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Metal Chelates of Dithiocarbazic Acid and Its Derivatives. VII. The Magnetism of Some Copper(II) Complexes of Salicylaldehyde Schiff Bases Derived from *N*-Methyl-*S*-methyldithiocarbazate and *S*,*S'*-Dimethyldithiocarbazate

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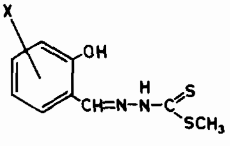
*The Schiff bases α-*N*-methyl-S-methyl-β-*N*-(2-hydroxyphenyl)methylendithiocarbazate o-HO.C_5H_4.CH = NNMeC(=S)SMe (HONMeS), its 3-methoxy derivative (3-MeOHONMeS), 1-(2-hydroxyphenyl)-2,3-diaza-4-methylthio-5-thiahexa-1,3-diene, o-HO.C_5H_4.CH = NN=C$(SMe)_2$ (HONSMe) and its 5-chloro and 5-bromo derivatives (5XHONSMe; X = Cl, Br) were prepared. By the loss of a proton the Schiff bases act as uni-negatively charged ONS tridentate ligands.*

The complexes Ni(ONMeS)X (X = Cl, Br, NCS) are diamagnetic and square-planar, while the complex $Ni(ONMeS)_2$ is paramagnetic and octahedral. The palladium complex Pd(ONSMe)Cl was also isolated.

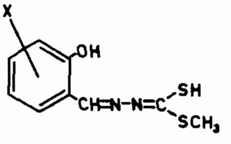
The copper complexes $Cu(ONMeS)NO_3$, $Cu(ONSMe)NO_3$, and $[Cu(ONMeS)py]ClO_4$ display normal magnetic behaviour. The compound $Cu(ONMeS)BF_4$ has an anomalously low moment (0.88 B.M.) at room temperature and the moment decrease to 0.38 B.M. at 93°K due to antiferromagnetic interaction. The compound $Cu_2(3MeOONMeS)Cl_3$ also displays antiferromagnetic interaction between the two copper atoms of the dimer. The complexes $Cu_3(ONMeS)_2Cl_4$ and $Cu_3(ONSMe)_2Cl_4$ most likely have a linear trimeric structure; the magnetic data for the latter compound fit an equation for a linear trimer with three antiferromagnetically interacting copper atoms. The compounds Cu(5ClONSMe)Cl and Cu(5BrONSMe)Cl are monomeric with normal magnetic moments.

Introduction

In part VI[1] of this series Schiff bases of the type (I) were reported. The tautomeric forms (II) of these compounds by the loss of two protons behave as doubly negatively charged ONS tridentates coordinating to metal ions via the phenolic oxygen, the β-nitrogen, and the thiolo sulphur atoms. The copper complexes CuL (L = I; X = 5-chloro, 5-bromo, 3-methoxy) display antiferromagnetic behaviour, while the complex CuL (L = I; X = 5-nitro) is ferromagnetic due to interaction between the copper atoms in a structure involving a tetrameric metal cluster.[1]



(I)



(II)

We have now prepared the *N*-methyl and *S*-methyl derivatives of some of these ligands in order to study the magnetic behaviour of the copper complexes.

Results and Discussion

The *N*-methyl and *S*-methyl derivatives, which are listed in Table I, were prepared by the condensation of the appropriate salicylaldehyde with 2-*N*-methyl-*S*-methyldithiocarbazate or *S*,*S'*-dimethyldithiocarbazate. They were obtained as beautifully crystalline solids which are quite stable in air.

Some nickel complexes of (I; HONMeS) were isolated (see Table II) in order to establish whether these Schiff bases, by losing a proton, would behave as singly negatively charged ONS tridentate ligands. The complexes Ni(ONMeS)X (X = Cl, Br, NCS) are diamagnetic and non-electrolytes. Their diamagnetism indicates that they possess a square-planar configuration. The infrared spectrum of the thiocyanato complex shows ν(C-N) at 2100 cm^{-1}, indicating a terminal N-bonded thiocyanate group.[2] There is also a band at 1520 cm^{-1} which is assigned as the phenolic C-O stretching frequency. The occurrence of a ν(C-O) band at 1520 cm^{-1} in the spectra of the Ni(ONMeS)X complexes is indicative of non-bridging oxygen;[1] in the case of a bridging oxygen this absorption is shifted to higher frequencies by 15-20 cm^{-1}. Consequently the mono-ligand nickel complexes are assigned monomeric square-planar structures with the ligand acting as a tridentate by coordinating via the phenolic oxygen, the β-nitrogen, and the thioether sulphur atoms.

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(1) M. Akbar Ali, S.E. Livingstone, and D.J. Phillips, *Inorg. Chim. Acta, 7*, 179 (1973).

(2) K. Nakamoto, «Infrared Spectra of Inorganic and Coordination Compound», Wiley Interscience, 2nd edn., New York (1970), p. 189.

Table I. Salicylaldehyde Schiff Bases.

