Contribution from the School of Chemistry, The University of New South Wales, Kensington, N.S.W., 2033, Australia

Metal Chelates of Dithiocarbazic Acid and Its Derivatives. VI. Antiferromagnetic and Ferromagnetic Interactions in Some Copper(II) Complexes of Salicylaldehyde and Acetylacetone Schiff Bases Derived from *S*-Methyldithiocarbazate

M. Akbar Ali, S. E. Livingstone, and D. J. Phillips

Received August 31, 1972

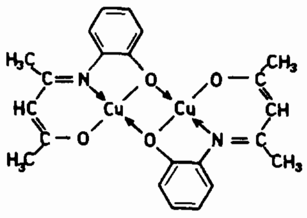
The Schiff base S-methyl-β-N-(2-hydroxyphenyl)methylenedithiocarbazate, $o\text{-}HO.C_6H_4CH{=}NNHC({=}S)SCH_3$, and the corresponding 5chloro, 5-bromo, 5-nitro, and 3-methoxy derivatives were prepared from the appropriate salicylaldehyde and S-methyldithiocarbazate. The acetylacetone Schiff base 2-hydroxy-4-methyl-5,6-diaza-7-thiono-8-thianona-2,4-diene, $CH_3C(OH){=}CHC(CH_3){=}NNHC({=}S)SCH_3$, was also prepared.

By the loss of two protons the ligands behave as doubly negatively charged ONS tridentates. Complexes of the type M(ONS).B (M = Cu,Ni; B = py, H_2O) and Co^{III}(ONS)(ONSH) were isolated. In addition, the complexes M(ONS) (M = Cu, Ni, Pd, Pt) were obtained. It is suggested that where M = Ni, Pd, Pt, the complexes possess square-planar, dimeric thiolo-bridged structures.

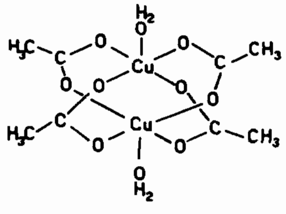
The copper complexes Cu(ONS) of the 5-chloro,5-bromo-, and 3-methoxy- salicylaldehyde Schiff bases are red and have anomalously low moments which decrease with decrease in temperature. This behaviour is attributed to antiferromagnetic interaction due to an oxygen-bridged dimeric structure. The moment of the green copper complex of the 5-nitrosalicylaldehyde Schiff base increases with decrease in temperature, indicating ferromagnetic interaction between the copper atoms. The value of the moment at 83°K is 2.43 B.M. and the magnetic data fit the expression for a tetrahedral cluster of four ferromagnetically interacting copper atoms. The green copper complex of the acetylacetone Schiff base is also ferromagnetic.

Introduction

Tridentate Schiff bases in which the donor atoms are oxygen and nitrogen (ONO donor set) have been extensively investigated as ligands, since many of them are known to form bivalent coper complexes with anomalous magnetic behaviour.[1,2] Thus the variation with temperature of the magnetic susceptibility of the copper(II) complex with 2-(acetylpropylideneamino)phenol[3] closely resembles that of copper(II) acetate and related compounds.[4,5] The predicted binuclear structure(I) was confirmed by an X-ray crysstallographic structure analysis.[3] The structure (I) involves two planar copper atoms side by side linked by oxygen atoms. This complex was the first known example to exhibit pairwise antiferromagnetic interaction and to possess a structure different from that of copper(II) acetate (II).



(I)



(II)

Although metal complexes of ONO tridentate ligands have been quite extensively investigated, considerably less is known about metal complexes of tridentate ligands which have oxygen, nitrogen, and sulphur donors (ONS set of donors).[5]

In order to study metal complexes of the derivatives of dithiocarbazic acid that will have oxygen, nitrogen, and sulphur as donor atoms, several Schiff base derivatives were prepared by the condenstation of appropriate salicylaldehydes (or acetylacetone) with *S*-methyldithiocarbazate. Metal complexes of these ligands are discussed herein.

Results and Discussion

All the Schiff bases were prepared by the condensation of *S*-methyldithiocarbazate with acetylacetone or appropriate salicylaldehydes in absolute ethanol. These are listed in Table I.

The infrared spectra of the compounds show ν(N-

---

[1] R.L. Martin in « New Pathways in Inorganic Chemistry », ed. E.A.V. Ebsworth, A.G. Maddock, and A.G. Sharpe, University Press, Cambridge (1966), Chap. 9.

[2] P.W Ball, *Coordination Chem. Rev.*, *4*, 361 (1969).

[3] G.A. Barclay, C.M. Harris, B.F. Hoskins, and E. Kokot, *Proc. Chem. Soc.*, 264 (1961); G.A. Barclay and B.F. Hoskins, *J. Chem. Soc.*, 1979 (1965).

[4] E. Kobot and R.L. Martin, *Inorg. Chem.*, *3*, 1306 (1964); L. Dubicki, C.M. Harris, E. Kokot, and R.L. Martin, *Inorg. Chem.*, *5*, 93 (1966).

[5] K. Ison and E. Kokot, *Austral. J. Chem.*, *23*, 661 (1970).

