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Contribution from the Departments of Chemistry, University of Wollongong, Wollongong, New South Wales 2500, Australia, and University of Virginia, Charlottesville, Virginia 22901

Five- and Six-Coordinated Cobalt(II), Nickel(II), Copper(II), and Zinc(II) Complexes of the Pentadentate Schiff Base Ligands

N,N'-Bis[(2-hydroxy-5-Y-phenyl)phenylmethylene]-4-azaheptane-1,7-diamine (Y = Chloro or Methyl) and *N,N'*-Bis[(5-chloro-2-hydroxyphenyl)phenylmethylene]-4-thiaheptane-1,7-diamine

EDWARD M. BOGE,^{1a} DEREK P. FREYBERG,^{1b} ERNEST KOKOT,^{1a} GARRY M. MOCKLER,^{1a} and EKK SINN^{1b}

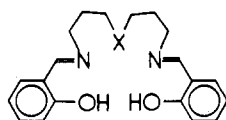
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Zinc(II), copper(II), nickel(II), and cobalt(II) complexes of the potentially pentadentate ligands H₂cbpN, H₂mbpN, and H₂cbpS and some Lewis base adducts (with pyridine (py) and 2-, 3-, and 4-methylpyridine (2-Mepy, 3-Mepy, 4-Mepy)) have been isolated and their spectral and magnetic properties investigated. The ligands are formed from the Schiff base condensation of 2-hydroxy-5-Y-benzophenone (Y = chloro, methyl) with 4-azaheptane-1,7-diamine (H₂cbpN and H₂mbpN) and 5-chloro-2-hydroxybenzophenone with 4-thiaheptane-1,7-diamine (H₂cbpS). These data indicate that the complexes ML (L = cbpN, mbpN, cbpS) are all five-coordinate. Previous x-ray structural data had shown that Ni(mbpN), Cu(mbpN), Zn(mbpN)·H₂O, and Zn(cbpN)·H₂O were five-coordinate. Spectral data indicate that the adducts with heterocyclic Lewis bases, ML·base (M = Co(II), Ni(II)), are octahedral with the Schiff base ligands acting as pentadentates. The postulated structures of the cbpX complexes differ unexpectedly from those previously postulated for the analogous salicylaldimines.

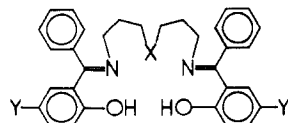
Introduction

Potentially pentadentate ligands salXH₂ (**1**) have been



1, salXH₂ (X = NH, NC₆H₅, S, O, PCH₃)

prepared by the Schiff base condensation of salicylaldehyde with tridentate amines. We have synthesized a series of ligands



2, H₂cbpN (X = NH, Y = Cl), H₂mbpN (X = NH, Y = CH₃),
H₂cbpS (X = S, Y = Cl)

2 based on substituted *o*-hydroxybenzophenones and amines containing central "NH" and thioether groups. These complexes of cbpX and mbpX invariably have greater solubility and are more suitable for the growth of crystals for x-ray crystallography than their salicylaldehyde analogues and were synthesized to take advantage of these properties. In this series of complexes the mbpN compounds are more soluble than their cbpN analogues.

Single-crystal x-ray diffraction studies on two nickel complexes^{2,3} with salX ligands (X = NH, NCH₃) have shown the metal environments to be intermediate between square-pyramidal and trigonal-bipyramidal geometries, while other studies^{4,5} have shown that Zn(cbpN)·H₂O, Zn(mbpN)·H₂O, Ni(mbpN), and Cu(mbpN) are all five-coordinate with the central donor atom coordinated to the metal atom. The water molecules in the two zinc complexes are not coordinated to the metal atom. The zinc complexes have trigonal-bipyramidal geometry, while the copper and nickel complexes have a distorted square-pyramidal geometry. In the copper complex the copper(II) to central nitrogen bond (2.37 Å) is significantly longer than in the corresponding nickel(II) (2.04 Å) or zinc(II) (2.16, 2.19 Å) complexes.

On the basis of spectral and magnetic data, Niswander et al.⁶ have concluded that for salX complexes where X = NH, NCH₃, NC₆H₅, PCH₃ the cobalt(II) complexes are five-coordinate and where X = S, O the central donor atom remains uncoordinated and the complexes are tetrahedral. From a spectroscopic study⁷ of similar copper(II) complexes, it was concluded that assignment of even gross stereochemical features is very difficult from electronic spectral data.

