1982

Synthesis and characterization of some cadmium II complexes by conventional and electrochemical methods.

Luis A. Bustos

University of Windsor

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LA THÈSE A ÉTÉ MICROFILMÉE TELLE QUE NOUS L'AVONS RÉCEUE
SYNTHESIS AND CHARACTERIZATION OF SOME CADMIUM(II) COMPLEXES BY CONVENTIONAL AND ELECTROCHEMICAL METHODS

by

Luis A. Bustos

A Thesis submitted to the Faculty of Graduate Studies through the Department of Chemistry in Partial Fulfillment of the requirements for the degree of Master of Science at The University of Windsor

Windsor, Ontario, Canada 1982
To my parents
ABSTRACT

This thesis reports investigations of complexes of cadmium(II) with the unsaturated bidentate sulphur ligand toluene-3,4-dithiolate (TDT), and bidentate oxygen ligands such as 2,4-pentanedionate (acac) and 1,1,1-trifluoro-2,4-pentanedionate (tfpd). The complexes have been prepared by different routes, and investigated by analytical and spectroscopic techniques to determine their coordination number and structure.

I. Synthesis of Neutral Dithiolato Cadmium(II) Compounds

Cadmium(II) halide reacts with toluene-3,4-dithiol (H₂TDT) in ethanol at 55°C to give the compound CdTDT.

Reaction of this compound with neutral bidentate ligands such as 2,2'-bipyridine (bipy) or 1,10-phenanthroline (phen) gives either the 1:1 adduct CdLv(bipy) or the 1:2 adduct CdLv(phen)₂. Other ligands also used were pyridine (py) and N,N,N,N'-tetramethylethylenediamine (TMED). Metal analysis and spectroscopic evidence support the formulation of these complexes as cadmium(II) species.

II. Synthesis of Anionic Cadmium(II) Compounds

Sodium hydroxide reacts with toluene-3,4-dithiol in ethanol to give Na₂(TDT). The reaction of this compound with CdTDT in the presence of a solution containing the
appropriate tetraphenylarsonium halide in ethanol yields 
(Ph₄As)₂[Cd(TDT)₂], which reacts with neutral bidentate
ligands such as 1,10-phenanthroline or 2,2'-bipyridine
to form 1:1 adducts such as (Ph₄As)₂[Cd(TDT)₂(Phen)].
Investigations using X-ray, ¹H NMR and other spectroscopic
techniques allowed the structures of these compounds to be
established.

III. Electrochemical Synthesis of Cadmium(II)

β-Diketonate Complexes

The electrochemical oxidation of cadmium metal in the
presence of 2,4-pentanedione (Hacac) or other β-diketones
(HL) leads to the formation of very stable CdL₂ compounds.
The sacrificial anode was cadmium, the cathode was platinum
and the solution phase was acetonitrile containing small
amount of tetraethylammonium perchlorate. Gram quantities
of product were obtained at room temperature. All the
compounds were isolated and characterized using infrared
(IR), nuclear magnetic resonance spectroscopy (¹H and
¹⁹F NMR) and in some cases mass spectrometry. Adducts of
the type CdL₂(phen) were also prepared, and the structure
established by X-ray methods.
ACKNOWLEDGEMENTS

I wish especially to express my sincere gratitude to my supervisor, Professor D. G. Tuck, for his continued guidance through the ups and downs of this research.

Special thanks go to Dr. R. C. Rummelfeldt, Dr. J. E. Drake, Dr. Akhtar Osman and Clovis Peppe, who have helped to solve the many problems encountered. I wish to thank the technicians for help during this project: M. Fuerth, M. Shutt and the secretaries, Maizie Lorondeau and Donna Dee. For help in typing this thesis I wish to thank Mrs. A. Zeleney. This acknowledgement includes many students and faculty members of the Chemistry Department and The University of Windsor who have made my stay a pleasant, interesting and exciting experience.
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acac 2,4-pentadionate
approx approximate(ly)
bipy 2,2'-bipyridine
\( \text{cm}^{-1} \) wave number
DMSO dimethysulfoxide
\( EF \) current efficiency
en ethylenediamine
Et ethyl
\( F \) Faraday constant
FD field desorption
\( g \) gram(s)
h hour(s)
\( ^1\text{H} \text{ NMR} \) proton nuclear magnetic resonance
\( \text{H}_2\text{TD} \text{T} \) toluene-3,4-dithiol
I.R. infrared
M metal(s)
mA millampere
Me methyl
\( m/e \) mass to charge ratio
mL millilitre \((10^{-3}\) litres\)
mp melting point
MS mass spectrometry
Ph phenyl
phen 1,10-phenanthroline
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<td>%RA</td>
<td>percentage relative abundance</td>
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CHAPTER I

THE GENERAL CHEMISTRY OF CADMIUM

1. Introduction

Cadmium (Z=48, atomic mass 112.40 gmol⁻¹) the second member of the group IIb of the periodic table, was discovered almost simultaneously by Stromeyer and Hofmann in Germany in 1817. The electronic configuration of the element is Kr₄d¹⁰₅s² (first ionization potential 865 Kj mol⁻¹). It is a silvery-white, soft metal, melting point 320.9°C and boiling point 765°C. The chemistry of cadmium is generally similar to that of the related group IIb elements zinc and mercury. The organic compounds of Group IIb elements show an interesting gradation of properties and chemical reactivity, running parallel to the electronegativity of the elements (1). Metals which are more electronegative than magnesium, e.g., zinc, cadmium and mercury, form organic compounds of comparatively low reactivity which undergo fewer useful chemical reactions. The organic derivatives of zinc, cadmium and mercury are covalent compounds of normal structure. The coordination chemistry of cadmium has been reviewed (2), with the stereochemistry being summarized in terms of 2,3,4,5 and
6-coordinate species. The use of X-ray crystallographic methods has given much useful information on the detailed stereo-chemistry, bond lengths and bond angles of such compounds. Since the cadmium(II) ion is a $d^{10}$ state, the stereochemistry should be determined by the balance of electrostatic forces if the bonding is strongly ionic, in absence of ligand field stabilization effects (2).

2. **Cadmium Compounds of Coordination Number 2**

Two types of two-coordinate cadmium compounds have been reported, namely dimethylcadmium (Cd(CH$_3$)$_2$, bond length, 211.4 pm) (3), and the dihalides (bond length 224 pm for CdCl$_2$, 239 pm for CdBr$_2$ and 256 pm for CdI$_2$ respectively) (4), all in the gas phase. The symmetry is $D_{oh}$ in each case, demonstrated by electron diffraction and high resolution Raman spectroscopy.

3. **Cadmium Compounds of Coordination Number 3**

Tuck and Contreras (5, 6) have reported the existence of CdX$_3^-$ and CdX$_2Y^-$ anionic complexes of cadmium with $C_{2v}$ symmetry in the solid state ($X \neq Y = Cl, Br, I$) on the basis of vibrational spectroscopy and force constant calculations.

4. **Cadmium Compounds of Coordination Number 4**

Many different four-coordinate compounds have been identified by X-ray diffraction or spectroscopic methods. Examples
include $\text{CdX}_4^{2-}$ anions in aqueous solutions ($X=\text{Cl, CN}$) (7,8), $\text{CdC}_4^-$ ($T_d$, polymeric structure) (9), $\text{CdS}_4^-$ (Approx. $T_d$) (10), and $\text{CdI}_4^-$ (bridged dimer of distorted $T_d$) (11). All have tetrahedral or pseudo-tetrahedral symmetry. Tetrahedral CdO$_4$ coordination has been identified in crystalline $\text{CdZn}_2(\text{PO}_4)_2$ (40). The CdS$_4^-$ unit is not uncommon, having been identified in $\text{Cu}_2\text{CdSiS}_4$ (10), and a wide number of such complexes with S-donor ligands have been reported (41-44).

5. **Cadmium Compounds of Coordination Number 5**

A number of five-coordinate compounds have been clearly identified, and monomeric, dimeric and polymeric structures are known. The CdCl$_5^{3-}$ (12) and SnCl$_5^{2-}$ (13) anions have $D_{3h}$ symmetry, different from InCl$_5^{2-}$ (14) although these three anions are isoelectronic.

Some examples of monomer, dimer and polymeric cadmium complexes with sulphur ligands include the following: Hoskins and Kelly (15) have reported $\text{Et}_4\text{N}(\text{O-Etxanthate})_3^{3+}$, ($\text{Cds}_5$ species) as distorted $C_{4v}$ monomer; Domenicano, et al. have identified $\text{Cd}[\text{S}_2\text{CNMe}_2]_2$, ($\text{Cds}_5$) as distorted $C_{4v}$ symmetry but dimeric (16); and Burgi (17) has reported Cd(thioglycollate)$_2$, ($\text{Cds}_4$O) as distorted $D_{3h}$, polymeric structure.
6. Cadmium Compounds of Coordination Number 6

A large number of six-coordinate compounds have been reported (2). They are classified into three different types:

a) Coordination kernels, CdX₆ (X=O, N, Cl, Br, etc.).

b) Adducts, which have a stoichiometry CdX₂L₂.

c) Coordination compounds involving polydentate ligands, hydrogen bonding, etc.

The CdN₆ species are known with monodentate and bidentate ligands, but no anionic structures have been reported. The CdCl₆ species occur in a number of salts of stoichiometry C₂CdCl₂; C₂CdCl₄; C₃CdCl₅ and C₄CdCl₆ (2), (where C represents cation(s) of appropriate charge).

The CdX₂L₂ species often involve halogen bridging, leading to an octahedral stereochemistry (approx.), even with bidentate nitrogen-donor ligands. The acetylacetone complexes are interesting in that the neutral Cd(acac)₂ (O₆) has CdO₆ coordination by bridging (45). However [Cd(acac)₃]⁻ is a mononuclear species where the coordination is close to trigonal prismatic (46). Also CdO₄N₂ species are well known, e.g., Cd(picolinate)₂ (47), Cd(L-methionate) (48) with a distorted O₆ symmetry. All have octahedral or pseudo octahedral symmetry. The CdCl₂(HCONH₂)₂ (18) compound, with a CdCl₄O₂ coordination kernel, is approximately octahedral with halogen bridging.
Finally, since cadmium has an important application in the bioinorganic field, several structures have been published (17-20) showing cadmium bonded to amino acids and similar molecules.

7. **Objective of Work**

   The purpose of this work was to prepare new cadmium(II) compounds with anionic bidentate sulphur or oxygen ligands, and to obtain structural information wherever possible. The effect of neutral donor ligands on the stereochemistry and the coordination number was also investigated. Finally the use of direct electrochemical methods in such syntheses was explored for Cd(acac)$_2$ and its derivatives.
CHAPTER II

DITHIOLATO COMPLEXES OF CADMIUM(II)

2.1 Introduction

In the last ten years, many papers have been published about unsaturated bidentate sulphur donor ligands such as those shown in Figures 1, 2 and 3.

![Figure 1](image1.png)

1,2-dicyanoethylene-1,2-dithiolate (MNT)

Figure 1

![Figure 2](image2.png)

1,1-dicyanoethylene-1,2-dithiolate (iMNT)

Figure 2
Toluene-3,4-dithiolate (TDT)$^{2-}$

Figure 3

Schrauzer and Mayweg (21) reported the first neutral complex (Figure 4), obtained by the reaction of nickel sulphide with diphenylacetylene or by the reaction of nickel carbonyl, sulphur and diphenylacetylene.

