

Metal Chelates of Dithiocarbamic Acid and Its Derivatives. IV. Complexes of the Tridentate Schiff Base α -N-Methyl-S-methyl- β -N-(6-methylpyrid-2-yl)methylendithiocarbazate

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

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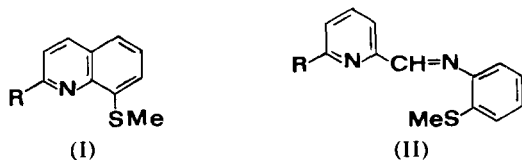
The Schiff base, α -N-methyl-S-methyl- β -N-(6-methylpyrid-2-yl)methylendithiocarbazate, 6-MeC₅H₃NCH=NN(Me)C(SMe)=S (MeN-NMe-S), acts as a tridentate ligand and forms stable, crystalline complexes with iron(II), cobalt(II), nickel(II), and copper(II).

The bis-ligand complexes [M(MeN-NMe-S)₂](ClO₄)₂·nH₂O (M = Fe, Co, Ni), [Co(MeN-NMe-S)₂](BF₄)₂, [Fe(MeN-NMe-S)₂][FeL₄], [Fe(MeN-NMe-S)₂][Fe^{III}-Cl₄]₂, and [Co(MeN-NMe-S)₂][CoX₄] (X = Cl, Br, NCS) were isolated. The iron(II) cation [Fe(MeN-NMe-S)₂]²⁺ is low-spin.

The mono-ligand complexes M(MeN-NMe-S)(NCS)₂ (M = Fe, Ni) are six-coordinate and probably polymeric with thiocyanato bridges. On the other hand, spectral evidence indicates that the halogeno-complexes M(MeN-NMe-S)X₂ (M = Fe, Ni, Cu; X = Cl, Br) are five-coordinate, probably with a distorted trigonal bipyramidal structure.

Introduction

The substitution of hydrogen by a methyl group in the α -position of the pyridine ring in a chelating ligand can affect the stereochemistry and the properties of the metal complexes. An example of the effect on the stereochemistry is provided by 2-methyl-8-methylthioquinoline (I, R = Me, mmtq) which is a weaker chelating agent than 8-methylthioquinoline (I, R = H).^{1,2} The steric influence of the methyl group causes the complexes MX₂mmtq (M = Co, Ni, Cu; X = Cl, Br) to adopt a pseudo-tetrahedral configuration.² The magnetic properties may also be affected.



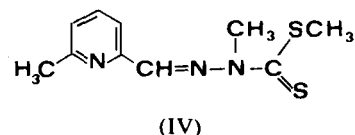
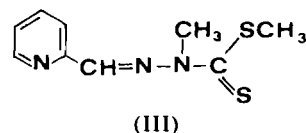
For example, the bis-ligand cobalt(II) complexes of 2-pyridyl-N-(2'-methylthiophenyl)methylenimine (II, R,

(1) L.F. Lindoy, S.E. Livingstone, and T.N. Lockyer, *Australian J. Chem.*, **19**, 1391 (1966).

(2) P.S.K. Chia and S.E. Livingstone, *Australian J. Chem.*, **21**, 339 (1968).

= H) are spin-paired, (μ at 293° K, 2.0-2.1 B.M.), whereas the corresponding complexes of 6-methylpyrid-2-yl-N-(2'-methylthiophenyl)methylenimine (II, R = Me) are spin-free at room temperature (μ at 293° K, 4.1-4.5 B.M.). However, the moments of the latter are temperature-dependent (μ at 80° K, 3.5-3.7 B.M.), due to a thermal equilibrium between the nearly equi-energetic spin-paired and spin-free states. The difference in magnetic behaviour arises from a lower effective ligand-field strength of the methyl derivative, due to the steric inter-ligand interference caused by the methyl group in the 6-position.^{3,4}

In Part III of this series⁵ metal chelates of the tridentate Schiff base α -N-methyl-S-methyl- β -N-(2-pyridyl)methylendithiocarbazate (III; N-NMe-S) were described. In order to study the effect of a methyl group in the 6-position of the pyridine ring in (III), we have synthesized the methyl derivative, α -N-methyl-S-methyl- β -N-(6-methylpyrid-2-yl)methylendithiocarbazate (IV; MeN-NMe-S). The metal chelates of (IV) are discussed herein.