It was concluded that, in general, M-X bonds did not form, especially when M = Cu, Co and X = S, though a weak M-X interaction was considered possible.⁶ The structures of the complexes ML were therefore presumed to be tetrahedral for M = Co(II) and planar for M = Cu(II). For M = Ni(II),

Table I. Analytical Data^a

Complex	% C		% H		% N		% M		Color
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	
Ni(cbpN)	62.27	62.56	4.74	4.71	6.81	6.80	9.5	9.7	Olive green
Ni(cbpN)·py	63.83	63.84	4.92	5.01	8.05	8.29	8.4	8.3	Yellow-brown
Ni(cbpN)·1.75(2-Mepy)	65.42	65.44	5.33	5.27	6.73	6.51	7.5	7.5	Yellow-brown
Ni(cbpN)·1.5(3-Mepy)	65.06	65.08	5.26	5.39	8.56	8.11	7.8	7.5	Brown
Ni(cbpN)·2(4-Mepy)	65.77	65.83	5.34	5.14	8.71	8.31	7.3	7.1	Red-brown
Cu(cbpN)	61.79	61.82	4.70	4.76	6.76	6.53	10.2	10.0	Light green
Co(cbpN)	62.23	61.77	4.73	4.76	6.81	6.68	9.5	9.3	Tan
Co(cbpN)·py	63.80	64.02	4.92	4.86	8.05	7.46	8.4	8.2	Red-brown
Co(cbpN)·2-Mepy	64.23	63.74	5.11	4.79	7.88	6.78	8.3	8.0	Yellow-brown
Co(cbpN)·3-Mepy	64.23	64.78	5.11	5.18	7.88	7.66	8.3	8.0	Brown
Co(cbpN)·4-Mepy	64.23	64.66	5.11	4.89	7.88	6.69	8.3	8.0	Red-brown
Zn(cbpN)	61.6	62.1	4.7	4.9	6.7	6.4			Yellow
Ni(mbpN)	70.86	70.90	6.12	6.20	7.29	7.08	10.2	10.4	Brown
Ni(mbpN)·2py	71.94	72.04	6.17	6.07	9.55	8.97	8.0	7.8	Red-brown
Ni(mbpN)·2-Mepy	71.76	71.70	6.32	6.48	8.37	8.09	8.8	8.9	Brown
Ni(mbpN)·3-Mepy	71.76	72.06	6.32	6.41	8.37	8.59	8.9	8.9	Red-brown
Ni(mbpN)·4-Mepy	72.90	72.89	6.61	6.34	9.82	9.28	6.9	7.0	Yellow-brown
Cu(mbpN)·0.5H ₂ O	69.19	69.10	6.15	6.02	7.12	7.31	10.8	10.5	Green
Zn(mbpN)·0.5H ₂ O	69.0	68.6	6.1	6.1	7.1	6.7			Yellow
Ni(cbpS)	60.60	60.55	4.45	4.64	4.42	4.34	9.3	9.0	Brown
Ni(cbpS)·py	62.28	61.90	4.66	4.72	5.88	5.27	8.23	8.05	Yellow
Ni(cbpS)·2-Mepy	62.74	62.41	4.85	4.88	5.78	5.68	7.9	8.1	Yellow-brown
Ni(cbpS)·3-Mepy	62.74	62.97	4.85	5.09	5.78	6.02	7.9	8.0	Red-brown
Ni(cbpS)·4-Mepy	62.74	63.29	4.85	5.10	5.78	6.05	7.9	7.5	Yellow-brown
Cu(cbpS)·0.5H ₂ O	59.28	58.94	4.59	4.52	4.38	4.32	9.8	9.6	Light green
Co(cbpS)	60.58	60.48	4.45	4.42	4.42	4.43	9.3	9.5	Brown
Co(cbpS)·1.5py	62.99	62.93	4.75	4.84	6.51	6.41	7.8	7.8	Orange
Co(cbpS)·2-Mepy	62.73	62.45	4.85	5.12	5.78	6.23	8.1	8.0	Brown
Co(cbpS)·3-Mepy	62.73	62.48	4.85	5.10	5.78	5.93	8.1	8.0	Red-brown

^a py = pyridine; 2-, 3-, 4-Mepy = 2-, 3-, 4-methylpyridine.

polymeric structures have been suggested,⁸ as in the case of tetradentate salicylaldehyde complexes with long-chain α , ω -diamines.⁹ The polymeric nature of the Ni(sal) complexes is now in doubt,^{10,11} and polymeric structures should therefore not be presumed for the Ni(cbp) complexes a priori. Despite a great similarity in properties between MsalX and McbpX, we show the cbpX complexes not to be tetrahedral for Co, planar for Cu, nor polymeric for Ni. The salX analogues are presumed to differ structurally only when their physical properties are observed to differ significantly from those of the cbpX complexes.

We describe here the preparation, characterization, and probable structures of the zinc(II), copper(II), nickel(II) and cobalt(II) complexes of the ligands **2**.

Experimental Section

3,3'-Iminobis(propylamine), 5-chloro-2-hydroxybenzophenone, and 5-methyl-2-hydroxybenzophenone were obtained from the Aldrich Chemical Co.

