

The Crystal and Molecular Structure of Chloro(2,4-dithiobiuret)copper(I)–*N,N*-Dimethylformamide: $[\text{Cu}(\text{Hdtb})\text{Cl}]_n \cdot n\text{DMF}$

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Abstract

The title complex, $[\text{Cu}(\text{C}_2\text{H}_4\text{N}_2\text{S}_2)\text{Cl}] \cdot \text{C}_3\text{H}_7\text{NO}$, $\text{C}_5\text{H}_{12}\text{ClCuN}_4\text{OS}_2$, crystallizes in the monoclinic space group $C2/c$ with $a = 14.926$ (1), $b = 10.925$ (1), $c = 15.208$ (1) Å, $\beta = 112.17$ (1)°, $Z = 8$. Data for 1363 reflexions were collected with a Philips PW 1100 automatic four-circle diffractometer. The structure was solved by direct methods and Fourier and difference Fourier syntheses. Refinement was carried out by least-squares methods with anisotropic thermal parameters for all the non-hydrogen atoms and only positional parameters for H atoms (excluding two DMF H atoms) to a final $R = 0.048$. The Hdtb molecule is planar within 0.27 Å, has a *trans* configuration and is S,S-bonded to two Cu atoms in an endless chain. Two parallel chains exchange 'long' Cu–S interactions (Cu–S = 2.880 Å) forming coordination dimers $(\text{CuS}_2\text{Cl})_2$ along the double chain. The Cu atom has trigonal-pyramidal coordination and is 0.326 Å from the basal S, S, Cl plane (Cu–S = 2.245, 2.258; Cu–Cl = 2.302 Å) belonging to its chain. Each Hdtb molecule is linked through a $\text{NH} \cdots \text{O}$ and a $\text{HNH} \cdots \text{O}$ bond to the O atom of the DMF molecule, which is planar within 0.03 Å.

Introduction

2,4-Dithiobiuret, $(\text{H}_2\text{N} \cdot \text{CS})_2\text{NH}$, (Hdtb) behaves as a S,S-chelating ligand in the neutral complexes $\text{Pd}(\text{dtb})_2$ (Girling & Amma, 1968), $\text{Ni}(\text{dtb})_2$ (Luth, Hall, Spofford & Amma, 1969), $\text{Ni}(\text{dtb})_2 \cdot \text{glycol}$ (Pignedoli, Peyronel & Antolini, 1972) and in the cationic complex $\text{Ni}(\text{Hdtb})_2(\text{ClO}_4)_2 \cdot \text{EtOH}$ (Pignedoli, Peyronel & Antolini, 1973). In a previous study (Pignedoli & Peyronel, 1976) we investigated the $\text{Cu}(\text{Hdtb})X$ ($X = \text{Cl}, \text{Br}, \text{I}$) complexes showing from their infrared spectra that the ligand is S,S-coordinated to the metal. At the same time other authors (Kowal & Kedzia, 1976) affirmed, on the basis of infrared and Raman investigations that in $\text{Cu}(\text{Hdtb})X$ ($X = \text{Cl}, \text{Br}$) the ligand is N,N-coordinated. As these complexes could not be obtained in crystals of suitable

size for single-crystal diffraction experiments, we have now prepared their DMF solvates and determined the crystal structure of $\text{Cu}(\text{Hdtb})\text{Cl} \cdot \text{DMF}$ in order to establish unequivocally the type of ligand coordination and also whether the molecule is bonded in this complex in the *cis* form as in other complexes or in the *trans* form as in the free ligand (Spofford & Amma, 1972).

Experimental

The compound was prepared by adding a solution of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (1 mmol) in DMF (2 ml) to a solution of Hdtb (2 mmol) in DMF (8 ml). Cu^{II} is instantaneously reduced to Cu^{I} by the excess of Hdtb giving a gold-yellow solution from which the yellow compound crystallizes. Analysis, found % (for $\text{C}_5\text{H}_{12}\text{ClCuN}_4\text{OS}_2$, calculated % in parentheses): C 19.49 (19.54), H 3.99 (3.94), N 18.07 (18.23). The substance is diamagnetic.

The crystals used for the X-ray experiments were obtained by slow recrystallization from a DMF solution and protected with a thin layer of Sicomet 85 in order to avoid loss of DMF.