Table I. Schiff Bases derived from *S*-Methyldithiocarbazate.

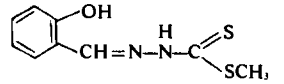
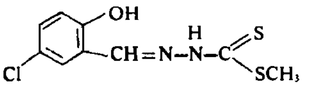
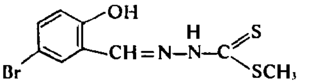
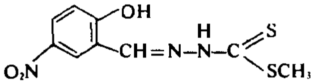
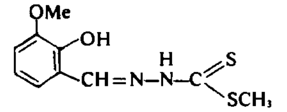
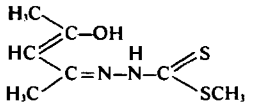
Compound		Structural formula	Abbreviation	M.p.	Analyses % Calc. Found C	H	N	S
(III)	*S*-Methyl-β-*N*-(2-hydroxyphenyl)methylendithiocarbazate		ONSH$_2$	202°	47.8	4.45	12.4	
					47.6	4.5	12.4	
(IV)	*S*-Methyl-β-*N*-(2-hydroxy-5-chlorophenyl)methylendithiocarbazate		5ClONSH$_2$	214	41.5	3.5	10.7	24.6
					41.7	3.7	10.45	24.4
(V)	*S*-Methyl-β-*N*-(2-hydroxy-5-bromophenyl)methylendithiocarbazate		5BrONSH$_2$	214	35.4	3.0	9.2	21.0
					35.65	2.9	8.7	21.3
(VI)	*S*-Methyl-β-*N*-(2-hydroxy-5-nitrophenyl)methylendithiocarbazate		5NO$_2$ONSH$_2$	185	39.8	3.3	15.5	23.6
					39.9	3.3	15.4	23.0
(VII)	*S*-Methyl-β-*N*-(2-hydroxy-3-methoxyphenyl)methylendithiocarbazate		3MeOONSH$_2$	189	46.85	4.7	10.9	25.0
					46.9	4.6	11.5	24.8
(VIII)	2-Hydroxy-4-methyl-5,6-diaza-7-thiono-8-thianona-2,4-diene		acacONSH$_2$	82	41.15	5.9	13.7	31.4
					41.25	5.8	13.2	31.4

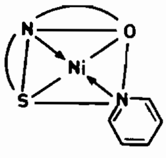
Table II. Metal Complexes of the Schiff bases derived from *S*-Methyldithiocarbazate.

Compound	Colour	Mol. conduct. Λ_{1000} at 25° (ohm^{-1}cm^{2}mole^{-1})	Analyses % Calcd. Found C	H	N	S	M
Ni(ONS)py	red	0.3 [a]	46.45	3.6	11.6	17.7	16.2
			46.8	3.6	11.6	17.0	16.1
Co(ONS)(ONSH)	brown	0.7 [a]	42.1	3.6	11.0	25.2	11.6
			42.1	3.6	10.7	24.9	11.3
Cu(ONS)H$_2$O	red	1.2 [b]	35.3	3.3	9.2	21.0	20.8
			35.5	3.2	8.75	20.5	20.9
Cu(ONS)py	yellowish green	1.5 [b]	45.8	3.6	11.45		17.3
			45.6	3.7	11.2		17.1
Cu(5ClONS)	red	1.1 [b]	33.5	2.2	8.7	19.9	19.7
			34.2	2.35	8.35	20.0	19.9
Cu(5BrONS)	red	1.0 [b]	29.5	1.9	7.6	17.5	17.3
			29.7	2.0	7.4	17.2	17.7
Cu(3MeOONS)	brown	0.3 [b]	37.8	3.2	8.8	20.2	20.0
			38.2	3.2	8.9	19.9	20.0
Cu(5NO$_2$ONS)	green	1.0 [b]	32.5	2.1	12.6	19.3	19.6
			32.6	2.4	12.85	18.7	19.4
Cu(acacONS)	dark green	3.5 [b]	31.6	3.8	10.5	24.1	23.9
			31.2	3.7	10.1	24.2	23.7
Ni(acacONS)	dark brown	4.0 [b]	32.1	3.8	10.7	24.5	22.4
			32.7	3.7	10.35	24.5	22.2
Pd(acacONS)	dark red	5.5 [b]	27.2	3.3	9.1	20.8	34.5
			27.4	3.4	8.2	19.8	34.0
Pt(acacONS)	orange	5.0 [b]	21.2	2.5	7.05		49.1
			21.6	2.9	6.8		48.8

[a] In nitrobenzene; [b] in dimethylformamide.

H) at *ca.* 3080 cm^{-1} but no ν(S-H) at *ca.* 2570 cm^{-1} indicating that in the solid state all of them remain in the thiono form. But in solution they probably exist as equilibrium mixtures of both the thiolo and thiono tautomeric forms. The metal complexes which were isolated are listed in Table II.

