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Metal Chelates of Dithiocarbazic Acid and Its Derivatives. II. Complexes of the Schiff Bases formed by Condensation of *S*-Methyldithiocarbazate with Acetone and Pyridine-2-aldehyde

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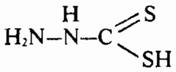
The acetone Schiff base S-*methyl*-N-*isopropylidendithiocarbazate,* $Me_2C=N-N=C(SMe)SH$ *(N–SH), forms the stable. crystalline complexes* $[M(N-S)_2]$ *(M=Co, Ni, Pd, Pt, Cu), which are non-electrolytes in nitrobenzene. The nickel, palladium, platinum, and copper complexes are square-planar but magnetic and spectral evidence indicates that the cobalt complex is tetrahedral.*

The pyridine-2-aldehyde Schiff base S-*methyl*-N-*(2-pyridyl)methylendithiocarbazate,* $C_5H_4NCH=N-N=C(SMe)SH$ *(N–N–SH), forms the square-planar 1:1 complexes* $[M(N-N-S)X]$ *(M = Ni, Pd, Pt, Cu; X = Cl, Br, I, NCS, or* NO_3*) and* $[Cu(N-N-S)\text{-}H_2O-ClO_4$ *and the octahedral 2:1 complexes* $[M(N-N-S)_2]$ *(M = Fe, Ni). The manganese(III) complex* $[Mn(N-N-S)Cl_2]$*. ½*H_2O *is probably octahedral and polymeric. With iron(III) the complexes* $[Fe(N-N-S)_2]ClO_4$ *and* $[Fe(N-N-S)_2][FeCl_4]$ *were obtained. Both the iron(II) complex and the iron(III) complex cation are spin-paired. Bivalent cobalt is oxidized to yield the cobalt(III) complexes ion* $[Co(N-N-S)_2]$*, which was isolated as* $[Co(N-N-S)_2]NO_3$ H_2O *and* $[Co(N-N-S)_2[CoX_4]$ *(X = Cl, Br, NCS).*

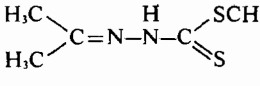
Introduction

In Part I of this series some metal complexes of dithiocarbazic acid(I) and its S-methyl ester were described.[1] As part of a detailed study of the metal complexes formed by derivatives of dithiocarbazic acid, we now report complexes of the Schiff bases formed by the condensation of *S*-methyldithiocarbazic acid with acetone and pyridine-2-aldehyde, *viz.* *S*-methyl-*N*-isopropylidendithiocarbazate(II) and *S*-methyl-*N*-(2-pyridyl)methylendithiocarbazate(III).

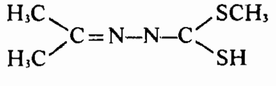
The infrared spectra of (II) and (III) show ν(N–H) at 3130 and 3080 cm^{-1}, respectively, but no ν(S–H) at *c.*2570 cm^{-1}, indicating that in the solid state both compounds exist in the forms (IIa) and (IIIa). However, in solution these compounds probably exist in equilibrium with the tautomeric forms (IIb) and (IIIb).



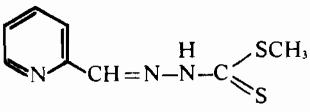
(I)



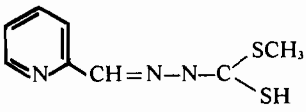
(IIa)



(IIb)



(IIIa)



(IIIb)

The acetone Schiff base, when in its tautomeric form (IIb), by loss of the thiol proton, might be expected to act as a singly negatively charged bidentate ligand by coordinating to a metal ion via the mercapto sulphur and the nitrogen bound to the isopropylidene group. Similarly, the tautometer (IIIb) of the pyridine-2-aldehyde Schiff base could act as a singly charged tridentate ligand by coordinating through the mercapto sulphur, the central nitrogen, and the pyridine nitrogen atoms. Our results show that these two ligands do, in fact, behave in this way.