Results and Discussion

The Schiff base (IV) was prepared by the condensation of 2-methyl-S-methyldithiocarbazate with 6-methylpyridine-2-aldehyde. The metal chelates of (IV) are not readily formed in the presence of water and in

(3) P.S.K. Chia and S.E. Livingstone, *Australian J. Chem.*, **22**, 1613 (1969).

(4) P.S.K. Chia and S.E. Livingstone, *Australian J. Chem.*, **22**, 1825 (1969).

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

Table I. Metal Complexes of α -N-Methyl-S-methyl- β -N-(6-methylpyrid-2-yl)methylendithiocarbazate (MeN-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 % | | | | |
|---|----------------|---|--|---------------|-------------|------------------|---------------|--------------|
| | | | | C | H | Calcd. Found. | S | M |
| Fe(MeN-NMe-S)Cl ₂ · 1/2H ₂ O | reddish-brown | 5.24 | insol. | 32.0 32.1 | 3.8 3.6 | 11.2 10.95 | 17.1 16.2 | 14.9 14.5 |
| Fe(MeN-NMe-S)Br ₂ | brown | 5.34 | 30 | 26.4 26.5 | 2.9 2.7 | 9.2 9.3 | 14.1 14.0 | 12.3 12.4 |
| Fe(MeN-NMe-S)(NCS) ₂ | green | 5.56 | insol. | 35.0 34.6 | 3.2 3.1 | 17.0 16.7 | 31.2 31.1 | 13.6 13.4 |
| [Fe(MeN-NMe-S) ₂](ClO ₄) ₂ · 3H ₂ O | bluish-black | 1.36 | 152 | <i>a</i> | <i>a</i> | 10.7 9.5 | 16.3 16.0 | 7.1 7.3 |
| [Fe(MeN-NMe-S) ₂][FeI ₄] | bluish-black | 3.90 | 190 | 21.9 22.5 | 2.4 2.7 | 7.65 7.7 | 11.7 11.7 | 10.2 9.9 |
| [Fe(MeN-NMe-S) ₂][FeCl ₄] ₂ | bluish-black | 4.80 | insol. | 25.8 26.05 | 2.8 2.85 | 9.0 8.9 | 13.8 13.5 | 18.0 18.3 |
| [Co(MeN-NMe-S) ₂](ClO ₄) ₂ · 2H ₂ O | orange | 4.50 | 172 | 31.1 30.6 | 3.9 3.9 | 10.9 10.7 | 16.6 16.7 | 7.6 8.1 |
| [Co(MeN-NMe-S) ₂][CoCl ₄] | green | 4.40 | insol. | 32.5 32.6 | 3.55 3.5 | 11.4 11.6 | 17.4 16.8 | 16.0 15.8 |
| [Co(MeN-NMe-S) ₂][CoBr ₄] | reddish-brown | 4.61 | 100 | 26.2 26.45 | 2.9 3.1 | 9.2 9.3 | | 12.9 12.9 |
| [Co(MeN-NMe-S) ₂][Co(NCS) ₄] | greenish-brown | 4.68 | 82 | 34.8 34.9 | 3.2 3.0 | 16.9 16.6 | 30.9 31.0 | 14.2 13.8 |
| [Co(MeN-NMe-S) ₂](BF ₄) ₂ | orange | 4.55 | 172 | 33.8 33.4 | 3.7 3.5 | 11.8 11.85 | 18.0 17.7 | 8.3 8.1 |
| Ni(MeN-NMe-S)Cl ₂ | red | 3.37 | 8 | 32.55 32.6 | 3.55 3.5 | 11.4 11.0 | 17.4 17.0 | 15.9 15.8 |
| Ni(MeN-NMe-S)Br ₂ | dark brown | 3.24 | 15 | 26.2 26.1 | 2.9 2.75 | 9.2 9.1 | 14.0 13.8 | 12.8 12.7 |
| Ni(MeN-NMe-S)(NCS) ₂ | greenish-brown | 3.08 | 23 ^b | 34.8 35.5 | 3.2 3.5 | 16.9 16.0 | 30.9 29.3 | 14.2 13.9 |
| [Ni(MeN-NMe-S) ₂](ClO ₄) ₂ · H ₂ O | yellow | 3.19 | 188 | 31.8 31.5 | 3.7 3.8 | 11.1 10.7 | 17.0 17.0 | 7.8 7.5 |
| Cu(MeN-NMe-S)Cl ₂ | reddish-brown | 1.83 | insol. | 32.1 32.2 | 3.5 3.45 | 11.2 10.8 | 17.15 16.9 | 17.0 16.9 |
| Cu(MeN-NMe-S)Br ₂ | reddish-brown | 1.83 | insol. | 26.0 25.9 | 2.8 2.6 | 9.1 8.8 | 13.9 13.9 | 13.7 13.7 |