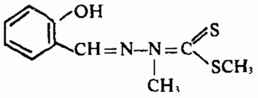
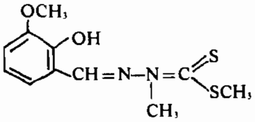
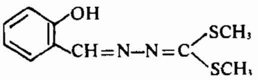
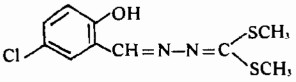
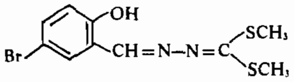
Compound		Structural formula	Abbreviation	M.p.	Analyses % Calcd. Found C	H	N	S
III	α-*N*-Methyl-S-methyl-β-*N*-(2-hydroxyphenyl)methylen-*dithiocarbazate*		HONMeS	121-2°	50.0 49.8	5.0 4.9	11.7 11.8	26.7 25.6
IV	α-*N*-Methyl-*S*-methyl-β-*N*-(2-hydroxy-3-methoxyphenyl)-methylendithiocarbazate		3MeOHONMeS	138	48.9 49.2	5.2 5.3	10.4 11.5	23.7 23.4
V	1-(2-Hydroxyphenyl)-2,3-diaza-4-methylthio-5-thiahexa-1,3-diene		HONSMe	72	50.0 49.8	5.0 5.0	11.7 11.8	26.7 25.9
VI	1-(2-Hydroxy-5-chlorophenyl)-2,3-diaza-4-methylthio-5-thiahexa-1,3-diene		5ClHONSMe	121	43.6 43.7	3.6 4.0	10.4 10.2	23.4 23.0
VII	1-(2-Hydroxy-5-bromophenyl)-2,3-diaza-4-methylthio-5-thiahexa-1,3-diene		5BrHONSMe	121	37.7 37.6	3.5 2.6	8.8 9.0	19.9 20.1

Table II. Nickel and Palladium Complexes of the Schiff Bases (III) and (V).

Compound	Colour	Mol. conduct. Λ_{1000} at 25° (ohm^{-1} cm^2 mole^{-1})	Analyses % Cald. Found C	H	N	S	M
[Ni(ONMeS)Cl]	reddish brown	0.2 [a]	36.0 36.4	3.3 3.3	8.4 8.6	19.2 19.1	17.6 17.45
[Ni(ONMeS)Br]	reddish brown	0.5 [a]	31.8 32.35	2.9 3.1	7.4 7.8	17.0 16.7	15.5 15.2
[Ni(ONMeS)NCS]	brown	0 [a]	37.1 37.1	3.1 3.1	11.8 11.8	27.0 26.8	16.5 16.3
[Ni(ONMeS)$_2$]	red	0.1 [a]	44.7 45.0	4.1 4.2	10.4 10.1	23.9 23.1	10.9 10.8
[Pd(ONSMe)Cl]	orange	1.0 [b]	31.5 31.7	2.9 3.0	7.35 7.4	16.8 16.6	27.9 27.8

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

Table III. Copper(II) Complexes of the Salicylaldehyde Schiff Bases.

Compound	Colour	Mol. conduct Λ_{1000} at 25° (ohm^{-1} cm^2 mole^{-1})	Magnetic moment per Cu atom at 298°K μ (B.M.)	Analyses % Calcd. Found C	H	N	S	Cu	Cl
Cu(ONMeS)NO$_3$	green	47 [a]	1.83	32.9 32.5	3.0 2.8	11.5 11.5	17.6 17.5	17.4 17.3	
[Cu(ONMeS)py]ClO$_4$	dark green	25 [b]	1.76	37.4 37.55	3.35 3.7	8.7 8.6	13.2 12.8		
Cu(NMeS)BF$_4$	yellowish green	83 [a]	0.88	30.8 31.0	2.85 3.2	7.2 6.5	16.45 15.7	16.3 16.0	
Cu$_3$(ONMeS)$_2$Cl$_4$	green	51 [c]	1.95	29.6 29.7	2.7 2.6	6.9 6.7	15.8 14.8	23.5 23.8	
Cu$_2$(3MeOONMeS)Cl$_3$	dark green	insol.	1.70	26.3 26.1	2.6 2.8	5.6 5.15	12.75 12.8	25.3 25.7	21.15 21.4
Cu(ONSMe)NO$_3$	green	10 [a]	1.87	32.9 33.2	3.0 3.2	11.5 11.1	17.6 17.6	17.4 17.1	
Cu$_3$(ONSMe)$_2$Cl$_4$	dark green	17 [a]	2.05	29.6 29.45	2.7 2.7	6.9 6.6	15.8 14.6	23.5 23.7	
Cu(5ClONSMe)Cl	green	0.2 [a]	1.87	32.2 32.7	2.7 2.9	7.5 7.3	17.2 16.9	16.9 16.9	19.0 19.3
Cu(5BrONSMe)Cl	green	0.1 [a]	1.84	28.8 28.8	2.4 2.6	6.7 6.0	15.4 15.1	15.2 15.1	

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

The bis-ligand complex $Ni(ONMeS)_2$ was also isolated; its magnetic moment (3.10 B.M.) is typical of octahedral nickel(II).

