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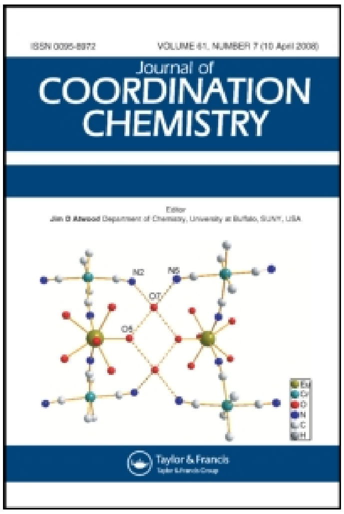

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# COMPLEXES OF COPPER(II), ZINC(II) AND CADMIUM(II) WITH 2-{[2-(N,N-DIMETHYL)- AMINOETHYL]IMINOMETHYL} PYRROLE, AND THE CRYSTAL STRUCTURE OF BIS{2-[[2- (N,N-DIMETHYL) AMINOETHYL]IMINOMETHYL]- PYRROLATO} CADMIUM(II)

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# COMPLEXES OF COPPER(II), ZINC(II) AND CADMIUM(II) WITH 2-{[2-(*N*,*N*-DIMETHYL)-AMINOETHYL]IMINOMETHYL}PYRROLE, AND THE CRYSTAL STRUCTURE OF BIS{2-[[2-(*N*,*N*-DIMETHYL)AMINOETHYL]IMINOMETHYL]-PYRROLATO}CADMIUM(II)

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The complexes $ML_2$ (M = Cu, Zn and Cd) were prepared by electrochemical oxidation of the appropriate metal in a solution of the Schiff base 2-{[2-(*N*,*N*-dimethyl)aminoethyl]iminomethyl}pyrrole (HL) in acetonitrile. The structure of $CdL_2$ was determined by X-ray diffraction methods. The cadmium atom lies in a distorted tetrahedral environment defined by the two azomethine nitrogens and the two pyrrole nitrogens, at distances of 2.277(5) and 2.266(4) Å, respectively. The two amino nitrogens lie much farther from the cadmium atom, at 2.731(5) Å. The vibrational, electronic and $^1H$ NMR spectra of the complexes are discussed and related to the structure.

**Keywords:** Copper, zinc, cadmium, Schiff bases, electrochemical synthesis, X-ray structure

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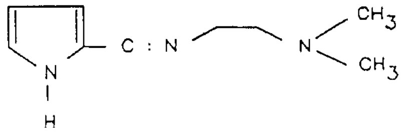
## INTRODUCTION

This work continues our studies of neutral complexes of Schiff bases derived from 2-pyrrolecarbaldehyde (pyr) by electrochemical oxidation of a sacrificial anode in non-aqueous solvents. The non-pyr moieties of the Schiff bases used previously have included anilines, in which case the only ligand donor atom are the pyrrole and imine nitrogens,[1–3] 2-aminophenol,[4] cysteamine and bis(2-aminophenyl)disulfide;[5] in the latter three cases coordination can also take place *via* oxygen or sulfur. We have now applied the same method to the synthesis of copper, zinc and cadmium complexes of the Schiff base 2-{[2-(*N*,*N*-dimethyl)amino]iminomethyl}pyrrole



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which can theoretically act as a mono-, bi- or terdentate ligand. The crystal structure of bis{2-[[2-(*N*,*N*-dimethyl)aminoethyl]iminomethyl]pyrrolato}cadmium(II) is also reported.

## EXPERIMENTAL

### *Materials and methods*

All solvents, 2-pyrrolecarbaldehyde and *N*,*N*-dimethylenediamine are commercially available and were used without further purification. The metals (Ega Chemie) were used as *ca* 2 × 2 cm plates. The ligand was prepared by reaction of equimolecular amounts of the aldehyde (1.902 g, 20 mmol) and amine (1.763 g, 20 mmol) until the theoretical amount of water had been collected in a Dean-Stark trap; the oily product was washed with diethyl ether and cyclohexane and its purity checked by recording its IR and $^1$H NMR spectra.