Bis(3-aminopropyl) Sulfide. Lithium aluminum hydride (2 mol) and 500 mL of sodium-dried ether were placed in a 1-L round-bottom flask with a side-arm tube to which was fitted a reflux condenser and CaCl₂ guard tube. 3,3'-Thiodipropionitrile (1 mol) was placed in the side-arm tube and the mixture was refluxed on a water bath until all of the nitrile had been extracted into the ether solution (about 24 h). Water and 1 M sodium hydroxide solution were added, with stirring, to destroy the unreacted LiAlH₄. The resulting sludge was ground with its own volume of anhydrous sodium sulfate, placed in the cup of a Soxhlet apparatus, and extracted with ether for 24 h. The ether solution was dried with anhydrous sodium sulfate, and the ether was removed on a rotary evaporator, leaving a pale yellow oil which was used without further purification. A portion of the oil was removed, acetylated with acetic anhydride, and titrated with standard sodium hydroxide solution. Yields in the range 70–85% were obtained.

Schiff Bases. With **3,3'-Iminobis(propylamine)**. The hydroxybenzophenone (2 mmol) and the amine (1.1 mmol) were refluxed in methanol (100 mL) for 1 h. The resulting Schiff base solution was used for the preparation of the metal complexes.

With **Bis(3-aminopropyl) Sulfide**. The hydroxybenzophenone (2 mmol) and the amine (1.3 mmol) were refluxed together for 30 min.

2,2-Dimethoxypropane (100 mL) was added to the resulting melt and the solution was used to prepare the metal complexes.

Metal Complexes. 1. ML. (a) General Method. The Schiff base solution (1 mmol in 100 mL) was added to a hot methanol solution of the metal acetate (1 mmol in 100 mL). Piperidine (2 mL) was then added to the solution and the volume reduced until the complex precipitated. The following complexes were prepared by this method: Ni(cbpN), Ni(mbpN), Cu(cbpN), Cu(mbpN)·¹/₂H₂O, Zn(cbpN), Zn(mbpN)·¹/₂H₂O, Co(cbpS), Cu(cbpS)·¹/₂H₂O.

(b) **Co(cbpN)** was prepared by the above method under a nitrogen atmosphere and without the addition of piperidine.

(c) **Ni(cbpS)**. The crude product was prepared by method (a) and then recrystallized from pyridine, and the pyridine was removed by heating in a drying pistol (140 °C) for 4 h.

2. ML·n(base). The parent compounds were dissolved in a minimum volume of hot heterocyclic base. Crystals of the adducts precipitated slowly upon partial evaporation of the solutions. With Co(cbpN), this procedure was carried out under nitrogen to avoid oxygenation.

Physical Measurements 1. Analyses. C, H, and N analyses (Table I) were carried out by Dr. E. Challen at the University of New South Wales. Metals were estimated by atomic absorption spectrometry apart from some nickel analyses which were carried out gravimetrically using dimethylglyoxime.

2. Visible and Near-Infrared Spectra. Solid-state reflectance spectra were measured on a Zeiss PMQII spectrophotometer with an RA3 reflectance attachment. Solution spectra were recorded on a Hitachi EPS3T spectrophotometer.

3. Magnetic Measurements. Room-temperature magnetic moments were determined using the Gouy method. Magnetic moments over the temperature range 80–300 K were determined using an apparatus similar to that described by Figgis and Nyholm.¹²

4. Mass Spectra. Electron impact mass spectra were determined on a Hitachi Perkin-Elmer RMU-6E mass spectrometer, using an electron beam of 70 eV. The spectra of the copper(II) complexes with cbpN, mbpN, and cbpS and of the zinc(II) complexes with cbpN and mbpN exhibited peaks due to the corresponding Fe complexes, presumably due to metal exchange with the source block at the temperature used (~280 °C). No exchange was observed for the nickel(II) or cobalt(II) complexes, indicating their relative stability compared with the copper(II) and zinc(II) complexes.