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

most instances it was found necessary to allow the metal salts to react with the Schiff base in a 1:1 mixture of absolute alcohol and 2,2-dimethoxypropane. The metal complexes, which were isolated, are listed in Table I.

Iron Complexes. The Schiff base (III; N-NMe-S) reacts readily with ferrous halides in aqueous alcohol solution to give the bis-ligand complexes [Fe(N-NMe-S)₂][FeX₄] (X = Cl, Br, NCS), in which the cation is diamagnetic.⁵ On the other hand, the 6-methyl derivative (IV) gives with ferrous halides only the high-spin mono-ligand complexes Fe(MeN-NMe-S)X₂ (X = Cl, Br, NCS). The diamagnetic bis-ligand complex ion [Fe(MeN-NMe-S)₂]²⁺ was isolated as the perchlorate only in the absence of water: *i.e.*, from a solution of ferrous perchlorate in alcohol containing 2,2-dimethoxypropane. The perchlorate is low-spin, although the values of the molar susceptibility (χ'_M at 293°K, 780) and the magnetic moment (μ , 1.36 B.M.) are somewhat high, but not abnormally so, for low-spin iron(II).

Treatment of a suspension of this complex perchlorate with lithium halides in alcohol-dimethoxypropane solution causes an immediate colour change with the concomitant formation of the high-spin mono-ligand complexes Fe(MeN-NMe-S)X₂ (X = Cl, Br, NCS).

The magnetic moment of the chloro-complex Fe(MeN-NMe-S)Cl₂ · 1/2H₂O is almost independent of temperature, ranging from 5.26 B.M. at 313°K to 5.06 B.M. at 93°K. The value of the Curie-Weiss constant θ is -10°. The compound could have one of a number of structures: (a) [Fe(MeN-NMe-S)₂][FeCl₄] - octahedral low-spin cation, high-spin tetrahedral anion; (b) [Fe(MeN-NMe-S)Cl₂] - five-coordinate; (c) [Fe(MeN-NMe-S)Cl₂]₂ - octahedral chlorobridged dimer; (d) [Fe(MeN-NMe-S)Cl]Cl - tetrahedral cationic. Since the cation [Fe(MeN-NMe-S)₂]²⁺ is low-spin, the magnetic moment expected for structure (a) is about 3.8 B.M. per iron atom. The observed moment (5.24 B.M.) rules out structure (a). The Mössbauer spectrum displays an isomer shift and quadrupole splitting typical of high-spin iron(II). The isomer shift varies from 1.193 mm sec⁻¹ at 293°K to 1.282 mm sec⁻¹ at 4.2°K. The quadrupole splitting is large and temperature-dependent, ranging from 2.419 mm sec⁻¹ at 293°K to 3.005 mm sec⁻¹ at 4.2°K.

The Mössbauer spectrum is inconsistent with structure (a) but does not distinguish unequivocally between structures (b), (c), and (d). The slight asymmetry which exists in the Mössbauer spectrum may be due to the presence of the dimeric structure (c) or the asymmetry may be due to the molecule's having an anisotropic site symmetry in the lattice. However, the temperature-dependence of the quadrupole

Table II. Solid State Reflectance Spectra of Iron Complexes

| Compound | Bands (cm ⁻¹) |
|---|--|
| [Fe(MeN-NMe-S) ₂](ClO ₄) ₂ · 3H ₂ O | 6700 w br, 8700 w br, 12200 sh, 16000, 18100 |
| Fe(MeN-NMe-S)Cl ₂ · 1/2H ₂ O | 4400, 8800, 13900, 16000 br, 19000 br |
| Fe(MeN-NMe-S)Br ₂ | 4300, 8900, 13800, 15800 br, 20500 br |
| Fe(MeN-NMe-S)(NCS) ₂ | 7700br, 12200 sh, 14600, 16000 sh, 20700 br |

w. weak; br, broad; sh, shoulder

splitting is not consistent with a distorted octahedral structure.