Toluene-3,4-dithiolate (TDT) is known to complex with main group metals such as tin (22) and indium (23). Toluene-3,4-dithiolate (TDT), was originally used by Clark in 1936 for the colorimetric determination of tin (26,27). Later, in the 1950's, Bahr and Schleitzer (49) prepared metal complexes of maleonitrite dithiolate (MNT), a ligand that they prepared themselves, but only in the 1960's were new transition metal complexes of dithiolate ligands reported. The
first isolation of a complex of coordination number six with unsaturated bidentate sulphur-donor ligand was by Gilbert and Sandell who made \( \text{Mo(TDT)}_3 \) (28). Other examples include the square planar complexes (24, 25) or neutral trigonal prismatic complexes shown in Figures 5 and 6.

![Figure 5](image)

\[ [\begin{array}{c}
\text{S} \\
\text{S} \\
\text{S} \\
\text{S} \\
\text{H}_3\text{C} \\
\text{M} \\
\end{array} ]^{-} \text{C}^+ \]

\( M = \text{Cu, Ni, Co, Fe}; \; C^+ = \text{Ph}_3\text{AsCH}_3^+ \)

\( M = \text{Au, Pt, Co, Fe}; \; C^+ = (\text{n-C}_4\text{H}_{10})_4\text{N}^+ \)

![Figure 6](image)

Finally, a recent report of \( R_4\text{N}^+[(\text{TDT})_2\text{SnX}]^- \) (29), (X=Cl, Br, I and R=Me, Et, Et) has been published. The structure was determined by X-ray study and it showed
the first tin compound having a rectangular-pyramidal geometry as shown in Figure 7.

![Chemical Structure](image)

Figure 7

This is a very interesting structure because until now only square planar (50), trigonal prismatic (51, 52), trigonal bipyramidal (53) and distorted octahedral (54) species had been reported for metal-TDT complexes.

2.2 Experimental

(a) Chemicals and Solvents

Chemical and solvents were of reagent grade. All solvents were purified, handled and stored under nitrogen (30).

(b) Acetonitrile

Acetonitrile "A.C.S." grade was dried by treating acetonitrile (1L) with phosphorus pentoxide, then re-fluxing with fine calcium hydride (4-5g) for approximately 7h. The solvent was finally distilled at boiling point (81.6°C) under nitrogen and stored over Linde 4A molecular sieves.
(c) **Acetone**

Analytical grade acetone (1L) was stirred with anhydrous MgSO₄ (8g) and then distilled at the boiling point (56°C). The distillate was stored over Linde molecular sieves.

(d) **Diethyl Ether**

Anhydrous diethyl ether (1L) was stirred for 10h with CaCl₂ (7g), filtered, refluxed over sodium wire for 2h and distilled at 34°C. It was stored over calcium hydride.

(e) **Methanol**

Anhydrous methanol was obtained from absolute methanol by refluxing it with calcium hydride for 2h, followed by distillation at the boiling point (64.5°C) under nitrogen; it was stored over Linde 4A molecular sieves.

(f) **Petroleum Ether**

Petroleum ether was stirred with CaCl₂ or Na₂SO₄ for 10h, filtered and further dried over sodium wire.

(g) **N,N,N,N'-Tetramethylethylenediamine**

N,N,N,N'-tetramethylethylenediamine was refluxed with KOH pellets and distilled under nitrogen at the boiling point (122°C).

(h) **Tetrahydrofuran**

Tetrahydrofuran (500mL) was refluxed with LiAlH₄ (3g) for 4h and then distilled under nitrogen at the boiling
point (65.4°C). The distillate was stored over calcium hydride.

(i) **Hexane**

Distilled from sodium under nitrogen at boiling point (63°C).

(j) **Dimethyl Sulphoxide**

Dimethyl sulphoxide was dried over Linde 4A molecular sieves.

(k) **Ethanol**

Ethanol, "A.C.S." grade, was dried over Linde molecular sieves.

(l) **Benzene**

Analytical grade benzene was dried by refluxing it with sodium naphtha-quinolone for 4h and then distilled under nitrogen at boiling point (80°C). The distillate was stored over sodium.

(m) **Chloroform**

Chloroform, "A.C.S." grade, was dried over Linde molecular sieves.

2.3 Physical Measurements

(a) **Infrared Spectra (IR)**

The infrared spectra were recorded between 400-4000 cm\(^{-1}\) with Beckman IR-12 and/or Perkin-Elmer 180 instruments, using Nujol Mull, KBr or CsI pellets as appropriate.
(b) **Nuclear Magnetic Resonance Spectra (NMR)**

The proton nuclear magnetic resonance spectra were recorded on a Varian EM-360 instrument operating at 60MHz. The resonance frequencies are relative to internal TMS (tetramethylsilane).

(c) **Analytical Techniques**

Metal analysis were carried out by atomic absorption spectroscopy, using an IL-250 atomic absorption emission spectrophotometer.

The apparatus was calibrated with standard solutions ranging in concentration from 0.5 to 2.5 mgmL⁻¹.

(d) **Microanalyses**

Microanalyses (carbon, hydrogen and sulphur) were carried out by Guelph Chemical Laboratories Ltd., Ontario, Canada.

2.4 **Preparative Chemistry**

(a) **Toluene-3,4-Dithiol**

The starting material, toluene-3,4-dithiol (H₂TDT) was obtained from Eastman Kodak Co. and used without further purification (mo 20-30°C).

(b) **Preparation of Cadmium(II) Toluene-3,4-Dithiol**

Cadmium chloride (4.3g) dissolved in ethanol (30mL) was slowly added to a mechanically stirred solution of H₂TDT (1.1g) in ethanol (20mL). The mixture was stirred
for approximately 12h at 55°C, the temperature at which precipitation took place. The yellow precipitate was collected, washed twice with ethanol and dried in vacuo.

Analysis showed that this substance is cadmium(II) toluene-3,4-dithiolate (CdTDTS, mp 225-227°C), which is soluble in DMSO, TMED, Py, en and insoluble in acetonitrile, acetone, chloroform, methanol, etc. (yield 2.1 g).

(c) Preparation of Bis (pyridine) Cadmium(II) Toluene-3,4-Dithiolate

Cadmium(II) toluene-3,4-dithiolate (0.43g) was dissolved in pyridine (py, 5mL), with stirring. Diethyl ether was added dropwise until a cloudiness was apparent in the solution. This was redissolved with a small amount of pyridine, and the solution cooled for 24h. The resultant yellow precipitate was filtered off and dried in vacuo. This substance is soluble only in pyridine. Analysis (Table II-1) and I.R. spectra showed that this solid was CdTDTS(py)$_2$ (yield 0.87 g).

(d) Preparation of Bis (1,10-phenanthroline) Cadmium(II) Toluene-3,4-Dithiolate

To a solution of 0.54g of 1,10-phenanthroline in 40mL of ethanol was added 0.25 g of cadmium(II) toluene-3,4-dithiolate. On being stirred the solution changed colour slowly, from pale yellow to orange. After 6h, the precipitate was filtered off, washed twice with ethanol
and dried in vacuo. This procedure was carried out for three different reaction times, namely 6h, 14h, 30h, but the same product was obtained in each case (yield 0.36 g).

(e) Preparation of \((2,2'^\prime\text{-bpyridine})\) Cadmium(II) Toluene-3,4-Dithiolate

The preparative method was exactly the same as that for the phenanthroline complex. The colour of the solution changed from pale yellow to deep yellow. This reaction was done twice for different reaction times, 7h and 16h, with the same result in each case. This substance is insoluble in all common organic solvents (yield 0.23 g).

(f) Preparation of \((N,N,N',N'^\prime\text{-Tetramethylene-diamine})\) Cadmium(II) Toluene-3,4-Dithiolate

Cadmium(II) toluene-3,4-dithiolate was dissolved in \(N,N,N',N'^\prime\text{-tetramethylene-diamine}\), and the excess of the solvent was pumped off over several hours. The drop-wise addition of petroleum-ether precipitated a yellow powder, which was dissolved in chloroform and reprecipitated with petroleum-ether. It was collected and dried in vacuo (yield 0.31 g).

(g) Preparation of \((\text{Dimethylsulphoxide})\) Cadmium(II) Toluene-3,4-Dithiolate

Cadmium(II) toluene-3,4-dithiolate (0.65g) was dissolved in 7mL of dimethyl sulphoxide (DMSO), and the excess of the solvent removed under vacuum over several hours. A brown heavy oil was collected and redissolved in chloroform.
Dropwise addition of diethyl ether precipitated a white powder, which is soluble only in chloroform (yield 0.24 g).

(h) Preparation of Ditetraphenylarsonium-Bis-(Toluene-3,4-Dithiolate) Cadmate(II)

Sodium hydroxide (0.8 g) dissolved in 30 mL of ethanol was added to a stirred solution of TDT in 15 mL of ethanol at room temperature. CdTDT (1.03 g) was then added slowly and the mixture was stirred until complete dissolution took place (approximately 16 h). A solution of tetraphenylarsonium chloride in ethanol was then added, and after five minutes, a yellow powder slowly precipitated. This yellow precipitate was filtered off and washed twice with ethanol. The product was redissolved in a mixture solution of EtOH/CH₂CN and cooled overnight at 0°C. The yellow crystals were filtered off and dried in vacuo (mp 230-232°C) (yield 0.32 g).

(i) Preparation of Ditetraphenylarsonium - Bis-(Toluene-3,4-Dithiolate)-1,10-Phenanthroline Cadmate(II)

To a stirred solution of 0.6 g of (Ph₄As)₂[Cd-(TDT)₂] in 30 mL of acetonitrile was added a solution of 0.08 g of 1,10-phenanthroline in 10 mL of ethanol. The solution changed color from yellow to orange after the addition of 1,10-phenanthroline. Diethyl ether was added dropwise until the appearance of cloudiness in the
solution, the solid redissolved in acetonitrile, and the resultant solution cooled for approximately 15h. The final yellow precipitate was filtered off, washed with ethanol and dried in vacuo (mp 256-258°C) (yield 0.35 g).

(j) Preparation of Ditetraphenylarsonium-Bis-(Toluene-3,4-Dithiolate)-2,2'-Bipyridine Cadmate(II)

To a solution of 0.59g of (Ph₄As)₂[Cd(TDT)₂] in 30mL of acetonitrile was added a solution of 0.07g of 2,2'-bipyridine in 10mL of ethanol. The yellow solution did not change colour after the addition of 2,2'-bipyridine. Diethyl ether was added; the precipitation procedures were essentially identical to those just described. The final yellow precipitate was collected, washed with ethanol and dried in vacuo (mp 218-220°C) (yield 0.42 g).

(k) Preparation of Ditetraphenylarsonium-Bis-(Toluene-3,4-Dithiolate)-N,N,N',N'-Tetramethylethylenediamine Cadmate(II)

To a solution of 0.3g of (Ph₄As)₂[Cd(TDT)₂] in 10mL of acetonitrile was added 3mL of N,N,N',N'-tetramethyl-ethylenediamine. The volume of the solution was reduced to approximately 5mL using a rota-vapor evaporator. The white precipitate obtained was collected, washed with ethanol and dried in vacuo (mp 215-217°C) (yield 0.27 g).
(1) **Attempted Preparation of Ditetraethylammonium-Bis (Toluene-3,4-Dithiolate) Cadmate(II)**

Toluene-3,4-dithiol (0.7g) 30 mL of ethanol was added dropwise to a solution of sodium hydroxide (0.4g) in 20 mL of ethanol. The solution was stirred and tetra-ethylammonium chloride (1.6g) in 40 mL of ethanol was added. The white precipitate of sodium chloride was filtered off and 0.4g of cadmium chloride in 20 mL of ethanol added to the filtrate. The pale yellow powder was filtered off and washed with ethanol until chloride ion could be identified in the washing. The product was dried in vacuo. (yield 0.58 g).