The copper complexes which were obtained are listed in Table III. The molecular conductivity of $Cu(ONMeS)NO_3$ in nitromethane (47 mho), although indicating appreciable ionic dissociation, is considerably below that expected (*c.* 85 mho) for a uni-univalent electrolyte in this solvent. The infrared spectrum displays strong bands at 1480 and 1280 cm^{-1}, indicative of a coordinated nitrato group.[3] The reflectance spectrum (Figure 1) is more indicative of square-planar than of any other configuration. Accordingly a four-coordinate structure $[Cu(ONMeS)NO_3]$ is assigned to this complex.

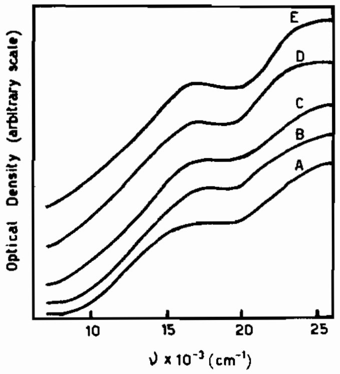


Figure 1. Solid state reflectance spectra of copper complexes: A, $[Cu(ONMeS)py]ClO_4$; B, $Cu_3(ONMeS)_2Cl_4$; C, $Cu_3(ONSMe)_2Cl_4$; D, $Cu(ONMeS)NO_3$; E, $Cu(ONSMe)NO_3$.

In the presence of pyridine the Schiff base (III) reacts with copper(II) perchlorate to give the complex $[Cu(ONMeS)py]ClO_4$ which is a uni-univalent electrolyte in nitrobenzene. The infrared spectrum shows a single broad absorption centred at 1070 cm^{-1}, indicating the presence of ionic perchlorate. The magnetic moment is at the low end of the range usually found for copper(II). The ν(C-O) frequency occurs at 1530 cm^{-1} indicating the presence of a non-bridging phenolic oxygen.[1] The electronic spectrum (Figure 1) is similar to that of $[Cu(ONMeS)NO_3]$ and is consistent with a square-planar configuration.

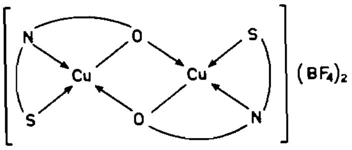
With copper(II) fluoroborate the ligand (III) yields a beautifully crystalline, yellowish-green complex having the stoicheiometry corresponding to $Cu(ONMeS)BF_4$. The infrared spectrum of the complex shows that the fluoroborate ions are not coordinated. The magnetic moment at room temperature (0.88 B.M.) is anomalously low and the moment decreases with decrease in temperature (see Table IV). This suggests that antiferromagnetic interactions are involved. However, the temperature dependence of the susceptibility could not be used to assign a definite structure to this complex because of the large errors involved in measuring such low susceptibilities. Nevertheless, the oxygen-bridged binuclear structure (VIII) is suggested for this compound. The occur-

Table IV. Magnetic Data for Copper Complexes.

T(°K)	$10^6\chi'_M$ per Cu atom	$1/\chi'_M$ per Cu atom	μ(B.M.) per Cu atom
	$[Cu_2(ONMeS)_2](BF_4)_2$		
373	408	2450	1.10
353	408	2450	1.08
343	426	2347	1.08
333	397	2519	1.03
323	374	2674	0.99
313	368	2717	0.96
303	356	2808	0.93
293	350	2857	0.91
283	327	3058	0.86
273	321	3115	0.84
263	315	3174	0.82
253	304	3289	0.76
233	280	3571	0.72
213	298	3360	0.72
193	280	3571	0.66
183	275	3635	0.64
173	240	4170	0.58
153	222	4501	0.52
123	211	4739	0.46
93	195	5128	0.38
	$Cu_3(ONMeS)_2Cl_4$		
333	1454	688	1.97
303	1574	635	1.96
283	1667	600	1.95
253	1884	531	1.96
223	1873	534	1.90
193	2429	412	1.95
163	2913	343	1.96
133	3523	284	1.94
103	4409	227	1.91
83	5428	184	1.91
	$Cu_2(3MeOONMeS)Cl_3$		
343	1037	964	1.70
313	1107	903	1.67
283	1193	832	1.65
253	1275	784	1.61
223	1304	767	1.53
193	1413	708	1.48
163	1493	670	1.40
133	1462	684	1.25
103	1366	732	1.07
83	1185	844	0.89
	$Cu(ONSMe)NO_3$		
303	1356	738	1.82
263	1554	644	1.81
213	1919	521	1.82
163	2492	401	1.81
113	3491	287	1.78
83	4633	216	1.76
	$Cu_3(ONSMe)_2Cl_4$		
313	1704	587	2.07
283	1852	540	2.05
253	2008	498	2.02
223	2175	460	1.98
193	2462	406	1.96
163	2786	359	1.91
133	3166	316	1.84
103	3694	271	1.75
83	4157	241	1.67
	$Cu(5BrONSMe)Cl$		
323	1266	790	1.81
297	1409	710	1.84
223	1818	550	1.81
173	2406	416	1.83
113	3614	277	1.81
83	4760	210	1.78

(3) B.M. Gatehouse, S.E. Livingstone, and R.S. Nyholm, *J. Chem. Soc.*, 4222 (1957).

rence of ν(C-O) at 1550 cm^{-1} in the infrared spectrum confirms the presence of bridging phenolic oxygen atoms.

