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Metal Chelates of Dithiocarbazic Acid and Its Derivatives. III. Complexes of the Tridentate Schiff Base α-*N*-Methyl-*S*-methyl-β-*N*-(2-pyridyl)-methylendithiocarbazate with Some 3d Metal Ions

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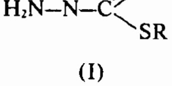
The Schiff base, α-N-methyl-S-methyl-β-N-(2-pyridyl)-methylendithiocarbazate, $C_5H_4NCH=NN(Me)C(S\text{-}Me)=S$ *(N—NMe—S), behaves as a neutral tridentate ligand, forming stable crystalline complexes with first-row transition metal ions. It forms the monoligand complexes* $Cr(N\text{—}NMe\text{—}S)Cl_3$, $Mn(N\text{—}NMe\text{—}S)X_2$ *(X = Cl, NCS),* $M(N\text{—}NMe\text{—}S)X_2$ *(M = Ni, Cu; X = Cl, Br, I, NCS), and* $[Cu(N\text{—}NMe\text{—}S)(H_2O)]SO_4$*. The manganese and nickel complexes are probably halogen-bridged, octahedral, and polymeric. The structures of the copper complexes are uncertain.*

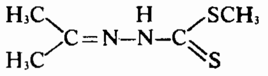
The bis-ligand complexes, which were isolated, are $[M(N\text{—}NMe\text{—}S)_2](ClO_4)_2$ *(M = Fe, Co, Ni),* $[Ni(N\text{—}NMe\text{—}S)_2](BF_4)_2\ 2H_2O$, $[M(N\text{—}NMe\text{—}S)_2][MX_4]$ *(M = Fe, Co; X = Cl, Br, I, NCS), and* $[Fe(N\text{—}NMe\text{—}S)_2][FeCl_4]_2$*. In these complexes the iron(II) cation is low-spin and diamagnetic but the cobalt(II) cation is high-spin.*

Introduction

In Part I of this series metal complexes of dithiocarbazic acid (I; R = H) and its *S*-methyl ester (I; R = Me) were described.[1] In part II[2] we reported the preparation of the Schiff bases, *S*-methyl-*N*-isopropylidendithiocarbazate (IIa) and *S*-methyl-*N*-(2-pyridyl)methylendithiocarbazate (IIIa). In the solid state these Schiff bases exist in the forms (IIa) and (IIIa). However, in solution the tautomeric forms (IIb) and (IIIb) are present and they readily lose a proton under neutral conditions to give stable metal complexes in which the metal ion is bound to the thiolo sulphur atom. The acetone Schiff base behaves as a bidentate ligand, while the pyridine Schiff base acts as a tridentate, coordinating through the mercapto sulphur and the β-imino and the pyridine nitrogen atoms.[2]



(I)



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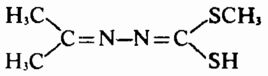

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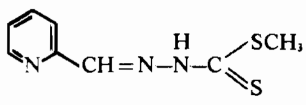
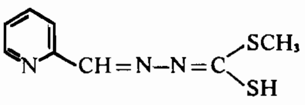
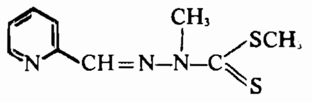


(IIIa)



(IIIb)



(IV)

In order to investigate further the types of metal complexes formed by derivatives of dithiocarbazic acid, we have prepared the α-*N*-methyl derivative of the Schiff base (IIIa), *viz.* α-*N*-methyl-*S*-methyl-β-*N*-(2-pyridyl)methylendithiocarbazate (IV; N—NMe—S). The compound (IV) cannot exhibit the same type of tautomerism as the compounds (IIa) and (IIIa) and thus cannot exist in a mercapto form analogous to (IIb) and (IIIb). The Schiff base (IV) readily forms metal complexes in which it behaves as a neutral tridentate ligand. These complexes are discussed below.

Results and Discussion

The Schiff base (IV) was prepared by the condensation of pyridine-2-aldehyde with 2-methyl-*S*-methyldithiocarbazate. The metal complexes, which were isolated, are listed in Table I.