Analysis showed that the material obtained was not the desired substance, and it is concluded that the Cd(TDT)$_2^-$ anion cannot be stabilized in the solid state with the tetraethylammonium cation. This is in contrast to the earlier preparation of Et$_4$N[In(TDT)$_2$] (60).
### TABLE II-1

Analytical Results for Cadmium(II) Dithiolate and Adducts

<table>
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<th>Compound</th>
<th>Metal Analysis (%)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Found</td>
<td>Calcd.</td>
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<tr>
<td>CdTDT</td>
<td>41.7</td>
<td>42.2</td>
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</tr>
<tr>
<td>CdTDT (py)$_2$</td>
<td>26.9</td>
<td>26.5</td>
<td></td>
</tr>
<tr>
<td>CdTDT (phen)$_2$</td>
<td>17.7</td>
<td>17.9</td>
<td></td>
</tr>
<tr>
<td>CdTDT (bipy)</td>
<td>26.7</td>
<td>26.6</td>
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<tr>
<td>CdTDT (TMED)</td>
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<td>29.4</td>
<td></td>
</tr>
<tr>
<td>CdTDT (DMSO)</td>
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<td>32.6</td>
<td></td>
</tr>
<tr>
<td>$\text{Ph}_4\text{As}_2\left[\text{Cd(TDT)}_2\right] \cdot 2\text{EtOH}$</td>
<td>9.6</td>
<td>8.8</td>
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<tr>
<td>$\text{Ph}_4\text{As}_2\left[\text{Cd(TDT)}_2(\text{phen})\right]$</td>
<td>8.4</td>
<td>8.2</td>
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</tr>
<tr>
<td>$\text{Ph}_4\text{As}_2\left[\text{Cd(TDT)}_2(\text{bipy})\right]$</td>
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<td>8.4</td>
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<tr>
<td>$\text{Ph}_4\text{As}_2\left[\text{Cd(TDT)}_2(\text{TMED})\right]$</td>
<td>8.9</td>
<td>8.8</td>
<td></td>
</tr>
<tr>
<td>$\text{Et}_4\text{N}_2\left[\text{Cd(TDT)}_2\right]$</td>
<td>29.8</td>
<td>16.5</td>
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# TABLE II-2

Elemental Analyses of CdTDT and \([\text{Cd(TDT)}_2]^{2-}\)

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<td>CdTDT</td>
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<td>(31.50)</td>
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<tr>
<td>([\text{Cd(TDT)}_2]^{2-})</td>
<td>61.91</td>
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<td>(61.94)</td>
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*(Ph₄As)₂[Cd(TDT)]₂·2(EtOH)*
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<th>Cd(TDT)$_{2}^{-}$</th>
<th>CdTDT (DMSO)</th>
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<td>710 m</td>
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<td>CdTDT(phen)$_2$</td>
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<td>CdTDT(TMED)</td>
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<td>1525 w</td>
<td>1585 m</td>
<td>1585 m</td>
<td></td>
</tr>
<tr>
<td>2910 w</td>
<td>2920 w</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE II-4

Summary of Crystal Data, Intensity Collection, and Structural refinement for [(C$_6$H$_5$)$_4$As]$_2$ [Cd(CH$_3$C$_6$H$_3$S)$_2$] \((C_2H_5OH)_2\)

<table>
<thead>
<tr>
<th>Cell constants</th>
<th>(a = 23.032(4) \text{ Å})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(b = 12.396(4) \text{ Å}, \beta = 111.106(2)^\circ)</td>
</tr>
<tr>
<td></td>
<td>(c = 22.529(5) \text{ Å})</td>
</tr>
<tr>
<td></td>
<td>(U = 6001(3) \text{ Å}^3)</td>
</tr>
<tr>
<td>Space group</td>
<td>(P2_1/c \ (C_2^h; \text{ No. 14}))</td>
</tr>
<tr>
<td>(Z)</td>
<td>4</td>
</tr>
<tr>
<td>(M)</td>
<td>1279.74 g. mol$^{-1}$</td>
</tr>
<tr>
<td>(\rho) (calc.)</td>
<td>1.410 g. cm$^{-3}$</td>
</tr>
<tr>
<td>(\rho) (meas.)</td>
<td>1.409 g. cm$^{-3}$</td>
</tr>
<tr>
<td>Absorption coeff. ((\mu))</td>
<td>16.96 cm$^{-1}$</td>
</tr>
<tr>
<td>Crystal dimensions</td>
<td>0.1x0.2x0.2 mm</td>
</tr>
<tr>
<td>Radiation</td>
<td>MoK$_\alpha$ ((\lambda=0.71069 \text{ Å}))</td>
</tr>
<tr>
<td>(2\theta)$_{\text{max}}$</td>
<td>45.0</td>
</tr>
<tr>
<td>Scan type</td>
<td>coupled (\theta) (crystal)/2(\theta) (counter)</td>
</tr>
<tr>
<td>Scan width</td>
<td>Ka$_1$ -1$^\circ$ to Ka$_2$ +1$^\circ$</td>
</tr>
<tr>
<td>Scan speed</td>
<td>2.02$^\circ$ - 4.88$^\circ$ min</td>
</tr>
<tr>
<td>Background time/s. time</td>
<td>0.5</td>
</tr>
<tr>
<td>Total reflections meas.</td>
<td>6884 ((h, \pm k, \pm l))</td>
</tr>
<tr>
<td>Unique averaged data</td>
<td>2523[((F_o^2)) - (\tau(F_q^2))]</td>
</tr>
<tr>
<td>(R) = (\Sigma\Delta/\Sigma</td>
<td>F_o</td>
</tr>
<tr>
<td>(R_w) = (\sum\omega \Delta^2/\sum\omega F_o^2)^{1/2}</td>
<td>0.0486</td>
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### TABLE II-4 (cont'd)

Interatomic Distances (Å) and Angles (°), with standard deviations in parenthesis

(a) Bonding

<table>
<thead>
<tr>
<th>Bonding</th>
<th>Distances (Å)</th>
<th>Bonding</th>
<th>Distances (Å)</th>
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<tr>
<td>Cd-S(1)</td>
<td>2.510(4)</td>
<td>Cd-S(3)</td>
<td>2.502(4)</td>
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<td>Cd-S(2)</td>
<td>2.488(5)</td>
<td>Cd-S(4)</td>
<td>2.531(4)</td>
</tr>
<tr>
<td>S(1)-C(01)</td>
<td>1.759(18)</td>
<td>S(3)-C(07)</td>
<td>1.757(13)</td>
</tr>
<tr>
<td>S(2)-C(06)</td>
<td>1.791(13)</td>
<td>S(4)-C(012)</td>
<td>1.773(15)</td>
</tr>
<tr>
<td>C(01)-C(02)</td>
<td>1.38(2)</td>
<td>C(07)-C(08)</td>
<td>1.41(2)</td>
</tr>
<tr>
<td>C(01)-C(06)</td>
<td>1.44(2)</td>
<td>C(07)-C(012)</td>
<td>1.39(2)</td>
</tr>
<tr>
<td>C(02)-C(03)</td>
<td>1.42(3)</td>
<td>C(08)-C(09)</td>
<td>1.35(2)</td>
</tr>
<tr>
<td>C(03)-C(03A)</td>
<td>1.56(2)</td>
<td>C(09)-C(09A)</td>
<td>1.56(3)</td>
</tr>
<tr>
<td>C(03)-C(04)</td>
<td>1.33(3)</td>
<td>C(09)-C(010)</td>
<td>1.38(2)</td>
</tr>
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<td>C(04)-C(05)</td>
<td>1.38(2)</td>
<td>C(010)-C(011)</td>
<td>1.39(2)</td>
</tr>
<tr>
<td>C(05)-C(06)</td>
<td>1.40(2)</td>
<td>C(011)-C(012)</td>
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<td>As(1)-C(11)</td>
<td>1.906(15)</td>
<td>As(2)-C(151)</td>
<td>1.907(16)</td>
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<td>As(1)-C(21)</td>
<td>1.865(16)</td>
<td>As(2)-C(61)</td>
<td>1.913(15)</td>
</tr>
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<td>As(1)-C(31)</td>
<td>1.921(13)</td>
<td>As(2)-C(71)</td>
<td>1.926(15)</td>
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<td>As(1)-C(41)</td>
<td>1.886(14)</td>
<td>As(2)-C(81)</td>
<td>1.890(14)</td>
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<td>C-C(ave)Ph1</td>
<td>1.39(3)</td>
<td>C-C(ave)Ph5</td>
<td>1.38(2)</td>
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<td>C-C(ave)Ph2</td>
<td>1.39(2)</td>
<td>C-C(ave)Ph6</td>
<td>1.38(2)</td>
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<td>C-C(ave)Ph3</td>
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<td>C-C(ave)Ph7</td>
<td>1.38(4)</td>
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<tr>
<td>C-C(ave)Ph4</td>
<td>1.39(1)</td>
<td>C-C(ave)Ph8</td>
<td>1.39(3)</td>
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</table>

(b) Bond Angles

<table>
<thead>
<tr>
<th>Angles (°)</th>
<th>Angles (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S(1)-Cd-S(2)</td>
<td>87.3(2)</td>
</tr>
<tr>
<td>S'(1)-Cd-S(4)</td>
<td>122.9(1)</td>
</tr>
<tr>
<td>S(2)-Cd-S(4)</td>
<td>119.1(1)</td>
</tr>
<tr>
<td>Cd-S(1)-C(01)</td>
<td>100.1(5)</td>
</tr>
<tr>
<td>Cd-S(3)-C(07)</td>
<td>100.4(5)</td>
</tr>
<tr>
<td>S'(1)-C(01)-C02</td>
<td>117(1)</td>
</tr>
<tr>
<td>C(02)-C(01)-C(06)</td>
<td>116(2)</td>
</tr>
<tr>
<td>C(02)-C(03)-C(03A)</td>
<td>119(2)</td>
</tr>
<tr>
<td>Bonding Distances</td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td>---</td>
</tr>
<tr>
<td>C(03A)–C(03)–C(04)</td>
<td>120(2)</td>
</tr>
<tr>
<td>C(04)–C(05)–C(06)</td>
<td>121(2)</td>
</tr>
<tr>
<td>S(2)–C(06)–C(05)</td>
<td>118(1)</td>
</tr>
<tr>
<td>S(3)–C(07)–C(08)</td>
<td>115(1)</td>
</tr>
<tr>
<td>C(08)–C(07)–C(012)</td>
<td>118(1)</td>
</tr>
<tr>
<td>C(08)–C(09)–C(09A)</td>
<td>120(1)</td>
</tr>
<tr>
<td>C(09A)–C(09)–C(010)</td>
<td>119(2)</td>
</tr>
<tr>
<td>C(010)–C(011)–C(012)</td>
<td>122(1)</td>
</tr>
<tr>
<td>S(4)–C(012)–C(011)</td>
<td>116(1)</td>
</tr>
<tr>
<td>C(11)–As(1)–C(21)</td>
<td>107.7(6)</td>
</tr>
<tr>
<td>C(11)–As(1)–C(41)</td>
<td>112.2(7)</td>
</tr>
<tr>
<td>C(21)–As(1)–C(41)</td>
<td>107.9(7)</td>
</tr>
<tr>
<td>C(51)–As(2)–C(61)</td>
<td>108.5(6)</td>
</tr>
<tr>
<td>C(51)–As(2)–C(81)</td>
<td>111.1(7)</td>
</tr>
<tr>
<td>C(61)–As(2)–C(81)</td>
<td>108.7(6)</td>
</tr>
<tr>
<td>C–C–C(Av)Ph</td>
<td>120(2)</td>
</tr>
</tbody>
</table>

(c) Non-bonding Distances

0(015)–S(4) | 3.322 | 0(017)–S(1) | 3.306 |

(a) ESD's on average values are calculated by using the "scatter" formula \( \sigma = \left\{ \sum (d_i - \bar{d})^2 / (N-1) \right\}^{1/2} \), where \( d_i \) is the \( i \)th and \( \bar{d} \) is the mean of \( N \) "equivalent" measurements.
Figure 8. ORTEP Plot of C_{66}H_{66}As_{2}C_{8}O_{2}S_{4}.
2.5 Results and Discussion

2.5.1 Preparative

The methods described have been successful in leading to the preparation of the neutral compound CdTDT, a salt of the anion Cd(TDT)$_2^{2-}$, and a number of adducts of these two species. None of these compounds has been reported previously.