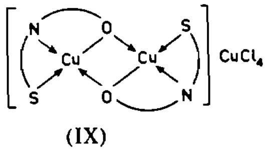


(VIII)

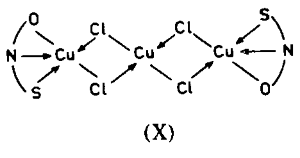
The equivalent conductivity (Λ_{1000}) of this complex (83 ohm^{-1}) does not distinguish between the monomeric ionic formulation [Cu(ONMeS)]BF$_4$ and a polymeric one [Cu$_n$(ONMeS)$_n$](BF$_4$)$_n$. The electrolyte type can be determined by the measurement of the equivalent conductivity (Λ) over a range of concentration (*c*) and the determination of the slope of the plot of Λ_o-Λ against $\sqrt{c}$ (Λ_o = equivalent conductivity extrapolated to infinite dilution).[4] Values for $(\Lambda_o\text{-}\Lambda)/\sqrt{c}$ have been obtained over a range of *c* from $10^{-3}M$ to $2\times10^{-2}M$ for tri-, bi-, and uni-univalent electrolytes in nitromethane.[4,5] The complex Cu(ONMeS)BF$_4$ was found to have Λ_o = 88 and $(\Lambda_o\text{-}\Lambda)/\sqrt{c}$ = 141 in nitromethane solution. These data indicate that this complex is a uni-univalent electrolyte. The value for $(\Lambda_o\text{-}\Lambda)/\sqrt{c}$ differs from these for [NBu$_4$]Br (183) and Na[BPh$_4$] (216) but is close to that for the complex [Ru$_2$Cl$_3$(PEt$_2$Ph)$_6$]Cl (151), which has a value of Λ_o of 85.5 ohm^{-1}.[5]

The magnetic and infrared evidence suggests that in the solid state our complex exists in the dimeric form [Cu$_2$(ONMeS)$_2$](BF$_4$)$_2$ but the conductivity data show that in nitromethane solution the complex exists as a uni-univalent electrolyte, possibly as [Cu(ONMeS)(MeNO$_2$)]BF$_4$.

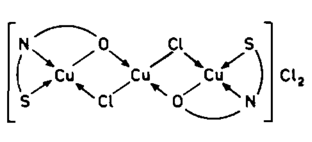
With copper(II) chloride the Schiff base (III) yields a green crystalline complex having the composition Cu$_3$(ONMeS)$_2$Cl$_4$. The structures (IX - XIII) are possible. ,The magnetic moment does vary slightly with temperature (see Table IV) and the Curie-Weiss law ($\chi_M = c/T\text{-}\theta$ is obeyed with a relatively small value for the Weiss constant (θ = –8°K). Accordingly, there is no appreciable antiferromagnetic interaction between the copper atoms in this complex. Therefore the structure (IX) can be excluded, since the bridging arrangement of the cation would be expected to lead to marked antiferromagnetic interaction as found for [Cu$_2$(ONMeS)$_2$](BF$_4$)$_2$. Moreover, a feature of the electronic spectrum of the pseudo-tetrahedral [CuCl$_4$]$^{2-}$ anion is the presence of a band at 7800 cm^{-1}.[6] This band does not appear in the spectrum of the complex (Figure 1).



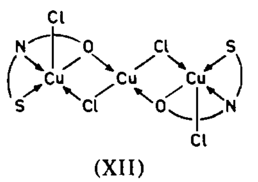
(IX)



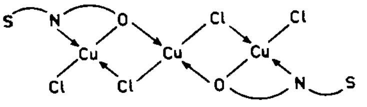
(X)



(XI)



(XII)



(XIII)

The infrared spectrum of Cu$_3$(ONMeS)$_2$Cl$_4$ shows the ν(C-O) frequency at 1540 cm^{-1} which is indicative of the presence of a bridging phenoxy group.[1] Acordingly structure (X) is unlikely. The complex is insoluble in most solvents but is slightly soluble in dimethylformamide. The conductivity (51 ohm^{-1}) in dimethylformamide, while appreciable, is below that expected (70-90 mho) for a bi-univalent electrolyte in this solvent[4,7] and may be due to some decomposition in dimethylformamide. Therefore the ionic structure (XI) is also unlikely. The most likely structures seem to be either (XII) in which the Schiff base ligands are tridentate and the two terminal copper atoms are five-cordinate or (XIII) in which the thioether group of the ligand is not coordinated and all three copper atoms have an approximately square-planar configuration.