N, C, and H contents of the complexes were determined on a Carlo-Erba EA1108 microanalyser. IR spectra were recorded in KBr mulls on a Perkin-Elmer 180 spectrophotometer. Proton NMR spectra were recorded on a Brucker WM 250 MHz apparatus using DMSO as solvent; chemical shifts were determined against TMS as internal standard. Solid reflectance spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. Magnetic moments were measured using a SQUID instrument.

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### *Preparation of the complexes*

The electrochemical method used was similar to that described previously.[6] Briefly, the cell was a 100 cm$^3$ tall-form beaker fitted with a rubber bung through which the electrochemical leads passed. The anode was suspended from a platinum wire and the cathode was another platinum wire. Direct current was obtained from a purpose-built D.C. power supply. The cell can be summarized as $\mathrm{Pt}_{(-)}/\mathrm{MeCN} + \mathrm{HL}/\mathrm{M}_{(+)}$; M = Cu, Zn, Cd; HL = Schiff base.

### *Copper(II) complex*

The electrochemical oxidation of copper in a solution of HL (0.26 g, 1.6 mmol) in $CH_3CN$ (50 cm$^3$) containing a small amount of tetraethylammonium perchlorate (20 mg) for 2 h at 22 V and 10 mA resulted in the loss of 49.6 mg of copper from the anode, ($E_f = 1.05$ mol F$^{-1}$). Hydrogen was evolved at the cathode during the electrolysis. The reaction mixture was filtered to remove any precipitated particles of metal, and the filtrate was left to concentrate by evaporation at room temperature. After concentration, the oil obtained was stirred with cyclohexane to precipitate a dark brown solid. Anal.: calcd. for $[CuL_2]\cdot 3H_2O$: C, 48.5; N, 18.9; H, 7.6%. Found: C, 48.8; N, 18.4; H, 7.4%.

### *Zinc complex*

The oxidation of zinc to produce $ZnL_2$ followed the same course as for copper. Electrolysis of a solution of HL (0.28 g, 1.7 mmol) and tetraethylammonium perchlorate (20 mg) in $CH_3CN$ (50 cm$^3$) for 2 h at 15 V and 20 mA led to the dissolution of 49.2 mg of zinc ($E_f = 0.50$ mol $F^{-1}$). By evaporation of the resulting solution, a powder identified as $ZnL_2$ was isolated. Anal.: calcd. for $[ZnL_2] \cdot 3H_2O$: C, 48.3; N, 18.8; H, 7.6%. Found: C, 48.4; N, 18.5; H, 7.6%.

### *Cadmium complex*

A similar experiment (25 V, 20 mA, 2 h) with cadmium as anode and 0.32 g (1.9 mmol) of HL in 50 $cm^3$ of $CH_3CN$, dissolved 0.83 mg of cadmium ($E_f = 0.49$ mol $F^{-1}$) to yield a yellow solution from which a powder precipitated on slow concentration and addition of diethylether. The precipitate was collected, washed with acetonitrile and diethylether, dried *in vacuo* and identified as $CdL_2$. The remaining solution phase was concentrated at room temperature to give yellow crystals of $CdL_2$ suitable for X-ray studies. Anal.: calcd. for $[CdL_2]$: C, 49.0; N, 19.1; H, 6.4%. Found: C, 48.8; N, 19.3; H, 6.8%.

### *Crystal data*

$Cd[C_9H_{14}N_3]_2$, $M = 440.86$, orthorhombic, space group *Pbcn*, (No. 60), $a = 9.5114(8)$, $b = 11.5136(7)$, $c = 18.279(2)$ Å, $U = 2002.1(5)$ Å$^3$ (by least-squares refinement of diffractometer angles for 20 automatically centred reflections, $12 < \Theta < 35°$, $\lambda = 1.54184$ Å), $Z = 4$, $Dc = 1.462$ g cm$^{-3}$. Prismatic crystals with dimensions 0.15 × 0.25 × 0.35 mm, $\mu(\mathrm{MoK}\alpha) = 90.54$ cm$^{-1}$.