The chromium (III) complex $Cr(N\text{—}NMe\text{—}S)Cl_3$ is a non-electrolyte in nitromethane. Its solid state reflectance spectrum displays strong bands at 15800 and 24500 cm^{-1}. These can be assigned, respectively, as the two spin-allowed transitions ${}^4T_{2g}\leftarrow{}^4A_{2g}$ and ${}^4T_{1g}(F)\leftarrow{}^4A_{2g}$, found for octahedral chromium (III).[3] The solubility, conductivity, and spectral data are consistent with a monomeric octahedral configuration.

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

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

(3) A.B.P. Lever, « Inorganic Electronic Spetcroscopy, » Elsevier, Amsterdam (1968), Chap. 9.

Table I. Metal Complexes of α-*N*-Methyl-*S*-methyl-β-N-(2-pyridyl)methylendithiocarbazate (N-NMe-S).

Compound	Colour	Magnetic moment per metal atom at 298°K μ (B.M.)	Mol. conduct. Λ_{1000} in $MeNO_2$ at 25° (ohm^{-1} cm^2 mole^{-1})	Analyses % Calcd. Found C	H	N	S	M
$[Cr(N{-}NMe{-}S)Cl_3]$	green	3.84	0.5	28.2 28.6	2.9 3.0	10.95 10.6	16.7 16.3	
$[Mn(N{-}NMe{-}S)Cl_2]$	orange	5.87	insol.	30.8 30.9	3.2 3.2	12.0 11.8	18.3 18.2	15.6 15.4
$[Mn(N{-}NMe{-}S)(NCS)_2] \cdot 1/2H_2O$	orange	5.91	insol.	32.6 32.5	3.0 2.8	17.3 17.5	31.6 32.0	
$[Fe(N{-}NMe{-}S)_2](ClO_4)_2 \cdot 5H_2O$	dark blue	diam.	171	 [a]	 [a]	10.8 9.8	16.5 15.7	7.2 7.0
$[Fe(N{-}NMe{-}S)_2][FeCl_4]$	dark blue	3.80	88	30.7 30.5	3.2 3.2	11.9 11.8	18.2 18.0	15.9 16.2
$[Fe(N{-}NMe{-}S)_2][FeBr_4]$	dark blue	3.81	76	24.5 25.2	2.5 2.6	9.5 11.0	14.5 14.4	
$[Fe(N{-}NMe{-}S)_2][Fe(NCS)_4]$	blue	3.65	110	33.2 33.0	2.8 2.7	17.6 17.3	32.3 32.4	14.05 13.95
$[Fe(N{-}NMe{-}S)_2][FeCl_4]_2$	deep blue	4.77	154	24.0 24.2	2.5 2.5	9.3 9.5	14.2 14.0	18.6 17.6
$[Co(N{-}NMe{-}S)_2](ClO_4)_2$	red	4.27	158	30.5 30.5	3.1 3.4	11.9 11.4	18.1 17.7	8.3 8.1
$[Co(N{-}NMe{-}S)_2][CoCl_4] \cdot H_2O$	brown	4.50	48[b]	29.7 29.9	3.3 3.3	11.5 11.1	17.6 17.6	16.2 16.0
$[Co(N{-}NMe{-}S)_2][CoBr_4]$	brown	4.42	186[b]	24.3 24.6	2.5 2.5	9.5 9.3	14.4 14.6	13.3 13.0
$[Co(N{-}NMe{-}S)_2][CoI_4]$	brown	4.43	232[b]	20.1 20.35	2.1 1.9	7.8 7.8	11.9 12.0	10.95 10.7
$[Co(N{-}NMe{-}S)_2][Co(NCS)_4]$	yellowish green	4.29	110[b]	33.0 33.4	2.8 3.1	17.5 17.5	32.0 31.7	14.7 14.4
$[Ni(N{-}NMe{-}S)Cl_2]$	yellowish brown	3.20	insol.	30.45 30.1	3.1 3.3	11.8 11.3	18.1 17.7	16.5 16.3
$[Ni(N{-}NMe{-}S)Br_2]$	yellowish brown	3.23	insol.	24.35 24.4	2.5 2.6	9.5 9.2	14.4 14.5	13.3 13.3
$[Ni(N{-}NMe{-}S)I_2]$	dark brown	3.12	insol.	20.1 20.1	2.1 2.3	7.8 7.8	11.9 12.7	10.9 10.8
$[Ni(N{-}NMe{-}S)(NCS)_2]$	yellowish green	3.16	insol.	33.0 33.0	2.8 2.7	17.5 17.2	32.0 30.0	14.7 14.8
$[Ni(N{-}NMe{-}S)_2](ClO_4)_2$	light brown	3.04	156	30.5 30.8	3.1 3.5	11.9 11.3	18.1 17.9	8.3 8.2
$[Ni(N{-}NMe{-}S)_2](BF_4)_2 \cdot 2H_2O$	light brown	3.16	160	30.0 29.6	3.6 3.5	11.7 11.5	17.8 17.2	8.2 7.9
$[Cu(N{-}NMe{-}S)Cl_2]$	yellowish green	1.87	insol.	30.0 29.9	3.1 3.0	11.7 11.4	17.8 17.8	17.7 17.3
$[Cu(N{-}NMe{-}S)Br_2]$	green	1.84	insol.	24.1 24.4	2.5 2.7	9.4 9.45	14.3 14.1	14.2 13.8
$[Cu(N{-}NMe{-}S)I_2]$	black	1.79	insol.	19.9 19.9	2.0 1.8	7.7 7.7	11.8 12.5	11.7 11.4
$[Cu(N{-}NMe{-}C)(NCS)_2] \cdot 2H_2O$	green	1.91	insol.	29.95 29.7	3.4 2.85	15.9 16.25		14.4 15.2
$[Cu(N{-}NMe{-}S)(H_2O)]SO_4$	green	1.87	insol.	26.8 26.6	3.25 3.25	10.4 10.25	23.9 23.2	15.8 15.5