With copper(II) chloride the Schiff base (IV) yields a dark green complex Cu$_2$(3MeOONMeS)Cl$_3$. This is in contrast to the Schiff base (III) which gives the trinuclear complex Cu$_3$(ONMeS)$_2$Cl$_4$. The change in colour and stoicheiometry of the complex with the replacement of hydrogen by methoxyl in the 3-position of the salicyldehyde moiety suggests a different structure for the complex of the 3-methoxy ligand (IV).

The magnetic moment of Cu$_2$(3MeOONMeS)Cl$_3$ falls from 1.70 B.M. at 343°K to 0.89 B.M. at 83°K (see Table IV). The magnetic data fit both the Bleaney-Bowers equation (1) for a dimeric arrangement of two interacting copper atoms and the Ising equation (2) for a linear polymeric arrangement.[8-10] The temperature independent paramagnetism *Nα* is taken as 60×10^{-6} c.g.s.u. The quality of

$$\chi_M = \frac{N\beta^2g^2}{kT}[3+\exp(-2J/kT)]^{-1}+N\alpha \qquad (1)$$

$$\chi_M = \frac{N\beta^2g^2[\exp(4K)+(2+K^{-1})\exp(2K)-K^{-1}\exp(-2K)+5]}{12\ kT\ [\exp(2K)+\exp(-2K)+2]}+N\alpha$$

$$(K=\frac{J}{kT}) \qquad (2)$$

the closest fit for the Bleaney-Bowers equation with *g* = 2.13 and *J* = –79 cm^{-1}—$\Sigma[(\chi_{obs}-\chi_{calc})T]^2$ = 0.14×10^{-3}—is better than that for the Ising equa-

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[4] W.J. Geary, *Coordination Chem. Rev.*, *7*, 81 (1971).
[5] R.D. Feltham and R.G. Hayter, *J. Chem. Soc.*, 4587 (1964).
[6] A. van der Avoird and P. Ros, *Theor. Chim. Acta*, *4*, 13 (1966).
[7] J.V. Quagliano, J. Fujita, G. Franz, D.J. Phillips, J.P. Walmsley, and S.Y. Tyree, *J. Amer. Chem. Soc.*, *83*, 3770 (1961).
[8] B. Bleaney and K.D. Bowers, *Proc. Roy. Soc.*, *A214*, 451 (1952).
[9] R.W. Jotham and S.F.A. Kettle, *Inorg. Chim. Acta*, *4*, 145 (1970).
[10] G.F. Newell and E.W. Montroll, *Rev. Mod. Phys.*, *25*, 353 (1953); G.G. Bararchlough and C.F. Ng, *Trans. Faraday Soc.*, *60*, 836 (1964); E. Sinn, *Coord. Chem. Rev.*, *5*, 313 (1970).

tion with $g = 2.24$ and $J = -98$ cm^{-1}—$\Sigma[\chi_{obs} - \chi_{calc}]T]^2 = 0.58 \times 10^{-3}$—(see Figure 2).

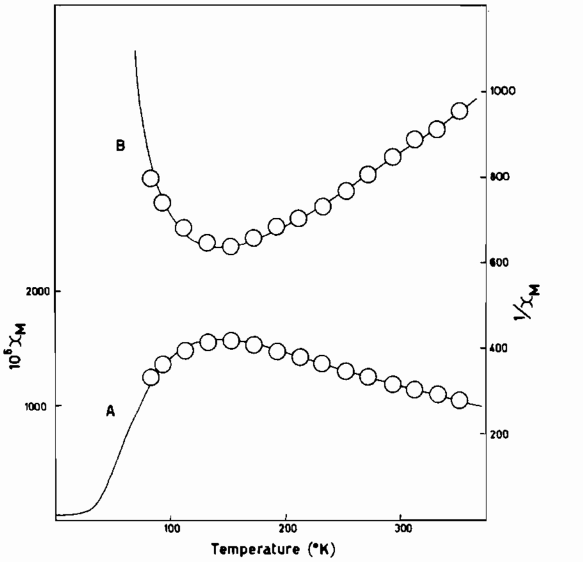
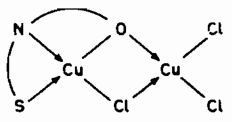


Figure 2. The temperature dependence of $10^6\chi_M$(A), and $1/\chi_M$ (B) for $Cu_2(3MeOONMeS)Cl_3$. Experimental values are indicated by open circles and the full curves are the calculated valves obtained from the Bleaney-Bowers equation (1) with $g = 2.13$ and $J = -79$ cm^{-1}.

The simplest dimeric structure which can be assigned to $Cu_2(3MeOONMeS)Cl_3$ is (XIV). The ν(C-O) frequency for this complex occurs at 1560 cm^{-1}, indicating the presence of a bridging phenolic oxygen. The low solubility of the complex precluded a molecular weight determination.