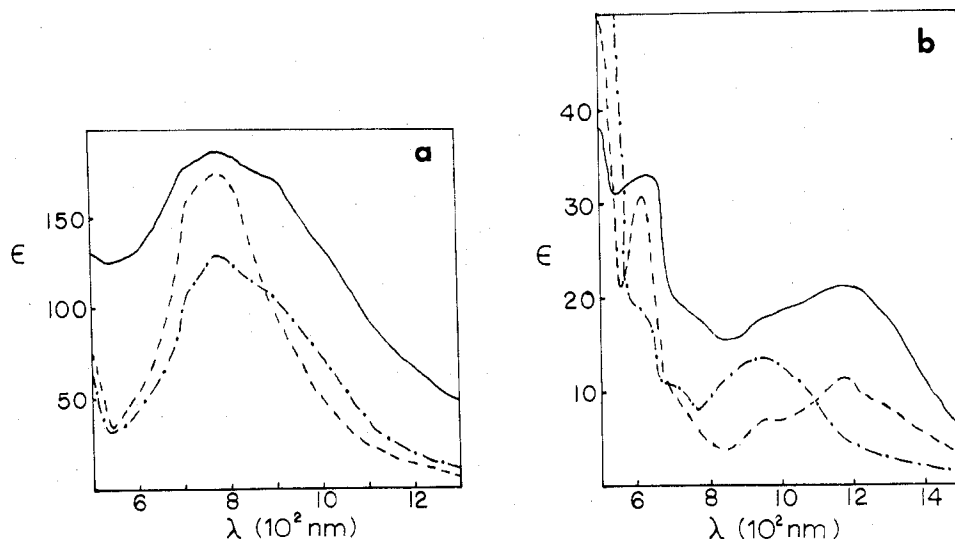


Figure 1. Electronic spectra of (a) Cu(cbpN) and (b) Ni(cbpN): —, solid state (OD, arbitrary scale); - - -, CH₂Cl₂ solution (ϵ , M⁻¹ cm⁻¹); - · - ·, py solution (ϵ , M⁻¹ cm⁻¹).

Results and Discussion

Copper(II) Complexes. The copper(II) complexes CuL are magnetically normal, obeying the Curie-Weiss law down to 80 K (Table II). Their visible spectra (Figure 1a, Table II) consist of one asymmetric band between 680 and 740 nm, which is consistent¹³ with the distorted square-pyramidal structure found for CumbpN.⁴ The similarity of the spectra of Cu(cbpS)· $\frac{1}{2}$ H₂O and Cu(cbpN) to that of Cu(mbpN)· $\frac{1}{2}$ H₂O suggests that these compounds are also approximately square pyramidal with the central sulfur or nitrogen atom coordinated to the copper atom. The hemihydrates (Cu(mbpN)· $\frac{1}{2}$ H₂O and Cu(cbpS)· $\frac{1}{2}$ H₂O) apparently have the water present as water of crystallization, similar to the case of the zinc complexes.

In dichloromethane solution, the spectra of the copper complexes resemble the solid-state spectra, indicating no change in stereochemistry. When the complexes are dissolved in the donor solvent, pyridine, there are small shifts to higher wavelengths (~ 30 nm) and a reduction in extinction coefficient for Cu(cbpN) and Cu(mbpN)· $\frac{1}{2}$ H₂O. There is a small shift to lower wavelength (10 nm) and higher extinction coefficient for Cu(cbpS). These small shifts in the spectra cannot be considered positive evidence for the formation of a six-coordinate adduct CuL·py. No solid adduct could be obtained from pyridine solution, and we therefore conclude that any pyridine adduct formed in solution must be of relatively low stability. This contrasts with the ready Lewis base adduct formation (with pyridine and methylpyridines) of the analogous cobalt(II) and nickel(II) complexes and (with water) of the nickel complex of a closely related ligand.¹⁴

Nickel(II) Complexes. NiL. The room-temperature magnetic moments are in the range 3.32–3.46 μ_B (Table II) compatible with a magnetically dilute monomeric five-coordinated structure. The visible-near-infrared spectra (Table III) have spectral bands near 600, 950, and 1150 nm (Figure 1b). These data are consistent with the distorted square-pyramidal structure found for Ni(mbpN) and suggest that the thioether group in Ni(cbpS) is coordinated to the nickel atom. The dichloromethane solution spectra suggest that the five-coordinate structure is retained in nondonor solvents. When the complexes are dissolved in heterocyclic base, the band near 1150 nm disappears, which is consistent with a change in coordination from square-pyramidal to nearly octahedral nickel(II).

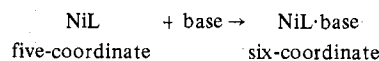
NiL·*n*(base). Complexes of formula NiL·*n*(base) (*n* = 1–3) are obtained when the five-coordinated complexes NiL are

Table II. Magnetic Moments

Complex	Magnetic moment range, ^a μ_B	Curie-Weiss const Θ , K
Ni(cbpN)	3.11–3.35	-21
Ni(mbpN)	2.93–3.23	-27
Ni(cbpS) ^b	3.46 (289.8 K)	
Ni(cbpN)·py	2.94–3.23	-27
Ni(cbpN)·1.75(2-Mepy)	2.98–3.19	-17
Ni(cbpN)·1.5(3-Mepy)	3.20–3.34	-11
Ni(cbpN)·2(4-Mepy)	3.21–3.39	-12
Ni(mbpN)·2py	3.05–3.34	-22
Ni(mbpN)·2-Mepy	2.92–3.12	-15
Ni(mbpN)·3-Mepy	3.10–3.32	-12
Ni(mbpN)·3(4-Mepy) ^b	3.24 (297 K)	
Ni(cbpS)·py ^b	3.01 (289.9 K)	
Ni(cbpS)·2-Mepy	2.86–3.20	-20
Ni(cbpS)·3-Mepy	3.15–3.35	-15
Ni(cbpS)·4-Mepy ^b	3.34 (289.9 K)	
Cu(cbpN)	2.01–2.10	-10
Cu(mbpN)·0.5H ₂ O	1.91–2.10	-12
Cu(cbpS)·0.5H ₂ O	1.76–2.17	-16
Co(cbpN)	3.99–4.41	-24
Co(cbpS)	4.61–4.85	-11
Co(cbpN)·py ^b	4.70 (290.3 K)	
Co(cbpN)·2-Mepy	4.54–4.87	-15
Co(cbpN)·3-Mepy	4.27–4.68	-21
Co(cbpN)·4-Mepy ^b	4.82 (290.3 K)	
Co(cbpS)·1.5py ^b	4.78 (289.9 K)	
Co(cbpS)·2-Mepy	4.37–4.70	-18
Co(cbpS)·3-Mepy	4.26–4.67	-22