The cell parameters were determined at 291 K and the intensities were recorded for $\sin \theta / \lambda \leq 0.57 \text{ \AA}^{-1}$ using a four-faced prismatic crystal approximately $0.25 \times 0.30 \times 0.80$ mm. A Philips PW 1100 automatic four-circle diffractometer connected on-line to a computer was used with monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$). The cell parameters were refined by least-squares methods from $2 \sin \theta$ values, each determined twice with independent measurements of 24 reflexions with medium–strong intensities using the *LSRET* program of A. Immirzi (1977, private communication).

Crystal data

Chloro(2,4-dithiobiuret)copper(I)–*N,N*-dimethylformamide $[\text{Cu}(\text{Hdtb})\text{Cl}]_n \cdot n\text{DMF}$, $\text{C}_5\text{H}_{12}\text{ClCuN}_4\text{OS}_2$, monoclinic, observed reflexions: hkl , $h + k = 2n$; $h0l$, $l = 2n$; the structure was solved in the space group $C2/c$ (C_{2h}^6 , No. 15); $a = 14.926$ (1), $b = 10.925$

(1), $c = 15.208$ (1) Å, $\beta = 112.17$ (1)°, $V = 2296.4$ Å³, $F(000) = 1248$, $FW = 307.1$, $Z = 8$, $d_c = 1.78$ Mg m⁻³. The number of molecules per cell was calculated ($Z = 8.06$) from the molecular volume (Immirzi, 1976) by assuming a covalent radius of 1.35 Å (Pauling, 1960) for the Cu^I ion.

The observed intensities were corrected for Lorentz and polarization factors; 1363 independent reflexions with $F_o > 1.5\sigma(F_o)$, from 1808 measured reflexions, were used for the calculations. Of the atomic scattering factors used (*International Tables for X-ray Crystallography*, 1974) those for the Cu, S, Cl and O atoms were corrected for the real part of the anomalous dispersion (*International Tables for X-ray Crystallography*, 1974); for H atoms the SDS coefficients were used.

The structure was solved by direct methods using the program *MULTAN* (Germain, Main & Woolfson, 1971). From 280 reflexions having $E > 1.26$ all the non-hydrogen atoms of the Cu(Hdtb)Cl part of the compound and the O atom of the DMF molecule were located and gave very good bond distances. The other non-hydrogen atoms of the DMF molecule were located with Fourier and difference Fourier syntheses. After isotropic and some anisotropic refinements of all the non-hydrogen atoms, all the Hdtb and most of the DMF H atoms were located in the difference Fourier syntheses. In the subsequent refinement H(O) was assumed to be in the position given by the difference Fourier syntheses and H(O21) in the calculated position.

The structure was then refined, anisotropically for the non-hydrogen and with fixed isotropic thermal parameters for the H atoms, by the block-diagonal least-squares method to a final $R = \sum |F_o| - |F_c| / \sum |F_o| = 0.048$. The program *MIQUAD* (Immirzi, 1967) was used with the weighting formula $1/w = 2|F_o|_{\min} + |F_o| + (2/|F_o|_{\max})|F_o|^2$ (Cruickshank, 1965). In the final cycle of computations the average

parameter shifts were about 0.1 of the e.s.d.'s for the non-hydrogen atoms and 0.10–0.15 of the e.s.d.'s for the Hdtb H atoms.

The final positional parameters of the atoms are given in Table 1.*

The interatomic distances and angles with their e.s.d.'s (Tables 2 and 3) were calculated with the program *MIQUAD* (Immirzi, 1967). The least-squares planes (Table 4) and the atom deviations from them were calculated with *PIAMED* (Immirzi, 1967). The orthographic projections of the polymeric chain (Fig. 1), the thermal ellipsoids of the asymmetric unit (Fig. 2) and the coordination dimer (CuS₂Cl)₂ (Fig. 3) were

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34379 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Interatomic distances (Å) and their e.s.d.'s*