### *Data collection and processing*

CAD4 diffractometer, $\omega/2\Theta$ mode with $\omega$ scan width $= 0.85 + 0.15 \tan \Theta$, graphite monochromated CuK$\alpha$ radiation, 1561 reflections measured ($0 < \Theta < 60°$, $-1 \leqslant h \leqslant 12$, $0 \leqslant k \leqslant 10$, $0 \leqslant l \leqslant 19$), 1383 unique ($R_{int} = 0.025$), 1163 and $I \leqslant 3\sigma(I)$; Lorentz and polarization corrections. Absorption corrections were applied at a later stage in the refinement[7] (max., min. transmission factors = 1.453, 0.859). The intensity of a standard reflection was essentially constant throughout the experiment.

### *Structure analysis and refinement*

Standard direct methods followed by normal difference Fourier techniques. Full-matrix least-squares refinement with all non-H atoms anisotropic and hydrogens included, as fixed contributors, at positions found in difference synthesis, with one overall isotropic temperature factor which refined to $U_{iso} = 0.15(1)$ Å$^2$. The function minimized, $\Sigma w(|F_0| - |F_c|)^2$, with the weighting scheme $w = 1/[\sigma^2(F_0) + 0.001F_0^2]$, gave satisfactory statistical analyses. Final $R = [\Sigma(|F_0| - |F_c|)/\Sigma|F_0|]$ and $R' = \{[\Sigma w(|F_0| - |F_c|)^2/\Sigma w|F_0|^2]^{1/2}\}$ values were 0.039 and 0.043, respectively. Program used: SHELX-76.[8] Scattering factors for non-H atoms were from Cromer and Mann[9] with corrections for anomalous dispersion from Cromer and Liberman,[10] for H from Stewart, Davidson and Simpson.[11] Crystallographic data can be obtained through the Fachinformationszentrum Energie, Physik, Mathematik D-7514 Eggenstein-Leopoldshafen.

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## RESULTS AND DISCUSSION

The electrochemical oxidation of copper, zinc or cadmium in the presence of the Schiff base HL led to complexes of general formula $ML_2$, where L is the monoanionic form of the ligand.

For copper the electrochemical efficiency, $E_f$, defined as moles of metal dissolved per Faraday of charge, was close to 1.0 mol $F^{-1}$, indicating that the formation of copper(I) at the anode is followed by oxidation to copper(II) in solution, in accordance with the following scheme.

$$\begin{aligned} &\text{Cathode:} && HL + e^- \rightarrow L^- + 1/2\,H_2 \\ &\text{Anode:} && L^- + Cu \rightarrow [CuL] + e^- \\ &[CuL] + HL \rightarrow [CuL_2] + 1/2\,H_2 && \end{aligned}$$

For zinc and cadmium $E_f$ was close to 0.5 mol $F^{-1}$, corresponding to the process below.

$$\begin{aligned} &\text{Cathode:} && 2HL + 2e^- \rightarrow 2L^- + H_2 \\ &\text{Anode:} && 2L^- + M \rightarrow [ML_2] + 2e^- \end{aligned}$$

Attempts to prepare mixed complexes by adding 1,10-phenanthroline or 2,2-bipyridine to the Schiff base solution were unsuccessful, analytical data showing that the compounds isolated still had the general formula $ML_2$.

