

TABLE 2 — IR DATA OF THE COMPLEXES

Complex	$\nu_{\max}$ (cm <sup>-1</sup> ) (assignment)
Hg(NO <sub>3</sub> ) <sub>2</sub> ·(C <sub>5</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>2</sub> ·4H <sub>2</sub> O	1520 (vs) $\nu$ NO <sub>2</sub> (asym) 1280 (mbr) $\nu$ NO <sub>2</sub> (sym) 820 (m) nonplanar-rocking 1640 (ms) lattice water
Zn(SCN) <sub>2</sub> (C <sub>5</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>2</sub>	2150 (s) $\nu$ CN 830 (ws) $\nu$ CS
Zn(NO <sub>3</sub> ) <sub>2</sub> (C <sub>5</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>4</sub>	1520 (vs) $\nu$ NO <sub>2</sub> (asym) 1280 (mbr) $\nu$ NO <sub>2</sub> (sym) 820 (m) nonplanar rocking
Zn(ClO <sub>4</sub> ) <sub>2</sub> (C <sub>5</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>4</sub>	1135 (s) $\nu$ ClO (sym) 930 (s) $\nu$ ClO (asym)
Zn(BF <sub>4</sub> ) <sub>2</sub> (C <sub>5</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>4</sub>	1115 (vs), $\nu$ BF <sub>4</sub> (asym) 1050 (vs), $\nu$ BF <sub>4</sub> (sym)
Zn(CH <sub>3</sub> COO) <sub>2</sub> (C <sub>5</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>4</sub> ·3H <sub>2</sub> O	1562 (ss), $\nu$ OCO (asym) 1400 (s), $\nu$ OCO (sym) 1648 (ms), lattice water
ZnSO <sub>4</sub> (C <sub>5</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>4</sub>	1160 (ss), ( $\nu_3$ ) 740 (m), ( $\nu_1$ )
Cd(NO <sub>3</sub> ) <sub>2</sub> (C <sub>5</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>4</sub>	1518 (vs), $\nu$ NO <sub>2</sub> (asym) 1270 (mbr), $\nu$ NO <sub>2</sub> (sym) 820 (m) nonplanar rocking
Cd(BF <sub>4</sub> ) <sub>2</sub> (C <sub>5</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>4</sub>	1115 (vs), $\nu$ BF <sub>4</sub> (asym) 1050 (vs), $\nu$ BF <sub>4</sub> (sym)
Cd(ClO <sub>4</sub> ) <sub>2</sub> (C <sub>5</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>4</sub>	1135 (s), $\nu$ ClO (sym) 930 (m), $\nu$ ClO (asym)
Cd(CH <sub>3</sub> COO) <sub>2</sub> (C <sub>5</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>4</sub>	1562 (ss), $\nu$ OCO (asym) 1400 (s), $\nu$ OCO (sym)
Cd <sub>2</sub> (SO <sub>4</sub> ) <sub>2</sub> (C <sub>5</sub> H <sub>8</sub> N <sub>2</sub> ) <sub>4</sub> ·6H <sub>2</sub> O	1180 (ss), ( $\nu_3$ ) 760 (m), ( $\nu_1$ ) 1640, lattice water

s=strong; m=medium; br=broad; w=weak; ss=strong sharp.

the fluoborato complexes are also 1:2 electrolytes in water. Their IR data do not conclusively indicate coordination of the anions. The sulphato and the acetato complexes lose their water of crystallization at 100-120°C. From all these considerations, distorted octahedral structures have been suggested for the compounds, except the perchlorato and the fluoborato complexes which are supposed to be tetrahedral.

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### Methyl 2-(N-Ethylamino)cyclopentene-1-dithio-carboxylate Complexes of Pd(II), Pt(II) & Hg(II)

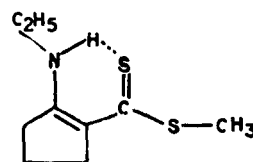
K. NAG & D. S. JOARDAR

Department of Inorganic Chemistry  
Indian Association for the Cultivation of Science  
Calcutta 700032

Received 29 March 1976; accepted 9 July 1976

The title ligand (EACDAME) forms complexes of the type M(EACDAME)<sub>2</sub>Cl<sub>2</sub> [M=Pd(II), Pt(II) and Hg(II)]. In these compounds the ligand acts in the unidentate form. While with Pd(II) and Pt(II) bonding takes place through the nitrogen atom, in the case of Hg(II) complex bond formation takes place through the sulphur atom.