The spectroscopic data which lead to the characterization of these compounds is discussed first before proposing structure for these molecules.

2.5.2 Infrared Spectra

The infrared spectra of CdTDT, Cd(TDT)$_2^{2-}$ and its adducts were recorded using KBr pellets, and the spectra are reported in Table II-3.

From infrared spectral studies, Davison, et al. (53) have assigned bands to $\nu$(C≡C) in some complexes of the type $[M(S_2C_2(CF_3)_2)m]^{n-}$, (with M=Ni, Co, Fe, Pd and Pt, and m=2 or 3, n=0, 1 or 2). Schrauzer and Mayweg (54) have partially assigned bands for $[Ni(C_2S_2R_2)]^{2-}$ (R=H, Me and Ph). Adams and Cornell (55) made a complete I.R. study of the complexes $[M(C_2S_2R_2)_2]^{n-}$, (R=H, CF and CN; M=Ni, Co, Cu, Pd and Pt).

The infrared spectra of the various maleonitrile dithiolate (MNT) complexes (23, 35) clearly show the presence of $\nu$(C≡N), $\nu$(C=C) and $\nu$(C=S) bands. The $\nu$(C≡N) bands
approximately 2200 cm\(^{-1}\) are present in all the complexes, with little or no shift from the spectrum of MNT\(^{2-}\) itself. The \(\nu(C=\C)\) mode is normally in the region 1600-1680 cm\(^{-1}\), but in MNT complexes this falls at 1430-1480 cm\(^{-1}\), suggesting that the double bond character is reduced due to delocalization of the \(\pi\)-bonding system. The two \(\nu(C-S)\) bands are known to be in the regions 1105-1120 cm\(^{-1}\) and 860-873 cm\(^{-1}\) in the compound Ni(S\(_2\)C\(_2\)H\(_2\))\(_2\) and M(MNT)\(_2\) (M=Ni,Cu,Pd or Pt). In the complex [In(MNT)\(_2\)]\(^{-}\), (60) there are two bands at 1115-1150 cm\(^{-1}\) and one very strong band at 855 cm\(^{-1}\), believed to be (C-S) stretching modes.

The information above was used as reference in the interpretation of the spectra of CdTDT complexes. For instance, [Cd(TDT)\(_2\)]\(^2-\) shows one band at 810 cm\(^{-1}\), believed to be (C-S), as in [In(TDT)\(_2\)]\(^{-}\) at 810 cm\(^{-1}\). The I.R. absorption spectra of cadmium(II) complexes are then compared with each other, with emphasis on the stretching modes of the C=C and C-S bonds. The data in Table II-3 show bands in this regions for each compound.

One major change found on complex formation is that the \(\nu(S-H)\) band at 2545 cm\(^{-1}\) disappears on coordination; furthermore, the phenyl ring vibration bands at 1620 and 1590 are at lower frequencies in the complexes. A detailed set of assignments is not justified, but the spectra clearly confirm the presence of TDT in each compound.
In CdTDt(DMSO), ν(S=O) is at 1010 cm\(^{-1}\), compared to 1050 cm\(^{-1}\) in the free ligand, corresponding to an O-bonded DMSO (36-38). The pyridine ligand shows no major shifts or splittings on complexing (56) and in fact most absorptions of free pyridine are faithfully reproduced in the complex CdTDtpy\(_2\).

The CdTDt complexes of 1,10-phenanthroline and 2,2'-bipyridine show the expected shifts (37-39) in the 700-800 cm\(^{-1}\) region, assigned to out-of-plane C-H bend, and in the 1500-1600 cm\(^{-1}\) region assigned to aromatic C=C stretching.

2.5.3 N.M.R. Studies

The \(^1\)H NMR spectrum of cadmium(II) - toluene-3,4-dithiolate, taken at room temperature in DMSO-d\(_6\) using TMS as internal standard, shows the expected single resonance at δ2.18 (–CH\(_3\)) and a multiplet at δ7.32 (aromatic protons). The spectrum of pure toluene-3,4-dithiol consisted of two sharp singlets at δ2.05 (–CH\(_3\)), δ3.90 (S-H), and a multiplet centred at δ7.11 due to aromatic protons. The most obvious change in the spectrum of toluene-3,4-dithiol on reacting with cadmium(II) is the disappearance of the S-H resonance. The spectrum of (Ph\(_4\)As)\(_2\)[Cd(TDT)]\(_2\) also shows a singlet at δ2.50 (–CH\(_3\)), and a multiplet between δ7.8-8.2 due to aromatic protons.

The NMR spectra of 1,10-phenanthroline in acetone (57)
and 2,2'-bipyridine in DMSO (35) had been reported previously. The eight protons of 1,10-phenanthroline and 2,2'bipyridine (Figures 10 and 11 respectively) can be considered as four pairs, thus, Ha and Ha'; Hb and Hb'; Hc and Hc'; and Hd and Hd' which behave as equivalent pairs giving one resonance signal from each pair.

![Figure 10](image)

![Figure 11](image)

The resonance absorptions of these protons are assigned in the region between 7.0 and 8.5 ppm (downfield from TMS). The complex series of resonances in this region, and the solubility problems encountered with the 1,10-phenanthroline and 2,2'-bipyridine complexes of CdTDT, resulted in a low
intensity spectra without adequate resolution of the ring protons. This means that a detailed analysis of the spectra is difficult, except for the toluene methyl group, which is identified at 2.2 ppm for 1,10-phenanthroline, and 2.15 ppm for 2,2'-bipyridine. Nevertheless in all the systems studied, the NMR spectra confirm the presence of both TDT and the appropriate neutral ligand. Since the spectra were run in DMSO-d$_6$, which itself complexes with CdTDT, the results cannot be used to make detailed structural assignments.

2.5.4 X-Ray Crystallography

A single crystal, thought to be (Ph$_4$As)$_2$[Cd(TDT)$_2$] was studied by Dr. M. Khan, using the conventional methods of X-ray crystallography. The structure only refined satisfactorily when two molecules of ethanol were allowed for in the lattice, although none of the previous spectroscopy had revealed the presence of these solvent molecules. A summary of crystal data, interatomic distances (Å) and angles (°), with standard deviations in parentheses, are reported in Table II-4.

The cadmium atom is coordinated by two sulfur atoms from each TDT ligand. Figure 8 shows the ORTEP projection of C$_{66}$H$_{64}$As$_2$CdO$_2$S$_4$, and Figure 9 shows the unit cell and the distribution of four [C$_6$H$_5$)$_4$As]$_2$[Cd(CH$_3$C$_6$H$_3$S$_2$)$_2$] (C$_2$H$_5$OH)$_2$ which correspond to a monoclinic cell. Figure 12
shows the ligand geometry in the molecule.

2.5.5 Structural Discussion

Since the structure of the Cd(TDT)$_2$$_2^{-}$ anion is established, it is reasonable to propose that the anions [Cd(TDT)$_2$phen]$^{2-}$ and [Cd(TDT)$_2$-bipy]$^{2-}$ are six-coordinate species with a CdS$_4$N$_2$ kernel (c.f. ref. (2)). A likely structure is that shown in Figure 13.

The structure of CdTDT itself is most probably polymeric, given the total insolubility in non-donor organic solvents. If one assumes a tetrahedral environment with each cadmium coordinated by four sulphur atoms, with bridging to the cadmium, a possible structure is that shown in Figure 14. Each cadmium is here coordinated by four sulphur atoms for three different TDT ligands.

The cadmium environment is tetrahedral, to a first approximation, composed of four bonded sulphurs, which are bridging to other cadmium atoms. Each cadmium atom
Figure 13 [Cd(TDT)$_2$phen]$^{2-}$ configuration

is thus coordinated by four sulfur atoms from each of three independent ligands.

Figure 14
The structure of the neutral adducts of CdTDT, which are themselves insoluble in non-donor solvents can then be tentatively described as a CdTDT polymeric chain to which one or more donor atoms can be coordinated at the cadmium (Figure 15).

![Diagram of polymeric chain of adducts of CdTDT](image)

**Figure 15** Polymeric chain of adducts of CdTDT

Further discussion of the structures of these adducts does not seem justified at this time.
CHAPTER III

THE ELECTROCHEMICAL SYNTHESIS OF
CADMIUM (II) - β-DIKETONATE COMPLEXES

3.1 Introduction

The electrochemical technique represents the simplest and most direct method of carrying out oxidation or reduction, since the removal or addition of electrons can be achieved without any of the complications involved in the use of redox reagents (31). An electrochemical system consists essentially of an electrolyte solution, voltage source, a cathode and an anode, either of which could be inert or active. The active case involves a sacrificial electrode, while in the former case the electrodes act as the source of, or sink for, electrons in the reduction or oxidation of solute species in the solution phase, which may be aqueous or non-aqueous.

In the synthesis of inorganic and organometallic compounds, relatively few methods use the metal as the starting material. Grignard reagents, and Frankland's synthesis of organo-zinc halides, are salutary examples of the ability of metals to cleave strong chemical bonds. In recent years, the use of metals has increased due to the development of
vapour phase synthesis, in which vaporization of the metal at elevated temperatures is followed by low temperature reactions in a condensed phase. Applications of such direct vapour phase synthesis require sophisticated apparatus, including a high vacuum system for efficient pumping and evaporating gram quantities of metals, and a cold trap for the collection of the product.

In electrochemical synthesis, in contrast, one normally works at or near room temperature, and the compounds are produced by the oxidation or reduction of metal electrode, using relatively unsophisticated apparatus. The method involved is a direct one in which the product(s) precipitate during the electrolysis in many cases, and the chemical yield is generally high in terms of metal consumed during electrolysis.

A number of different solvents and supporting electrolytes have been used in non-aqueous studies. The most common solvents used are acetonitrile, methanol, acetone, benzene, tetrahydrofuran, dimethylsulfoxide and pyridine. The choice of any particular combination of solvent and electrolyte is empirical and each combination has its own characteristics. The supporting electrolyte most often used has been tetraethylammonium perchlorate which offers the widest potential range.
3.2 Experimental

(a) **Mass Spectra (MS)**

Mass spectra were recorded with Varian MAT CH-5DF Mass Spectrometer, equipped with a combined F.D./F.I. source. All spectra were recorded through an Incos Model 2000 computer interfaced with the mass spectrometer.

(b) $^{19}\text{F NMR}$

The $^{19}\text{F}$ NMR spectra were recorded on a Bruker CXP-100 instrument operating at 84.7 MHz. The resonance frequencies are based on external trifluoro-acetic acid (TFA).

(c) Infrared, $^1\text{H}$ Nuclear Magnetic Resonance spectroscopy and metal analysis were as described in Chapter II.

(d) **Power Supply**

The power supply used was a Coutant LQ 50/50, capable of supplying 50V DC and 500 mA (maxima).