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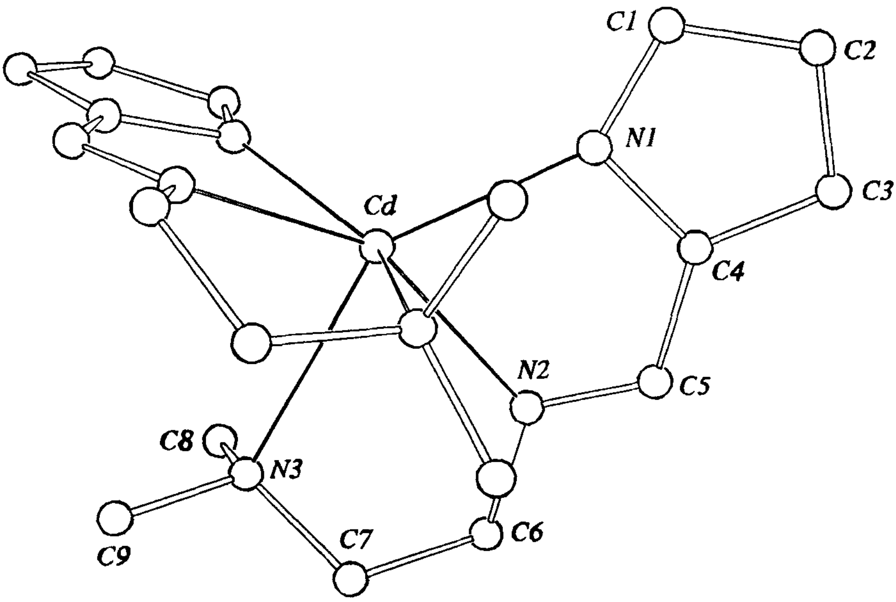

FIGURE 1 View of the structure of $CdL_2$.

### *Description of the structure of* [$CdL_2$]

Crystals of bis{2-[[2-(*N*,*N*-dimethyl)aminoethyl]iminomethyl]pyrrolato} cadmium(II) consist of monomeric [$CdL_2$] units (Figure 1). Final atomic coordinate sites and bond lengths and angles are listed in Tables I, II and III, respectively. The cadmium atom is located on a two-fold crystallographic axis and is coordinated

TABLE I
Fractional atomic coordinates and isotropic temperature factors (Å$^2$)

| Atom | $x/a$ | $y/b$ | $z/c$ | $B_{iso}$ |
|---|---|---|---|---|
| Cd | 0.5 | 0.1375(1) | 0.75 | 3.53(2) |
| N1 | 0.4404(4) | 0.2683(5) | 0.6534(2) | 3.7(2) |
| N2 | 0.3128(4) | 0.0723(5) | 0.7286(2) | 3.9(2) |
| N3 | 0.4213(4) | −0.0501(5) | 0.8517(3) | 4.6(2) |
| C1 | 0.4750(5) | 0.3635(7) | 0.6039(4) | 4.7(2) |
| C2 | 0.3943(6) | 0.3761(8) | 0.5459(3) | 5.6(3) |
| C3 | 0.3060(5) | 0.2856(7) | 0.5619(3) | 4.9(2) |
| C4 | 0.3348(4) | 0.2188(6) | 0.6274(3) | 3.9(2) |
| C5 | 0.2721(5) | 0.1183(6) | 0.6684(3) | 4.1(2) |
| C6 | 0.2464(6) | −0.0249(7) | 0.7746(3) | 5.0(2) |
| C7 | 0.3268(7) | −0.1200(7) | 0.8139(4) | 6.8(3) |
| C8 | 0.3803(7) | 0.032(1) | 0.9134(4) | 8.5(4) |
| C9 | 0.5020(7) | −0.155(1) | 0.8734(8) | 11.3(6) |

TABLE II
Selected bond distances (Å) with e.s.d.'s in parentheses

| | | | |
|---|---|---|---|
| Cd-N1 | 2.266(4) | Cd-N2 | 2.277(5) |
| Cd-N3 | 2.731(5) | N1-C1 | 1.341(8) |
| N1-C4 | 1.388(7) | N2-C5 | 1.274(7) |
| N2-C6 | 1.465(8) | N3-C7 | 1.450(9) |
| N3-C8 | 1.451(9) | N3-C9 | 1.42(1) |
| C1-C2 | 1.415(9) | C2-C3 | 1.364(9) |
| C3-C4 | 1.395(8) | C4-C5 | 1.413(8) |
| C6-C7 | 1.48(1) | | |