^a Temperature range 79–300 K. ^b Magnetic moments measured at room temperature.

recrystallized from heterocyclic base. The NiL·*n*(base) solid-state spectra (Table II) closely resemble those of NiL complexes in base solution, indicating adduct formation via the reaction



X-ray crystallographic data¹⁴ obtained for [Ni(cbpS)·py]·*m*-xylene and [Ni(cbpS)·3-Mepy]· $\frac{1}{2}$ (3-Mepy) show that these complexes have octahedral geometry with the pentadentate ligand wrapped around the metal in a square-pyramidal geometry with approximately linear N–Ni–N and O–Ni–O arrangements. The heterocyclic base occupies the sixth octahedral site, opposite the sulfur atom, and the additional solvent is present in the crystal lattice and is not coordinated to the nickel. The thioether group is coordinated

Table III. Visible-Near-Infrared Spectra (nm)

Complex	Solid state	Dichloromethane ^a	Heterocyclic base ^a
Ni(cbpN)	600 sh, 950 sh, 1170	605 (30.2), 950 (6.5), 1175 (12.5)	925 (10.8) ^b
Ni(mbpN)	600 sh, 950 sh, 1180	600 (75), 950 sh, 1180 (26.6)	600 sh, 920 (6.7) ^b
Ni(cbpS)	600 sh, 950 sh, 1150	600 sh, 1150 (130)	600, 980 (10.2) ^b
Ni(cbpN)·py	600 sh, 890	610 sh, 950 (7.6), 1170 (9.2)	925 (10.4)
Ni(cbpN)·1.75(2-Mepy)	600 sh, 920	600 (40), 900 (7.0), 1180 (13.0)	940 (11.0)
Ni(cbpN)·1.5(3-Mepy)	600 sh, 910	650 sh, 1000 (5.6), 1180 (7.0)	650 sh, 950 (10.2)
Ni(cbpN)·2(4-Mepy)	610 sh, 890	950 (10.2)	950 (10.2)
Ni(mbpN)·2py	620 sh, 900	600 (60), 950 sh, 1170 (19.0)	600 sh, 920 (6.8)
Ni(mbpN)·2-Mepy	610 sh, 910	600 (65), 950 sh, 1180 (23.0)	600 sh, 950 (14.2)
Ni(mbp)·3-Mepy	620 sh, 900	600 (47), 950 sh, 1180 (17.5)	920 (5.5)
Ni(mbpN)·3(4-Mepy)	620 sh, 910	600 (50), 1180 (18)	650 sh, 920 (8.0)
Ni(cbpS)·py	650 sh, 980	990 (12.8)	600, 980 (19.2)
Ni(cbpS)·2-Mepy	610 sh, 980	600 sh, 1150 (12.1)	950 sh, 1010 (8.2)
Ni(cbpS)·3-Mepy	670 sh, 980	650 sh, 950 sh, 1020 (7.0)	980 (11.1)
Ni(cbpS)·4-Mepy	670 sh, 980	650 sh, 900 sh, 980 (11.7)	630 sh, 990 (10.3)
Co(cbpN)	650 sh, 1540	650 sh, 1550 (8.2)	650 sh, 1000 (9.8), 1580 (6.9) ^b
Co(cbpS)	650 sh, 1470	650 sh, 1500 (12.0)	680 sh, 1030 (19) ^b
Co(cbpN)·py	650 sh, 990	650 sh, 1570 (9.1)	650 sh, 1000 (9.8), 1580 (6.8)
Co(cbpN)·2-Mepy	650 sh, 1000	650 sh, 1570 (17.0)	650 sh, 1000 (5.6), 1570 (4.1)
Co(cbpN)·3-Mepy	670 sh, 1000	650 sh, 1580 (13.6)	660 sh, 1000 (7.2), 1580 (5.5)
Co(cbpS)·1.5py	690 sh, 1010	670 sh, 1490 (12.3)	680 sh, 1030 (19.0)
Co(cbpS)·2-Mepy	620 sh, 1020	650 sh, 1500 (14.3)	650 sh, 1050 (10.5)
Co(cbpS)·3-Mepy	650 sh, 1020	650 sh, 1480 (12.8)	680 sh, 1030 (12.5)
Cu(cbpN)	745, 870 sh	745 (172)	775 (137), 900 sh
Cu(mbpN)·0.5H ₂ O	740, 850 sh	740 (192)	770 (130)
Cu(cbpS)·0.5H ₂ O	690, 790 sh	680 (153)	670 (215)

^a The solutions were 0.01 M. Extinction coefficients are in parentheses. ^b In pyridine.