Results and Discussion

The acetone Schiff base (II) has been reported by Sandström, who investigated its electronic spectrum, but no metal complexes were prepared. The pyridine-2-aldehyde Schiff base (III), which has not been previously reported, was prepared by condensation of *S*-methyldithiocarbazate with pyridine-2-aldehyde. Both Schiff bases (II) and (III) readily lose a proton in the presence of metal ions under neutral conditions with the concomitant formation of a metal chelate.

The Schiff base (II) gives inner complexes of the type $[M(N-S)_2]$ (N–SH = *S*-methyl-*N*-isopropylidenthiocarbazate; M = Co, Ni, Pd, Pt, Cu). These compounds, which are listed in Table I, were obtained as beautifully crystalline products which are quite stable on standing. All are non-electrolytes in nitrobenzene (Λ_{1000}, 0–0.5 ohm^{-1} cm^2 mole^{-1}).

The diamagnetism of the nickel complex indicates a square planar configuration. The palladium and platinum complexes are also doubtless square-planar. The ready solubility of the copper complex in chloro-

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(1) M. Akbar Ali, S.E. Livingstone, and D.J. Phillips, *Inorg. Chim. Acta*, *4*, 119 (1970).

(2) J. Sandström, *Acta Chem. Scand.*, *17*, 937 (1963).

Table I. Metal Complexes of *S*-Methyl-*N*-isopropylidendithiocabazate (N–SH).

Compound	Colour	M.p.	Magnetic moment at 298°K μ (B.M.)			Analyses % Calcd. Found		
				C	H	N	S	M
$[Co(N-S)_2]$	bluish-green	195°	4.94	31.5	4.8	14.7	33.6	15.4
				31.7	4.9	14.9	32.5	15.5
$[Ni(N-S)_2]$	brown	212 d.	diam.	31.5	4.8	14.7	33.6	15.4
				31.2	4.7	15.2	32.8	15.4
$[Pd(N-S)_2]$	orange	220 d.	diam.	28.0	4.2	13.1	29.9	24.8
				28.1	4.1	12.8	28.7	24.8
$[Pt(N-S)_2]$	yellow	205	diam.	23.2	3.5	10.8	24.8	37.7
				23.7	3.8	10.5	24.0	37.5
$[Cu(N-S)_2]$	black	125	1.85	31.1	4.7	14.5	33.2	16.5
				30.9	4.7	14.8	32.3	16.5

d. decomposes.

Table II. Electronic Spectral Bands of Bis(*S*-methyl-*N*-isopropylidendithiocarbazato)cobalt(II).

State	$^4T_1(F \leftarrow {}^4A_2$ ν_2 $\nu(cm^{-1})$	ε	$^4T_1(P \leftarrow {}^4A_2$ ν_3 $\nu(cm^{-1})$	ε
Solid	8500	—	16000	—
	9900	—	17000 sh	500
Chrloroform solution	8350	57	16100	—
	9900	62	17000 sh	—

form suggests a square-planar rather than a polymeric octahedral structure. This is supported by a molecular weight determination which showed that the complex is monomeric in dichloroethane (Calcd: *M*, 386. Found, *M*, 407).

However, the colour and the magnetic moment (4.94 B.M.) of the cobalt complex are in accord with a tetrahedral but not with a square-planar configuration. Further evidence for a tetrahedral structure is provided by the electronic spectrum. The spectral bands for the cobalt complex in the solid state and in chloroform solution are listed in Table II. The frequencies and intensities of the bands are typical of tetrahedral cobalt(II). Both the transitions ν_2 and ν_3 usually occur as multiple absorptions.[3]

Attempts to prepare complexes of manganese(II) and iron(III) were unsuccessful. No colour developed when manganese(II) chloride was added to a solution of the ligand (I). Ferric chloride gave a reddish colouration but no compound could be isolated.

Attempts to isolate 1:1 complexes of the type M(N–S)X, by means of the use of excess metal halide, were also unsuccessful. Similarly, attempts to prepare complexes containing the neutral ligand were abortive: preparations under acid conditions and attempts to protonate the complexes led to decomposition. However, metal complexes are known with the neutral and deprotonated forms of the acetone Schiff base of thiosemicarbazide, $(CH_3)_2C=NN=C(NH_2)SH$.[4]

The metal complexes which were obtained with *S*-methyl-*N*-(2-pyridyl)methylendithiocarbazate (N–N–SH) are listed in Table III. The formulae, derived from the analytical data, indicate that the ligand behaves as a uni-negatively charged tridentate chelating agent. All the compounds are beautifully crystalline and stable in air.