TABLE III
Selected bond angles (°) with e.s.d.'s in parentheses

| | | | |
|---|---|---|---|
| N1-Cd-N2 | 74.3(2) | N1-Cd-N3 | 142.0(2) |
| N1-Cd-N1[i] | 113.4(2) | N2-Cd-N1[i] | 124.8(2) |
| N3-Cd-N1[i] | 85.9(2) | N2-Cd-N3 | 68.0(2) |
| N2-Cd-N2[i] | 148.4(2) | N2-Cd-N3[i] | 91.1(2) |
| N3-Cd-N3[i] | 98.4(1) | C1-N1-C4 | 105.0(5) |
| C5-N2-C6 | 121.4(5) | C7-N3-C8 | 111.9(5) |
| C7-N3-C9 | 107.6(6) | C8-N3-C9 | 112.0(7) |
| N1-C1-C2 | 111.6(5) | C1-C2-C3 | 106.0(6) |
| C2-C3-C4 | 107.1(5) | N1-C4-C3 | 110.3(5) |
| N1-C4-C5 | 119.7(5) | C3-C4-C5 | 129.9(5) |
| N2-C5-C4 | 120.2(5) | N2-C6-C7 | 109.7(5) |
| N3-C7-C6 | 114.9(6) | | |

[i] Symmetry operation: $1-x$, $y$, $1.5-z$.

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strongly, and roughly tetrahedrally, to the pyrrole and imine nitrogen atoms of two symmetry-related ligands. Though the coordination sphere also includes the amino nitrogen atoms of both ligand molecules, any interaction with the cadmium atom must be very weak, and the ligand is best considered as bidentate.

The deviation from strictly tetrahedral geometry is caused by the small bite of the Schiff base (the N1–Cd–N2 angles are 74.3(2)°, which leads to N1–Cd–N2$^i$, N1–Cd–N1$^i$ and N2–Cd–N2$^i$ angles of 124.7(2), 113.5(1) and 148.4(2)°, respectively), and by the weak interaction between the cadmium atom and the amino nitrogens. Whether this latter fact is due to some real chemical bonding or to simply orientational demands of the amino group is not clear.

The Cd–N(pyrrole) bond length of 2.266(4) Å is considerably longer than those found in 5,10,15,20-tetraphenylporphinatocadmium(II)bis(dioxan), [Cd(TPP)·2-dioxan], in which there is also a four coordinate $CdN_4$ core (average Cd–N 2.14 Å), and very weak interaction with axial (dioxan) molecules,[12] and is even slightly greater than those found in [Cd(TPP)], 2.187(2) Å,[13] and five-coordinate [Cd(TPP)·piperidine], 2.203 Å,[14] but is similar to that observed in seven-coordinate [bis(pyridine) (5,9,10,14-tetraethyl-4,15-dimethyl-8,11-imino-6,3:13,16-dinitrilo-1,18-benzodiazacycloeicosinato)cadmium], 2.258(8) Å.[15] We have found no published data for Cd(azomethine) distances in tetrahedral complexes, but the value in $CdL_2$, 2.277(5) Å, is slightly shorter than that found in hexacoordinate [(1,2-benzenediamine-*N*)[*N*,*N*″-(2,6-pyridinediyldimethylidene)bis[1,2-benzenediamine]diperchlorate]cadmium(II), 2.377(10) Å,[16] and in seven-coordinate [bis[$\mu$-(acetato)]bis(acetato)bis[$\mu^4$-[(2,2′-[2,6-pyridinediylbis(ethylidynenitrilo)]bis[phenolato]tetracadmium(II), (2.36 Å) and [bis[$\mu$-(acetato)]bis(*N*,*N*-dimethylformamide)bis[$\mu$-[(2,2′-[2,6-pyridinediylbis(ethylidynenitrilo)]bis[phenolato]tetracadmium(II) (2.358 Å).[17]

The Cd–N(amine) distance, 2.731(3) Å, is smaller than the sum of the covalent radius of the metal in octahedral structures (*ca* 1.55 Å) and the van der Waals radius of the nitrogen atom (1.50 Å), but is much greater than the upper limit found for Cd–N(amine) bond lengths in hexacoordinate cadmium(II) complexes, 2.43 Å.[16,18,19] Therefore, these nitrogen atoms cannot be considered as fully bound to the cadmium atom, and it is difficult to assess the degree of bonding actually involved. The position of these atoms is nevertheless probably a consequence of the tendency of cadmium(II) to six-coordination rather than a packing effect.