[a] Analysis for carbon and hydrogen could not be done due to the explosive nature of the compound; [b] in dimethylformamide

This indicates that the Schiff base is acting as a tridentate.

The orange manganese (II) compounds, $Mn(N{-}NMe{-}S)Cl_2$ and $Mn(N{-}NMe{-}S)(NCS)_2 \cdot 1/2H_2O$ have moments close to the spin-only value (5.92 B.M), expected for high-spin manganese(II). The thiocyanato complex displays $C{\equiv}N$ stretching frequencies at 2052 and 2082 cm^{-1}. The occurrence of two $\nu(C{\equiv}N)$ bands indicates the presence of both terminal *N*-bonded and bridging thiocyanato groups. This, together with the insolubility, points to a polymeric bridged octahedral structure rather than a five-coordinate monomeric configuration for these compounds

The bis-ligand iron(II) complexes $[Fe(N{-}NMe{-}S)_2](ClO_4)_2 \cdot 5H_2O$ and $[Fe(N{-}NMe{-}S)_2][FeX_4]$ (X= Cl, Br, NCS) were obtained. The perchlorate is diamagnetic, while the other complexes have magnetic moments of 3.65-3.80 B.M. per iron atom. The moment of $[Fe(N{-}NMe{-}S)_2][FeCl_4]$ is almost independent of temperature, ranging from 3.83 B.M. at 303 °K to 3.63 B.M. at 83°K. This indicates that neither spin-state equilibrium nor antiferromagnetic interaction are involved. The paramagnetism of these compounds arises solely from the high-spin iron(II) atom in the anion. Table II lists the magnetic data. If the small value (260×10^{-6}) of the susceptibility for the cation $[Fe(N{-}NMe{-}S)_2]^{2+}$ is subtracted from the observed values for these complexes, the moments for the anions can be calculated:

these are found to be 5.10-5.34 B.M., *i.e.* within the range expected for high-spin iron(II) (see Table II). The conductivities of these compounds (see Table I) indicate that they behave as electrolytes in nitromethane. Although the complex $[Fe(N{-}NMe{-}S)_2][FeCl_4]_2$ has the conductivity expected for a bi-univalent electrolyte in this solvent (150-180 mho), the values for $[Fe(N{-}NMe{-}S)_2][FeX_4]$ (X = Cl, Br, NCS) are between those expected for a uni-univalent and a bi-bivalent electrolyte. This is probably due to ion-pair association between two large doubly charged ions. Thus the magnetic and conductivity data are consistent with the formulation of these complexes as the salts $[Fe(N{-}NMe{-}S)_2][FeX_4]$, rather than as neutral five-coordinate monomers $[Fe(N{-}NMe{-}S)X_2]$.

