

Metal Complexes of Sulphur-Nitrogen Chelating Agents. Part 14. Nickel(II), Palladium(II), Copper(II), Cobalt(II), and Cobalt(III) Complexes of the Tetradentate Schiff Bases Having ONNS Donor Sites

Santosh K. Mondal, Parimal Paul, Rita Roy and Kamalaksha Nag*

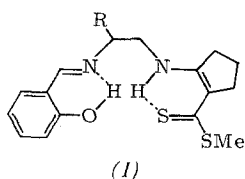
Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta 700 032, India

Summary

Complexes of nickel(II), palladium(II), copper(II), cobalt(II), and cobalt(III) with methyl-2-(β-salicylaldiminoethyl)cyclopent-1-en-dithiocarboxylate (H_2L^1) and methyl-2-(β-salicylaldiminoisopropyl)cyclopent-1-en-dithiocarboxylate (H_2L^2) have been prepared. They contain the donor sites ONNS. The metal(II) ions from neutral, monomeric square planar chelate complexes. The cobalt(III) complexes $[CoL^1(H_2O)_2]X$ ($X = Cl$ or ClO_4) appear to be *trans*-diaqua-species. All compounds have been characterized by a number of physico-chemical methods.

Introduction

Complexes of open-chain tetradentate ligands containing heterodonor atoms have been the subject of many studies^(1–4). A great deal of information is available on metal complexes of dianionic Schiff bases containing the N_2O_2 donor unit^(5–10). Similar information, although not to the same extent, has also been accumulated for $[N_2S_2]^{2-}$ donor systems^(2,3,11–18). However, very little is known about metal complexes of non-symmetrical ligands $[ONNS]^{2-}$ ⁽²⁰⁾. In previous publications of this series we have reported^(21–23) the chemistry of several metal(II) complexes of the tridentate ligands methyl-2-amino(β-alkylamino)cyclopent-1-en-dithiocarboxylates. The terminal amino-group of these ligands can be condensed with *o*-hydroxyphenyl aldehydes or ketones to obtain Schiff bases that have the desired set of coordination sites. The present paper deals with the complexes of nickel(II), palladium(II), copper(II), cobalt(II), and cobalt(III) obtained from methyl-2-(β-salicylaldiminoethyl)aminocyclopent-1-en-dithiocarboxylate and methyl-2-(β-salicylaldiminoisopropyl)aminocyclopent-1-en-dithiocarboxylate, hereafter abbreviated as H_2L^1 (*1a*) and H_2L^2 (*1b*), respectively.



a: R = H; *b*: R = Me

Experimental

Preparation of the ligands ($H_2L^{1,2}$)

Salicylaldehyde (6.1 g, 5 mmol) was added to a solution (300 cm³) of methyl-2-amino(β-alkylamino)cyclopent-1-en-dithiocarboxylate⁽²²⁾ (5 mmol) in EtOH. The solution was stir-

red for 0.5 h and then cooled in an icebath. The precipitated Schiff base was filtered and recrystallised from $C_6H_6/EtOH$ (1:1). Yield 75%; m.p. 128–129°C (H_2L^1), 98°C (H_2L^2).

Preparation of the metal complexes

$[NiL^1]^{1,2}$. $NiCl_2 \cdot 6H_2O$ (0.48 g, 2 mmol) in MeOH (20 cm³) was added to a stirred solution (20 cm³) of the ligand (0.46/0.67 g, 2 mmol) in C_6H_6 . The solution became deep green during stirring (0.5 h) and on partial removal of the solvent shining green crystals deposited. The compound was recrystallised from $CHCl_3$.

$[PdL^1]^{1,2}$. The preparation was carried out in the same way as described above using $Na_2[PdCl_4]$ (0.59 g, 2 mmol). The orange coloured compound deposited was collected by filtration and washed thoroughly with MeOH and H_2O . It was finally recrystallised from $CHCl_3$.

$[CuL^1]^{1,2}$. A few drops of strong aqueous ammonia were added to a MeOH solution (20 cm³) of $Cu(NO_3)_2 \cdot 3H_2O$ (0.48 g, 2 mmol) in order to convert it to the cuprammine complex. To this solution was added a solution of the ligand (2 mmol) in C_6H_6 (20 cm³). After stirring for 1 h the precipitated red complex was filtered and recrystallised from $CHCl_3$.