The conformation of the ligand is such as to make it unlikely that it would coordinate around three tetrahedral sites because of the severe strain involved. Furthermore, the conductivity (30 ohm⁻¹) of the bromo-complex in nitromethane, although indicating appreciable ionic dissociation in solution, is much less than half that expected for a uni-univalent electrolyte in this solvent. Hence structure (d) seems improbable.

The electronic spectral bands of the iron complexes are listed in Table II. The spectrum of the bis-ligand perchlorate is indicative of low-spin octahedral iron(II). Two principal spin-allowed bands are to be expected, corresponding to transitions from the ¹A_{1g} ground state to the ¹T_{1g} and ¹T_{2g} excited states. In addition, two weak bands assigned to the spin-forbidden transitions ³T_{1g} ← ¹A_{1g} and ³T_{2g} ← ¹A_{1g} are sometimes observed at lower frequencies as well as several charge-transfer bands above 17000 cm⁻¹.⁶ The two weak bands at 6700 and 8700 cm⁻¹ in the spectrum of [Fe(MeN-NMe-S)₂](ClO₄)₂ · 3H₂O are assigned as the spin-forbidden singlet-triplet transitions, while the band at 12200 cm⁻¹ is assigned to the transition ¹T_{1g} ← ¹A_{1g}. The band arising from the transition ¹T_{2g} ← ¹A_{1g} appears to be under the envelope of the charge-transfer bands at 16500 and 18100 cm⁻¹.

The spectra of the complexes Fe(MeN-NMe-S)X₂ (X = Cl, Br) are more indicative of five-coordinate than six-coordinate iron(II). Six-coordinate, high-spin iron(II) complexes usually display two bands in the region 8000-11000 cm⁻¹; these bands are considered to represent transitions from the ⁵T_{2g} state to the ⁵E_g state whose degeneracy has been lifted by the Jahn-Teller effect.⁶ On the other hand, five-coordinate, high-spin complexes display a band in the region 8000-10000 cm⁻¹ and a weaker band some 4000 cm⁻¹ on the low-energy side of this band.^{3,7,8} The spectra of the complexes Fe(MeN-NMe-S)X₂ (X = Cl, Br) display a well-defined band at c. 8800 cm⁻¹ and a weaker band at c. 4400 cm⁻¹. The bands at c. 14000 cm⁻¹ and at higher frequencies probably arise from charge-transfer transitions of the metal to ligand type. The spectra of these complexes closely resemble those of complexes having the chromophores N₃Cl₂, N₄Cl,⁷ N₂SCl₂, and N₂SBr₂.⁹ The spectral evidence indicates that the complexes Fe(MeN-NMe-S)X₂ (X = Cl, Br) have the five-coordinate structure (b) rather than the

octahedral dimeric structure (c) and the other evidence cited above is not inconsistent with this assignment.

The electronic spectrum of the thiocyanato-complex Fe(MeN-NMe-S)(NCS)₂ is more indicative of six-coordinate than of five-coordinate, high-spin iron(II). The two rather poorly resolved components of the ⁵E_g ← ⁵T_{2g} band occur at 7700 and 12200 cm⁻¹. The large separation of 4500 cm⁻¹ between the two components is not uncommon for a chromophore of this type, viz. FeN₄S₂.⁶ The infrared spectrum shows two ν(C≡N) absorptions: at 2080 and 2122 cm⁻¹, indicating the presence of both terminal N-bonded and bridging thiocyanato groups.⁹ Consequently, this complex is considered to possess an octahedral thiocyanato-bridged polymeric structure.

The addition of ferrous perchlorate to a solution of the Schiff base (IV) containing excess lithium iodide yields the bluish-black complex [Fe(MeN-NMe-S)₂][FeI₄]. The conductivity of this compound in nitromethane (190 ohm⁻¹) is that expected for a bivalent electrolyte. The magnetic moment per iron atom is 3.90 B.M. The moment is independent of temperature, the Curie-Weiss constant θ having a value of -4°. The value of the moment is consistent with the above formulation having low-spin iron(II) in the cation and high-spin iron(II) in the anion. The molar susceptibility at 298°K is 12700. If the susceptibility of the cation (780), as measured for the perchlorate, is subtracted, the value of the susceptibility for the anion is 11920, giving a magnetic moment of 5.36 B.M. for the [FeI₄]²⁻ anion. This value is similar to those previously reported for [FeCl₄]²⁻ (5.33,¹⁰ 5.34,⁵ and 5.40 B.M.¹⁰) and for [FeBr₄]²⁻ (5.34 B.M.⁵).