Table II. Magnetic Data on Iron Complexes.

Compound	T°*K*	$10^6\chi'_M$	μ for anion* (B.M.)
$[Fe(N{-}NMe{-}S)_2](ClO_4)_2 \cdot 5H_2O$	295	260	—
$[Fe(N{-}NMe{-}S)_2][Fe^{II}Cl_4]$	292	12320	5.34
$[Fe(N{-}NMe{-}S)_2][Fe^{II}Br_4]$	295	12200	5.34
$[FeN{-}NMe{-}S)_2][Fe^{II}(NCS)_4]$	290	11350	5.10
$[Fe(N{-}NMe{-}S)_2][Fe^{III}Cl_4]_2$	291	291100	5.82

* The cation is diamagnetic.

If the Schiff base (IV) is treated with ferric chloride, the complex which is obtained, *viz.* $[Fe(N{-}NMe{-}S)_2][FeCl_4]_2$, does not contain iron(III) in the cation but iron(II) in the cation and iron(III) in the anion (see Table II).

The Mössbauer spectrum of $[Fe(N{-}NMe{-}S)_2][FeCl_4]$ shows the presence of both low-spin and high-spin iron(II). The isomer shift for the low-spin cation ranges from 0.53 mm sec^{-1} at 293°K to 0.61 mm sec^{-1} at 4.2°K, while the quadrupole splitting is surprisingly small, ranging from 0.215 mm sec^{-1} at 293°K to 0.228 mm sec^{-1} at 4.2°K. The small quadrupole splitting indicates that the iron atom is in a site of high symmetry, since for low-spin iron(II) the quadrupole splitting arises solely from anisotropic bonding effects and non-cubic distribution of charges around the iron atom. The quadrupole splitting for the high-spin anion ranges from 1.201 mm sec^{-1} at 293°K to 3.108 mm sec^{-1} at 4.2°K. The increase in quadrupole splitting as the temperature is lowered can be ascribed to distortion from tetrahedral symmetry.[4,5]

The Mössbauer spectrum of $[Fe(N{-}NMe{-}S)_2][FeCl_4]_2$ shows similar isomer shift and quadrupole splitting for the cation (0.226 and 0.244 mm sec^{-1} at 293° and 4.2°K, respectively), indicating the presence of low-spin iron(II). The anion $[Fe^{III}Cl_4]^-$ absorbs in the same region as the cation and the absorption due to this species could not be separated from that of the cation. A fuller discussion of the Mössbauer spectra of these and other iron complexes of similar ligands will be given in another communication.[6]

The red bis-ligand cobalt(II) perchlorate, $[Co(N{-}NMe{-}S)_2](ClO_4)_2$, was obtained by the reaction of the Schiff base with cobalt perchlorate hexahydrate. Its reflectance spectrum (see Table III) is typical of octahedral cobalt(II).[3] The ν_3 band appears as a shoulder on the strong ligand absorption above 23000 cm^{-1}. The magnetic moment (4.27 B.M.) is somewhat low for octahedral cobalt(II) but the analytical figures show that the compound is not contaminated with a cobalt(III) species. The compound obeys the Curie-Weiss law with a value for θ of −16°K. The magnetic data over the temperature range 303-83°K are given in Table IV.

When the Schiff base reacts with cobalt(II) halides in alcohol solution, compounds are obtained having the stoicheiometric composition $Co(N{-}NMe{-}S)X_2$ (X = Cl, Br, I, NCS). However, the complexes are considered to have the structure $[Co(N{-}NMe{-}S)_2][CoX_4]$. They are insoluble in most common organic solvents but are slightly soluble in dimethylformamide, in which they behave as electrolytes, although it seems that some decomposition may occur in this solvent. The infrared spectrum of the thiocyanato complex shows only one $\nu(C{\equiv}N)$ band at 2074 cm^{-1}, indicating the presence of terminal *N*-bonded thiocyanato groups. The solid state reflectance spectral data are

Table III. Solid State Reflectance Spectra of Cobalt Complexes.