(XIV)

In complexes of (III) and (IV) the ligand could coordinate via either the thioether or the thione sulphur atom. However, in (V), (VI) and (VII) no thione groups are present and if sulphur coordination occurs in complexes of these ligands, it must be via the thioether sulphur. The pyridine-2-aldehyde Schiff base of *S,S'*-dimethyldithiocarbazate behaves as an NNS donor to nickel(II) and as an NN donor to cobalt(II).[11]

The complex Pd(ONSMe)Cl is a non-electrolyte in nitromethane. Its infrared spectrum displays ν(C-O) at 1520, indicating the presence of non-bridging phenolic oxygen. Therefore it is most likely that the complex has a square-planar monomeric structure with the ligand behaving as a uninegatively charged ONS donor. The complex $Cu(ONSMe)NO_3$ has a conductivity in nitrobenzene (10 ohm^{-1} cm^2 mole^{-1}) which indicates partial dissociation in solution. However, the infrared spectrum has bands at 1480 and 1275 cm^{-1}, showing that the nitrato group is coordinated in the solid state;[3] the ν(N-O) band at *ca.* 1010 cm^{-1} is obscured by ligand absorption. The electronic reflectance spectrum (Figure 1) is similar to that of $Cu(ONMeS)NO_3$; accordingly a square-planar structure is postulated with the ligand acting as an ONS donor. The magnetic data are given in Table IV; the complex obeys the Curie-Weiss law with a small value for the Weiss constant ($\theta = -5$°K).

With the copper chloride the Schiff base (V) yields the complex $Cu_3(ONSMe)_2Cl_4$. The complex has a low conductivity in nitromethane and its electronic spectrum (Figure 1) shows no bands attributable to the $[CuCl_4]^{2-}$ ion, while the infrared spectrum displays ν(C-O) at 1540 cm^{-1}. Hence the structures (IX) and (X) are unlikely for the same reasons given above in connection with the analogous compound $Cu_3(ONMeS)_2Cl_4$. The magnetic moment of $Cu_3(ONSMe)_2Cl_4$ decreases from 2.05 B.M. at room temperature to 1.67 B.M. at 83°K (see Table IV).

The temperature dependence of the susceptibility of $Cu_3(ONSMe)_2Cl_4$ has been compared with that expected for a dimeric structure (Equation 1) and that for a linear trimeric structure (Equation 3).[8,9]

$$\chi_M = \frac{N\beta^2 g^2[1 + \exp(2J/kT) + 10\exp(3J/kT)]}{12kT[1 + \exp(2J/kT) + 2\exp(3J/kT)]} + N\alpha \qquad (3)$$

The quality of the fit for the linear trimer equation (3)—$\Sigma[(\chi_{obs} - \chi_{calc})T]^2 = 0.21 \times 10^{-3}$, with $g = 2.48$ and $J = -37$ cm^{-1}—is better than for the dimer equation (1)—$\Sigma[(\chi_{obs} - \chi_{calc})T]^2 = 0.50 \times 10^{-3}$, with $g = 2.44$ and $J = -38$ cm^{-1} (see Figure 3). This is in accord with the other evidence supporting structures (XII) or (XIII). The reflectance spectra of Cu$_3$(ON-

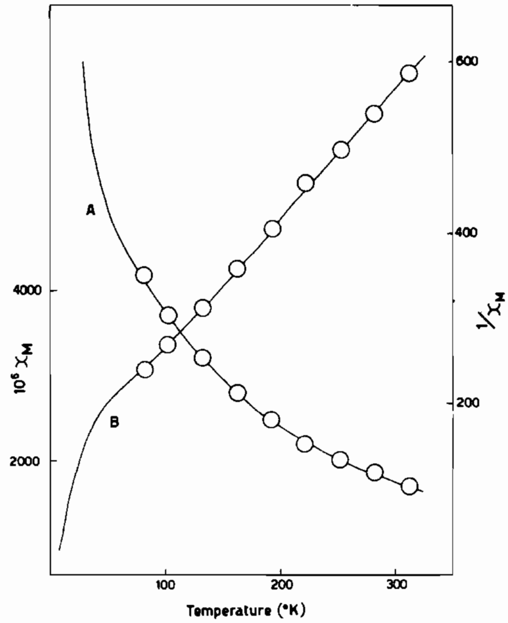


Figure 3. The temperature dependence of $10^6\chi_M$ (A) and $1/\chi_M$ (B) for $Cu_3(ONSMe)_2Cl_4$. Experimental values are indicated by open circles and the full curves are the calculated values obtained from equation (3) for a linear trimer structure, with $g = 2.48$ and $J = -37$ cm^{-1}.

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[11] M. Akbar Ali, S.E. Livingstone, and D.J. Phillips *Inorg. Chim. Acta, 6,* 552 (1972).