The addition of ferric chloride to the Schiff base (IV) gives the bluish-black complex [Fe^{III}(MeN-NMe-S)₂][Fe^{III}Cl₄]₂. The magnetic moment is 4.80 B.M. per iron atom. The molar susceptibility at 298°K is 28830, from which a value of 5.80 B.M. is obtained for the moment of the [Fe^{III}Cl₄]⁻ ion. A moment of 5.82 B.M. was reported for the anion in the analogous compound of (III): [Fe^{II}(N-NMe-S)₂][Fe^{III}Cl₄]₂.⁵

Cobalt Complexes. The orange bis-ligand cobalt(II) complexes [Co(MeN-NMe-S)₂]₂X₂ (X = ClO₄, BF₄) were obtained by the reaction of the Schiff base (IV) with cobalt perchlorate or fluoborate. Their reflectance spectra (see Table III) are typical of octahedral cobalt(II).⁶

With cobalt halides the Schiff base yields the beautifully crystalline complexes [Co(MeN-NMe-S)₂][CoX₄] (X = Cl, Br, NCS). The electronic reflectance spectra (see Table III) are similar to those of the ana-

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(8) P.S.K. Chia, S.E. Livingstone, and J.D. Nolan, *Proc. XII Internat. Confer. Coord. Chem.*, Sydney, 1969, H.C. Freeman, ed., Science Press, Sydney, p. 117.

(9) A. Sabatini and I. Bertini, *Inorg. Chem.*, **4**, 959, 1665 (1965).

(10) N.S. Gill, *J. Chem. Soc.*, 3512 (1961).

Table III. Solid State Reflectance Spectra of Cobalt Complexes

| | Bands of octahedral cobalt(II) (cm ⁻¹) | | | Bands of tetrahedral cobalt(II) (cm ⁻¹) | | | | | | |
|---|--|--|--|---|------|-------|----------|-------|-------|--|
| | ν_1 ${}^4T_{1g} \leftarrow {}^4T_{1g}$ | ν_2 ${}^4T_{1g}(P) \leftarrow {}^4T_{1g}$ | ν_2 ${}^4T_{1g} \leftarrow {}^4A_2$ | ν_1 ${}^4T_1(P) \leftarrow {}^4A_2$ | | | | | | |
| [Co(MeN-NMe-S) ₂](ClO ₄) ₂ | 9800 | 11600 sh | 19000 sh | | | | | | | |
| [Co(MeN-NMe-S) ₂](BF ₄) ₂ | 9800 | 11500 sh | 18700 sh | | | | | | | |
| [Co(MeN-NMe-S) ₂][CoCl ₄] | 9900 | 11500 sh | | 4750 | 5400 | 14500 | 15600 sh | 16400 | 17500 | |
| [Co(MeN-NMe-S) ₂][CoBr ₄] | 9900 | 11500 sh | 18500 sh | 4700 | 5500 | 14000 | 15000 | 15550 | | |
| [Co(MeN-NMe-S) ₂][Co(NCS) ₄] | 10000 w sh | | 19400 sh | 6800 | 8000 | | 15600 sh | 16600 | | |

sh, shoulder; w, weak

Table IV. Solid State Reflectance Spectra of Nickel and Copper Complexes.

| Compound | Bands (cm ⁻¹) |
|--|---|
| [Ni(MeN-NMe-S) ₂](ClO ₄) ₂ · H ₂ O | 6600w, 11800, 13500w sh, 18500sh |
| Ni(MeN-NMe-S)Cl ₂ | 6000, 8600, 10800sh, 12400, 13500sh, 17600, 21800 |
| Ni(MeN-NMe-S)Br ₂ | 5800, 8500, 10800sh, 12500, 13400sh, 17400sh |
| Ni(MeN-NMe-S)(NCS) ₂ | 6800w, 10100, 16400 |
| Cu(MeN-NMe-S)Cl ₂ | 9200, 12000, 19500sh |
| Cu(MeN-NMe-S)Br ₂ | 9500, 12300, 18800sh |

logous complexes [Co(N-NMe-S)₂][CoX₄]⁵ and display bands of the octahedral bis-ligand cation and bands attributable to the tetrahedral [CoX₄]²⁻ anions.^{11,12} The chloro-complex is insoluble but the bromo- and thiocyanato-complexes have conductivities in nitromethane which are little more than half those of the perchlorate and fluoborate. These low values could be due to ion-pair association; this phenomenon has been observed with similar compounds.⁵