$[CoL^1]^{1,2}$. Et_3N (0.3 cm³) was added to a nitrogen purged solution (20 cm³) of the ligand (2 mmol) and the solution heated to boiling. The solution was then treated with an air-free EtOH solution (30 cm³) of $Co(OAc)_2 \cdot 4H_2O$ (0.5 g, 2 mmol). Continuing the reflux for 1 h glistening maroon crystals separated. These were collected by filtration after cooling to ambient temperature. Recrystallisation of the product from $CHCl_3$ was accomplished under nitrogen atmosphere.

$[Co^{III}L^1(H_2O)_2](ClO_4)$. To a MeOH solution (100 cm³) of the ligand (0.64 g, 2 mmol) an aqueous solution (20 cm³) of $Co(ClO_4)_2 \cdot 6H_2O$ (0.73 g, 2 mmol) was added with stirring. The deep brown solution was stirred in air for 6 h. A dark brown, almost black compound deposited. This was collected by filtration, washed successively with C_6H_6 , MeOH and H_2O , and was finally dried *in vacuo*. The compound could not be recrystallised due to its poor solubility.

$[Co^{III}L^1(H_2O)_2]Cl$ was prepared in the same way.

C and H analyses were performed by Mrs. C. Datta of the Department of Organic Chemistry. Nitrogen (semimicro) and metal analyses were carried out in our own laboratory.

Physical measurements

The equipment used was that reported recently^(12,24). Molecular weight determinations were carried out with $CHCl_3$ solutions using a Knauer Vapour phase osmometer.

Results and Discussion

The analytical data (Table 1) indicate the formation of 1:1 chelates with the bivalent metal ions. These are highly crys-

* Author to whom all correspondence should be directed.

Table 1. Analytical data for the complexes.

Complex	Found (calcd.) %		N	M
	C	H		
[NiL] ¹	51.2(50.9)	5.0(4.8)	7.5(7.4)	15.7(15.6)
[NiL] ²			7.0(7.2)	14.9(15.0)
[PdL] ¹	45.1(45.2)	4.6(4.5)	6.7(6.6)	25.2(25.1)
[PdL] ²			6.3(6.4)	24.2(24.3)
[CuL] ¹	50.1(50.3)	4.5(4.7)	6.7(6.6)	25.2(25.1)
[CuL] ²			6.9(7.1)	16.0(16.1)
[CoL] ¹	50.6(50.9)	5.1(4.8)	7.3(7.4)	15.8(15.6)
[CoL] ²			7.3(7.2)	15.2(15.0)
[CoL ¹ (H ₂ O) ₂]ClO ₄			5.4(5.3)	11.4(11.2)
[CoL ¹ (H ₂ O) ₂]Cl			6.2(6.0)	12.6(12.7)

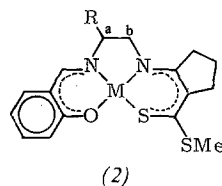
talline compounds, fairly soluble in organic solvents and are nonelectrolytes. The diaqua-cobalt(III) complexes are 1:1 electrolytes ($\Lambda_M = ca. 80 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ in *N,N*-dimethylformamide). Preliminary studies showed that the water molecules in [CoL¹(H₂O)₂]⁺ can be replaced by other nucleophiles such as pyridine and imidazole. However, due to the poor solubility of the precursor, kinetic studies of the replacements could not be carried out.

Molecular weight determinations in chloroform solution established the mononuclear nature of [NiL]¹ (obs. 360; calcd. 377) and [CuL]² (obs. 410; calcd. 396). The nickel(II), palladium(II), and cobalt(III) compounds are diamagnetic. Room temperature magnetic moments of [CoL]¹ (2.02 B.M.) and [CoL]² (2.06 B.M.) indicate a square planar configuration. The normal magnetic moments of the copper(II) complexes, [CuL]¹ (1.92 B.M.) and [CuL]² (1.88 B.M.) probably indicate no antiferromagnetic interaction and probably no dimerisation through phenoxy bridges. It should be mentioned, however, that in the case of Cu(salen) although the x-ray structure determination revealed^(25,26) a dinuclear structure with an approximately square pyramidal stereochemistry around copper, there is no evidence of antiferromagnetic interaction in magnetic measurements⁽²⁷⁾. Nevertheless, the e.p.r. spectrum of the compound does indicate⁽²⁸⁾ the presence of signals that are attributable to transitions within the triplet state.