Treatment of the Schiff base *S*-methyl-β-*N*-(2-hydroxyphenyl)methylendithiocarbazate (III; ONSH$_2$) with a nickel salt in the presence of potassium hydroxide and pyridine, yields a bright red crystalline nickel(II) complex Ni(ONS)py. The diamagnetism and red colour of this compound indicate that it has a square-planar configuration. The compound is soluble in absolute alcohol and in most of the common polar and non-polar organic solvents. Its very small conductivity (0.3mho) in nitrobenzene indicates that it is an inner complex. All these suggest that the ligand is acting as a dinegatively charged tridentate, coordinating through the thiolo sulphur, the β-nitrogen, and the phenolic oxygen atoms. The pyridine molecule probably occupies the fourth coordination position about the nickel(II) atom as shown in (IX).



(IX)

The interaction of cobalt(II) acetate with the Shiff base $ONSH_2$ yields the dark brown diamagnetic cobalt(III) complex Co(ONS)(HONS). Similar rapid oxidation of cobalt(II) to give a cobalt(III) complex occurs with *S*-methyl-*N*-(2-pyridyl)methylendithiocarbazate[6] and with monothio-β-diketones.[7,8] The negligible conductivity (0.7 mho) in nitrobenzene indicates that it is an inner complex. The compound can be assigned with the structure (X) in which one of the ligands behaves as a tridentate dibasic acid and the other a monobasic acid. A similar structure was proposed for the analogous salicylaldehydethiosemicarbazonecobalt(III) complex.[9]

All the Schiff bases (IV-VIII) react with cupric perchlorate in alcohol to give CuL (LH_2 = Schiff base). However, with (III) the hydrated complex $Cu(ONS)H_2O$ was obtained. The red colours of these compounds suggest the presence of copper(II) rather than copper(I), since copper(I) complexes are usually either colourless or yellow.

Apart from $Cu(5NO_2ONS)$ and Cu(acacONS) the CuL complexes have anomalously low magnetic moments of *ca* 0.6 to 1.0 B.M. (Table III). The magnetic properties of $Cu(ONS).H_2O$ and Cu(3MeOONS) were examined over the temperature range 313-93°K and 373-193°K, respectively. The data are included in Tables IV and V. The decrease of magnetic moments with decrease in temperature indicates that antiferromagnetic interactions are involved, since in antiferromagnetic materials the electron spins are aligned in an antiparallel fashion, so that the susceptibilities decrease with decreasing temperature. Unfortunately the temperature dependence of the susceptibility data could not be used properly to elucidate the structures of the $Cu(ONS).H_2O$, Cu(5ClONS), Cu(5BrONS) and Cu(3MeOONS) complexes, since the errors involved in the measurements of such low moments were far too large. However, an oxygen-bridged binuclear structure (XI) similar to (I) is proposed for the complexes.

Table III. Magnetic Data on the Complexes of Salicylaldehyde and Acetylacetone Schiff Bases

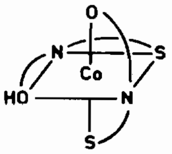
Compound	$10^6\chi'_M$	T(°K)	μ(B.M.)
$Cu(ONS)H_2O$	283	293	1.01
Cu(ONS)py	1873	293	2.00
Ni(ONS)py	—	292	diam.
Co(ONS)(ONSH)	—	—	diam.
Cu(5ClONS)	260	289	0.77
Cu(5BrONS)	276	295	0.79
$Cu(5NO_2ONS)$	1907	294	2.01
Cu(3MeOONS)	276	292	0.79
Ni(acacONS)	—	294	diam.
Cu(acacONS)	1110	294	1.62
Pd(acacONS)	—	—	diam.
Pt(acacONS)	—	—	diam.

Table IV. Magnetic Data for $Cu(ONS)H_2O$.

T(°K)	$10^6\chi'_M$	$\frac{1}{\chi'_M}$	μ(B.M.)
313	467	2141	1.09
293	437	2270	1.01
273	417	2398	0.96
253	387	2584	0.89
233	382	2618	0.85
213	372	2688	0.80
193	372	2688	0.72
173	412	2427	0.76
153	362	2763	0.67
133	382	2618	0.64
113	402	2488	0.45
93	492	2032	0.60

Table V. Magnetic Data for Cu(3MeOONS).

T(°K)	$10^6\chi'_M$	$\frac{1}{\chi'_M}$	μ(B.M.)
373	341	2933	1.01
353	330	3030	0.97
343	322	3106	0.94
333	266	3759	0.84
313	268	3731	0.82
303	237	4222	0.76
293	253	3952	0.77
273	202	4950	0.67
253	169	5917	0.59
233	144	6944	0.52
193	103	9709	0.40



(X)

The phenolic ν(C-O) frequency occurs at *ca.* 1530 cm^{-1} in the infrared spectra of mononuclear complexes of salicylaldehyde Schiff bases,[10,11] whereas the spectra of bi- and tri- nuclear phenolic oxo-bridged

---

(6) M. Akbar Ali, S.E. Livingstone, and D.J. Phillips, *Inorg. Chim. Acta, 5,* 493 (1971).

(7) R.K.Y. Ho, S.E. Livingstone, and T.N. Lockyer, *Austral J. Chem., 19,* 1179 (1966).