(e) **Current Efficiency**

The current efficiency is defined as the number of moles of metal dissolved per Faraday of electricity. The measurement was carried out at controlled constant current and under the same conditions in which the products were isolated and characterized. The cadmium anode was weighed before and after electrolysis, and the number of moles dissolved thus calculated. The amount of electri-
city passed through the cell (in Faradays) is given by
number of Faradays = \( \frac{I \times t}{F} \)
where,
\( I = \) controlled constant current
\( t = \) time of electrolysis
\( F = \) Faraday's constant = 96,480 Coulomb mol\(^{-1}\),
then,
\( E_F = \frac{\text{Moles Metal Dissolved}}{\text{Faradays}} \)

(f) **Electrochemical Cell**

The electrochemical cell used in this case, is shown in Figure 16.

A 100 mL Pyrex beaker containing approximately 50 mL of solution phase served as reaction vessel. The cathode was a thin platinum plate approximately 2 cm wide and 3 cm long. The cadmium anode (1-2g) was a flattened sheet suspended on a platinum wire. The two electrodes were supported by a rubber bung fitted tightly into the neck of the beaker, and provided with a glass inlet and outlet tubes to maintain an inert atmosphere of nitrogen in the electrochemical cell. The outlet tube was connected to a non-return glass bubbler.

An important experimental point is the control of current by adjusting the voltage. Too high a current causes disintegration of the anode, with consequent contamination of the product. The currents quoted gave a reasonable rate of reaction without such complications.
Figure 16  Electrochemical Cell
3.3 Preparative Chemistry

(a) Electrochemical Preparation of bis-acetylácetonato-cadmium(II)

The electrochemical oxidation of cadmium metal in a solution containing 40 mL of acetonitrile, 10 mL of acetylacetone (2,4-pentanediione) and 20 mg of $\text{Et}_4\text{NClO}_4$ was carried out for 4h using an initial voltage of 15V and a current of 20 mA. The precipitate which formed in the reaction mixture was then collected by filtration at room temperature, and dried in vacuo. This compound was very stable to the air and room temperature. Analytical results are collected in Table III-1, and the experimental conditions in Table III-2.

(b) Electrochemical Preparation of 2,2'-bipyridine Adduct of $\text{Cd(acac)}_2$

A mixture consisting of 0.79g of 2,2'-bipyridine, 10 mL of $\text{Hacac}$, 40 mL of acetonitrile and 25 mg of $\text{Et}_4\text{NClO}_4$ was electrolyzed for 2.35h using an initial voltage of 8V and a current of 20 mA. The product deposited at the bottom of the cell, and was collected, washed with acetonitrile to remove excess of 2,2'-bipyridine and then dried in vacuo.

(c) Electrochemical Preparation of 1,10-phenanthroline Adduct of $\text{Cd(acac)}_2$

A solution of 1.0g of 1,10-phenanthroline, 5 mL of
Hacac, 40 mL of acetonitrile and 30 mg of \( \text{Et}_4\text{NClO}_4 \) was electrolyzed for 12h at 11V and 20 mA current. After this period the product was filtered off, washed with acetonitrile to remove any excess of 1,10-phenanthroline and dried in vacuo.

(d) **Electrochemical Preparation of** \( \text{N,N,N',N'}-\text{Tetramethylethylene diamine Adduct of} \quad \text{Cd(acac)}_2 \)

The electrochemical oxidation of cadmium metal in a solution containing 40 mL of acetonitrile, 5 mL of Hacac, 5 mL of TMED and 25 mg of \( \text{Et}_4\text{NCIO}_4 \) was carried out for 6.45h using an initial voltage of 16V and a current of 20 mA. The mixture was then filtered to isolate the product, which was washed with acetonitrile and dried in vacuo.

(e) **Electrochemical Preparation of** \( \text{bis}^{4,4,4-\text{trifluoro-1-}(2 \text{ naphthyl})-1,3-\text{butanedionato}} \quad \text{Cadmium(II)} \)

Using an initial voltage of 10V and a current of 20 mA, a solution of 1.4g of \( 4',4',4'-\text{trifluoro-1-}(2 \text{ naphthyl})-1,3-\text{butanedione} \) in 40 mL of acetonitrile and 20 mg of \( \text{Et}_4\text{NCIO}_4 \) was electrolyzed for 14h. A white product precipitated in the cell. The compound was filtered, washed with petroleum-ether and dried in vacuo, yielding 1.65 g of product.
(f) **Electrochemical Preparation of bis (4,4,4-Trifluoro-1-phenyl-1,3-butanedionate Cadmium(II))**

A mixture consisting of 1.76g of 4,4,4-trifluoro-1-phenyl-1,3-butanedione 45 mL of acetonitrile and 25 mg of Et₄NClO₄ was electrolyzed for 15h, using an initial voltage of 11V and a current of 20 mA. The product was deposited at the bottom of the cell as the electrolysis progressed. This material was collected, washed with petroleum-ether and dried in vacuo.

(g) **Electrochemical Preparation of bis (1,1,1-Trifluoro-6-methyl-2,4-heptanedionate) Cadmium(II))**

A solution of 2 mL of 1,1,1-trifluoro-6-methyl-2,4-heptanedione, 20 mL of acetonitrile and 10 mg of Et₄NClO₄ was electrolyzed for 16h, using an initial voltage of 45V and a current of 30 mA. After this period the solution was evaporated in vacuo at room temperature. The product was collected, washed with petroleum-ether and dried in vacuo. A total yield of 0.45g was obtained.

(h) **Electrochemical Preparation of bis (1,1,1-Trifluoro-5-methyl-2,4-hexanedionate) Cadmium(II))**

Electrochemical oxidation of cadmium metal in a solution containing 3 mL of 1,1,1-trifluoro-5-methyl-2,4-hexanedione, 20 mL of acetonitrile and 10 mg of Et₄NClO₄...
was carried out for 16h, using an initial voltage of 26V and a current of 30 mA. After this period the solution was treated in the same way as described in (g). The product was dried in vacuo and analyzed for cadmium.

(i) Electrochemical Preparation of bis (1,1,1-
Trifluoro-5,5-dimethyl-2,4-hexanedionate)

Cadmium(II)

Using an initial voltage of 44V and a current of 20 mA, a solution of 1 mL of 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione in 20 mL of acetonitrile and 10 mg of Et₄NClO₄ was electrolyzed for 5h. After this period the solvent was evaporated at room temperature. The solid was collected, washed with petroleum-ether and dried in vacuo. Approximately 0.11g of cadmium was dissolved from the anode.

(j) Electrochemical Preparation of bis (1,1,1-
Trifluoro-2,4-pentanedionate) Cadmium(II)

Electrochemical oxidation of cadmium metal in a solution mixture consisting of 2 mL of 1,1,1-trifluoro-2,4-pentadione, 20 mL of acetonitrile and 15 mg of Et₄NClO₄ was carried out for 12h, using an initial voltage of 18V and a current of 10 mA. The solution was then treated in the same way as described in (g). The product was dried in vacuo and analyzed for cadmium.
(k) **Attempted Electrochemical Preparation of Triethylammonium-tris-acetylacetonate-Cadmate(II)**

Using an initial voltage of 12V and a current of 20 mA, a solution containing 40 mL of acetonitrile, 3 mL of Hacac, 1 mL of Et$_3$N and 30 mg of Et$_4$NClO$_4$ was electrolyzed for 18h. The reaction mixture was filtered to isolate the product, which was washed with acetonitrile and subsequently dried in vacuo. The solid obtained was found to contain 34.76% of cadmium (calcd. 21.82). This suggests that the product found could be Cd(acac)$_2$, for which the calculated metal content is 36.2%.

Thus the attempt to prepare the Et$_3$NH$^+$ salt of Cd(acac)$_3$ by this route was clearly unsuccessful (see section 3.4).
TABLE III-1
Analytical Results for Cadmium(II)-β-Diketonates and some Adducts

<table>
<thead>
<tr>
<th>Compound</th>
<th>Cd Analysis (%)</th>
<th>Mol. Wt.*</th>
<th>Melting Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(acac)$_2$</td>
<td>36.4</td>
<td>36.2</td>
<td>e</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>310.6</td>
</tr>
<tr>
<td>Cd(acac)$_2$ bipy</td>
<td>24.3</td>
<td>24.1</td>
<td>e</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>468.8</td>
</tr>
<tr>
<td>Cd(acac)$_2$ phen</td>
<td>22.9</td>
<td>22.8</td>
<td>e</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>492.8</td>
</tr>
<tr>
<td>Cd(acac)$_2$ TMED</td>
<td>26.5</td>
<td>26.3</td>
<td>e</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>426.8</td>
</tr>
<tr>
<td>Cd(CF$_3$COCHCOR$_a$)$_2$</td>
<td>17.4</td>
<td>17.5</td>
<td>644</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>644</td>
</tr>
<tr>
<td>Cd(CF$_3$COCHCOR$_b$)$_2$</td>
<td>20.8</td>
<td>20.7</td>
<td>544</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>544</td>
</tr>
<tr>
<td>Cd(CF$_3$COCHCOR$_c$)$_2$</td>
<td>22.5</td>
<td>22.4</td>
<td>503</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>503</td>
</tr>
<tr>
<td>Cd(CF$_3$COCHCOR$_d$)$_2$</td>
<td>23.9</td>
<td>23.7</td>
<td>476</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>476</td>
</tr>
<tr>
<td>Cd(CF$_3$COCHCOR$_e$)$_2$</td>
<td>22.5</td>
<td>22.4</td>
<td>504</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>504</td>
</tr>
<tr>
<td>Cd(CF$_3$COCHCOR$_f$)$_2$</td>
<td>26.7</td>
<td>26.8</td>
<td>420</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>420</td>
</tr>
</tbody>
</table>

* mass spectrometry

e not recorded

$^a_{\text{2-naphthyl}}; \quad ^b_{\text{phenyl}}; \quad ^c_{\text{C}_4\text{H}_9}; \quad ^d_{\text{i-C}_3\text{H}_7}; \quad ^e_{\text{t-C}_4\text{H}_9}; \quad ^f_{\text{CH}_3}$
### TABLE III-2

Reaction Conditions for Direct Electrochemical Synthesis of Cadmium(II) \(-\beta\)-Diketonates