The infrared spectrum of the thiocyanato-complex displays two $\nu(\text{C}\equiv\text{N})$ bands, at 2087 and 2130 cm⁻¹, suggesting the presence of both terminal N-bonded and bridging thiocyanato groups. It is possible that in the solid state both the forms [Co(MeN-NMe-S)₂][Co(NCS)₄] and [Co(MeN-NMe-S)(NCS)₂]_n are present. The latter form would contain octahedral cobalt(II) with one thiocyanato group forming a bridge between adjacent metal atoms.

Nickel Complexes. With nickel perchlorate the Schiff base (IV) yields the bis-ligand complex [Ni(MeN-NMe-S)₂](ClO₄)₂ · H₂O, which is a bi-univalent electrolyte in nitromethane. With nickel halides the mono-ligand complexes Ni(MeN-NMe-S)X₂ (X = Cl, Br, NCS) are formed. The chloro- and bromo-complexes have but slight conductivity in nitromethane. The electronic spectral bands of the nickel complexes are listed in Table IV.

The perchlorate and the thiocyanato-complex have spectra which are indicative of octahedral nickel(II).⁶ These compounds have lower symmetry than regular octahedral (O_h); however, the spectra of pseudo-octahedral nickel(II) complexes very often retain the simple form found in O_h symmetry.¹³ Accordingly, the spectra of these two complexes are discussed in terms of O_h symmetry, since they are considered to obey the average environment rule.¹⁴ The bands at 11800 and 18500 cm⁻¹ in the spectrum of the per-

chlorate are assigned as ν_1 (${}^3T_{2g} \leftarrow {}^3A_{2g}$) and ν_2 (${}^3T_{1g} \leftarrow {}^3A_{2g}$), respectively; the weak shoulder at 13500 cm⁻¹ probably arises from the spin-forbidden transition ${}^1E_g \leftarrow {}^3A_{2g}$. The bands at 10100 and 16400 cm⁻¹ in the spectrum of the thiocyanato-complex can be assigned to the ν_1 and ν_2 transitions of octahedral nickel(II). The infrared spectrum of this complex displays two $\nu(\text{C}\equiv\text{N})$ absorptions, at 2102 and 2121 cm⁻¹, suggesting that one of the thiocyanato groups is bridging.

The spectra of the chloro- and bromo-complexes contain more bands and are similar to the spectra of known five-coordinate, high-spin nickel(II) complexes.^{6,13,15} For trigonal bipyramidal complexes (D_{3h} symmetry) a total of six-spin-allowed transitions—four 3F and two 3P —are expected,¹⁶ although the 3P transitions occur at higher energies (>20000 cm⁻¹).¹³ Known five-coordinate, high-spin nickel(II) complexes usually have irregular trigonal bipyramidal structures, hence their symmetry is lower than D_{3h} and accordingly, their spectra are more irregular than predicted from the regular model.¹⁷ The number of bands and the frequencies at which they occur in the spectra of the chloro- and bromo-complexes (see Table IV) are inconsistent with a six-coordinate structure but are indicative of five-coordination. Consequently, these compounds are considered to possess a five-coordinate structure which is probably irregular trigonal bipyramidal.