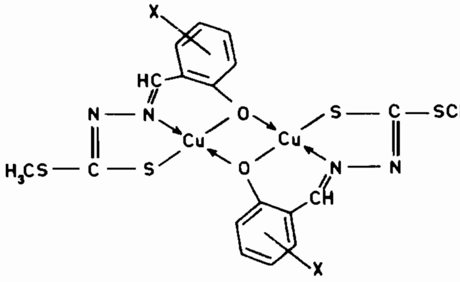
(8) S.H.H. Chaston and S.E. Livingstone, *Austral. J. Chem., 20,* 1079 (1967).,

(9) A.V. Ablov and N.V. Gerbeleu, *Russ. J. Inorg. Chem., 9,* 1260 (1964), *10,* 33 (1965).

(10) S.J. Gruber, C.M. Harris, and E. Sinn, *J. Inorg. Nucl. Chem., 30,* 1805 (1968).

(11) G.E. Batley and D.P. Graddon, *Austral. J. Chem., 20,* 877 (1967).

complexes display the ν(C-O) frequency within the range 1545-1550 cm.$^{-1}$[12] The green pyridine adduct Cu(ONS)py has a moment of 2.0 B.M. at room temperature; the ν(C-O) band occurs at 1535cm^{-1}. In the spectrum of the nickel complex Ni(ONS)py, for which structure (IX) has been proposed, the ν(C-O) frequency occurs at 1538cm^{-1}, indicating the presence of non-bridging oxygen. The C-O stretching frequency for the CuL complexes (L = 5ClONS, 5BrONS, 5NO$_2$ONS, and 3MeOONS) occurs in the range 1545-1560cm^{-1} (Table VI). This shift in the C-O frequency is strong evidence that bridging occurs through the phenolic oxygen atoms. The C-O frequency for Cu-(ONS)H$_2$O occurs at 1560cm^{-1}, indicating the presence of oxo-bridging; this suggests that the structure of this compound differs from that of Cu(ONS)py.



(XI)

The green colour of the complex Cu(5NO$_2$ONS) and its room-temperature magnetic moment (1.99 B.M.) suggest that its structure is different from those of he other CuL complexes. The copper o ligand ratio is 1:1 and thus at least dimerization is required for the copper atoms to be four-coordinate. However, a binuclear structure of the type (XI) cannot be assigned to this compound because the bridging arrangement which it involves is known to lead to strong pairwise antiferromagnetic interaction. The magnetic moment of this compound was measured over the temperature range 333-83°K (see Table VII). The remarkable feature of the magnetic data is that the moment increases with decrease in temperature and rises to 2.43 B.M. at 83°K. This increase in the effective magnetic moment $\mu_{eff} = 2.83\sqrt{\chi_M T}$ with decreasing temperature indicates that ferromagnetic exchange interactions are involved. The field dependence magnetic data are included in Table VIII. The increase in the moment witeh decrease in temperature appears to be the largest for a copper complex.[1,13,15] In spite of the difference in colour, the electronic spectrum of Cu-5NO$_2$ONS) is not markedly different from the spectra of CuL (L = ONS, 5ClONS, 5BrONS and 3Me-OONS) complexes, all being dominated by the tail of a strong absorption in the ultra-violet.

Table VI. C-O Stretching Frequencies in the Salicylaldehyde Schiff Base Complexes.

Compound	ν(C-O)(cm^{-1})
Ni(ONS)py	1538
Cu(ONS)py	1535
Cu(ONS)H$_2$O	1560
Cu(3MeOONS)	1558
Cu(5ClONS)	1545
Cu(5BrONS)	1560
Cu(5NO$_2$ONS)	1550

Table VII. Magnetic Data for Cu(5NO$_2$ONS).

T(°K)	$10^6\chi'_M$	$\frac{1}{\chi'_M}$	μ(B.M.)
333	1519	658.3	2.02
323	1525	655.7	1.99
313	1601	624.6	2.01
303	1650	606.1	2.01
293	1691	591.4	2.00
283	1757	569.0	2.00
273	1815	551.0	2.00
263	1915	522.1	2.01
253	2009	497.8	2.02
243	2117	472.3	2.03
233	2212	452.1	2.04
223	2380	420.1	2.07
213	2526	395.9	2.08
203	2686	372.3	2.10
193	2882	347.0	2.12
183	3105	322.1	2.14
173	3327	300.6	2.15
163	3570	280.1	2.17
153	3869	258.5	2.19
143	4290	233.1	2.22
133	4659	214.6	2.24
123	5260	190.1	2.28
113	5798	172.5	2.30
103	6583	151.9	2.34
93	7473	133.8	2.39
83	8763	114.1	2.43

Table VIII. Magnetic Moment at Different Field Strengths for Cu(5NO$_2$ONS).

Field Strength H^2 (gauss^2)	μ(B.M.)
(a) Temperature: 293°K	
1.174×10^7	2.03
2.345×10^7	2.03
2.98×10^7	2.04
3.46×10^7	2.06
4.08×10^7	2.05
(b) Temperature: 83°K	
1.174×10^7	2.38
2.345×10^7	2.41
2.980×10^7	2.41
3.460×10^7	2.44
4.08×10^7	2.44

Ferromagnetic coordination complexes are known and the few previous examples with copper(II) exhibit only a small increase of magnetic moment at low temperature.[1,15]

The Cu(5NO$_2$ONS) complex is not sufficiently so-

---

[12] C.M. Harris and E. Sinn, *J. Inorg. Nucl. Chem.*, *30*, 2723 (1968).