The orange manganese(III) complex Mn(N–N–S)Cl$_2$. ½H$_2$O was obtained from the reaction of the Schiff base with manganese(II) chloride. Its magnetic moment is within the range expected for manganese (III). The diffuse reflectance spectrum shows some broad absorption below 8000 cm^{-1} but any band which might be attributed to the $^5T_{2g} \leftarrow {}^5E_g$ transition of octahedral manganese(III)[3] is masked by strong ligand absorption above 17000 cm^{-1}. The insolubility of the complex is consistent with a polymeric structure and it is likely that the complex is six-coordinate with bridging chloro or thiolo groups.

Ferrous chloride yields the low-spin octahedral iron (II) complex $[Fe(N-N-S)_2]$. The Mössbauer spectrum shows a quadrupole splitting of 0.57 mm sec^{-1} at 293°K, indicating that there is some anisotropy in the bonding, as expected for an NNS donor ligand.[5]

The iron(III) complex $[Fe(N-N-S)_2]ClO_4$, which is also low-spin, was prepared from ferric perchlorate. The magnetic moment (1.86 B.M.) is rather low, since most spin-paired iron(III) complexes have moments within the range 2.2–2.5 B.M. However, the analyses show that the compound is not likely to be contaminated with the iron(II) species. The Mössbauer spectrum shows large quadrupole splitting (2.42 mm sec^{-1} at 293°K), indicating that the symmetry of the complex is well removed from octahedral (O_h). The isomer shift of 0.36 mm sec^{-1} at 293°K is a little less than that found for the iron(II) complex (0.47 mm sec^{-1}). The values for both compounds are typical for low-spin iron compounds.[5]

Ferric chloride gives the complex $[Fe(N-N-S)_2][FeCl_4]$ which is a uni-univalent electrolyte in nitromethane. The magnetic moment per iron atom is 4.43 B.M. at room temperature. The moment is almost independent of temperature (see Table IV). The molar susceptibility (χ'_M) at 298°K is 16400. The susceptibility of the cation $[Fe(N-N-S)_2]^+$, as determined for $[Fe(N-N-S)_2]ClO_4$, is 1420, making the susceptibility of the anion 14980; this gives a moment of 6.00 B.M. for the anion. Previous measurements of the susceptibility of the $[FeCl_4]^-$ anion have

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Table III. Metal Complexes of *S*-methyl-*N*-(2-pyridyl)methylendithiocarbazate (N—N—SH).