Copper Complexes. The mono-ligand complexes Cu(MeN-NMe-S)X₂ (X = Cl, Br) were readily obtained but attempts to isolate bis-ligand complexes were unsuccessful. Similar attempts to obtain bis-ligand complexes of (III) with copper were also unsuccessful.⁵ It is noteworthy that the complexes Cu(MeN-NMe-S)X₂ (X = Cl, Br) are reddish-brown but the analogous complexes of (III) are yellowish-

(11) F.A. Cotton, D.M.L. Goodgame, and M. Goodgame, *J. Amer. Chem. Soc.*, **83**, 4690 (1961).(12) F.A. Cotton, D.M.L. Goodgame, M. Goodgame, and A. Sacco, *J. Amer. Chem. Soc.*, **83**, 4157 (1961).(13) L. Sacconi, *Transition Metal Chem.*, **4**, 199 (1968).(14) O. Bostrup and C.K. Jørgensen, *Acta Chem. Scand.*, **11**, 1223 (1957).(15) M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966).(16) M. Ciampolini, *Inorg. Chem.*, **5**, 35 (1966).(17) M. Ciampolini and N. Nardi, *Inorg. Chem.*, **6**, 445 (1967).

green or green. Furthermore, the spectra of the former (see Table IV) are considerably different from those of the corresponding complexes of (III). The latter display one almost symmetrical band centred at 13600 cm^{-1} . The spectra of $\text{Cu}(\text{MeN}-\text{NMe}-\text{S})\text{X}_2$ display a broad band, centred at 10500 cm^{-1} , which is split into two components at *c.* 9400 and *c.* 12000 cm^{-1} . These spectra are similar to that of the trigonal bipyramidal complex $[\text{Cu}(\text{Me}_6\text{tren})-\text{Br}]\text{Br}$ [$\text{Me}_6\text{tren} = \text{tris}(2\text{-dimethylaminoethyl})\text{amine}$], which has a band at 9800 cm^{-1} with a pronounced shoulder at 12800 cm^{-1} .⁶ Consequently, a five-coordinate configuration is assigned to the complexes $\text{Cu}(\text{MeN}-\text{NMe}-\text{S})\text{X}_2$.

Conclusion

The Schiff base (IV) forms the bis-ligand complexes $[\text{M}(\text{MeN}-\text{NMe}-\text{S})_2](\text{ClO}_4)_2$ ($\text{M} = \text{Fe}, \text{Co}, \text{Ni}$ but not Cu), $[\text{Co}(\text{MeN}-\text{NMe}-\text{S})_2][\text{CoX}_4]$ ($\text{X} = \text{Cl}, \text{Br}, \text{NCS}$), and $[\text{Fe}(\text{MeN}-\text{NMe}-\text{S})_2][\text{FeI}_4]$. The mono-ligand complexes $\text{M}(\text{MeN}-\text{NMe}-\text{S})(\text{NCS})_2$ ($\text{M} = \text{Fe}, \text{Ni}$) are six-coordinate and probably polymeric with thiocyanato bridges. However, spectral evidence indicates that the halogeno-complexes $\text{M}(\text{MeN}-\text{NMe}-\text{S})\text{X}_2$ ($\text{M} = \text{Fe}, \text{Ni}, \text{Cu}$; $\text{X} = \text{Cl}, \text{Br}$) are five-coordinate, probably with a distorted or irregular trigonal bipyramidal structure. When a comparison is made between complexes formed by the Schiff bases (III) and (IV), it is apparent that the methyl group in the 6-position of the pyridine moiety of the ligand increases the tendency to form five-coordinate metal complexes.

Experimental Section

α -N-Methyl-S-methyl- β -N-(6-methylpyrid-2-yl)methylendithiocarbazate. 6-Methylpyridine-2-aldehyde (9g) in alcohol was added to a solution of 2-methyl-S-methyldithiocarbazate⁵ (10 g) in alcohol (130 ml). The mixture was heated on the steam bath for 5 min. and then allowed to stand overnight. The yellow crystals which had formed were filtered off, washed with 1:1 alcohol-ligroin and recrystallized from alcohol to give bright yellow crystals of the compound; yield, 15.0 g; m.p., 116° (Found: C, 50.35; H, 5.4; N, 17.8; S, 26.6. Calcd for $\text{C}_{10}\text{H}_{13}\text{N}_3\text{S}_2$: C, 50.2; H, 5.5; N, 17.6; S, 26.8%).

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-S-methyl- β -N-(6-methylpyrid-2-yl)methylendithiocarbazate Complexes of Nickel(II) and Copper(II) and of Bis{ α -N-methyl-S-methyl- β -N-(6-methylpyrid-2-yl)methylendithiocarbazate}cobalt(II)-Tetrachloro- and Tetrabromocobaltate(II). The Schiff base (0.67 g, 0.0028 mole) in hot alcohol (20 ml) was added to a solution of the metal halide (0.006 mole) in hot alcohol (50 ml). The mixture, after being heated

on the steam bath for 5 min. and then cooled, deposited the crystalline complex; yield, 60-80%.