[13] A.P. Ginsberg, *Inorg. Chim. Acta Rev.*, *5*, 45 (1971).

[14] E. Sinn, *Coordination Chem. Rev.*, *5*, 313 (1970).

[15] W.E. Hatfield, J.A. Barnes, D.Y. Jeter, and R. Whyman, *J. Amer. Chem. Soc.*, *92*, 4982 (1970); J.A. Barnes, W.C. Barnes, and W.E. Hatfield, *Inorg. Chim. Acta*, *5*, 276 (1971); J.A. Barnes, D.J. Hodgson, and W.E. Hatfield, *Inorg. Chem.*, *11*, 144 (1972); W.E. Hatfield, *Inorg. Chem.*, *11*, 216 (1972).

luble in suitable solvents for molecular weight measurements to be made.

The maximum spin-only magnetic moment for a ferromagnetic cluster is given by the expression:[1,16]

$$\mu^2_{eff} = n(n+2)$$

where n = the number of unpaired electrons in the cluster. For copper(II) $n = 1$ per copper atom, thus for two copper atoms in a cluster $\mu^2 = 2(2+2) = 8$; hence μ^2 per copper atom = 4 and μ = 2.00 B.M. per copper atom. Similarly, the maximum spin-only value of the moment per copper atom is 2.24 B.M. for a trimer and 2.45 B.M. for c tetrameter. In view of this, the magnetic data (Table VII) suggest that the complex Cu(5NO_2ONS) contains a cluster of a least three, but more likely four ferromagnetically interacting copper atoms. The data do not fit equations for three interacting copper atoms but agree reasonably well with the equation for a linear polymeric structure but more closely with the equation for a tetrahedral cluster of copper atoms.[17]

By the use of the Ising equation[18] (1) for a linear

$$\underset{\text{(per Cu atom)}}{\chi_M} = \frac{N\beta^2 g^2}{4kT}\exp\,(2J/kT) + N\alpha \qquad (1)$$

where N = Avagadro number
β = Bohr magneton
g = spectroscopic splitting factor
k = Boltzmann constant
T = absolute temperature
J = exchange coupling constant
$N\alpha$ = the temperature-independent paramagnetism of the metal ion

polymer of interacting copper atoms the closest fit to the data was obtained with $g = 2.10$ and $J = 17$ cm^{-1}; the sum of the weighted squares of the deviations $\Sigma[(\chi_{obs} - \chi_{calc})T]^2$ was found to be 0.39 × $10.^{-2}$ $N\alpha$ for copper(II) was taken as 60 × 10^{-6} c.g.s.u.

Equation (2) describes the magnetic behaviour of a tetrahedral cluster of copper atoms with allowance for intercluster interaction.[13,17]

$$\chi_M = \frac{N\beta^2 g^2[30 + 18\exp(-4J/kT)]}{12k(T-\theta)[5 + 9\exp(-4J/kT) + 2\exp(-6J/kT)]} + N\alpha \qquad (2)$$

A non-zero value for θ (the Weiss constant) indicates that there is magnetic interaction between the clusters. If intercluster interaction is assumed to be absent, i.e. θ is zero, the magnetic data agree closely with those predicated with $g = 2.00$ and $J = 38$cm^{-1}. In a short communication[19] we recently reported that the quality of the fit - $\Sigma[(\chi_{obs} - \chi_{calc})T]^2 = 0.31 \times 10^{-2}$ - is slightly better than that for a linear polymer. However, if θ is allowed to vary, a considerable improvement in fit - $\Sigma[(\chi_{obs} - \chi_{calc})T]^2 = 0.062 \times 10^{-2}$ - is obtained with $g = 1.95$, $J = 40$ cm^{-1}, and $\theta = +6.6°$. A similar modification of the Ising equation (1), by the inclusion of a Weiss constant term θ, produced no improvement in fit. In the lowest permissable value for g is taken as 2.00, then the best fit with equation (2) (see Figure 1) is obtained with $g = 2.00$, $J = 33$ cm^{-1}, and $\theta = +6.5°$ and the quality of the fit - $\Sigma[(\chi_{obs} - \chi_{calc})T]^2 = 0.084 \times 10^{-2}$ is still better than for the linear polymeric structure. The small positive value of θ suggests weak ferromagnetic intercluster interaction in addition to the strong intracluster interaction indicated by the positive value of J. Measurements at lower temperatures would be necessary to confirm that this weak interaction is present and that the apparently closer fit to the tetramer equation is meaningful. Furthermore, the magnestism of compounds with linear polymeric structures often does not fit the Ising equation closely. However, on the basis of measurements down to 83°K, the tetramer structure seems more likely than a linear polymeric arrangement.