I.r. spectra of the metal complexes show a plethora of bands, of which a few that are diagnostic of metal-ligand binding are presented in Table 2. The band near 1530 cm⁻¹ (which is absent in the free ligand) is due to C—O stretch of the phenolate and is used^(7,29) for distinguishing between mononuclear and phenoxy-bridged binuclear Schiff base copper(II) chelate complexes. In mononuclear complexes this band is

observed at *ca.* 1530 cm⁻¹, whereas in the phenoxy-bridge compounds this is invariably shifted to a higher frequency by *ca.* 20 cm⁻¹. On this basis all the compounds investigated appear to be mononuclear species. Again it should be noted that [Co(salen)] has at least two different types of crystal structure. A monomeric structure with solvated chloroform is obtained⁽³⁰⁾ from chloroform. In contrast, crystallisation from acetone yields a dimeric structure⁽³¹⁾ with oxygen bridges. The i.r. spectra also show the presence of three new bands in the metal chelate complexes in the range 600–300 cm⁻¹. The bands appearing at 560 ± 20, 520 ± 15 and 350 ± 10 cm⁻¹ are most likely due to contributions from $\nu(\text{M—O})$, $\nu(\text{M—N})$, and $\nu(\text{M—S})$ respectively.

¹H n.m.r. spectral features of the ligands and their nickel(II) and palladium(II) chelates are summarised in Table 3. It may be noted that the two hydrogen-bonded protons in H₂L¹ overlap at 12.3 ppm while in H₂L² these appear at still lower fields, *viz.* 14.0 (N—H···S) and 14.5 ppm (O—H···N) indicating stronger hydrogen bonding. On complex formation the ethylene-bridge protons in [NiL]¹ and [PdL]¹ experience profound shielding. The resonances due to (3,5)—CH₂ (of the cyclopentene moiety) and CH=N protons also undergo shift, to higher fields. Similar shielding effects are noticed in CH [labelled a in (2)], (3,5)—CH₂ and CH=N protons of [NiL]². These observations are consistent with extensive delocalisation of double bonds in the chelate ring (2).



The electronic spectral data of the compounds are given in Table 4. The nickel(II) complexes are characterised by single d-d bands at 16000 ([NiL]¹) and 16450 cm⁻¹ ([NiL]²) which evidently are due to $d_{xy} \rightarrow d_{x^2-y^2}$ transitions in square planar complexes. In the palladium(II) chelates the d-d bands are obscured by the charge-transfer transitions at *ca.* 24500 cm⁻¹. In the visible region the copper(II) complexes exhibit two absorption bands which probably arise from transition involving $d_{z^2} \rightarrow d_{xy}$ (*ca.* 19000 cm⁻¹) and $d_{x^2-y^2}$ (*ca.* 14500 cm⁻¹) in square planar complexes^(32,33). The electronic structures of low-spin, planar Schiff base cobalt(II) complexes have been the subject of considerable research^(10,33-35). By analogy with the observations made for [Co(salen)]⁽³³⁾ we assign the absorption at 9900 cm⁻¹ to the $d_{yz} \rightarrow d_{x^2-y^2}$ transition and that

Table 2. I.r. data^{a)} for the metal complexes.

Compound	$\nu(\text{C=N})$	$\nu(\text{C=C})/\text{phenyl ring}$	$\nu(\text{C}\cdots\text{C})$	$\nu(\text{C—O})$	$\nu(\text{C}\cdots\text{N} + \text{C}\cdots\text{C})$
[H ₂ L] ¹	1630s	1600s			1490s
[H ₂ L] ²	1620s	1580s			1470s
[NiL] ¹	1625s	1600m	1565m	1530m	1470s
[NiL] ²	1610s	1590s	1545s	1530s	1450s
[PdL] ¹	1630s	1595s	1570m	1530m	1460s
[PdL] ²	1620s	1590s	1565s	1525s	1450s
[CuL] ¹	1630s	1600s	1575s	1535s	1460s
[CuL] ²	1620s	1590s	1570s	1530s	1455s
[CoL] ¹	1610s	1600s		1535s	1450s
[CoL ¹ (H ₂ O) ₂]Cl	1630s	1600s		1530m	1450s

^{a)} cm⁻¹.