In earlier communications we have reported<sup>1-5</sup> the coordination behaviour of 2-aminocyclopentene-1-dithiocarboxylic acid (ACDA), 2-(N-ethylamino)cyclopentene-1-dithiocarboxylic acid and the S-methyl ester of ACDA toward several metal ions. With the acids both (N, S<sup>-</sup>) and (S, S<sup>-</sup>) type metal chelates have been obtained depending on the metal ions<sup>1-4</sup>. The S-methyl ester of ACDA can act both as bidentate and monodentate ligand<sup>5</sup>. Here we wish to report the preparation and characterization of the complexes of methyl 2-(N-ethylamino)cyclopentene-1-dithiocarboxylate (I, EACDAME) with Pd(II), Pt(II) and Hg(II).



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The ligand was prepared by the method of Bordas *et al.*<sup>6</sup>

$\text{Pd}(\text{EACDAME})_2\text{Cl}_2$  — Sodium tetrachloropalladate(II) (2 mmoles) dissolved in 35 ml of ethanol was added to an ethanolic solution of the ligand (4 mmoles in 50 ml of ethanol) with constant stirring during 30 min. The dark product obtained after removal of two-thirds of the solvent under reduced pressure was filtered and washed first with

ethanol and then with water till the compound was free from chloride. It was recrystallized from acetone, yield 70% [Calc. for  $\text{Pd}(\text{EACDAME})_2\text{Cl}_2$ : Pd, 18.4; N, 4.8; S, 22.1; Cl, 12.2. Found: Pd, 18.5; N, 4.0; S, 21.9; Cl, 12.0%].

$\text{Pt}(\text{EACDAME})_2\text{Cl}_2$  — Potassium tetrachloroplatinate(II) (2 mmoles) and the ligand (4 mmoles) in acetone were stirred for 2 hr. The solution became deep red. Removal of the major portion of the solvent gave a brownish red product which was filtered and washed successively with warm water, ethanol-water (1:1) and petroleum ether. The compound was recrystallized from acetone, yield 80% [Calc. for  $\text{Pt}(\text{EACDAME})_2\text{Cl}_2$ : C, 32.3; H, 4.5; N, 4.2; Cl, 10.6. Found: C, 32.5; H, 4.4; N, 4.3; Cl, 10.4%].

$\text{Hg}(\text{EACDAME})_2\text{Cl}_2$  — A mixture of mercuric chloride (2 mmoles) and the ligand (4 mmoles) in ethanol was stirred for 1 hr. The solution was then concentrated under reduced pressure to about one-third of the original volume (45 ml). A yellow crystalline compound thus separated was collected and washed with ethanol; yield 75% [Calc. for  $\text{Hg}(\text{EACDAME})_2\text{Cl}_2$ : Hg, 29.8; N, 4.2. Found: Hg, 29.6; N, 4.4%].

The analytical data of the compounds prepared agree with the composition  $\text{M}(\text{EACDAME})_2\text{Cl}_2$  [M = Pd(II), Pt(II) and Hg(II)]. The complexes are non-electrolytic in nature, indicating that the ligand acts in the unidentate form in these compounds. Attempt to isolate the Ni(II) complex was unsuccessful, although with the S-methyl ester of 2-aminocyclopentene-1-dithiocarboxylic acid a bis-chelate of the deprotonated ligand was obtained readily<sup>5</sup>. It thus appears that the substitution of the amino proton of methyl 2-aminocyclopentene-1-dithiocarboxylate with an alkyl group significantly affects the coordination behaviour particularly in its ability to get deprotonated.