Compound	Colour	Magnetic moment per metal atom at 298°K μ (B.M.)	Mol. conduct. Λ_{1000} in $MeNO_2$ at 25° ($ohm^{-1}cm^2mole^{-1}$)	Analyses % Calcd. Found C	H	N	S	M
$[Mn(N–N–S)Cl_2]\,.\,\frac{1}{2}H_2O$	orange	4.80	insol.	27.8	2.6	12.2	18.6	
				27.8	2.8	12.3	18.3	
$[Fe(N–N–S)_2]$	deep green	0.7	0	40.3	3.4	17.6	26.9	11.7
				39.9	3.4	17.2	27.2	12.0
$[Fe(N–N–S)_2]ClO_4$	dark brown	1.86	24 [a]	33.4	2.8	14.6	22.3	9.7
				33.8	3.0	14.2	21.9	9.5
$[Fe(N–N–S)_2][FeCl_4]$	dark brown	4.43	70	28.5	2.4	12.5	19.0	16.6
				28.5	2.4	12.5	19.0	16.8
$[Co(N–N–S)_2]NO_3\,.\,H_2O$	red	diam.	80	34.3	3.2	17.5	22.9	10.5
				34.4	3.2	17.5	23.0	10.8
$[Co(N–N–S)_2]_2[CoCl_4]$	reddish-brown	2.98	111	33.1	2.8	14.5	22.1	15.2
				31.6	2.6	13.8	20.4	14.9
$[Co(N–N–S)_2]_2[CoBr_4]$	brown	2.88	126	28.7	2.4	12.6	19.2	13.2
				28.2	2.3	12.4	18.4	13.6
$[Co(N–N–S)_2]_2[Co(NCS)_4]$	black	2.71	132	34.6	2.6	17.9	30.8	14.1
				34.4	2.7	17.9	29.9	14.2
$[Ni(N–N–S)Cl]$	reddish-brown	diam.	0	31 6	2.6	13.8	21.1	19.3
				31.7	2.6	13.7	21.1	19.4
$[Ni(N–N–S)Br]$	brown	diam.	2	27.5	2.3	12.0	18.4	16.8
				27.4	2.6	11.9	18.2	16.9
$[Ni(N–N–S)I]$	brown	diam.	19	24.3	2.0	10.6	16.2	14.8
				24.6	2.5	10.6	16.1	14.9
$[Ni(N–N–S)NCS]$	dark brown	diam.	2	33.1	2.5	17.1	29.4	17.9
				33.1	2.5	17.0	29.6	17.8
$[Ni(–N–S)_2]$	reddish-brown	3.10	1	40.1	3.4	17.5	26.8	12.2
				40.2	3.6	17.6	25.8	12.3
$[Pd(N–N–S)Cl]$	orange	diam.	2	27.3	2.3	11.9		30.1
				27.2	2.4	12.2		30.0
$[Pt(N–N–S)Cl]$	dark red	diam.	1.5	21.8	1.8	9.5		44.3
				22.5	1.9	9.6		44.1
$[Cu(N–N–S)Cl]$	green	1.90	0.5	31.1	2.6	13.6	20.7	20.6
				31.0	2.7	13.4	20.0	20.4
$[Cu(N–N–S)Br]$	green	2.13	0.6	27.2	2.3	11.9	18.1	18.0
				27.3	2.5	11.4	18.1	17.8
$[Cu(N–N–S)NO_3]$	dark green	1.82	7	28.6	2.4	16.7	19.1	18.8
				28.2	2.4	16.4	18.7	18.9
$[Cu(N–N–S)H_2O]ClO_4$	green	2.12	72	24.6	2.6	10.7	16.4	
				24.5	2.8	10.1	15.5	

[a] In nitrobenzene.

Table IV. Magnetic Data for the Complex $[Fe(N–N–S)_2]$-$[FeCl_4]$.

T (°K)	$10^6\chi'_M$	μ (B.M.) per iron atom
303	16308	4.46
273	18006	4.45
243	20162	4.49
213	22828	4.43
183	26488	4.41
153	31500	4.40
103	44942	4.30

given values within the range 5.9-6.0 B.M.[6] The Mössbauer spectrum shows the presence of two types of iron atom. The values for the isomer shift and the quadrupole splitting of the low-spin iron(III) atom were found to be 0.34 and 2.38 mm sec^{-1}, respectively, at 293°K, in close agreement with the values found for $[Fe(N–N–S)_2]ClO_4$. The isomer shift for the high-spin iron(III) atom in the $[FeCl_4]^-$ anion was found to be 0.49 mm sec^{-1} at 293°K; the small quadrupole splitting (0.22 mm sec^{-1}) indicates only slight distortion from tetrahedral symmetry.

The interaction of cobalt(II) nitrate with the Schiff base (III) yields the red, diamagnetic cobalt(III) complex $[Co(N–N–S)_2]NO_3\,.\,H_2O$. Similar rapid oxidation of cobalt(II) to give a cobalt(III) complex occurs with monothio–β–diketones.[7] On the other hand, cobalt(II) chloride, bromide, and thiocyanate react to give the complexes $[Co(N–N–S)_2]_2[CoX_4]$ (X = Cl, Br, NCS), which contain diamagnetic cobalt (III) in the cation and high-spin cobalt(II) in the anion. This formulation of these complexes is confired by the magnetic and spectral data. Calculations of the moment of the cobalt(II) atom in the anion from the molar susceptibilities of the complexes give the following values: $[CoCl_4]^{2-}$, 5.10 B.M.; $[CoBr_4]^{2-}$, 4.88 B.M.; $[Co(NCS)_4]^{2-}$, 4.58 B.M. No T.I.P. corrections were applied in these calculations. The values are close to those previously reported for these $[CoX_4]^{2-}$ anions.[8-10]