Compnud	Bands of octahedral cobalt(II) (cm^{-1})		Bands of tetrahedral cobalt(II) (cm^{-1})						
	ν_1 $^4T_{2g} \leftarrow {}^4T_{1g}$	ν_3 $^4T_{1g}(P) \leftarrow {}^4T_{1g}$	ν_2 $^4T_1(F) \leftarrow {}^4A_2$				ν_3 $^4T_1(P) \leftarrow {}^4A_2$		
$[Co(N{-}NMe{-}S)_2](ClO_4)_2$	10400 11300sh	19500sh							
$[Co(N{-}NMe{-}S)_2][CoCl_4] \cdot H_2O$	10300sh 11400	19500sh	4700		5400	6100	14400	14900sh	15800
$[NEt_4]_2[CoCl_4]$[7] [a]			4780	5100	5400	5920	14300	14900	15750
$[Co(N{-}NMe{-}S)_2][CoBr_4]$	10300sh 11200	19300sh		4700	5300sh	5600	14000	15000	15500
$[NEt_4]_2[CoBr_4]$[7] [a]			4390	4880		5460	14200	14900	15530
$[Co(N{-}NMe{-}S)_2][CoI_4]$	10800sh	19500sh	4400	4650	5300		12500sh	13400	14300sh
$[NEt_4]_2[CoI_4]$[7] [a]				4100-5000br				13800	14300
$[Co(N{-}NMe{-}S)_2][Co(NCS)_4]$	11300sh	19500sh		6800	7800			16000	17000sh
$[NMe_4]_2[Co(NCS)_4]$[8]					7780			16250	

[a] In hexachlorobutadiene mull; sh, shoulder; br, broad.

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(4) P.R. Edwards and C.E. Johnson, *J. Chem. Phys.*, *49*, 211 (1968).
(5) R.B. Ingalls, *Phys. Rev.*, *133A*, 787 (1964).
(6) R.L. Martin and I.A.G. Roos, to be published.
(7) F.A. Cotton, D.M.L. Goodgame, and M. Goodgame, *J. Amer. Chem. Soc.*, *83*, 4690 (1961).
(8) F.A. Cotton, D.M.L. Goodgame, M. Goodgame, and A. Sacco, *J. Amer. Chem. Soc.*, *83*, 4157 (1961).

given in Table III. The spectra display bands attributable to the octahedral cation $[Co(N{-}NMe{-}S)_2]^{2+}$ and stronger bands characteristic of the tetrahedral $[CoX_4]^{2-}$ ions. Data for $[NR_4]_2[CoX_4]$ are included for comparison.

The magnetic moment of the thiocyanato complex decreases only slightly with decrease in temperature. The graph of $1/\chi'_M$ gainst T gives a straight line with a rather large value (–44°K) for the Curie-Weiss constant θ. The data are listed in Table IV.

Table IV. Magnetic Data for Cobalt Complexes.

T(°K)	$10^6\chi'_M$	μ(B.M.)
	$[Co(N{-}NMe{-}S)_2][ClO_4)_2$	
303	7668	4.26
263	8650	4.28
223	10278	4.30
183	12337	4.27
143	15427	4.22
103	20768	4.15
83	25390	4.13
	$[Co(N{-}NMe{-}S)_2][Co(NCS)_4]$	
303	7427	4.26
273	8121	4.22
243	8892	4.17
223	9540	4.14
203	10300	4.10
173	11720	4.05
143	13599	3.96
113	16584	3.88
83	21324	3.78

Table V. Solid State Reflectance Spectra of Nickel Complexes.