<table>
<thead>
<tr>
<th>Compound</th>
<th>Vol. Acetonitrile (mL)</th>
<th>Vol. and/or Wt. of Ligand</th>
<th>Voltage (V)</th>
<th>Initial Current (mA)</th>
<th>Time (h)</th>
<th>Cd Dissolved (g)</th>
<th>Wt. Product Obtained (g)</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd(acac)_2</td>
<td>40</td>
<td>10 mL</td>
<td>16</td>
<td>20</td>
<td>4.0</td>
<td>0.15</td>
<td>0.26</td>
<td>62.5</td>
</tr>
<tr>
<td>Cd(acac)_2 bipy</td>
<td>40</td>
<td>10 mL/0.79 g</td>
<td>8</td>
<td>20</td>
<td>2.3</td>
<td>0.11</td>
<td>0.28</td>
<td>60.9</td>
</tr>
<tr>
<td>Cd(acac)_2 phen</td>
<td>40</td>
<td>5 mL/1.0 g</td>
<td>11</td>
<td>20</td>
<td>12.0</td>
<td>0.37</td>
<td>0.57</td>
<td>64.8</td>
</tr>
<tr>
<td>Cd(acac)_2 TMED</td>
<td>40</td>
<td>5 mL/5 mL</td>
<td>16</td>
<td>20</td>
<td>6.4</td>
<td>0.18</td>
<td>0.38</td>
<td>55.9</td>
</tr>
<tr>
<td>Cd(CF₃COCHRₐ)₂</td>
<td>40</td>
<td>1.4 g</td>
<td>10</td>
<td>20</td>
<td>14.0</td>
<td>0.41</td>
<td>1.65</td>
<td>70.1</td>
</tr>
<tr>
<td>Cd(CF₃COCHRₐ)₂</td>
<td>45</td>
<td>1.8 g</td>
<td>11</td>
<td>20</td>
<td>15.0</td>
<td>0.31</td>
<td>0.89</td>
<td>60.3</td>
</tr>
<tr>
<td>Cd(CF₃COCHRₐ)₂</td>
<td>20</td>
<td>2.0 mL</td>
<td>45</td>
<td>30</td>
<td>16.0</td>
<td>0.16</td>
<td>0.45</td>
<td>63.2</td>
</tr>
<tr>
<td>Cd(CF₃COCHRₐ)₂</td>
<td>20</td>
<td>3.0 mL</td>
<td>26</td>
<td>30</td>
<td>16.0</td>
<td>0.16</td>
<td>0.46</td>
<td>67.6</td>
</tr>
<tr>
<td>Cd(CF₃COCHRₐ)₂</td>
<td>20</td>
<td>1.0 mL</td>
<td>44</td>
<td>20</td>
<td>5.0</td>
<td>0.11</td>
<td>0.36</td>
<td>73.5</td>
</tr>
<tr>
<td>Cd(CF₃COCHRₐ)₂</td>
<td>20</td>
<td>2.0 mL</td>
<td>18</td>
<td>10</td>
<td>12.0</td>
<td>0.12</td>
<td>0.29</td>
<td>68.8</td>
</tr>
</tbody>
</table>

R = \(^{a}\)2-naphthyl, \(^{b}\)phenyl, \(^{c}\)i-C₄H₉, \(^{d}\)i-C₃H₇, \(^{e}\)t-C₄H₉ and \(^{f}\)CH₃
TABLE III-3

I.R. Spectra of Cadmium(II) Complexes of β-Diketonates and some Adducts

<table>
<thead>
<tr>
<th>Hacac</th>
<th>Cd(acac)$_2$</th>
<th>Cd(acac)$_2$ bipy</th>
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</thead>
<tbody>
<tr>
<td>480 m</td>
<td>510 s</td>
<td>500 w</td>
</tr>
<tr>
<td>625 m</td>
<td>625 m</td>
<td>630 m</td>
</tr>
<tr>
<td>730 m</td>
<td>760 s</td>
<td>730 w</td>
</tr>
<tr>
<td>905 s</td>
<td>900 s</td>
<td>770 s</td>
</tr>
<tr>
<td>990 s</td>
<td>995 s</td>
<td>905 s</td>
</tr>
<tr>
<td>1160 s</td>
<td>1220 s</td>
<td>1000 s</td>
</tr>
<tr>
<td>1200 s</td>
<td>1360 s</td>
<td>1040 w</td>
</tr>
<tr>
<td>1230 w</td>
<td>1410 s</td>
<td>1150 w</td>
</tr>
<tr>
<td>1290 w</td>
<td>1490 s</td>
<td>1230 m</td>
</tr>
<tr>
<td>1350 m</td>
<td>1590 s</td>
<td>1310 w</td>
</tr>
<tr>
<td>1410 m</td>
<td>2990 m</td>
<td>1350 vw</td>
</tr>
<tr>
<td>1600 s</td>
<td></td>
<td>1440 m</td>
</tr>
<tr>
<td>1690 s</td>
<td></td>
<td>1510 m</td>
</tr>
<tr>
<td>1710 w</td>
<td></td>
<td>1590 m</td>
</tr>
<tr>
<td>2990 s</td>
<td></td>
<td>2995 w</td>
</tr>
</tbody>
</table>

s = strong; m = medium; w = weak; vw = very weak
### TABLE III-3 (cont'd)

<table>
<thead>
<tr>
<th>Cd(acac)$_2$phen</th>
<th>Cd(acac)$_2$TMED</th>
<th>CdL$_2^b$</th>
<th>CdL$_2^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>500 m</td>
<td>510 m</td>
<td>590 w</td>
<td>590 m</td>
</tr>
<tr>
<td>635 w</td>
<td>540 w</td>
<td>675 vw</td>
<td>645 m</td>
</tr>
<tr>
<td>720 w</td>
<td>635 w</td>
<td>700 s</td>
<td>710 s</td>
</tr>
<tr>
<td>730 m</td>
<td>660 s</td>
<td>770 w</td>
<td>730 m</td>
</tr>
<tr>
<td>765 m</td>
<td>710 w</td>
<td>805 s</td>
<td>775 s</td>
</tr>
<tr>
<td>790 w</td>
<td>760 m</td>
<td>870 m</td>
<td>805 w</td>
</tr>
<tr>
<td>855 m</td>
<td>810 w</td>
<td>910 w</td>
<td>820 w</td>
</tr>
<tr>
<td>915 m</td>
<td>915 s</td>
<td>970 m</td>
<td>940 m</td>
</tr>
<tr>
<td>990 w</td>
<td>950 m</td>
<td>1055 w</td>
<td>1010 m</td>
</tr>
<tr>
<td>1010 m</td>
<td>1025 s</td>
<td>1135 s</td>
<td>1030 m</td>
</tr>
<tr>
<td>1100 w</td>
<td>1095 w</td>
<td>1190 s</td>
<td>1075 m</td>
</tr>
<tr>
<td>1145 w</td>
<td>1135 w</td>
<td>1210 vw</td>
<td>1100 w</td>
</tr>
<tr>
<td>1195 w</td>
<td>1165 m</td>
<td>1240 m</td>
<td>1125 w</td>
</tr>
<tr>
<td>1220 w</td>
<td>1195 w</td>
<td>1260 m</td>
<td>1155 w</td>
</tr>
<tr>
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<td>1225 s</td>
<td>1300 s</td>
<td>1200 w</td>
</tr>
<tr>
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<td>1245 s</td>
<td>1390 w</td>
<td>1290 m</td>
</tr>
<tr>
<td>1395 s</td>
<td>1290 m</td>
<td>1430 m</td>
<td>1310 vw</td>
</tr>
<tr>
<td>1450 m</td>
<td>1360 m</td>
<td>1455 s</td>
<td>1440 w</td>
</tr>
<tr>
<td>1510 s</td>
<td>1390 w</td>
<td>1525 m</td>
<td>1470 m</td>
</tr>
<tr>
<td>1590 s</td>
<td>1455 w</td>
<td>1545 m</td>
<td>1490 m</td>
</tr>
<tr>
<td>2990 w</td>
<td>1510 m</td>
<td>1600 s</td>
<td>1540 m</td>
</tr>
<tr>
<td></td>
<td>1600 s</td>
<td>1580 s</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2990 w</td>
<td>1615 s</td>
<td></td>
</tr>
</tbody>
</table>

$^{b}$CF$_3$COCHCOC$_{10}$H$_7$

$^{c}$CF$_3$COCHCOC$_6$H$_5$
TABLE III-3 (cont'd)

<table>
<thead>
<tr>
<th>CdL&lt;sub&gt;d&lt;/sub&gt;</th>
<th>CdL&lt;sub&gt;e&lt;/sub&gt;</th>
<th>CdL&lt;sub&gt;f&lt;/sub&gt;</th>
<th>CdL&lt;sub&gt;g&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>590 s</td>
<td>535 m</td>
<td>580 m</td>
<td>580 m</td>
</tr>
<tr>
<td>610 w</td>
<td>570 w</td>
<td>630 w</td>
<td>660 w</td>
</tr>
<tr>
<td>705 m</td>
<td>590 w</td>
<td>705 s</td>
<td>735 m</td>
</tr>
<tr>
<td>745 w</td>
<td>640 w</td>
<td>740 w</td>
<td>780 m</td>
</tr>
<tr>
<td>790 s</td>
<td>720 s</td>
<td>785 w</td>
<td>810 w</td>
</tr>
<tr>
<td>840 m</td>
<td>770 w</td>
<td>805 s</td>
<td>860 s</td>
</tr>
<tr>
<td>870 s</td>
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<td>940 w</td>
</tr>
<tr>
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<td>810 s</td>
<td>950 m</td>
<td>1030 w</td>
</tr>
<tr>
<td>975 m</td>
<td>900 s</td>
<td>1020 w</td>
<td>1140 s</td>
</tr>
<tr>
<td>1080 w</td>
<td>950 m</td>
<td>1100 w</td>
<td>1190 m</td>
</tr>
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<td>1145 s</td>
<td>1040 m</td>
<td>1140 m</td>
<td>1230 m</td>
</tr>
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<td>1140 s</td>
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</tr>
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<td>1190 m</td>
<td>1260 m</td>
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<td>1235 w</td>
<td>1300 s</td>
<td>1500 m</td>
</tr>
<tr>
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<td>1280 w</td>
<td>1370 m</td>
<td>1535 m</td>
</tr>
<tr>
<td>1375 w</td>
<td>1300 s</td>
<td>1400 m</td>
<td>1635 s</td>
</tr>
<tr>
<td>1395 w</td>
<td>1390 m</td>
<td>1465 m</td>
<td></td>
</tr>
<tr>
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<td>1525 m</td>
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<td>1495 m</td>
<td>1630 s</td>
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</tr>
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<td>1500 m</td>
<td>1520 m</td>
<td>2990 m</td>
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</tr>
<tr>
<td>1535 s</td>
<td>1550 w</td>
<td></td>
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</tr>
<tr>
<td>1630 s</td>
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</tr>
<tr>
<td>2985 m</td>
<td>2990 m</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>d</sup>CF<sub>3</sub>COC<sub>CH</sub>CH<sub>(CH<sub>3</sub>)<sub>2</sub></sup>
<sup>e</sup>CF<sub>3</sub>COC<sub>CH</sub>(CH<sub>3</sub>)<sub>2</sub>
<sup>f</sup>CF<sub>3</sub>COC<sub>CH</sub>(CH<sub>3</sub>)<sub>3</sub>
<sup>g</sup>CF<sub>3</sub>COC<sub>CH</sub>CH<sub>3</sub>
TABLE III-4

$^{19}$F Resonance of Trifluoromethyl-$\beta$-Diketonates
Cd(CF$_3$COCHCOR)$_2$

<table>
<thead>
<tr>
<th>R</th>
<th>Chemical Shift$^a$</th>
<th>$\Delta$ Shift</th>
<th>This Work</th>
<th>Tanner (3Z)$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HL</td>
<td>CdL$_2$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Naphthyl</td>
<td>1.73</td>
<td>2.31</td>
<td>0.58</td>
<td>1.10</td>
</tr>
<tr>
<td>Phenyl</td>
<td>1.44</td>
<td>2.31</td>
<td>0.87</td>
<td>0.94</td>
</tr>
<tr>
<td>i-C$_4$H$_9$</td>
<td>1.15</td>
<td>2.31</td>
<td>1.16</td>
<td>0.94</td>
</tr>
<tr>
<td>i-C$_3$H$_7$</td>
<td>1.15</td>
<td>2.31</td>
<td>1.15</td>
<td>c</td>
</tr>
<tr>
<td>t-C$_4$H$_9$</td>
<td>1.44</td>
<td>2.31</td>
<td>0.87</td>
<td>c</td>
</tr>
<tr>
<td>CH$_3$</td>
<td>1.15</td>
<td>2.31</td>
<td>1.16</td>
<td>1.31</td>
</tr>
</tbody>
</table>

$^a$ reported in ppm ($\delta$) downfield from trifluoro acetic acid.