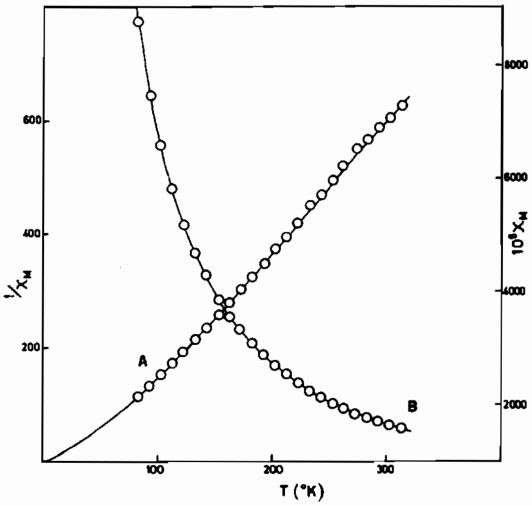


Figure 1. The temperature dependence of $1/\chi_M$ (A) and $10^6\chi_M$ (B) for the complex Cu(5NO_2ONS). Experimental values are indicated by open circles and the full curves are the calculated values obtained from Equation (2) with $g = 2.00$, $J = 33$ cm^{-1}, and $\theta = 6.5$°K.

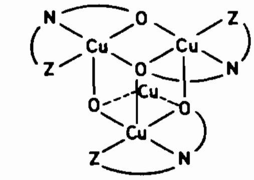
We are not aware of any copper complexes with linear polymeric structures in which ferromagnetic interactions are present. In contrast both ferromagnetic and antiferromagnetic interactions have been detected in complexes involving tetrahedral clusters of copper atoms.[1,13,14,20,21,22] The nature of the interaction in copper(II) tetrameric complexes appears to depend critically upon the coordination of the copper ion.

The most likely structure for the complex is one with pairs of oxygen-bridged $[Cu(5NO_2ONS)]_2$ units aligned to give a tetrahedral arrangement of metal

---

(16) R.L. Martin, *Proc. Roy. Austral. Chem. Inst.*, *38*, 33 (1971).
(17) R.W. Jotham and S.F.A. Kettle, *Inorg. Chim. Acta*, *4*, 145 (1970).
(18) G.F. Newell and E.W. Montrol, *Rev. Mod. Phys.*, *25*, 353 (1953); C.G. Barraclough and C.F. Ng, *Trans. Faraday Soc.*, *60*, 836 (1964).
(19) M. Akbar Ali, S.E. Livingstone, and D.J. Phillips, *Chem. Commun.*, 909 (1972).
(20) C.M. Harris and E. Sinn, *Inorg. Nuclear Chem. Letters*, *5*, 125 (1969).
(21) M.E. Lines, A.P. Ginsberg, and R.L. Martin, *Phys. Rev. Letters*, *28*, 684 (1972).
(22) M.E. Lines, A.P. Ginsberg, R.L. Martin, and R.C. Sherwood, *J. Chem. Phys.*, *57*, 1 (1972).

atoms (XII; Z = S), as found for the copper complex of the Shiff base derived from 2-aminoethanol and acetylacetone (XII; Z = O).[23]



(XII)

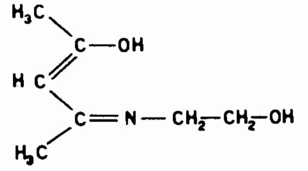
The copper atoms in the latter complex form a distorted tetrahedral cluster with D_{2d} symmetry. The magnetic data for this complex over the temperature range 300 - 1.5°K fit an equation for a cluster of four copper atoms having D_{2d} symmetry with two values for J, indicating the presence of both ferromagnetic and antiferromagnetic interactions ($J_L = 4\text{cm}^{-1}$; $J_S = -15\text{cm}^{-1}$).[24] When this equation was used to interpret the data obtained for the complex Cu(5NO$_2$ONS) on the assumption that the complex had D_{2d} symmetry, no improvement in fit was obtained over that given by Equation (2) for a regular tetrahedral cluster. The values which were derived for J_L and J_S were both positive and comparable to the value of J obtained from Equation(2). Measurements at lower temperatures would be necessary to confirm which equation gives the closer fit, since the temperature range studied is the least sensitive to the effects of a second exchange integral.

Complexes of the acetylacetone Schiff base (VIII) were also isolated (see Table II). The complexes are insoluble in the common polar and non-polar organic solvents; this suggests that they do not possess monomeric structures.

Table IX. Magnetic Data on Cu(acacONS).

T(°K)	$10^6\chi'_M$	$\frac{1}{\chi'_M}$	μ(B.M.)
333	947	1056.0	1.59
313	1028	972.8	1.61
294	1110	900.9	1.62
273	1175	851.1	1.61
253	1240	806.5	1.59
233	1419	704.7	1.63
213	1559	645.6	1.63
193	1736	576.0	1.64
163	2094	477.6	1.66
133	2770	361.0	1.72
113	3446	290.2	1.77
103	3968	252.0	1.82
83	4877	205.0	1.81

The magnetic moment of the green copper complex Cu(acacONS) increases from 1.59 B.M. at 333°K to 1.81 B.M. at 83°K (see Table IX). The increase of the moment with decrease in temperature indicates the presence of ferromagnetic interactions. The reduced value of the moment at room temperature could be due to the presence of antiferromagnetic interactions as well. The Shiff base (VIII) has a similar structural skeleton to that of the Schiff base derived from acetylacetone and 2-aminoethanol, viz. 5-aza-2,7-dihydroxy-4-methylhepta-2,4-diene (XIII;EIAH$_2$). The structure of Cu(EIA) is known[23] and has been described above (XII; Z = O).