Compounds	Bands (cm^{-1})				
$[Ni(N{-}NMe{-}S)_2](ClO_4)_2$	10400sh	12200	13000sh		18500sh
$[Ni(N{-}NMe{-}S)_2](BF_4)_2 . 2H_2O$	10200sh	12400			18500sh
$Ni(N{-}NMe{-}S)Cl_2$	8200sh	10500	13900br	15000br	18800sh
$Ni(N{-}NMe{-}S)Br_2$	8150	10700	12000	13800vbr	16600sh
$Ni(N{-}NMe{-}S)I_2$	6900	7600	11400sh		16800sh
$Ni(N{-}NMe{-}S)(NCS)_2$		10400	11500sh		17600

With nickel perchlorate and nickel tetrafluoborate the Schiff base yields the bis-ligand complexes $[Ni(N{-}NMe{-}S)_2](ClO_4)_2$ and $[Ni(N{-}NMe{-}S)_2](BF_4)_2 \cdot 2H_2O$, which are bi-univalent electrolytes in nitromethane. The infrared spectra indicate that the anions are not coordinated. The electronic spectrum of $[Ni(N{-}NMe{-}S)_2](ClO_4)_2$ is typical of octahedral nickel(II) (see Table V).

On the other hand, nickel halides yield the mono-ligand complexes $Ni(N{-}NMe{-}S)X_2$ (X = Cl, Br, I, NCS). Their insolubility in all common solvents suggest that they do not possess a monomeric five-coordinate structure. The infrared spectrum of the thiocyanato complex displays two $\nu(C{\equiv}N)$ bands at 2085 and 2140 cm^{-1}, indicating the presence of both terminal *N*-bonded and bridging thiocyanato groups. This suggests that the complex has a polymeric octahedral structure with one of the thiocyanato groups acting as a bridge between two nickel atoms. It seems likely that the other complexes have similar structures with bridging halogen atoms.

The solid state reflectance spectral data are listed in Table V. The bands cannot be assigned with certainty, especially on account of the low symmetry of the N_2SX_3 chromophore. However, the spectra are more characteristic of six-coordinate than five-coordinate high-spin nickel(II).

Although bis-ligand complexes were obtained with iron(II), cobalt(II), and nickel(II), attempts to isolate bis-ligand copper(II) complexes were unsuccessful. Under anhydrous conditions both copper perchlorate and copper fluoborate react with the Schiff base (IV), yielding evil-smelling products which could not be characterized. Copper sulphate pentahydrate reacts with the Schiff base in methanol solution to give a complex having the composition $Cu(N{-}NMe{-}S)SO_4 \cdot H_2O$. Its infrared spectrum indicates that the sulphate group is ionic; consequently, it has been formulated as the aqua complex $[Cu(N{-}NMe{-}S)(H_2O)]SO_4$. It is assumed to possess an essentially square-planar configuration.

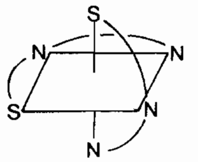
The crystalline halogeno complexes $Cu(N{-}NMe{-}S)X_2$ (X = Cl, Br, I, NCS) were obtained. They are insoluble in common organic solvents. The infrared spectrum of the thiocyanato complex displays only one $\nu(C{\equiv}N)$ band at 2060 cm^{-1}, indicating that bridging thiocyanato groups are not present. The electronic spectra display a fairly broad, almost symmetrical band centred at *c.* 13600 cm^{-1}. These spectra do not resemble those of known five-coordinate copper(II) complexes.[9] The data are insufficient to warrant the assignment of a stereochemical configuration to these complexes but it seems unlikely that they are five-coordinate.

Conclusion

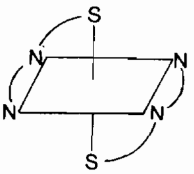
The structures of the metal complexes cannot be assigned with certainty in the absence of complete X-ray structural data. Nevertheless the results indicate that the Schiff base (IV), although acting as a tridentate, shows little tendency to form five-coordinate neutral complexes with bivalent metal ions. It forms bis-ligand complexes with iron(II), cobalt(II), and nickel(II) but not with copper(II). The reluctance to form a bis-ligand complex with copper(II) can be ascribed to the Jahn-Teller effect which causes elongation of the bonds in the apical sites about copper(II). This may place too great a strain on the one ligand

(9) M. Ciampolini, *Structure and Bonding*, 6, 52, (1969).

molecule which must occupy both apical sites as in (V). Since the three bonds about the β-nitrogen atom must be planar, the ligand cannot coordinate as shown in (VI).