$^b$ the shifts of the $^{19}$F resonances are in reasonable agreement with the values obtained by Tanner in analogous complexes of InL$_3$, where L is CF$_3$COCHCOR$^-$. 

$c$ not recorded.
# TABLE II-5

Mass Spectrum of bis(4,4,4-Trifluoro-1-(2-Naphthyl)-1,3-Butanedionato) Cadmium(II)

<table>
<thead>
<tr>
<th>m/e</th>
<th>% R.A.</th>
<th>Provisional Assignment</th>
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<tbody>
<tr>
<td>266.00</td>
<td>28.48</td>
<td>$\text{CF}_3\text{COCHCOC}_7\text{H}_7^+$</td>
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<tr>
<td>267.00</td>
<td>3.40</td>
<td></td>
</tr>
<tr>
<td>320.00</td>
<td>6.60</td>
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</tr>
<tr>
<td>321.00</td>
<td>8.83</td>
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</tr>
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<td>322.00</td>
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</tr>
<tr>
<td>639.00</td>
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</tr>
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<td>68.67</td>
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</tr>
<tr>
<td>644.00</td>
<td>100.00</td>
<td>$\text{Ca}$(CF$_3$COCHCOC$_7$H$_7$)$_2^+$</td>
</tr>
<tr>
<td>645.00</td>
<td>26.60</td>
<td></td>
</tr>
</tbody>
</table>

Field Desorption

Base m/e: 644
Solvent: CHCl$_3$
TABLE III-6

Mass Spectrum of bis(4,4,4-Trifluoro-l-Phenyl-1,3-Butanedionate) Cadmium(II)

<table>
<thead>
<tr>
<th>m/e</th>
<th>% R.A.</th>
<th>Provisional Assignment</th>
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</thead>
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<td>35.00</td>
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</tr>
<tr>
<td>38.00</td>
<td>32.88</td>
<td></td>
</tr>
<tr>
<td>50.00</td>
<td>77.48</td>
<td></td>
</tr>
<tr>
<td>216.00</td>
<td>45.95</td>
<td>CF₃COHCOC₆H₅⁺</td>
</tr>
<tr>
<td>217.00</td>
<td>20.27</td>
<td></td>
</tr>
<tr>
<td>540.00</td>
<td>42.79</td>
<td></td>
</tr>
<tr>
<td>541.00</td>
<td>63.96</td>
<td></td>
</tr>
<tr>
<td>542.00</td>
<td>54.95</td>
<td></td>
</tr>
<tr>
<td>543.00</td>
<td>32.43</td>
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</tr>
<tr>
<td>544.00</td>
<td>100.00</td>
<td>Cd(CF₃COHCOC₆H₅)₂⁺</td>
</tr>
<tr>
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<td>18.92</td>
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</tr>
<tr>
<td>546.00</td>
<td>27.48</td>
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</tr>
</tbody>
</table>
TABLE III-7

Mass Spectrum of bis(1,1,1-Trifluoro-6-Methyl-2,4-Heptanedionate) Cadmium(II)

<table>
<thead>
<tr>
<th>m/e</th>
<th>% R.A.</th>
<th>Provisional Assignment</th>
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</thead>
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<td></td>
</tr>
<tr>
<td>72.00</td>
<td>1.50</td>
<td></td>
</tr>
<tr>
<td>130.00</td>
<td>17.02</td>
<td></td>
</tr>
<tr>
<td>195.00</td>
<td>2.22</td>
<td></td>
</tr>
<tr>
<td>196.00</td>
<td>3.76</td>
<td>( \text{CF}_3\text{COCHCOCH}_2\text{CH(CH}_3)_2\text{H}^{+} )</td>
</tr>
<tr>
<td>221.00</td>
<td>1.43</td>
<td></td>
</tr>
<tr>
<td>252.00</td>
<td>1.86</td>
<td></td>
</tr>
<tr>
<td>496.00</td>
<td>2.36</td>
<td></td>
</tr>
<tr>
<td>499.00</td>
<td>25.97</td>
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</tr>
<tr>
<td>500.00</td>
<td>41.42</td>
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</tr>
<tr>
<td>502.00</td>
<td>85.41</td>
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<tr>
<td>503.00</td>
<td>100.00</td>
<td>( \text{Cd(CF}_3\text{COCHCOCH}_2\text{CH(CH}_3)_2\text{H}^{+} )</td>
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<tr>
<td>504.00</td>
<td>46.28</td>
<td></td>
</tr>
<tr>
<td>505.00</td>
<td>18.81</td>
<td></td>
</tr>
</tbody>
</table>
TABLE III-8
Mass Spectrum of bis(1,1,1-Trifluoro-5-Methyl-2,4-Hexanedioniate) Cadmium(II)

<table>
<thead>
<tr>
<th>Field Desorption</th>
<th>Provisional Assignment</th>
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<tbody>
<tr>
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<tr>
<td>Solvent: CHCl₃</td>
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<table>
<thead>
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<th>m/e</th>
<th>% R.A.</th>
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<td>180.95</td>
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<tr>
<td>182.00</td>
<td>8.74</td>
<td>CF₃COCHCOCH(CH₃)₂⁺</td>
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<tr>
<td>237.84</td>
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</tr>
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<td>298.12</td>
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<td></td>
</tr>
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<td>384.34</td>
<td>3.68</td>
<td></td>
</tr>
<tr>
<td>467.87</td>
<td>5.06</td>
<td></td>
</tr>
<tr>
<td>470.00</td>
<td>2.30</td>
<td></td>
</tr>
<tr>
<td>472.03</td>
<td>65.75</td>
<td></td>
</tr>
<tr>
<td>473.56</td>
<td>93.10</td>
<td></td>
</tr>
<tr>
<td>474.75</td>
<td>63.91</td>
<td></td>
</tr>
<tr>
<td>476.00</td>
<td>100.00</td>
<td>Cd(CF₃COCHCOCH(CH₃)₂)⁺</td>
</tr>
<tr>
<td>477.75</td>
<td>28.74</td>
<td></td>
</tr>
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</table>
TABLE III-9

Mass Spectrum of bis(1,1,1-Trifluoro-5,5-Dimethyl-2,4-Hexanedionate) Cadmium(II)

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</tr>
<tr>
<td>85.00</td>
<td>3.23</td>
<td></td>
</tr>
<tr>
<td>100.00</td>
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</tr>
<tr>
<td>130.00</td>
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<td>CdO⁺</td>
</tr>
<tr>
<td>219.00</td>
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</tr>
<tr>
<td>376.00</td>
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</tr>
<tr>
<td>408.00</td>
<td>3.23</td>
<td></td>
</tr>
<tr>
<td>418.00</td>
<td>3.23</td>
<td></td>
</tr>
<tr>
<td>445.00</td>
<td>4.99</td>
<td></td>
</tr>
<tr>
<td>498.00</td>
<td>6.01</td>
<td></td>
</tr>
<tr>
<td>500.00</td>
<td>33.28</td>
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</tr>
<tr>
<td>501.00</td>
<td>51.47</td>
<td></td>
</tr>
<tr>
<td>502.00</td>
<td>71.70</td>
<td></td>
</tr>
<tr>
<td>503.00</td>
<td>55.57</td>
<td></td>
</tr>
<tr>
<td>504.00</td>
<td>100.00</td>
<td>Cd(CF₃COCHCO(CH₃)₃)₂⁺</td>
</tr>
<tr>
<td>506.00</td>
<td>21.11</td>
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</tr>
</tbody>
</table>
TABLE III-10

Mass Spectrum of bis(1,1,1-Trifluoro-2,4-Pentanedionate Cadmium(II))

<table>
<thead>
<tr>
<th>m/e</th>
<th>% R.A.</th>
<th>Provisional Assignment</th>
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</thead>
<tbody>
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<tr>
<td>130.08</td>
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</tr>
<tr>
<td>153.86</td>
<td>8.98</td>
<td>$\text{CF}_3\text{COCHCOCH}_3^+$</td>
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<tr>
<td>375.64</td>
<td>13.67</td>
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</tr>
<tr>
<td>378.09</td>
<td>10.55</td>
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</tr>
<tr>
<td>379.71</td>
<td>7.81</td>
<td></td>
</tr>
<tr>
<td>415.69</td>
<td>35.94</td>
<td></td>
</tr>
<tr>
<td>416.71</td>
<td>30.86</td>
<td></td>
</tr>
<tr>
<td>419.75</td>
<td>67.58</td>
<td></td>
</tr>
<tr>
<td>420.00</td>
<td>100.00</td>
<td>$\text{Cd}($$\text{CF}_3\text{COCHCOCH}_3$$)_2^+$</td>
</tr>
<tr>
<td>421.81</td>
<td>16.02</td>
<td></td>
</tr>
<tr>
<td>Compound</td>
<td>-CH&lt;sub&gt;3&lt;/sub&gt;</td>
<td>-CH</td>
</tr>
<tr>
<td>------------</td>
<td>-----------------</td>
<td>------</td>
</tr>
<tr>
<td>Hacac&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.30 (s)</td>
<td>5.9 (s)</td>
</tr>
<tr>
<td>Cd(acac)&lt;sub&gt;2&lt;/sub&gt;&lt;sup&gt;a&lt;/sup&gt;</td>
<td>2.10 (s)</td>
<td>5.2 (s)</td>
</tr>
<tr>
<td>Cd(acac)&lt;sub&gt;2&lt;/sub&gt;bipy&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.70 (s)</td>
<td>5.1 (s)</td>
</tr>
<tr>
<td>Cd(acac)&lt;sub&gt;2&lt;/sub&gt;phen&lt;sup&gt;b&lt;/sup&gt;</td>
<td>1.60 (s)</td>
<td>5.0 (s)</td>
</tr>
<tr>
<td>Cd(acac)&lt;sub&gt;2&lt;/sub&gt;TMED&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.98 (s)</td>
<td>5.4 (s)</td>
</tr>
<tr>
<td></td>
<td>2.25 (s)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.41 (s)</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> run in MeOH-d<sub>4</sub>
<sup>b</sup> run in DMSO-d<sub>6</sub>
<sup>c</sup> run in CDCl<sub>3</sub>
<sup>s</sup> singlet
<sup>m</sup> multiplet

Spectra are reported in ppm (δ) downfield from internal TMS
3.4 Results and Discussion

3.4.1 General

Complexes of metal ions with acetylacetones have been studied for many years. Metal acetylacetonates have been used as polymerisation initiators after irradiation with high energy rays (33). They are also used in hydrogenating catalysts, and as bactericides.

The acetylacetonates are regarded as having delocalised bonding in the chelate rings, resulting in equalization of the pairs of C-C, C-O and M-O distances.

![Diagram](image)

**Figure 17**

According to the result of an X-ray analysis of Fe(acac)$_3$ (50), the chelate ring is planar and symmetrical ($C_{2v}$) and the two C=O are equivalent, as are the two C≡C bonds in the ring. This result provides evidence for the existence of delocalisation in the chelate ring (Figure 17), and confirms the proposal of Calvin and Wilson (34) that the
M-O bond is also involved, thus explaining the high stability of acetylacetone chelates in general.