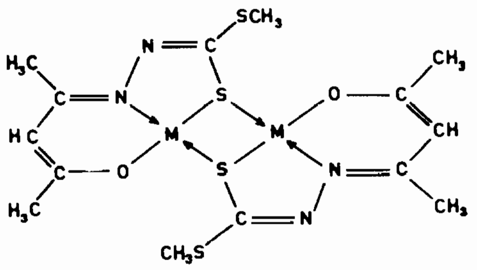


(XIII)

The structure of Cu(acacONS) is uncertain, although an oxygen or thiolo-bridged dimeric structure seems unlikely, since this would be expected to lead to strong antiferromagnetism. A tetrameric structure analogous to that of Cu(EIA) (XII) is possible and this would be consistent with the ferromagnetic interaction observed with Cu(acacONS).

In dimeric structures of the type (I) the copper atoms are essentially four-coordinate, whereas in a tetrameric structure of the type (XII) they are five-coordinate. It would be reasonable to expect that the electronic spectra might distinguish between dimeric and tetrameric structures. Indeed the antiferromagnetic compounds Cu(ONS), which are considered to be dimeric, are red, while the ferromagnetic complexes Cu(5NO$_2$ONS) and Cu(acacONS), which are considered to be tetrameric, are green. However, the electronic spectrum of Cu(5NO$_2$ONS), which shows a broad absorption centred at 21,200cm^{-1} with a sholder at *ca* 14,000cm^{-1}, is not markedly different from the spectra of the antiferromagnetic complexes Cu(ONS). In all the spectra the *d-d* bands are largely obscured by strong charge-transfer absorption extending from the ultraviolet.

In the diamagnetic complexes M(acacONS) (M = Ni,Pd,Pt) the metal atom is assumed to have its usual square-planar arrangement. It is suggested that this is achieved by the formation of bridged dimers. A dimeric oxygen-bridged structure for the related Ni(EIA) complex has been confirmed by an X-ray crystal structure determination.[25] However, it is most likely that the complexes M(acacONS) have the thiolo-bridged structure (XIV) rather than an oxygen-bridged



(XIV)

---

[23] J.A. Bertrand and J.A. Kelley, *Inorg. Chim. Acta, 4,* 203 (1970).

[24] A.P. Ginsberg, R.L. Martin, and R.C Sherwood, unpublished results cited in ref. (13).

[25] J.A. Bertrand and C.E. Kirkwood, *Inorg. Chim. Acta, 4,* 192 (1970).

structure because of the pronounced (b) class behaviour of these three metals[26] and their strong tendency to form very stable thiolo-bridges.[27] Polymeric thiolo-bridged structures are also possible.

Experimental Section

General Method of Preparation of the Schiff Bases (III), (IV), (V), and (VI). A solution of the appropriate salicylaldehyde (10g) in alcohol (50ml) was added to a hot solution of *S*-methyldithiocarbazate (10g) in alcohol (250ml). The solution was heated on the steam bath for 10 min and upon cooling yielded a crystalline product which was recrystallized from alcohol; yield, 75-90%.

S-Methyl-β-N-(2-hydroxy-3-methoxyphenyl)methylendithiocarbazate (VII). *S*-Methyldithiocarbazate[28] (2.1g) in alcohol (25ml) was added to a hot solution of 3-methoxysalicylaldehyde (3.3g) in hot alcohol (25 ml). The mixture was heated on a steam-bath for 5 min and then allowed to cool. The pale yellow crystals which had formed were filtered off and recrysstallized from alcohol to yield the pure ligand; yield, 3.8g.

2-Hydroxy-4-methyl-5,6-diaza-7-thiono-8-thianona-2,-4-diene (VIII). *S*-Methyldithiocarbazate (5.0 g) was dissolved in a mixture of acetylacetone (5 ml) and alcohol (25 ml). The solution was heated on a steam-bath for 5 min. Water (50ml) was added, whereupon two layers formed. The lower layer was separated, and on being scratched with a glass rod it solidified. Recrystallization of the solid from absolute alcohol afforded the pure compound; yield, 60%.

Preparation of the Metal Complexes. Unless otherwise stated all the complexes after filtration were washed with alcohol and dried *in vacuo* over phosphorus pentoxide.

Preparation of S-Methyl-β-N-(2-hydroxophenyl)methylendithiocarbazatomonopyridinenickel(II). *S*-Methyl-β-*N*-(2-hydroxyphenyl)methylendithiocarbazate (1.0g) in alcohol (50ml) was added to a solution prepared by dissolving potassium hydroxide (0.25g) in alcohol (50ml). The mixture was stirred for 15 min and then filtered into a solution of nickel perchlorate hexahydrate (1.6g) in alcohol (50ml). Pyridine (2ml) was added and the mixture was heated on the steam-bath for 5 min and, on cooling, yielded red needles of the complex; yield, 1.0g.