Cu–Cl	2.302 (2)	O–C(O)	1.26 (1)
Cu–S(1)	2.245 (2)	C(O)–N(O)	1.31 (1)
Cu–S(2)	2.258 (2)	N(O)–C(O1)	1.50 (1)
Cu–S(1'')	2.880 (3)	N(O)–C(O2)	1.38 (2)
S(1)–C(1)	1.719 (8)	C(O)–H(O)	1.18 (8)
S(2)–C(2)	1.682 (5)	C(O1)–H(O11)	1.06 (8)
C(1)–N(1)	1.294 (8)	C(O1)–H(O12)	1.14 (8)
C(2)–N(3)	1.316 (10)	C(O1)–H(O13)	1.03 (12)
C(1)–N(2')	1.365 (10)	C(O2)–H(O21)	1.06
C(2)–N(2)	1.385 (10)	C(O2)–H(O22)	1.15 (11)
N(2)–H(2)	0.91 (6)	C(O2)–H(O23)	0.98 (9)
N(1)–H(11)	0.77 (10)	O–N(2)	2.807 (5)
N(1)–H(12)	0.94 (8)	O–N(3)	2.922 (7)
N(3)–H(31)	0.95 (6)	O–H(2)	1.95
N(3)–H(32)	0.84 (10)	O–H(31)	2.13
Cl–N(1)	3.216 (5)	Cl–H(12)	2.34 (8)
Cl–N(3)	3.227 (8)	Cl–H(32)	2.40 (10)

Positions of S(1''): 1.5 – x, 0.5 – y, 1 – z; N(2'): x – 0.5, 0.5 – y, z – 0.5.

Table 1. *Fractional coordinates for non-hydrogen ($\times 10^4$) and for hydrogen atoms ($\times 10^3$)*

Estimated standard deviations are given in parentheses.

	x	y	z		x	y	z
Cu	7371 (1)	2978 (1)	6054 (1)	H(2)	1017 (5)	475 (6)	895 (5)
Cl	6548 (1)	4773 (1)	6012 (1)	H(11)	466 (5)	323 (6)	404 (5)
S(1)	6587 (1)	1404 (1)	5138 (1)	H(12)	569 (5)	351 (6)	472 (5)
S(2)	8624 (1)	2564 (1)	7423 (1)	H(31)	892 (5)	567 (7)	807 (5)
C(1)	5476 (4)	1899 (5)	4363 (4)	H(32)	807 (5)	495 (6)	731 (5)
C(2)	9067 (4)	3888 (6)	7984 (4)	H(O)	975	834	867
N(1)	5178 (3)	3013 (5)	4354 (3)	H(O11)	1044 (5)	974 (7)	856 (5)
N(2)	9919 (3)	3985 (4)	8774 (3)	H(O12)	1114 (5)	990 (7)	785 (5)
N(3)	8644 (4)	4956 (5)	7715 (4)	H(O13)	1160 (5)	993 (7)	915 (5)
O	10287 (5)	6504 (5)	8794 (5)	H(O21)	1203	664	893
C(O)	10362 (7)	7640 (9)	8694 (6)	H(O22)	1257 (5)	816 (7)	921 (5)
N(O)	11156 (5)	8155 (7)	8690 (5)	H(O23)	1197 (5)	767 (7)	806 (5)
C(O1)	11128 (10)	9510 (11)	8543 (8)				
C(O2)	11977 (10)	7560 (18)	8697 (12)				

drawn with *ORTEP* (Johnson, 1965). In the asymmetric unit used for the description of the structure the Hdtb moiety is divided into two parts in order to emphasize the coordination of the metal, which is the principal interest of this work, and the intramolecular hydrogen bonds. A difference Fourier synthesis of the Hdtb H atoms gave well resolved and centered peaks.

Results and discussion

The structure consists of four infinite polymeric zigzag chains; the axes of two lie in the $x, \frac{1}{2}, z$ and those of the other two in the $x, \frac{3}{2}, z$ plane. The non-hydrogen atoms of the chain are coplanar within 0.35 Å, their least-squares mean plane making an acute angle of 56.5°

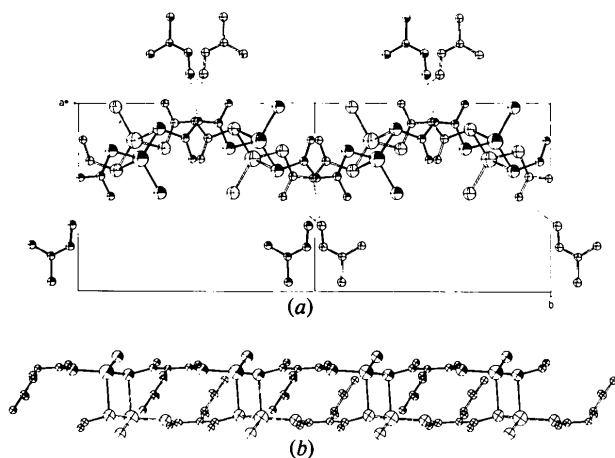


Fig. 1. Orthographic projection of the double chain on (a) the $a (\sin \beta) b$ and (b) the ac planes.