The synthesis of neutral chelate compounds normally begins with an aqueous solution of a salt of the metal in question; addition of the chelating agent is followed by extraction, precipitation, crystallisation, etc., as appropriate. Since the parent neutral compounds are weakly acid, the direct reaction

\[ M + nHL + ML_n + n/2H_2 \]

is rarely possible, but for ligands such as 2,4-pentanedionate, etc., this reaction goes directly when the metal is the anode of a non-aqueous solution cell (51). As with other electrochemical methods, the preparation is simple and usually rapid, and affords the products in gram quantities from the readily available metals. The current efficiency is always low, and equal to \( 1/n \) mol-Faraday\(^{-1} \), where \( n \) is the oxidation number of the metal in the product. This leads to the overall stiochiometric equations

Cathode: \( n\text{Hacac} + n\text{e}^- + n\text{acac}^- + n/2\text{H}_2(g) \)

Anode: \( n\text{acac}^- + M + M(\text{acac})_n + n\text{e}^- \)

In the present work, the measured current efficiencies are
\[
\text{Cd}(+) / \text{acac} / \text{Pt}(-) + 0.54 \text{ mol F}^- \quad \text{(theory 0.50)}
\]
\[
\text{Cd}(+) / \text{acac+bipy} / \text{Pt}(-) + 0.52 \text{ mol F}^- \quad \text{(theory 0.50)}
\]

These results are in a good agreement with the mechanism proposed above, as is the production of a gas, believed to be hydrogen, at the cathode. The most important feature of this method of synthesis is that it offers a rapid convenient and simple route for the direct electrochemical synthesis of these cadmium complexes, especially since the oxidation of metal occurs at room temperature and good samples are obtained.

In this chapter, characterization of the products was established by metal analysis (Table III-1), mass spectra (Tables III-5-10) and infrared spectroscopy (Table III-3). In view of interest in the synthesis of Cd(II) complexes with bidentate ligands, we made a number of attempts to prepare Cd(acac)\textsubscript{3} by direct electrochemical synthesis in the hope of investigating the stereochemical aspects of the method, but without any success. The reaction condition changes involved solvent (acetone, acetonitrile), concentration of ligand (acac, 3mL and 9mL), time of electrolysis (5h, 18h), and amount of Et\textsubscript{3}N (1mL and 4mL). The same product was obtained in each case, Cd(acac)\textsubscript{2}.

This problem was not investigated further. Electrochemical oxidation of cadmium under various conditions gave rise to a series of compounds and adducts, and the spectroscopic information on these will now be discussed.
3.5 Vibrational Spectroscopy

The frequencies of coordinated TMED have been reported previously (58), and we assume that the ligand is coordinated as a bidentate donor in the present complex. Chelate-type diamines display two bands, assigned as CH$_2$ rocking vibrations at approximately 810 and 770 cm$^{-1}$, while intermolecular bridging leads to a trans conformation in the diamine, with I.R. bands at 870 and 790 cm$^{-1}$ (58). In our case, the TMED complex show bands at 810 and 760 cm$^{-1}$, which suggest the presence of bidentate TMED.

In phenanthroline' (39), two intense bands appeared at approximately 725 cm$^{-1}$ assigned to the out-of-plane deformation of the hydrogen atoms on the heterocyclic rings, and at 850 cm$^{-1}$ to the hydrogens on the centre ring. Also the 1500-1600- cm$^{-1}$ region is assigned to aromatic C=C stretching. In 2,2'-bipyridine (39), three strong bands are present, one near 760 cm$^{-1}$ assigned to out-of-plane bending of ring hydrogens, one near 1450 cm$^{-1}$ which is probably a ring frequency, and a ring frequency near 1600 cm$^{-1}$.

The infrared spectra of the 2,2'-bipyridine', 1,10-phenanthroline and N,N,N',N'-tetramethylethylenediamine adducts by Cd(acac)$_2$ confirm the bidentate coordination of these ligands and thus the compounds are formulated as the six-coordinate L$_2$Cd.bipy, etc., species (L=acac). The
I.R. also showed a group of intense absorptions between 1610 and 1410 cm\(^{-1}\), corresponding to \(\nu(C=O)\) and \(\nu(C=C)\) of the ligand.

### 3.6 Mass Spectral Studies on CdL\(_2\)

The mass spectra for ML\(_2\) compounds typically showed ML\(_2^+\) and HL\(^+\). The main feature of these spectra is the calculation of molecular weight; a strong molecular ion peak \(M^+\) at 644 m/e for Cd(CF\(_3\)COCHCOC\(_{10}H_7\))\(_2\); 544 m/e for Cd(CF\(_3\)COCHCOC\(_6H_5\))\(_2\) with a relative intensity of 100%, suggests and supports the formulation as CdL\(_2\).

### 3.7 \(^1\)H NMR Spectroscopy

The \(^1\)H NMR spectra of Cd(acac\(_2\))\(_2\)TMED and of TMED itself, taken at ambient temperature in the solvent CDCl\(_3\) using TMS as internal standard, showed the expected resonance pattern (Table III-11). The free ligand spectrum consisted of two sharp singlets at \(\delta=2.61\) (NMe\(_2\)) and 2.80 (\(-CH_2-CH_2-\)) ppm from TMS. The Cd(acac\(_2\))\(_2\)TMED adduct presented three sharp singlets between 2.0-2.5 ppm. Integration values allowed us to assign the signal at 2.41 ppm as the methylene protons of the nitrogen ligand. Due to the similarity of the chemical shifts of the CH\(_3\) groups from TMED and acac, it is difficult to assign properly the resonances, but we propose 2.25 and 1.98 ppm for -NMe\(_2\) and -Me resonances respectively.

The \(^1\)H NMR spectra of the bipy and phen complexes,
Figure 18 ORTEP Plot of C_{22}H_{22}CdO_{4}N_{2}
although giving less detailed information, also confirm the formulation as adducts of Cd(acac)$_2$.

3.8 $^{19}$F NMR of Diketones

Use of the partially fluorinated diketones allows the $^{19}$F resonances of free and complexed ligand to be used to investigate the chemical shift. Table III-4 shows the $^{19}$F chemical shifts for chelates of cadmium(II) and the parent diketones $\text{CF}_3\text{COCH}_2\text{COR}$, with reference to trifluoroacetic acid.

The $^{19}$F spectrum of each CdL$_2$ complex is a singlet (half width 113.2 Hz). The change in the $^{19}$F resonance frequency on complex formation is typically 0.8 ppm which is of the same order of magnitude as reported earlier by Tanner, Tuck and Wells (32) for the analogous InL$_3$ complexes. The accuracy of the experimental results does not allow any detailed interpretation at this point.

3.9 X-Ray Crystallographic Results

The crystal structure of Cd(acac)$_2$phen has been determined by Dr. M. Khan from single crystal X-ray diffractometer data. The cadmium atom is coordinated by two oxygen atoms from each acac ligand, with the remaining two sites about six-coordinate cadmium being occupied by the two nitrogen atoms from 1,10-phenanthroline. Figure 18 shows the ORTEP projection of $\text{C}_{22}\text{H}_{22}\text{CdO}_4\text{N}_2$. 
E. N. Maslen, et al. (52), reported the crystal structure of bis-acetylacetonatocadmium(II). The structure is comprised of linear chains of cadmium atoms spaced at 3.768 and 3.718 Å; the cadmium atoms are bridged by one oxygen atom from each ligand [Cd-O 2.288-2.353Å], the other two coordination sites around cadmium are occupied by the other two non-bridging oxygen atoms [Cd-O 2.221, 2.250Å]. Figure 19 shows the general stereochemistry of this structure.

The cadmium environment is octahedral in Cd(acac)$_2$ to a first approximation, and is composed by four bridging ligand and the cis pair of non-bridging ligand oxygen atoms. The angular geometry of the octahedron is quite distorted, the angles between adjacent Cd-O bonds ranging from 72.8 to 113.1° and the angles between opposed Cd-O from 153.3 to 171.4°.

Unlike Cd(acac)$_2$, the structure of Cd(acac)$_2$phen reveals a mononuclear six-coordinate species with a CdO$_4$N$_2$ kernel. The stereochemistry is essentially octahedral, with distortions due to the bite of the bidentate acac and phen ligands. The structural details are summarized in Tables III-12 and III-13. In addition to the comparison of this molecule with the polymeric Cd(acac)$_2$, there is a third relevant structure, that of the [Cd(acac)$_3$]$^{2-}$ anion (46), which has approximately trigonal prismatic
six-coordinate stereochemistry. A comparison of the M-O bond lengths and angles is given in Table III-14. It appears that the type of coordination has little effect on the ligand bite angle, but these are substantial variations in the Cd-O bond distances. Further work on this topic is clearly needed. Figure 20 shows the mean ligand geometry of the two ligand systems and the associated cadmium atoms. (Distances in (Å), angles in (°)).

3.10. General Conclusions

The electrochemical method has been shown to be a simple and useful route to various β-diketonate complexes of cadmium(II), and to adducts of these species. The Cd(acac)₂ molecule is clearly a Lewis acid, and a study of the solution equilibria.

Cd(acac)₂ + L ⇌ Cd(acac)₂L by Cd NMR spectroscopy could be of interest. Equally one should investigate the effect of substituent groups on the β-diketonate (CF₃, phenyl, etc.) on this Lewis acid behaviour, and on the degree of association in solution.
Figure 19

Figure 20
**TABLE III-12**

Summary of Crystal Data, Intensity Collection, and Structural refinement for Cd(acac)$_2$(phen)·(Cd$_{22}$H$_{24}$N$_2$O$_4$).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cell constants</strong></td>
<td></td>
</tr>
<tr>
<td>a</td>
<td>16.159(3) Å</td>
</tr>
<tr>
<td>b</td>
<td>10.292(2) Å</td>
</tr>
<tr>
<td>c</td>
<td>12.694(3) Å</td>
</tr>
<tr>
<td>U</td>
<td>2111(2) Å$^3$</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>Pbcn(D$^{14}_2$h; No. 60)</td>
</tr>
<tr>
<td><strong>Z</strong></td>
<td>4</td>
</tr>
<tr>
<td><strong>M</strong></td>
<td>492.84 g. mol$^{-1}$</td>
</tr>
<tr>
<td>$\rho$(calc.)</td>
<td>1.55 g. cm$^{-3}$</td>
</tr>
<tr>
<td><strong>Absorption coeff. ($\mu$)</strong></td>
<td>9.61 cm$^{-1}$</td>
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<tr>
<td><strong>Crystal dimensions</strong></td>
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</tr>
<tr>
<td><strong>Radiation</strong></td>
<td>MoK$_\alpha$(λ=0.71069 Å)</td>
</tr>
<tr>
<td>$2\theta$ max</td>
<td>50.0°</td>
</tr>
<tr>
<td><strong>Scan type</strong></td>
<td>coupled $\theta$ (crystal)/2$\theta$(counter)</td>
</tr>
<tr>
<td><strong>Scan width</strong></td>
<td>K$\alpha_1$-1° to K$\alpha_2$+1°</td>
</tr>
<tr>
<td><strong>Background time/s.time</strong></td>
<td>0.5</td>
</tr>
<tr>
<td><strong>Total reflections meas.</strong></td>
<td>1563 (h,k,l)</td>
</tr>
<tr>
<td><strong>Unique averaged data</strong></td>
<td>1324[($F_o^2$) &gt; $\sigma(F_o)^2$]</td>
</tr>
<tr>
<td>R = $[\Sigma</td>
<td>F_o</td>
</tr>
<tr>
<td>$R_w = [\Sigma w^2(F_o^2 - \langle F_o^2 \rangle)]^{1/2}$</td>
<td>0.0277</td>
</tr>
</tbody>
</table>
TABLE III-13

Interatomic Distances (Å) and Angles (°), with standard deviations in parenthesis

(a) Bonding

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distance (Å)</th>
<th>Bond</th>
<th>Distance (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd-O(1)</td>
<td>2.223(3)</td>
<td>Cd-O(2)</td>
<td>2.272(3)</td>
</tr>
<tr>
<td>Cd-N</td>
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(b) Bond Angles

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### TABLE III-14

A Comparison of Bond Lengths and Angles in Cd-acac species

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REFERENCES


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Post Graduate Scholarships