Table 3. ^1H n.m.r. data of the ligands and some metal chelates.

Compound ^{a)}	Chemical shifts, δ (ppm)
$[\text{H}_2\text{L}]^1$ ^{b)}	1.8m (4-CH ₂), 2.57s (SMe), ca. 2.7m (3,5-CH ₂) ^{c)} , 3.7m (CH ₂ -CH ₂ bridge) ^{c)} , 6.7–7.4m (<i>o</i> -disubstituted phenyl), 8.36s (CH=N), 12.3b (O—H \cdots N + N—H \cdots S)
$[\text{NiL}]^1$ ^{d)}	1.87m (4-CH ₂), 2.57s (SMe), ca. 2.6m (3,5-CH ₂) ^{c)} , ca. 3.4(CH ₂ -CH ₂ bridge), 6.35–7.5m (<i>o</i> -disubstituted phenyl), 8.2s (CH=N)
$[\text{PdL}]^1$ ^{d)}	1.9m (4-CH ₂), 2.55s (SMe), 6.3–7.5m (<i>o</i> -disubstituted phenyl), 8.16s (CH=N)
$[\text{H}_2\text{L}]^2$ ^{b)}	1.37d (Me), 1.77m (4-CH ₂), 2.55s (SMe), 2.63m (3,5-CH ₂) ^{c)} , 3343m (a-CH + b-CH ₂) ^{c)} , 6.7–7.4m (<i>o</i> -disubstituted phenyl), 8.38s (CH=N), 14b (N—H \cdots S), 14.5b (O—H \cdots N)
$[\text{NiL}]^2$ ^{b)}	1.4d (Me), 1.78m (4-CH ₂), 2.57m (3,5-CH ₂) ^{c)} , 2262s (SMe), 2.95m(b-CH) ^{c)} , 3.47m (a-CH ₂), 6.3–7.4m (<i>o</i> -disubstituted phenyl), 8.16s (CH=N)

^{a)} Me₄Si ($\delta=0$) used as the internal standard; ^{b)} In CDCl₃; ^{c)} Overlapping multiplets; ^{d)} In DMSO-d₆.

appearing at 17250 cm⁻¹ as a shoulder is probably due to the $d_{yz} \rightarrow d_{xy}$ transition. For $[\text{Co}^{\text{III}}\text{L}(\text{H}_2\text{O})_2]^+$ the absorption spectrum shows the presence of a band at 630 nm, a shoulder at 595 nm and another band at 455 nm. The shoulder possibly arise from splitting of the band at 630 nm. In $\text{Co}^{\text{III}}\text{L}_4\text{X}_2$ complexes such splitting occurs for the lower energy band when the complexes have a *trans*-configuration⁽³⁶⁾.

The e.p.r. spectrum of $[\text{CuL}]^1$ in undiluted polycrystalline form at 77 K is axial and is typical of square-planar copper(II) complexes with D_{4h} symmetry. In the half-field region no resonance due to the $\Delta M_s = \pm 2$ transition could be observed. The g -values of this compound are: $g_{\parallel} = 2.151$ and $g_{\perp} = 2.027$. Figure 1 shows the spectrum of $[\text{CuL}]^1$ doped in $[\text{NiL}]^1$ at ambient temperature. The spectrum appears to be slightly rhombic. The $g_z(g_{\parallel})$ value is 2.156 and the corresponding hyperfine splitting (A_z) is 200×10^{-4} cm⁻¹; other g - and A -values could not be determined reliably. However, estimating the value of g_{\perp} as that obtained for the undiluted specimen, it appears that $g_y \approx g_x \approx 2.03$. It is relevant to compare the e.p.r. spectral parameters of $[\text{CuL}]^1$ with $[\text{Cu}(\text{salen})]$ and N,N -ethanebis(methyl-2-aminocyclopent-1-en-dithiocarboxylato)-copper(II), $[\text{CuL}]^3$. The spectrum of dimeric $[\text{Cu}(\text{salen})]$ has been interpreted⁽²⁸⁾ in terms of its doublet state transitions ($g_{\parallel} = 2.34$, $g_{\perp} = 2.07$) and triplet state transitions ($g_{\parallel} = 2.04$, $g_{\perp} = 2.03$). For mononuclear $[\text{Cu}(\text{salen})]$ doped in $[\text{Ni}(\text{salen})]$,