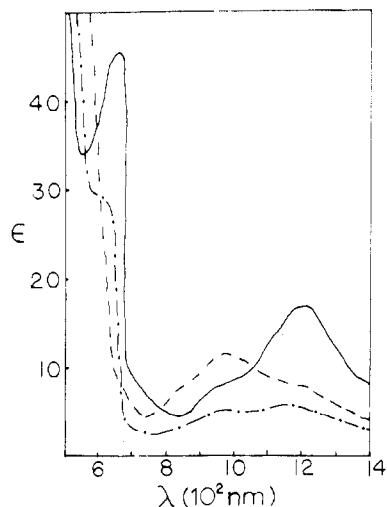


Figure 2. Dichloromethane solution spectra (ϵ , $M^{-1} \text{ cm}^{-1}$): —, Ni(mbpN)·3-Mepy; - - -, Ni(cbpN)·2(4-Mepy); - · - ·, Ni(cbpN)·1.5(3-Mepy).

to the metal (2.47 Å). The spectra of the adducts when dissolved in dichloromethane (Table III, Figure 2) indicate varying degrees of dissociation to the five-coordinate complex, as evidenced by the reappearance of the 1150-nm band. The position of the ${}^3A_2 \rightarrow {}^3T_2$ band¹⁶ in the spectra of the octahedral adducts (920–950 nm for Ni(cbpN)·base and Ni(mbpN)·base and 980–1010 nm for Ni(cbpS)·base) indicates a weaker ligand field in cbpS than in cbpN.

Cobalt(II) Complexes. CoL. These complexes exhibit normal Curie–Weiss behavior (Table II). Their spectra (Table III, Figure 3) with bands near 620 and 1500 nm are consistent with a distorted square-pyramidal geometry,¹⁶ for L = cbpS and cbpN, both in the solid state and in solution. Attempts to obtain suitable crystals for x-ray structure determinations have so far been unsuccessful.

Heterocyclic Base Solution. (1) Co(cbpS). New spectral bands near 650 and 1030 nm (Table II, Figure 4) indicate the formation of an octahedral species

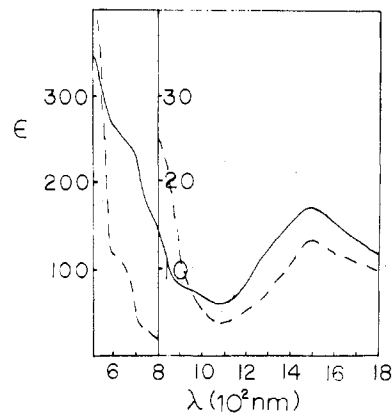
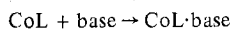


Figure 3. Electronic spectra of Co(cbpN): —, solid state (OD, arbitrary scale); - - -, CH_2Cl_2 solution (ϵ , $M^{-1} \text{ cm}^{-1}$).

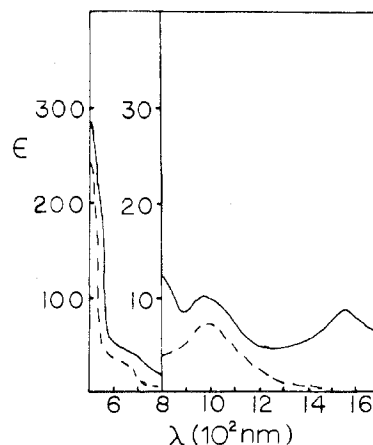


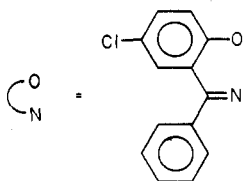
Figure 4. Pyridine solution spectra of CoL (ϵ , $M^{-1} \text{ cm}^{-1}$): —, Co(cbpN); - - -, Co(cbpS).