$MeS)_2Cl_4$ and $Cu_3(ONSMe)_2Cl_4$ are very similar, suggesting that the two compounds have similar structures. Whereas the latter compound shows distinct antiferromagnetic behaviour, the data for the former compound do not show any marked antiferromagnetic interaction over the temperature range studied; data are required for temperatures below 83°K to establish the presence of any antiferromagnetic interaction in $Cu_3(ONMeS)_2Cl_4$.

Whereas dimeric or trimeric complexes were obtained from the reaction of copper chloride with the Schiff base (III), (IV), and (V), the ligands (VI) and (VII) yield the 1:1 complexes Cu(5ClONSMe)Cl and Cu(5BrONSMe)Cl). The complexes are non-electrolytes in nitromethane and their infrared spectra display ν(C-O) at *ca.* 1520 cm^{-1}, indicating non-bridging phenoxy groups. The compounds are assumed to possess a square-planar configuration with the ligands acting as ONS donors. The magnetic data show that the compound Cu(5BrONSMe)Cl obeys the Curie-Weiss law with a value of −10°K for the Weiss constant θ.

The ONSMe ligands (V), (VI), and (VII), derived from *S,S'*-dimethyldithiocarbazate, cordinate to copper(II) as tridentates involving coordination via the thioether sulphur atom. This behaviour is in contrast to that of the pyridine-2-aldehyde Schiff base of *S,S'*-dimethyldithiocarbazate, which shows little tendency to bind to copper via the thioether sulphur atom.[11]

Experimental Section

Unless otherwise stated all the compounds, after filtration, were washed with alcohol and dried *in vacuo* over phosphorus pentoxide.

α-N-*Methyl*-S-*methyl*-β-N-(*2-hydroxyphenyl*)*methylendithiocarbazate.* Salicyldehyde (10 g) was added to a solution of *N*-methyl-*S*-methyldithiocarbazate (10 g) in alcohol (250 ml). The solution was heated on the steam bath for 15 min and then allowed to stand overnight at room temperature. The pale yellow crystals which had formed were then filtered off; yield, 17.0 g.

α-N-*Methyl*-S-*methyl*-β-N-(2-hydroxy-3-methoxyphenyl)-*methylendithiocarbazate.* This compound was prepared in a manner similar to the above except that a solution of 3-methoxysalicylaldehyde (12.2 g) was used instead of salicylaldehyde. The ligand formed as beautifully crystalline needles; yield, 13.0 g.

1-(2-Hydroxyphenyl)-2,3-diaza-4-methylthio-5-thiahexa-1,3-diene. S-Methyldithiocarbazate[12] (5.0 g), in alcohol (50 ml) was added with stirring to a solution of potassium hydroxide (2.3 g) in alcohol (50 ml). The stirring was continued for 5 min and then methyl iodide (5.0 g) was added, followed by the addition of excess of salicyldeyde (20 g). The mixture was allowed to stand overnight and then the ligand was precipitated by the addition of water (200 ml). Recrystallization of the crude product from alcohol afforded white crystals; yield, 6.0 g.

1-(2-Hydroxy-5-chlorophenyl)-2,3-diaza-4-methylthio-5-thiahexa-1,3-diene and 1-(2-Hydroxy-5-bromophenyl)-2,3-diaza-4-methylthio-5thiahexa-1,3-diene. The compounds were prepared by the same general method. *S*-Methyldithiocarbazate (5.0 g) was dissolved in alcohol (100 ml) containing potassium hydroxide (2.5 g). After the mixture was stirred for 20 min, methyl iodide (50 g) was added. 5-Chlorosalicylaldehyde (7.0 g) or 5-bromosalicylaldchyde (9.0 g) in alcohol (100 ml) was added to the mixture which was left overnight. The compound was precipitated by the addition of water (500 ml). The crude product was purified by recrystallization from alcohol; yield, 9.0 g.

*General Method for the Preparation of Chloro-Bromo-, and Thiocyanato-*α-N-*methyl*-S-*methyl*-β-N-(*2-hydroxophenyl*)-*methylendithiocarbazatenickel*(*II*). A solution of the ligand (1.0 g) in hot alcohol (50 ml) was added to the hot solution of metal halide or thiocyanate (2.0 g) in alcohol (20 ml). After being heated on the steam bath for 5 min, the brown solution slowly deposited the crystalline complexes. After 1 hr the crystals were filtered off; yield, 60-80%.

*General Method for the Preparation of Dichloro-and Dibromo-*α-N-*methyl*-S-*methyl*-β-N-(*2-hydroxophenyl*)*methyldithiocarbazateiron*(*III*). A solution of the Schiff base (1.0 g) in a mixture of alcohol (20 ml) and 2,2-dimethoxypropane (30 ml) was added to a hot solution of ferric halide (3.0 g) in the same solvent (50 ml). After being heated on the steam bath for 3 min, the brown solution deposited dark brown crystals; yield, 80%.

Bis-{α-N-*methyl*-S-*methyl*-β-N-(*2-hydroxophenyl*)*methylendithiocarbazate*}*nickel*(*II*). The ligand (2.0 g) was stirred into a solution, prepared by dissolving sodium hydroxide (0.3 g) in 90% alcohol (100 ml). After the mixture was stirred for 10 min, it was filtered into a solution of nickel nitrate hexahydrate (1.0 g). The solution, on being heated on the steam bath for 5 min and cooled, deposited red crystals of the pure complex; yield, 1.5 g.