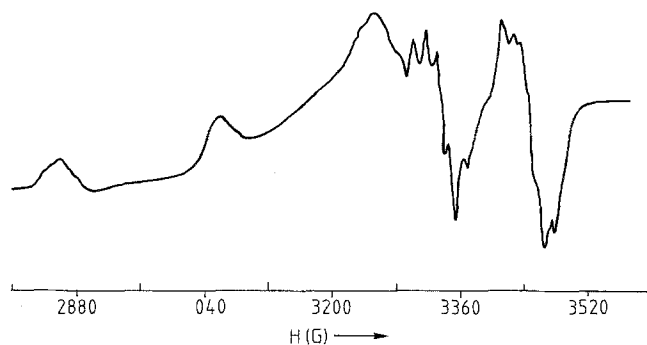


Figure 1. The room temperature e.p.r. spectrum of CuL^1 doped in NiL^1 using a frequency of 9.522 GHz.

which is relevant to us, a slightly rhombic spectrum with the following g -values was obtained⁽³⁷⁾: $g_z = 2.192$, $g_y = 2.046$, $g_x = 2.049$. In the case of $[\text{CuL}]^3$ again a slightly rhombic spectrum was observed⁽¹⁵⁾; $g_z = 2.117$ (other g -values not reported). It should be noted that $[\text{CuL}]^1$ has a chromophore $[\text{CuON}_2\text{S}]$ which is intermediate between $[\text{CuN}_2\text{O}_2]$ of $[\text{Cu}(\text{salen})]$ and $[\text{CuN}_2\text{S}_2]$ of $[\text{CuL}]^3$. Thus one would expect the e.p.r. spectral features of CuL^1 to lie between those of $[\text{Cu}(\text{salen})]$ and $[\text{CuL}]^3$. Indeed the observed g_z value of $[\text{CuL}]^3$ (2.156) is almost equal to the expected value (2.154) showing the validity of the “average environment rule”.

Table 4. Electronic spectral data of the metal chelates^{a)}.

Compound	ν_{max} , cm ⁻¹ (ϵ , M ⁻¹ cm ⁻¹)
$[\text{NiL}]^1$	16000(110) ^{b)} ; 23500(6610) ^{c)} ; 30500(17780) ^{d)}
$[\text{NiL}]^2$	16450(115) ^{b)} ; 23150(7250) ^{c)} ; 28570(10730) ^{d)} ; 30490(18230) ^{d)}
$[\text{PdL}]^1$	24400(8320) ^{c)} ; 32900(20890) ^{d)}
$[\text{PdL}]^2$	24500(7780) ^{c)} ; 33110(20450) ^{d)}
$[\text{CuL}]^1$	14300(55) ^{c)} ; 18900(450) ^{b)} ; 26670(13800) ^{c)} ; 34480(14120) ^{d)}
$[\text{CuL}]^2$	14710(55) ^{c)} ; 19230(460) ^{b)} ; 26880(15160) ^{c, d)} ; 30490(15520) ^{d)} ; 34250(13510) ^{d)}
$[\text{CoL}]^1$ ^{b)}	9900(12) ^{b)} ; 17240(600) ^{b)} ; 20000(2280) ^{c)} ; 23250(6660) ^{c, d)}
$[\text{CoL}^1(\text{H}_2\text{O})_2]\text{ClO}_4$	15870(215), 17700sh(390); 21930(2250); 25250(5200) ^{c)}

^{a)} In CHCl₃ unless stated otherwise; ^{b)} $d_{xy} \rightarrow d_{x^2-y^2}$; ^{c)} CT band; ^{d)} $L \rightarrow L^*$; ^{e)} $d_{z^2} \rightarrow d_{xy}$; ^{f)} $d_{x^2-y^2} \rightarrow d_{xy}$; ^{g)} In MeNO₂; ^{h)} $d_{yz} \rightarrow d_{x^2-y^2}$; ⁱ⁾ $d_{yz} \rightarrow d_{xy}$; ^{j)} in DMF.