with the ab plane. Each chain is formed by alternating CuCl groups and bridging metal-S,S-bonded Hdtb molecules which have a *trans* configuration, their NH_2 groups forming weak hydrogen bonds with the Cl atom (Fig. 2).

The Hdtb and DMF molecules are almost planar (Table 4). Each Hdtb molecule is linked through a $\text{NH}\cdots\text{O}$ and a $\text{HNH}\cdots\text{O}$ bond to the O atom of the same DMF molecule, the ring $\text{O}-\text{H}(2)-\text{N}(2)-\text{C}(2)-\text{N}(3)-\text{H}(31)$ being planar within an r.m.s. atom deviation of 0.19 Å from its least-squares plane.

The Cu atom is bonded with normal distances to the S(1), S(2) and Cl atoms belonging to its chain at a

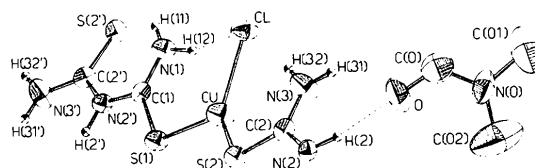


Fig. 2. *ORTEP* plot of the thermal ellipsoids of the asymmetric unit (xyz) scaled to include 50% probability. Atoms (') at the $x = 0.5, 0.5 - y, z = 0.5$ position are included in order to show a complete Hdtb molecule.

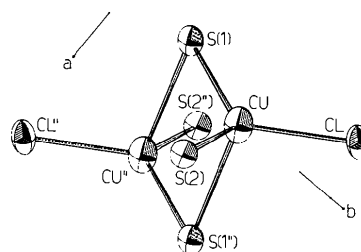


Fig. 3. *ORTEP* plot of the thermal ellipsoids scaled to include 40% probability of the coordination dimer $(\text{CuS}_2\text{Cl})_2$ projected on the ab plane. Atoms (') are at the position $1.5 - x, 0.5 - y, 1 - z$.

Table 3. *Interatomic angles (°) and their e.s.d.'s*

Cl—Cu—S(1)	119.18 (4)	C(1)—N(1)—H(11)	124 (8)	O—C(O)—H(O)	122 (4)
Cl—Cu—S(2)	116.35 (5)	C(1)—N(1)—H(12)	110 (3)	N(O)—C(O)—H(O)	114 (4)
S(1)—Cu—S(2)	118.39 (5)	C(2)—N(3)—H(31)	120 (4)	N(O)—C(O1)—H(O11)	102 (3)
S(1'')—Cu—Cl	101.06 (3)	C(2)—N(3)—H(32)	117 (7)	N(O)—C(O1)—H(O12)	120 (3)
S(1''')—Cu—S(1)	93.90 (4)	H(11)—N(1)—H(12)	126 (5)	N(O)—C(O1)—H(O13)	109 (5)
S(1''')—Cu—S(2)	99.87 (4)	H(31)—N(3)—H(32)	122 (6)	H(O11)—C(O1)—H(O12)	107 (3)
Cu—S(1)—C(1)	109.1 (2)	C(1)—N(2')—H(2')	112 (4)	H(O11)—C(O1)—H(O13)	102 (4)
Cu—S(2)—C(2)	109.0 (2)	C(2)—N(2)—H(2)	118 (5)	H(O12)—C(O1)—H(O13)	115 (5)
S(1)—C(1)—N(1)	122.8 (4)	Cl—H(12)—N(1)	155 (3)	N(O)—C(O2)—H(O21)	114
S(2)—C(2)—N(3)	123.6 (3)	Cl—H(32)—N(3)	171 (6)	N(O)—C(O2)—H(O22)	101 (3)
S(1)—C(1)—N(2')	114.7 (6)	H(12)—Cl—H(32)	142 (3)	N(O)—C(O2)—H(O23)	105 (4)
S(2)—C(2)—N(2)	124.2 (3)	Cu—Cl—H(12)	69 (1)	H(O21)—C(O2)—H(O22)	112
N(1)—C(1)—N(2')	122.5 (5)	Cu—Cl—H(32)	73 (1)	H(O21)—C(O2)—H(O23)	115
N(2)—C(2)—N(3)	112.2 (3)	N(2)—H(2)—O	155	H(O22)—C(O2)—H(O23)	109 (5)
C(1)—N(2')—C(2')	130.3 (8)	N(3)—H(31)—O	141		
O—C(O)—N(O)	123.0 (4)	H(2)—O—H(31)	62		
C(O)—N(O)—C(O1)	116.7 (4)				
C(O)—N(O)—C(O2)	126.6 (6)				
C(O1)—N(O)—C(O2)	116.2 (7)				