The N2–C5 bond lengths are within the accepted range for an N=C bond, 1.30 ± 0.04 Å.[20] The other bond lengths and angles in the ligands are also close to the expected values.[21] The pyrrole rings are essentially planar, the maximum deviation of any atom from the best squares-plane being 0.01 Å.

The IR spectra of the complexes are consistent with the structural data presented above. The spectra show no bands attributable to $\nu$(N–H), indicating that the pyrrole hydrogen atom is lost during electrolysis, and the band attributable to the azomethine $\nu$(C=N) is at lower frequency than in the free ligand; these facts indicate coordination through the pyrrole and azomethine nitrogen atoms.[3] In addition, the spectra show bands at 2780 and 2810 $cm^{-1}$ which are characteristic of the $\nu$(C–H) vibrations of a methyl group bound to a nitrogen atom that retains its lone pair;[22] this suggests that the dimethylamine nitrogen atom is not coordinated to the metal, in agreement with the X-ray diffraction findings for the cadmium complex.

For the zinc and cadmium complexes, $^1H$ NMR data reinforce the above conclusions (Table IV). The peak at 11.5 ppm assignable to the pyrrole N proton

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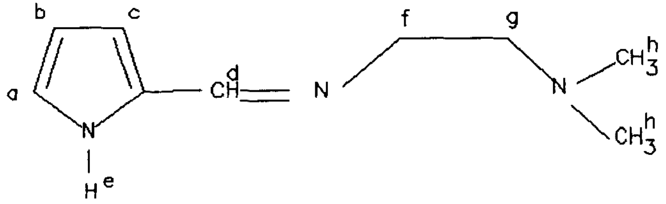
TABLE IV

Significant i.r. bands ($cm^{-1}$) and proton NMR chemical shifts for the Schiff base and its metal complexes

| | IR ($cm^{-1}$) | | | $^1H$ NMR (ppm) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Compound | $\nu(C{=}N)$ | $\nu(N{-}CH_3)$ | $\nu(N{-}H)$ | $H^a$ | $H^b$ | $H^c$ | $H^d$ | $H^e$ | $H^f$ | $H^g$ | $H^h$ |
| HL | 1604 | 2780, 2825 | 3200 | 6.4 | 6.1 | 6.8 | 8.0 | 11.5 | 3.5 | 2.4 | 2.2 |
| $CuL_2$ | 1610 | 2780, 2825 | | | | | | | | | |
| $ZnL_2$ | 1605 | 2785, 2825 | | 6.5 | 6.1 | 6.7 | 8.2 | | 3.5 | 2.3 | 1.9 |
| $CdL_2$ | 1605 | 2790, 2820 | | 6.5 | 6.1 | 6.7 | 8.2 | | 3.5 | 2.3 | 1.9 |



of the free ligand is not observed in the spectra of the complexes. The complexes retain the three widely separated signals of equal intensity between 6 and 7 ppm assignable to the three non-equivalent hydrogens of the pyrrole ring. The signal attributable to the imino hydrogen shifts downfield from its position in the free ligand, but the singlet assigned to the methyl groups shifts only very slightly upfield, in keeping with the non-coordination of the amino nitrogen atoms.[23]

These results show that the ligand is bidentate, binding to the metals through its pyrrole and imine nitrogens, and hence that the metal is tetracoordinate in these compounds.

The effective magnetic moment of the copper(II) complex at room temperature, 1.8 BM, and its diffuse reflectance spectrum, which shows a very broad band at 16200 $cm^{-1}$, is compatible with this complex having a square-planar structure.[24]

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