The bands in the electronic spectra of the cobalt complexes are listed in Table V. All the spectra

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(9) F.A. Cotton, D.M.L. Goodgame, M. Goodgame, and A Sacco, *J. Amer. Chem. Soc.*, *83*, 4157 (1961).

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Table V. Reflectance Spectral Bands of the Cobalt and Copper Complexes of *S*-methyl-*N*-(2-pyridyl)methylendithiocarbazate.

Compound	Bands ν (cm^{-1})				
$[Co(N{-}N{-}S)_2]NO_3 . H_2O$	20000sh				
$[Co(N{-}N{-}S)_2]_2[CoCl_4]$	4800sh	5500	14700	15800	20000sh
$[Co(N{-}N{-}S)_2]_2[CoBr_4]$	4500sh	5600	14000	15000	19500sh
$[Co(N{-}N{-}S)_2]_2[Co(NCS)_4]$	6800sh	7600	15800	19500sh	
$[Cu(N{-}N{-}S)Cl]$	15500				
$[Cu(N{-}N{-}S)Br]$	15500				
$[Cu(N{-}N{-}S)NO_3]$	16000				
$[Cu(N{-}N{-}S)H_2O]ClO_4$	16500				

display an absorption at *c.* 20000 cm^{-1}, which appears as a shoulder on the low frequency side of the strong ligand absorption in this region. This is assigned as the ${}^1T_{1g} \leftarrow {}^1A_{1g}$ transition of low-spin octahedral cobalt (III). The spectra of the complexes $[Co(N{-}N{-}S)_2]_2$-$[CoX_4]$ in addition dislay ν_2 bands. (${}^4T_1(F) \leftarrow {}^4A_2$ transition) in the region 4500-7600 cm^{-1} and ν_3 bands (${}^4T_1(P) \leftarrow {}^4A_2$ transition) within the range 14000-15800 cm^{-1}. The frequencies of these bands agree closely with those reported for these anions.[3,9,10]

With nickel (II) the brown, diamagnetic, four-coordinate complexes $[Ni(N{-}N{-}S)X]$ (X = Cl, Br, I, NCS) and the high-spin, six-coordinate complex $[Ni(N{-}N{-}S)_2]$ were obtained. All except the iodo-complex are virtually non-electrolytes in nitromethane. The small yet appreciable conductivity (19 mho) of the iodo-complex suggests some dissociation in solution. The infrared spectrum of the thiocyanato-complex displays bands at 2090 and 845 cm^{-1}, indicative of *N*-bonded thiocyanate.

Palladium(II) and platinum(II) yield the mono-ligand complexes $[M(N{-}N{-}S)Cl]$ (M = Pd, Pt), similar to the diamagnetic nickel complexes. These two compounds are unusual in that the platinum complex is deeper in colour (dark red) than its palladium analogue, which is orange. This has been observed in only a few instances: *viz.* with maleonitriledithiol[11] and monothio-β-diketones.[12,13] The absorption spectra of the Schiff base complexes were measured in nitromethane solution. The lowest energy band of the palladium complex occurs at 20800 cm^{-1} (ε, 2200), while the spectrum of the platinum complex displays a shoulder at 17800 cm^{-1} and a maximum at 18700 cm^{-1} (ε, 900). These bands are attributed to the $M \rightarrow L_\pi{}^*$ charge-transfer transition.