Preparation of {S-Methylβ-N-(2-hydroxyphenyl)methylendithiocarbazato}-{S-Methyl-β-N-(2-hydroxophenyl)methylendithiocarbazato}cobalt(III). Cobalt acetate (1.0g) in alcohol (100ml) was added to a solution of ligand (2.0g) in hot alcohol (50ml). The mixture was heated on a steam bath for 15 min to give a brown solution which was filtered. The filtrate was concentrated to about 50ml and the complex which had formed was filtered off; yield: 1.0g.

S-Methyl-β-N-(2-hydroxophenyl)methylendithiocarbazatocopper(II) Monohydrate. Cupric tetrafluoborate hexaydrate (2.0g) was disolved in a hot mixture of alcohol (30ml) and 2,2-dimethoxypropane) (20ml). The mixture was filtered into a solution of the ligand (1.0g) in alcohol (150ml). The solution, after being heated for 5 min, turned red and, upon coling, deposited light red crystals of the complex; yield, 0.6g.

General Method for the Preparation of S-Methyl-β-N-(2-hydroxo-5-chlorophenyl)methylendithiocarbazatocopper(II) and S-Methyl-β-N-(2-hydroxo-5-bromophenyl)methylendithiocarbazatocopper(II). Cupric perchlorate hexahydrate (2.0g) in a hot mixture of alcohol (20ml) and 2,2-dimethoxypropane (10ml) was added to the solution of the ligand (1.0g) in alcohol (250ml). After being heated on the steam-bath for 10 min, the red solution deposited light red fibrous crystals of the copper complex, which were filtered off; yield: 80%.

S-Methyl-β-N-(2-hydroxo-3-methoxyphenyl)methylendithiocarbazatocopper(II). A solution of cupric perchlorate hexahydrate (3.0g) in a hot 1:1 mixture of alcohol and 2,2-dimethoxypropane (30ml) was added to a solution of the ligand (1.5g) in alcohol (125ml). After the solution had been heated for 5 min, it was allowed to stand overnight. Reddish-brown crystals resulted; yield, 1.0g.

S-Methyl-β-N-(2-hydroxo-5-nitrophenyl)methylendithiocarbazatocopper(II). A solution of the ligand (1.0g) in alcohol (20ml) was added to a solution of cupric perchlorate hexahydrate (2.0g) in a 1:1 mixture of alcohol and 2,2-dimethoxypropane (30ml). The solution was heated on a steam-bath for 2 min and then stood for 2hr whereupon the green crystals which had formed were filtered off; yield, 0.9g.

S-Methyl-β-N-(2-hydroxophenyl)methylendithiocarbazatomonopyridinecopper(II). *S*-Methyl-β-N-2-hydroxophenyl)methylendithiocarbazatocopper(II) monohydrate (0.5g) was dissolved in pyridine (10ml). Addition of petroleum ether (20ml) caused precipitation of a green complex which was filtered off, washed with cyclohexane, then with ligroin, and dried in air; yield 0.4g.

General Method for the Preparation of the Platinum(II) and Palladium(II) Complexes of 2-Hydroxy-5,6-diaza-7-thiono-8-thianona-2,4-diene. A hot solution of potassium tetrachlorometallate (1.0g) in water (50ml) was added, with stirring, to a boiling solution of ligand (1.0g) in acetone (10ml). The mixture was heated on a steam bath for 3 min whereupon crystals of the complex were deposited. These were filtered off, washed first with water and then with acetone; yield 50-60%.

2-Hydroxo-5,6-diaza-7-thiolo-8-thianona-2,4,6-triene-copper(II). A saturated solution of cupric acetate was made by heating cupric acetate hydrate (2.0g) in a

---

[26] S. Ahrland, J. Chatt, and N.R. Davies, *Quart. Rev.*, *12*, 265 (1958).

[27] S.E. Livingstone, *Quart. Rev.*, *19*, 386 (1965).

[28] G. Bähr and G. Schleitzer, *Z. anorg. u. allgem. Chem.*, *280*, 176 (1955).

mixture of alcohol (100ml) and 2,2-dimethoxypropane (20ml). To this solution was added, with stirring, a solution of the ligand (1.0g) in alcohol (20ml). The solution was heated on a steam-bath for 5 min and allowed to cool. The dark green product which had formed was then filtered off; yield, 1.2g.

2-Hydroxo-5,6-diaza-7-thiolo-8-thianona-2,4,6-triene-nickel(II). A saturated solution of nickel acetate was prepared by heating nickel acetate tetrahydrate (2.0g) in a boiling mixture of alcohol (100ml) and 2,2-dimethoxypropane (50ml). The hot solution was then added to a solution of the ligand (1.0g) in alcohol (10ml). After the solution had been heated for 15 min a brown solution was obtained, which on being left standing for 24 hr, yielded dark brown crystals of the nickel complex; yield, 0.32g.

Magnetic Measurements. The magnetic measurements were made on a Newport variable-temperature Gouy balance.

Spectral Measurements. The infrared spectra were obtained on a Perkin-Elmer 337 spectrophotometer and the electronic spectra were obtained on a Zeiss PMQII spectrophotometer.