References

- S. G. Murray and F. R. Hartley, *Chem. Rev.* 81, 365 (1981).
- M. Akbar Ali and S. E. Livingstone, *Coord. Chem. Rev.*, 13, 101 (1974).
- R. Morassi, I. Bertini and L. Sacconi, *Coord. Chem. Rev.*, 11, 343 (1973).
- C. A. McAuliffe, *Adv. Inorg. Radiochem.*, 17, 165 (1970).
- R. H. Holm, G. W. Everett, Jr. and A. Chakravorty, *Progr. Inorg. Chem.*, 7, 83 (1966).
- S. Yamada, *Coord. Chem. Rev.*, 1, 415 (1966).
- E. Sinn and C. M. Harris, *Coord. Chem. Rev.*, 4, 391 (1969).
- M. D. Hobday and T. D. Smith, *Coord. Chem. Rev.*, 9, 311 (1972–73).
- R. D. Jones, D. A. Summerville and F. Basolo, *Chem. Rev.*, 79, 135 (1979).
- C. Dawl, W. P. Schlapfer and A. V. Zelewsky, *Struct. Bonding (Berlin)*, 36, 129 (1979).
- S. K. Mondal, D. S. Joarder and K. Nag, *Inorg. Chem.* 17, 191 (1978).
- R. Roy, P. Paul and K. Nag, *Transition Met. Chem.*, in press.
- R. D. Bereman, M. R. Churchill and G. Shields, *Inorg. Chem.*, 18, 3117 (1979).
- R. D. Bereman, G. Shields, J. Bordner and J. R. Dorfman, *Inorg. Chem.*, 20, 2165 (1981).
- R. D. Bereman, D. P. Rillema, P. McCarthy and G. Shields, *J. Inorg. Biochem.*, 16, 47 (1982).
- P. R. Blum, R. M. C. Wei and S. C. Cummings, *Inorg. Chem.*, 13, 450 (1974).
- L. S. Chen and S. C. Cummings, *Inorg. Chem.*, 17, 2358 (1978).
- M. F. Corrigan and B. O. West,

Aust. J. Chem., 29, 1413 (1976). – ⁽¹⁹⁾ P. J. Marini, K. S. Murray and B. O. West, *J. Chem. Soc., Dalton Trans.*, 143, (1983). – ⁽²⁰⁾ R. C. Coombes, J. P. Costes and D. E. Fenton, *Inorg. Chim. Acta Lett.*, 77, L 173 (1983).

⁽²¹⁾ R. Roy, S. K. Mandal and K. Nag, *J. Chem. Soc., Dalton Trans.*, 1935 (1983). – ⁽²²⁾ R. Roy, M. Chaudhury, S. K. Mandal and K. Nag, *J. Chem. Soc., Dalton Trans.*, in press. – ⁽²³⁾ P. Paul, R. Roy and K. Nag, *Indian J. Chem., Sect A*, communicated. – ⁽²⁴⁾ S. K. Mandal and K. Nag, *Inorg. Chem.*, 22, 2567 (1983); *J. Chem. Soc., Dalton Trans.*, 2429 (1983). – ⁽²⁵⁾ D. Hall and J. N. Waters, *J. Chem. Soc.*, 2444 (1960). – ⁽²⁶⁾ R. Dingle, *Acta Chem. Scand.*, 20, 33 (1966). – ⁽²⁷⁾ S. J. Gruber, C. M. Harris and E. Sinn, *Inorg. Chem.*, 7, 268 (1968). – ⁽²⁸⁾ G. O. Carlisle and W. E. Hatfield, *Inorg. Nucl. Chem. Lett.*, 6, 633 (1970). – ⁽²⁹⁾ S. K. Mandal and K. Nag, *J. Chem. Soc., Dalton Trans.*,

in press. – ⁽³⁰⁾ W. P. Schaeffer and R. E. Marsh, *Acta Crystallogr. Sect. B*, 25, 1675 (1969).