Copper(II) chloride, bromide, and nitrate yield the four-coordinate complexes $[Cu(N{-}N{-}S)X]$ (X = Cl, Br, NO_3), which are non-electrolytes in nitromethane. The infrared spectrum of the nitrato complex shows strong bands at 1485 cm^{-1} (ν_4), 1275 cm^{-1} (ν_1), and 1007 cm^{-1} (ν_3); these bands confirm the presence of a coordinated nitrato group.[14]

Copper(II) perchlorate yields the perchlorate $Cu(N{-}N{-}S)ClO_4 . H_2O$, which is a uni-univalent electrolyte in nitromethane. The single broad band centred at 1125 cm^{-1} and the strong band at 622 cm^{-1} in the infrared spectrum indicate the presence of ionic perchlorate. Accordingly, it appears that the water molecule occupies the fourth coordination site.

The electronic spectra of all the copper complexes (see Table V) show a single broad absorption at *c.* 16000 cm^{-1}. The spectra and the magnetic moments are consistent with square-planar copper(II) and it seems most likely that the copper complexes have this configuration.

Conclusions

Both the ligands (IIb) and (IIIb) readily lose a proton under neutral conditions and coordinate via the thiolo sulphur to give stable, highly crystalline complexes. The acetone Schiff base (IIb) forms a diamagnetic square-planar nickel(II) complex but gives a spin-free tetrahedral complex with cobalt(II). On the other hand, cobalt(II) is readily oxidized in the presence of the pyridine-2-aldehyde Schiff base (IIIb) to yield the cobalt(III) cationic complex $[Co(N{-}N{-}S)_2]^+$. This ligand forms spin-paired complexes with nickel(II), iron(II), and iron(III). The ability of a ligand to cause spin-pairing is related to its degree of « softness », together with its capacity for metal→ligand π-bonding.[12,15] Only the softest ligands, such as cyanide ion[16] and *o*-phenylenebisdimethylarsine,[17] cause spin-pairing with iron(III). Others, such as dialkyldithiocarbamates[15] and monothio-β-diketones,[18] form iron(III) complexes whose moments are temperature-dependent due to a thermal equilibrium between the nearly equi-energetic spin-paired ($t_{2g}{}^5$) and spin-free ($t_{2g}{}^3 e_g{}^2$) configurations. Consequently, the spin-pairing ability of the Schiff base (IIIb) can be considered to be quite high, at least greater than that of either dialkyldithiocarbamates or monothio-β-diketones.

Experimental Section

Analyses. Carbon, hydrogen, and nitrogen were determined by Dr. E. Challen of the Microanalytical Laboratory, University of New South Wales. Sulphur was determined by the Australian Microanalytical Service, Melbourne. Iron and cobalt were determined by atomic absorption spectrophotometry after the complex had been dissolved in boiling concentrated hydrochlo-

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ric acid. Nickel and copper were estimated gravimetrically after the complex had been decomposed by heating with a mixture of sulphuric and nitric acids. Palladium and platinum were determined gravimetrically by direct ignition of the complex.

S-*Methyl*-N-*isopropylidendithiocarbazate.* A solution of hydrazinium dithiocarbazate (14 g), prepared as previously described,[1] in water (50 ml) was added to a solution of methyl iodide (14.2 g) in alcohol (80 ml). The solution was stirred for 8 hr and stood overnight. Acetone (12 ml) was added dropwise, with stirring, to the solution over 10 min. The resulting crystalline product was filtered off, washed with water, and recrystallized from alcohol to give colourless crystals of the Schiff base; yield, 12.8 g (80%); m.p., 114° (lit.[2] 117°) (Found: C, 37.0; H, 6.2; N, 17.3. Calcd for $C_5H_{10}N_2S_2$: C, 37.3; H, 6.6; N, 17.5%).

S-*Methyl*-N-*(2-pyridyl)methylendithiocarbazate.* A solution of *S*-methyldithiocarbazate (12.2 g), prepared as previously described,[1] in alcohol (250 ml) was added to a solution of pyridine-2-aldehyde (10.7 g) in alcohol (30 ml). The solution, after being heated on a steam bath for 30 min, deposited crystals, which were filtered off, washed with a little alcohol, and recrystallized from alcohol to give pale yellow crystals of the Schiff base; yield, 16 g (75%); m.p. 180° (Found: C, 45.6; H, 4.3; N, 19.4; S, 30.3. Calcd for $C_8H_9N_3S_2$: C, 45.5; H, 4.3; N, 19.9; S, 30.3%).