(V)



(VI)

Experimental Section

2-Methyl-S-methyldithiocarbazate. This compound was prepared by a different method to that reported previously.[10]

Methyl hydrazine (17 g) was added to a solution of potassium hydroxide (20.7 g) in 90% aqueous alcohol (130 ml). The mixture was cooled to 10°, then carbon disulphide (28.1 g) was added dropwise, with vigorous stirring, over 1 hr, while the temperature of the mixture was not allowed to exceed 10°. The resulting yellow solution was diluted with water (300 ml) and then methyl iodide (53 g) was added slowly from a burette while the mixture was stirred vigorously. After the stirring had been continued for 3 hr, the white crystals of 2-methyl-*S*-methyldithiocarbazate were filtered off, washed with a 1:1 mixture of alcohol and ligroin, and recrystallized from alcohol; yield, 30 g (78%); m.p., 92° (lit.,[10] 93°).

α-N-*Methyl*-S-*methyl*-β-N-(*2-pyridyl*)*methylendithiocarbazate.* Pyridine-2-aldehyde (20g) in alcohol (50ml) was added to a solution of 2-methyl-*S*-methyldithiocarbazate (20 g) in alcohol (500 ml). The mixture was heated on the steam bath for 30 min then allowed to stand for 2 hr. Water (200 ml) was added and the mixture was placed in an ice bath for 1 hr. The yellowish-white product, which had separated was washed with a little alcohol, then with ligroin, and recrystallized from alcohol to give pale cream crystals of the *compound;* yeld, 20 g (55%); m.p., 104° Found: C, 47.9; H, 5.1; N, 18.85. Calcd for $C_9H_{11}N_3S_2$: C, 48.0; H, 4.9; N, 18.65%).

Preparation of Metal Complexes. All complexes, after being filtered off from the reaction mixture, were washed with alcohol, and dried *in vacuo* over phosphorus pentoxide.

*Method of Preparation of Dichloro- and Dibromo-α-*N-*methyl*-β-N-(*2-pyridyl*)*methylendithiocarbazate Complexes of Manganese*(*II*), *Nickel*(*II*), *and Copper*(*II*). The Schiff base (0.67 g, 0.003 mole) in alcohol (50 ml) was added to a solution of the metal halide (0.004 mole) in alcohol (50 ml). The solution, after being heated on the steam bath for 15 min and cooled, deposited the crystalline complex; yield, 80-95%.

*Method of Preparation of Diiodo- and Dithiocyanato-α-*N-*methyl*-β-N-(*2-pyridyl*)*methylendithiocarbazate Complexes of Manganese*(*II*), *and Nickel*(*II*). The Schiff base (0.003 mole) in hot alcohol (20 ml) was added to a solution of the metal nitrate (0.006 mole) and lithium iodide or thiocyanate (0.01 mole) in hot alcohol (30 ml). The mixture was kept on the steam bath for 15 min and allowed to cool. whereupon the crystalline complex was deposited; yield, 50-80%.

*Trichloro-α-*N-*methyl*-β-N-(*2-pyridyl*)*methylendithiocarbazatechromium*(*III*). The Schiff base (0.45 g, 0.002 mole) in alcohol (20 ml) was added to a solution containing an excess of chromic chloride hexahydrate (2 g) in alcohol (30 ml). The mixture was heated on the steam bath for 15 min and, on cooling, deposited well formed green crystals of the complex; yield, 70%.

Bis{α-N-*methyl*-β-N-(*2-pyridyl*)*methylendithiocarbazate*}*nickel*(*II*) *Perchlorate and Fluoborate.* A solution of nickel perchlorate or fluoborate (0.002 mole) in alcohol (20 ml) was added to a solution of the Schiff base (0.004 mole) in alcohol (25 ml). The solution was heated on the steam bath for 15 min and cooled, whereupon the crystalline complex was isolated by filtration; yield, 75-85%.

Bis{α-N-*methyl*-β-N-(*2-pyridyl*)*methylendithiocarbazate*}*cobalt*(*II*) *and -iron*(*II*) *Perchlorate.* A solution of the metal perchlorate hexahydrate (0.003 mole) in a hot 1:1 mixture of alcohol and 2,2-dimethoxypropane (20 ml) was added to a solution of the Schiff base (0.006 mole) in the same solvent (30 ml). The mixture was heated on the steam bath for 15 min and then cooled, whereupon the crystalline metal complex, which had separated, was filtered off under nitrogen and washed with alcohol; yield, 90%.