⁽³¹⁾ R. DeIasi, S. L. Holt and B. Port, *Inorg. Chem.*, 10, 1498 (1971). – ⁽³²⁾ B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev.*, 5, 143 (1970). – ⁽³³⁾ M. A. Hitchman, *Inorg. Chem.*, 16, 1985 (1977); *Inorg. Chim. Acta*, 26, 237 (1978). – ⁽³⁴⁾ B. R. McGarvey, *Can. J. Chem.*, 53, 2498 (1975). – ⁽³⁵⁾ F. Cariati, F. Morazzoni, C. Busetto, G. del Piero and A. Zazzetta, *J. Chem. Soc., Dalton Trans.*, 342 (1976). – ⁽³⁶⁾ A. B. P. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 1968. – ⁽³⁷⁾ M. I. Scullen and H. C. Allen, Jr., *J. Coord. Chem.*, 4, 255 (1975).

(Received January 6th, 1984)

TMC 1092

Bis *N*(chlorophenyl)dithiocarbamato Complexes of Cobalt(II), Nickel(II), Palladium(II) and Platinum(II)

Narender K. Kaushik*, Bharat Bhushan and Anand K. Sharma

Department of Chemistry, University of Delhi, Delhi-110007, India

Summary

Cobalt(II), nickel(II), palladium(II) and platinum(II) complexes with *o*-(OCD), *m*-(MCD) and *p*-chlorophenyldithiocarbamate (PCD) ligands have been synthesised and characterised by chemical analyses, molecular weight determinations, conductance measurements, electronic and i.r. spectral studies. The thermal behaviour of the complexes has been studied by t.g. and d.t.a. techniques in a static air atmosphere and heats of reaction of different decomposition steps have been calculated from the d.t.a. curves. The thermal decomposition products of the complexes were identified by elemental analyses and i.r. spectra.

Introduction

In recent years there has been considerable interest in metal dithiocarbamates because of their diverse applications such as accelerators in vulcanisation, high pressure lubricants in industries and fungicides and pesticides in biological and biochemical fields⁽¹⁾. Although many metal dithiocarbamates have been reported, little attention has been paid to their thermal behaviour^(2–13). In continuation of our previous work on this theme^(5–13) we describe the preparation, characterisation and thermal investigation of bis [*N*(chlorophenyl)dithiocarbamato] cobalt(II), nickel(II), palladium(II) and platinum(II) complexes.

Experimental

Reagents and general techniques

The ligands ammonium [*N*(*o*-, *m*-, *p*-chlorophenyl)dithiocarbamates] were prepared by reacting equimolar amounts of the *o*-, *m*-, or *p*-chloroaniline with CS₂ and NH₃ as described by Kloppping and Kerk⁽¹⁴⁾. Analytical grade materials were used.

The ligands were estimated by Shankaranarayana and Patel's⁽¹⁵⁾ method. Cobalt, nickel, palladium and platinum were estimated by standard gravimetric methods⁽¹⁶⁾ after digestion of the complexes, as reported by Erdey⁽¹⁷⁾. Nitrogen was estimated by Kjeldahl's method and sulphur as BaSO₄.

Physical measurements

Molecular weights were determined using a Gallenkemp (U.K.) ebulliometer. Conductance measurements were made in PhNO₂ at 25 ± 0.5 °C with a Beckmann Conductivity bridge model RC-18A. I.r. spectra were recorded in the solid state (KBr pellets) in the 4000–200 cm⁻¹ region with a Perkin Elmer 621 grating spectrometer. The electronic spectra were recorded in Me₂CO on a Perkin-Elmer 4000 Å instrument. Magnetic measurements were made by Gouy's method using Hg[Co(SCN)₄] as calibrant.

The thermogravimetric curves were obtained on a Stanton automatic thermorecording balance, Model TR-I, with a 80–102 mg sample size and a heating rate of 4 K min⁻¹ in a self-produced air atmosphere. A silica crucible was used for

* Author to whom all correspondence should be directed.