Method of Preparation of Bis(S-*methyl*-N-*isopropylidendithiocarbazato*) *Complexes of Cobalt*(*II*), *Nickel*(*II*), *and Copper*(*II*). A hot solution of the metal nitrate hexahydrate (0.001 mole) in alcohol (10 ml) was added to a hot solution of the Schiff base (0.32 g, 0.002 mole) in alcohol (20 ml). The solution was heated on the steam bath for 10 min and, on cooling, deposited crystals of the metal complex. The product was filtered off, washed with alcohol, and recrystallized from chloroform; yield, 70-80%.

Method of Preparation of Bis(S-*methyl*-N-*isopropylidendithiocarbazato*) *Complexes of Palladium*(*II*) *and Platinum*(*II*). A hot solution of potassium tetrachlorometallate(II) (0.015 mole) in water (10 ml) was added to a solution of the Schiff base (0.48 g, 0.003 mole) in hot acetone (10 ml). The mixture was warmed on the steam bath for 10 min and then cooled. The resulting metal complex was filtered off, washed with water, then dissolved in chloroform and reprecipitated with ligroin; yield, 80-85%.

Dichloro-S-*methyl*-N-*(2-pyridyl)methylendithiocarbazatomanganese*(*III*) *Hemihydrate.* The Schiff base (1 g) in alcohol (100 ml) was added to a hot solution of manganese(II) chloride hexahydrate (1.4 g) in alcohol (50 ml). The mixture was stood 4 hr, whereupon the orange crystals of the complex, which had deposited, were filtered off and washed with alcohol; yield, 1.5 g (92%).

Bis{S-*methyl*-N-*(2-pyridyl)methylendithiocarbazato*}-*iron*(*II*). Ferrous chloride tetrahydrate (0.5 g) in water (5 ml) was added to a hot solution of the Schiff base (1.05 g) in alcohol (100 ml). The solution immediately turned deep green and slowly deposited deep green crystals of the complex. The crystals were filtered off, washed with alcohol, and dried *in vacuo;* yield, 0.9 g (75%).

Bis{S-*methyl*-N-*(2-pyridyl)methylendithiocarbazato*}-*iron*(*III*) *Perchlorate.* Ferric perchlorate hexahydrate (1 g) in alcohol (20 ml) was added to a solution of the Schiff base (0.9 g) in alcohol (100 ml). To this solution was added lithium perchlorate (2 g) in alcohol (10 ml). Overnight the mixture deposited dark brown crystals of the complex; these were filtered off, washed with alcohol, and dried *in vacuo;* yield, 0.9 g (72%).

Bis{S-*methyl*-N-*(2-pyridyl)methylendithiocarbazato*}-*iron*(*III*) *Tetrachloroferrate*(*III*). Anhydrous ferric chloride (2 g) in hot alcohol (20 ml) was added to a solution of the Schiff base (1 g) in alcohol (100 ml). The mixture was heated on a steam bath for 15 min and then allowed to cool, whereupon shining dark brown crystals of the complex separated. The product was filtered off, washed with alcohol, and dried *in vacuo;* yield, 1.5 g (94%).

Bis{S-*methyl*-N-*(2-pyridyl)methylendithiocarbazato*}*cobalt*(*III*) *Nitrate Monohydrate.* Cobalt nitrate hexahydrate (1 g) in alcohol (20 ml) was added to a solution of the Schiff base (1.4 g) in alcohol (100 ml). The dark red solution was concentrated on the steam bath to 30 ml, cooled, and treated with ligroin (10 ml), whereupon an oil separated. Crystallization was induced by scratching of the inside of the beaker with a glass rod. The red crystals so obtained were filtered off, washed with alcohol, and dried *in vacuo* over phosphorus pentoxide; yield, 0.59 g (31%).