(2) Co(cbpN). The spectra (Figure 4) consist of bands near both 1000 and 1500 nm, indicating the presence of both CoL and CoL·base. Thus the five-coordinate cobalt complexes are less susceptible to coordination in the sixth donor site than the

Table IV. Monoisotopic Mass Spectra of McbpN Complexes (Principal Peaks)

Co	Ni	Cu	Zn	Proposed ion structure ^a
616	615	620	621 604	McbpN ⁺
598	597			
582	581	586	587 550	McbpNHCl
			536	
399, 400				
384, 385	384	389	389	
357, 358	357	362	363	
289	289			

^a In these structures and those in Table V



corresponding nickel(II) complexes. This is consistent with the observations of Sacconi et al.¹⁶ and Niswander et al.⁶ that the related cobalt(II) salicylaldimine complexes showed little or no adduct formation with pyridine, while adducts with the nickel(II) complexes formed readily.

Co(cbpN) oxygenates¹⁴ in base solution over a period of several hours, requiring solution spectra to be measured under nitrogen. Co(cbpS) in base solution was much less susceptible to oxygenation¹⁴ (it oxygenates over a period of several days) and spectral measurements could be made in air.

(3) CoL·n(base) (n = 1–1.5). The spectra (Figure 5) and magnetic properties of the adducts (Tables II, III) are consistent with an octahedral structure. This conclusion is supported by an x-ray structural determination¹⁵ of [Co(cbpS·3-Mepy)]^{1/2}(3-Mepy), which shows the metal atom to be six-coordinated with the central thioether sulfur coordinated

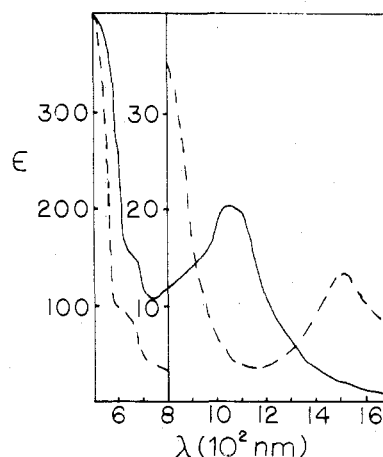


Figure 5. Electronic spectra of Co(cbpS)·1.5(3-Mepy): —, solid state (OD, arbitrary scale); - - -, CH₂Cl₂ solution (ϵ , M⁻¹ cm⁻¹).

Table V. Monoisotopic Mass Spectra of McbpS Complexes (Principal Peaks)

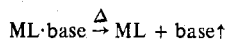
Co	Ni	Cu	Proposed ion structure ^a
633 417	632	637	McbpS
		368	
362	361		
329, 330	329	332	
		306	
270	269, 270		

^a See footnote to Table IV.

to the cobalt atom. This thioether coordination can be contrasted with the behavior of the salicylaldimine complex Co(salS), for which it has been suggested,⁶ from spectral data, that the sulfur atom was not coordinated to the cobalt atom.

Spectral data (Figure 5) show that the adducts dissociate in dichloromethane solution to give the five-coordinated species.

Mass Spectra. The fragmentation patterns of the complexes exhibited close similarities to those reported for the analogous salicylaldimines,¹⁷ facilitating the interpretation of the present spectra and supporting the earlier work. The principal mass spectral peaks and proposed ion structures are shown in Tables IV and V, for the cbpN and cbpS compounds, respectively. The mbpN complexes gave spectra corresponding to those for the cbpN complexes, though no MmbpN - CH₃ peak was seen. The heaviest ion observed from the ML-base complexes was the five-coordinate ML⁺ ion, the base having been removed from the complex by heat and vacuum in each case before ionization occurred



Each complex ML may be unambiguously identified by its molecular ion, while fragmentation patterns are characteristic of both M and L.

The cbpN complexes (except Co(cbpN)) all show a loss of NH₃ or NH₄; but only Zn(cbpN) shows a further degradation

of the amide chain while still retaining both benzophenone imine groups. This is presumably due to lack of stability of the five-coordination in the zinc(II) complex. However, in all cases, once one of the benzophenone end groups breaks off, the linear triamine chain degrades atom by atom.

The cbpS complexes, in contrast, do not show loss of H₂S to any great extent. This is in agreement with the observation that the M-S bond is considerably stronger than the M-N bond. The spectra show, first, a loss of one of the benzophenone groups and then degradation of the aliphatic chains. Although atom-by-atom degradation does occur, loss of the entire propyl group is seen to be the principal process. Also, a peak corresponding to benzophenone *N*-propylimine appears, which is not seen in the cbpN complexes. The similarity of the mass spectra of the Co- and Cu-cbpS complexes to those of the analogous salS's indicates that any differences in the behavior of the potentially coordinating sulfur atom in cbpS and salS is quite subtle. The extent of the difference between the two ligands and the reasons for it warrant closer study.