Bis{α-N-*methyl*-β-N-(*2-pyridyl*)*methylendithiocarbazate*}*iron*(*II*) *Tetrachloroferrate*(*II*). Ferrous chloride tetrahydrate (1.19 g, 0.006 mole) in water (5 ml) was added to a hot solution of the Schiff base (0.45 g, 0.002 mole) in alcohol (40 ml). The mixture turned blue and, on standing, deposited blue crystals of the complex; yield, 0.42 g (60%).

Bis{α-N-*methyl*-β-N-(*2-pyridyl*)*methylendithiocarbazate*}*iron*(*II*) *Tetrabromoferrate*(*II*) *and Tetrathiocyanatoferrate*(*II*). Ferrous perchlorate hexahydrate (1.09 g, 0.003 mole) in water (5 ml) was added to a solution of the Schiff base (0.67 g, 0.003 mole) in alcohol (20 ml). Lithium bromide or thiocyanate (1.5 g) in alcohol (20 ml) was then added and the mixture was heated on the steam bath for 15 min, then stood for one hour, whereupon the blue crystals of the complex were separated by filtration; yield, 70%.

Bis{α-N-*methyl*-β-N-(*2-pyridyl*)*methylendithiocarbazate*}*iron*(*II*) *Tetrachloroferrate*(*III*). A solution of anhydrous ferric chloride (0.97 g, 0.006 mole) in a 1:1 mixture of alcohol and 2,2-dimethoxypropane (15 ml) was added to a solution of the Schiff base (0.45 g, 0.002 mole) in the same solvent (20 ml). The solution, which at first became red then slowly changed

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(10) A.J. Sandström, *Arkiv. Kemi,* 9, 255 (1956).

to deep blue, was heated on the steam bath for 15 min, then allowed to stand for 1 hr, whereupon the deep blue crystals of the complex were separated by filtration; yield, 0.54 g (60%).

Bis{α-N-*methyl*-β-N-(*2-pyridyl*)*methylenditiocarbazate*}*cobalt*(*II*)*Tetrachloro-, Tetrabromo-, Tetraiodo-, and Tetrathiocyanatocobaltate*(*II*). The Schiff base (0.45 g, 0.002 mole) in alcohol (20 ml) was added to a solution of cobalt halide or thiocyanate (0.004 mole) in hot alcohol (50 ml). The mixture was heated on the steam bath for 15 min and allowed to cool whereupon the crystalline complex was separated by filtration; yield, 90-95%.

α-N-*Methyl*-β-*N*-(2-*pyridyl*)*methylenditiocarbazatemonoaquacopper*(*II*) Sulphate. A saturated solution of copper sulphate pentahydrate in methanol (50ml) was added to a hot solution of the Schiff base (0.45g) in methanol (20ml). The mixture was heated on the steam bath for 15min then allowed to stand 1 hr during which green crystals of the complex slowly deposited; yield, 0.41 g (60%).

Method of Preparation of Diiodo- and Dithiocyanato-α-N-*methyl*-β-*N*-(2-*pyridyl*)*methylenditiocarbazatecopper*(*II*). To a hot solution of copper nitrate trihydrate (0.96g, 0.004 mole) in alcohol (20ml) was added a hot solution of the Schiff base (1.34g, 0.006 mole) in alcohol (50 ml). Excess of lithium iodide or thiocyanate in alcohol (10 ml) was added dropwise, with stirring, to the reaction mixture. After the addition, the mixture was allowed to cool and the crystalline complex was removed by filtration; yield, 70-80%.

Spectral Measurements. The electronic diffuse reflectance spectra were measured on a Zeiss PMQII spectrophotometer from the sample diluted with magnesium carbonate and spread on filter paper. The infrared spectra were obtained from nujol or halocarbon mulls on a Perkin-Elmer 337 spectrophotometer.

Magnetic Measurements. The magnetic susceptibilities were measured by the Gouy method. The measurements other than at room temperature were made on a Newport variable-temperature Gouy balance.

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