Method of Preparation of Bis{S-*methyl*-N-*(2-pyridyl)methylendithiocarbazato*}*cobalt*(*III*) *Tetrachloro-, Tetrabromo, and Tetrathiocyanato-cobaltates*(*II*). Hydrated cobalt(II) chloride, bromide, or thiocyanate (1 g) in alcohol (20 ml) was added to a hot solution of the Schiff base (0.5 g) in alcohol (100 ml). After 5 min, the crystalline complex, which had deposited, was filtered off in an atmosphere of nitrogen, and washed with alcohol. The complex was dried initially in a stream of nitrogen and finally *in vacuo* over phosphorus pentoxide; yield, 75-80%.

Method of Preparation of Chloro- and Bromo-S-*methyl*-N-*(2-pyridyl)methylendithiocarbazato Complexes of Nickel*(*II*) *and Copper*(*II*). The Schiff base (0.84 g, 0.004 mole) in hot alcohol (100 ml) was added to a solution of the metal halide (0.004 mole) in alcohol (20 ml). The solution, after being heated on a steam bath for 15 min and cooled, deposited the crystalline complex, which was filtered off, washed with alcohol, and dried *in vacuo;* yield, 65-80%.

Iodo-S-*methyl*-N-*(2-pyridyl)methylendithiocarbazatonickel*(*II*). A solution of nickel nitrate hexahydrate (2 g) and sodium iodide (2 g) in alcohol (50 ml) was boiled for 15 min, then chilled in ice. The precipitated sodium nitrate was filtered off and the filtrate was treated with a solution of the Schiff base (1 g) in hot alcohol (100 ml). The solution slowly deposited dark brown crystals of the iodo complex; these were filtered off, washed with alcohol, and dried *in vacuo;* yield, 1.4 g (75%).

Thiocyanato-S-*methyl*-N-*(2-pyridyl)methylendithiocarbazatonickel(II).* This complex was prepared in a similar manner to that described for the iodo complex; yield, 1.3 g (85%).

*Bis{*S-*methyl*-N-*(2-pyridyl)methylendithiocarbazato}-nickel(II).* Nickel nitrate hexahydrate (1 g, 0.034 mole) in alcohol (20 ml) was added to a hot solution of the Schiff base (2.1 g, 0.010 mole) in alcohol (150 ml). The solution was heated on a steam bath for 15 min, then allowed to stand for 2 hr, during which the complex deposited as reddish-brown crystals. These were filtered off, washed with alcohol, and dried *in vacuo;* yield, 0.99 g (60%).

Method of Preparation of Chloro-S-*methyl*-N-*(2-pyridyl)methylendithiocarbazato Complexes of Palladium(II) and Platinum(II).* Potassium tetrachlorometallate(II) (0.0015 mole) in water (10 ml) was added to a solution of the Schiff base (0.32 g, 0.0015 mole) in acetone (30 ml). The mixture was heated on a steam bath for 10 min, then cooled, whereupon the crystalline complex deposited. The crystals were filtered off, washed with 1:1 acetone-water, and dried *in vacuo* over phosphorus pentoxide; yield, 80%.

Nitrato-S-*methyl*-N-*(2-pyridyl)methylendithiocarbazatocopper(II).* Copper nitrate hexahydrate (1 g, 0.034 mole) in alcohol (10 ml) was treated with a solution of the Schiff base (0.72 g, 0.034 mole) in 2:1 alcohol-dimethoxypropane mixture. The solution was heated on a steam bath for 10 min and cooled, whereupon deep green crystals of the complex deposited. The crystals were filtered off, washed with chloroform, then with alcohol, and dried *in vacuo* over phosphorus pentoxide; yield, 0.79 g (70%).

S-*Methyl*-N-*(2-pyridyl)methylendithiocarbazatoaquacopper(II) Perchlorate.* Copper perchlorate hexahydrate (1.12 g, 0.003 mole) in alcohol (15 ml) was added to a hot solution of the Schiff base (0.64 g, 0.003 mole) in alcohol (100 ml). The solution was chilled in ice and ligroin (20 ml) was added. Dark green crystals of the complex separated. The complex was filtered off, dissolved in alcohol, and reprecipitated by the addition of ligroin; yield, 0.78 g (66%).

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.

Molecular Weight Determination. The molecular weight was determined in dichloroethane at 37° on a Mechrolab vapour phase osmometer.

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