Nitrato-α-N-*methyl*-S-*methyl*-β-N-(*2-hydroxophenyl*)-*methylendithiocarbazatecopper*(*II*). Cupric nitrate tetrahydrate (1.7 g) in a hot 1:1 mixture of alcohol and 2,2-dimethoxypropane (40 ml) was added to a boiling solution of the ligand (0.8 g) in alcohol (50 ml). Green crystals of the complex formed immediately; these were filtered off; yield, 1.7 g.

Tetrachloro-bis{α-N-*methyl*-S-*methyl*-β-N-(*2-hydroxophenyl*)*methylendithiocarbazate*}*tricopper*(*II*). Cupric chloride dihydrate (1.7 g) in alcohol (100 ml) was added with stirring to a hot solution of the ligand 1.0 g) in alcohol (50 ml); a green precipitate formed. The mixture was heated on the steam bath for 5 min and the crystalline precipitate was filtered off; yield, 1.2 g.

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(12) M. Akbar Ali ,S.E. Livingstone, and D.J. Phillips, *Inorg. Chim. Acta, 5,* 119 (1971).

α-N-*Methyl*-S-*methyl*-β-N-(2-*hydroxophenyl*)*methylendithiocarbazatemonopyridinecopper*(*II*) *Perchlorate.* Copper perchlorate hexahydrate (1.0 g) in a mixture of alcohol (20 ml) and 2,2-dimethoxypropane (5 ml) was added to a hot solution of the ligand (1.0 g) in a mixture of alcohol (50 ml) and pyridine (2 ml). The mixture, on being heated on a steam bath, deposited dark green crystals of the complex which was filtered off; yield, 1.2 g.

α-N-*Methyl*-S-*methyl*-β-N-(2-*hydroxophenyl*)*methylendithiocarbazatecopper*(*II*) *Tetrafluoborate.* Copper tetrafluoborate (2.0 g) was stirred into a hot mixture of alcohol (20 ml) and 2,2-dimethoxypropane (10 ml). The mixture was then filtered hot into a solution of the ligand (0.7 g) in alcohol (50 ml)). The mixture was heated on a steam bath for 5 min, whereupon the dark brown solution deposited yellowish-green crystals of the complex; yield, 0.8 g.

Nitrato-1-(2-hydroxophenyl)-2,3-diaza-4-methylthio-5-thiahexa-1,3-dienecopper(II). A solution of cupric nitrate tetrahydrate (1.5 g) in a mixture of alcohol (30 ml) and 2,2-dimethoxypropane (20 ml) was treated with a solution of the ligand (1.0 g) in alcohol (20 ml). The mixture was heated on the steam bath for 5 min to give a deep green solution. Ligroin (10 ml) was added to the solution which, on cooling, deposited green crystals of the complex; yield, 0.4 g.

Tetrachloro-1-(2-hydroxophenyl)-2,3-diaza-4-methylthio-5-thiahexa-1,3-dienetricopper(II). A solution of the ligand (0.5 g) in hot alcohol (10 ml) was added to a hot solution of cupric chloride dihydrate (1.5 g). On cooling, the solution deposited deep green crystals of the complex; yield, 0.5 g.

General Method for the Preparation of Chloro-1-(2-hydroxo-5-bromophenyl)-2,3-diaza-4-methylthio-5-thiahexa-1,3-dienecopper(II) and Chloro-1-(2-hydroxo-5-chlorophenyl)-2,3-diaza-4-methylthio-5-thiahexa-1,3-dienecopper(II). A solution of the appropriate Schiff base (1.5 g) in hot alcohol (200 ml) was mixed with a solution of cupric chloride dihydrate (1.0 g) in alcohol (100 ml). The resulting solution was heated on a steam bath for 10 min, whereupon shining, needle-shaped crystals of the complex were deposited; yield, 0.4-0.5 g.

Trichloro-α-N-*methyl*-S-*methyl*-β-N-(2-*hydroxo-3-methoxyphenyl*)*methylendithiocarbazatedicopper*(*II*). A solution of the ligand (1.0 g) in alcohol (100 ml) was added to a hot solution of cupric chloride dihydrate (3.0 g) in alcohol (150 ml). The mixture, after being heated on the steam bath for 5 min, deposited fine, greenish-black crystals of the complex; yield, 1.6 g.

Chloro-1-(2-hydroxophenyl)-2,3-diaza-4-methylthio-5-thiahexa-1,3-dienepalladium(II). Potassium chloropalladate(II) (0.5 g) in water (10 ml) was added, with stirring, to a boiling solution of the ligand (0.5 g) in acetone (15 ml). The resulting orange precipitate of the complex was filtered off, washed with water, then with acetone, and finally with ligroin; yield, 0.3 g.