Method of Preparation of Dithiocyanato- α -N-methyl-S-methyl- β -N-(6-methylpyrid-2-yl)methylendithiocarbazatenickel(II) and of Bis{ α -N-methyl-S-methyl- β -N-(6-methylpyrid-2-yl)methylendithiocarbazate}cobalt(II) Tetrathiocyanatocobaltate(II). The metal thiocyanate (0.003 mole) in hot 1:1 alcohol-dimethoxypropane mixture (10 ml) was added to a warm solution of the Schiff base (0.72 g, 0.003 mole) in the same solvent (20 ml). The mixture, after being heated on the steam bath for 5 min. and cooled, yielded the crystalline compound; yield, 75-85%.

Method of Preparation of the Bis{ α -N-methyl-S-methyl- β -N-(6-methylpyrid-2-yl)methylendithiocarbazate} Perchlorates of Iron(II), Cobalt(II), and Nickel(II). The metal perchlorate hexahydrate (0.55 g, 0.0015 mole) in warm 1:1 alcohol-dimethoxypropane (10 ml) was added to a warm solution of the Schiff base (0.72 g, 0.003 mole) in the same solvent. The mixture was heated on the steam bath for 2 min. and cooled, whereupon the crystalline complex was removed by filtration; yield, 70-90%.

Bis{ α -N-methyl-S-methyl- β -N-(6-methylpyrid-2-yl)methylendithiocarbazate}cobalt(II) Fluoborate. Cobalt(II) fluoborate (0.7 g, 0.0021 mole) in warm 1:1 alcohol-dimethoxypropane (10 ml) was added to a solution of the Schiff base (1.0 g, 0.0042 mole) in the same solvent. The mixture was heated on the steam bath for 1 min. and cooled, whereupon orange crystals of the complex deposited; yield, 0.9 g (60%).

Dichloro- α -N-methyl-S-methyl- β -N-(6-methylpyrid-2-yl)methylendithiocarbazateiron(II) Hemihydrate. Ferrous chloride tetrahydrate (0.5 g, 0.0025 mole) in warm alcohol (10 ml) was added to a solution of the Schiff base (0.57 g, 0.0024 mole) in warm alcohol (20 ml). The mixture was heated on the steam bath for 5 min. and allowed to cool, whereupon red crystals of the complex deposited; yield, 0.67 g (75%).

Dibromo- and Dithiocyanato- α -N-methyl-S-methyl- β -N-(6-methylpyrid-2-yl)methylendithiocarbazateiron(II). Ferrous perchlorate hexahydrate (2 g, 0.0055 mole) in 1:1 alcohol-dimethoxypropane (25 ml) was added to a hot solution containing the Schiff base (1.2 g, 0.005 mole) and lithium bromide or thiocyanate (2 g) in the same solvent (50 ml). After the mixture had been heated on the steam bath for 5 min. and cooled, the complex was removed by filtration; yield, 75-80%.

Bis{ α -N-methyl-S-methyl- β -N-(6-methylpyrid-2-yl)methylendithiocarbazate}iron(II) Tetraiodoferrate(II). Ferrous perchlorate hexahydrate (2 g, 0.0055 mole) in 1:1 alcohol-dimethoxypropane (20 ml) was added to a hot solution containing the Schiff base (0.6 g, 0.0025 mole) and lithium iodide (2 g). After the mixture had been heated on the steam bath for 5 min. and cooled, the dark bluish-black crystals of the complex were removed by filtration; yield 1.24 g, (90%).

Bis{ α -N-methyl-S-methyl- β -N-(6-methylpyrid-2-yl)-

methylendithiocarbamate{*iron(II) Tetrachloroferrate* - (III). The Schiff base (0.6 g, 0.0025 mole) in alcohol (15 ml) was added to a solution of anhydrous ferric chloride (1 g, 0.006 mole) in alcohol (20 ml). After the mixture had been heated on the steam bath for 10 min. and cooled, the dark bluish-black crystals of the complex were removed by filtration; yield, 0.58 g (50%).

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. Measurements other than at ambient temperature were made on a Newport variable-temperature Gouy balance.

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