Positions of S(1''): $1.5 - x, 0.5 - y, 1 - z$; C(2'), N(2'), H(2'): $x = 0.5, 0.5 - y, z = 0.5$.

Table 4. *Least-squares planes*

The equation in the form $Ax + By + Cz + D = 0$ is referred to the crystallographic axes a, b, c ; plane coefficients A, B, C, D are $\times 10^4$. Deviations of the atoms from the planes and r.m.s. deviations are in \AA ($\times 10^3$).

<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	R.m.s.	S(1)	C(1)	N(1)	N(2')			
-7006	-2344	8885	-3072	11	3	-10	4	3			
					S(2)	C(2)	N(3)	N(2)			
-7937	-1349	8488	-10114	3	-1	3	-1	-1			
					C(1)	N(2')	C(2')	H(2')			
-8080	-850	8449	-11744	3	1	-2	1	1			
					C(1)	N(1)	H(11)	H(12)			
-5972	-1850	9481	10307	26	-5	22	-10	-7			
					C(2)	N(3)	H(31)	H(32)			
-7300	-1398	8950	3809	64	14	-55	20	22			
					S(1)	C(1)	N(1)	N(2')	C(2')	N(3')	S(2')
-7981	-532	8570	-9957	271	-235	49	327	-4	-24	191	-304
					C(O)	N(O)	C(O1)	C(O2)			
26	1035	9201	130843	47	-15	41	-12	-14			
					O	C(O)	N(O)	C(O1)	C(O2)		
20	1027	9204	130702	33	-1	-13	41	-13	-14		

Positions of atoms ('): $x - 0.5, 0.5 - y, z - 0.5$.

Table 5. *A comparison of some distances (Å) in Cu(Hdtb)Cl.DMF with those in related compounds*

	Cu(SUra) ₂ Cl.DMF	Cu(Hdtb)Cl.DMF	Cu(tu) ₂ Cl	Cu(dmt) ₃ Cl
Cu-S	2.225, 2.228 (1)	2.245, 2.258 (2)	2.229, 2.265, 2.309 (5)	2.360 (1)
Cu-Cl	2.260 (1)	2.302 (2)		2.406 (5)
Long bond		(Cu-S) 2.880 (3)	(Cu-Cl) 2.828 (5)	
Cu distance	0.116	0.326	0.316	0.899
from plane	S, S, Cl	S, S, Cl	S, S, S	S, S, S

distance of 0.326 Å from the S(1)S(2)Cl plane. The CuS₂Cl groups belonging to two parallel chains lying in the same $x, \frac{1}{4}, z$ or $x, \frac{3}{4}, z$ plane exchange long Cu-S bonds forming a coordination dimer (Fig. 3). The apical S(1'') atom lies approximately on the line perpendicular to the basal S(1)S(2)Cl plane as shown by the angles made by the S(1'')-Cu bond with the Cu-S(1), Cu-S(2), Cu-Cl bonds (Table 3).

With thioamidic ligands copper(I) chloride forms complexes in which the metal has almost planar trigonal coordination as in chlorobis(2-thiouracil)-copper(I) dimethylformamide solvate, Cu(SUra)₂Cl.DMF (Hunt, Griffith & Amma, 1976) or almost tetrahedral S₃Cl coordination as in chlorotris(*N,N'*-dimethylthiourea)copper(I), Cu(dmt)₃Cl (Girling & Amma, 1971). The basal Cu-S and the Cu-Cl distances of Cu(Hdtb)Cl.DMF are intermediate between those of the above-mentioned complexes (Table 5).