The PMR spectrum of the ligand showed the following signals:  $\delta$  1.33 (t, 3H,  $J = 6$  Hz,  $\text{N-CH}_2\text{CH}_3$ ), 3.37 (q, 2H,  $J = 6$  Hz,  $\text{N-CH}_2\text{CH}_3$ ), 2.47 (s, 3H,  $\text{CSSCH}_3$ ), 1.83 (q, 2H,  $J = 7$  Hz,  $4\text{-CH}_2$ ), 2.70 (m, 4H,  $3\text{-CH}_2$ ,  $5\text{-CH}_2$ ), 11.8 (1H, NH). In the S-methyl ester of 2-aminocyclopentene-1-dithiocarboxylic acid, the NH proton is located at  $\delta$  10.7 (ref. 5). The larger downfield shift of the NH proton in EACDAME indicates its higher basicity which explains its reluctance to form deprotonated chelate. The IR spectrum ( $\nu_{\text{max}}$  in  $\text{cm}^{-1}$ ) of the ligand shows a weak band at 3460 indicating that the secondary amino group is involved in hydrogen bonding with thiocarbonyl sulphur.

The  $\nu(\text{N-H})$  is observed at 3410 in the Pt(II) complex and at 3415 in the Pd(II) complex. In the Hg(II) complex, however, this band is considerably shifted to higher frequency range and appears at 3480. In the free ligand there is strong delocalization effect in the hydrogen bonded chelate ring and as a result  $\text{C}=\text{C}$  assumes partial double bond character. The strong band at 1592 in the free ligand is probably due to the combination of  $\delta(\text{N-H})$  and  $\nu(\text{C}=\text{C})$ . In the Pd(II) and Pt(II) complexes, a medium intensity band is observed  $\sim 1670$  and also a strong band  $\sim 1550$ . In the Hg(II) complex, although a strong band is observed at 1620, no band could be detected in the range

1550-1570. It may be mentioned that the ligand also shows no such band. Since EACDAME acts as an unidentate ligand with all the three metal ions, therefore, it coordinates with the metal ions either through nitrogen or through thiocarbonyl sulphur. If the bonding takes place through the nitrogen atom,  $\delta(\text{N-H})$  vibration should be observed at lower frequency compared to the free ligand and the  $\text{C}=\text{C}$  stretching frequency should be displaced to a higher energy, since the hydrogen bonded structure of the ligand is lost. The Pd(II) and Pt(II) complexes show such a behaviour. Hence in these complexes bonding through nitrogen is indicated. On the other hand, bonding through thiocarbonyl sulphur atom would result in the displacement of  $\delta(\text{N-H})$  to a higher energy, which is the case with the Hg(II) complex. Further confirmation of bonding through nitrogen in Pd(II) and Pt(II) complexes and through sulphur in Hg(II) complex gets support from (N-H) stretching frequencies of the complexes.

The electronic spectrum of the ligand shows two bands in methanol at 25.3 and 32 kK with the molar extinctions ( $\log \epsilon$ ) 4.4 and 4.0 respectively. The Pd(II) and Pt(II) complexes exhibit no  $d-d$  type transitions. In the Pd(II) complex three bands are observed at 25.1, 32.4 and 38.5 kK with the corresponding extinctions ( $\log \epsilon$ ) 4.4, 4.3 and 4.4 respectively; these are probably due to internal ligand transitions. The Pt(II) complex also displays three bands at 23.7 ( $\log \epsilon$  4.0), 25.5 (4.0) and 40 kK (4.37) and the first one appears to be a charge-transfer band.

Thanks are due to the CSIR, New Delhi, for the award of a senior research fellowship to one of the authors (D.S.J.).

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### Polarographic Study of the Complexes of Zn(II) & Pb(II) with Hexamethylenetetramine: A Kinetic Study

K. SARASWATHI & D. RAJENDRA PRASAD

Department of Chemistry, Sri Venkateswara University  
Tirupati 517502

Received 17 April 1976; accepted 21 July 1976

The electrode reactions are diffusion-controlled and are highly irreversible. The kinetic parameters ( $\alpha n$ , and  $K_{f,h}^0$ ) have been calculated by Koutecky's theoretical treatment as extended by Meites and Israel. Since the reduction is diffusion-controlled,  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  ions in HMTA can be determined polarographically.

A NUMBER of workers<sup>1-7</sup> have investigated the complexes of hexamethylenetetramine (HMTA) with Zn(II) and Pb(II). However, a polarographic