Conclusion

The structures of Cu(mbpN) and Ni(mbpN) reveal both complexes to be five-coordinate. From their spectral and magnetic properties and those of the corresponding cbpN and cbpS complexes with M = Cu(II), Ni(II) or Co(II) we predict that the latter will also be five-coordinate and that M-S, M-N bonding is general in such complexes. This prediction is supported by structural determinations of [McbpS·3-Mepy]^{1/2}(3-Mepy) (M = Ni(II), Co(II)), where, in each case, the thioether sulfur is coordinated to the metal. In the same way, where the properties of the two series are the same, we can postulate that thioether coordination occurs in the salX complexes. Specifically ruled out for these cases would be four-coordinated structures for Cu(II) and Co(II) and,

probably, polymeric structures for Ni(II).

Registry No. Ni(cbpN), 62561-26-6; Ni(cbpN)·py, 62520-63-2; Ni(cbpN)·(2-Mepy), 62520-64-3; Ni(cbpN)·(3-Mepy), 62520-65-4; Ni(cbpN)·(4-Mepy), 62520-66-5; Cu(cbpN), 62600-31-1; Co(cbpN), 62600-30-0; Co(cbpN)·py, 62520-67-6; Co(cbpN)·(2-Mepy), 62520-68-7; Co(cbpN)·(3-Mepy), 62520-69-8; Co(cbpN)·(4-Mepy), 62520-70-1; Zn(cbpN), 56937-89-4; Ni(mbpN), 56811-16-6; Ni(mbpN)·py, 62561-23-3; Ni(mbpN)·(2-Mepy), 62520-71-2; Ni(mbpN)·(3-Mepy), 62520-72-3; Ni(mbpN)·(4-Mepy), 62561-24-4; Cu(mbpN), 56811-15-5; Zn(mbpN), 56811-17-7; Ni(cbpS), 61218-51-7; Ni(cbpS)·py, 61218-54-0; Ni(cbpS)·(2-Mepy), 62520-79-0; Ni(cbpS)·(3-Mepy), 61218-53-9; Ni(cbpS)·(4-Mepy), 62520-80-3; Cu(cbpS), 62520-81-4; Co(cbpS), 61218-50-6; Co(cbpS)·py, 62549-81-9; Co(cbpS)·(2-Mepy), 62520-82-5; Co(cbpS)·(3-Mepy), 61218-52-8; bis(3-aminopropyl) sulfide, 13643-20-4; 3,3'-thiodipropionitrile, 111-97-7.

References and Notes

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Contribution from the Departments of Chemistry, University of Wollongong, Wollongong, NSW 2500, Australia, and the University of Virginia, Charlottesville, Virginia 22901

Crystal and Molecular Structures of [N,N'-Bis((5-chloro-2-hydroxyphenyl)phenylmethylene)-4-thiaheptane-1,7-diamino]copper(II)

D. P. FREYBERG,^{1a} G. M. MOCKLER,^{1b} and E. SINN^{*1a}

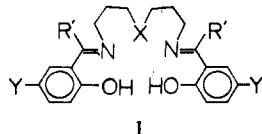
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The title complex has been synthesized and studied by single-crystal x-ray diffraction. Crystal data for Cu(cbpS), CuCl₂SO₂N₂C₃₈H₂₈, are as follows: space group C2/c, Z = 8, a = 18.689 (4) Å, b = 13.735 (5) Å, c = 22.669 (9) Å, β = 100.61 (2)°, V = 5720 Å³, R = 3.1%, 2606 reflections. The complex molecule contains the metal atom in a distorted square pyramid with the Cu-S bond pointing at the apex. The O₂N₂ base of the pyramid is distorted so as to give some trigonal-bipyramidal character to the geometry, the N atoms being raised above (0.07 Å) the Cu atom and the O atoms below it (0.3 Å). Although the Cu-S bond is elongated (2.686 (1) Å), it is no weaker than the Cu-N bonds in related copper Schiff base complexes. The observation of a Cu-S bond at all is unexpected from the interpretation of earlier physical data on complexes containing the same type of thioether chain in the ligand. It now appears likely that such a bond occurs in some other complexes where its existence had not previously been proposed from the available data.

Introduction

Complexes McbpX and MmbpX of the ligands H₂cbpX (1,



with R' = C₆H₅, Y = Cl) and H₂mbpX (1, with R' = C₆H₅, Y = CH₃) have been found to contain MX bonds when M = Co(II) or Ni(II) and X = S²⁻ and when M = Ni, Cu,³ or Zn⁴

and X = NH. Such a bond has also been postulated for the case M = Cu(II) and X = S⁵. On the other hand, for the unsubstituted MsalX complexes (1, R' = Y = H), the structures were previously proposed to be four-coordinated and hence presumably square planar for M = Cu(II) and tetrahedral for M = Co(II) and X = S⁶⁻⁸. The Ni(II) analogues were proposed to be polymeric,⁸ like the NiSalR complexes⁹ (SalRH₂ is 2 with R' = Y = H). No Ni-X bond would then be required to explain the magnetic or spectral properties. However, there is evidence that the SalR, cbpX (X = NH, S), cbpR (2, R' = C₆H₅, Y = Cl), and mbpR (2, R' = C₆H₅,