The long Cu-S bond in Cu(Hdtb)Cl.DMF is comparable to the long Cu-Cl bond observed for one of the two differently coordinated Cu^I atoms in the thiourea complex Cu(tu)₂Cl (Spofford & Amma, 1970). Also the distances of Cu from the basal plane are very similar in these two complexes, in which the Cu atom has almost trigonal-pyramidal coordination.

The Cl ion has two Cl-N intramolecular distances (Table 2) comparable with the distances (3.157 Å) observed in Cu(dmt)₃Cl (Girling & Amma, 1971) and suggesting the possibility of NH...Cl hydrogen bonding. The corresponding Cl distances from the refined H atom positions are in fact much shorter than Pauling's (1960) van der Waals radii sum (3.0 Å). These intramolecular Cl...H bonds may be at least partially responsible for the configuration of the almost planar polymeric chain of the complex. The DMF O atom has two short intermolecular O...N distances (Table 2), the corresponding O...H distances being shorter than Pauling's (1960) van der Waals radii sum (2.60 Å) and comparable to the NH...O distance (1.80 Å) observed in bis(quinoxaline-2,3-dithiolato)nickel(II)-bis(*N,N*-dimethylformamide) (Pignedoli & Peyronel, 1977). These intermolecular hydrogen bonds may be responsible for the relative stability of these DMF solvates.

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Schiff-Base Complexes of Calcium: Crystal Structure Analysis of Dinitrato[*N,N'*-propane-1,3-diylbis(salicylideneimine)]calcium(II) and the Spectroscopic Properties of Some Related Complexes

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Abstract

The title compound, $[\text{Ca}(\text{C}_{17}\text{H}_{18}\text{N}_2\text{O}_2)(\text{NO}_3)_2]$, $\text{C}_{17}\text{H}_{18}\text{CaN}_4\text{O}_8$, is orthorhombic with $a = 37.166$ (3), $b = 10.181$ (1), $c = 5.111$ (0) Å, $Z = 4$, space group $P2_12_12_1$. The structure was refined to $R = 0.026$ for 1511 counter reflections. The Schiff base is present in a hitherto unreported charge-separated form with the ligand bridging two Ca ions through negatively charged O atoms. The azomethine N atoms are not coordinated; they carry the protons which are transferred from the phenolic groups on complex formation and form intramolecular hydrogen bonds with the O atoms. A bidentate, chelating nitrate ion is coordinated to each Ca ion while a pair of equivalent, bridging nitrate ions complete eight-coordination about Ca^{II} by the formation of chelate rings to the separate Ca ions. The stereochemistry around Ca is best described as a distorted hexagonal bipyramid. Nine Schiff-base complexes have been prepared with *N,N'*-propane-1,3-diylbis(salicylideneimine) and related bases, H_2L , with

the stoichiometries $\text{Ca}(\text{H}_2\text{L})\text{X}_2 \cdot n\text{EtOH}$ [$\text{X} = (\text{NO}_3)^-$ or Cl^- , $n = 0$ or 2] and $\text{Ca}(\text{H}_2\text{L})_2\text{X}_2 \cdot n\text{S}$ [$\text{X} = (\text{NO}_3)^-$ or Cl^- , $n = 0$ or 1, $\text{S} = \text{EtOH}$ or H_2O]. Since the infrared spectra of the coordinated Schiff bases are so similar, it is concluded that the complexes are closely related structurally. The mode of coordination of Schiff bases in a large number of similar compounds of other metal ions is discussed.

Introduction

Schiff bases containing phenolic groups, such as *N,N'*-ethylenebis(salicylideneimine), H_2salen , form metal-ion complexes in two ways. In the first (and better understood), the ligand is ionized by the removal of the acidic protons attached to O, giving complexes such as $\text{Cu}(\text{salen})$. In the second, the base is apparently either un-ionized or partly ionized. In this case, the metal ion usually has class A character [$\text{La}^{\text{III}} - \text{Lu}^{\text{III}}$ (except Pm); $M^{\text{IV}} = \text{Ti}, \text{Nb}, \text{Th}, \text{U}, \text{Sn}, \text{Zr}, \text{Hf}; \text{Fe}^{\text{III}}; \text{Co}^{\text{II}}$;