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

Metal Chelates of Dithiocarbazic Acid and Its Derivatives. V. Complees of the NNS Ligand 2-(2,3-Diaza-4-methylthio-5-thiahexa-1,3-dienyl)pyridine with 3d Metal Ions

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

Received February 16, 1972

The Schiff base, 2-(2,3-diaza-4-methylthio-5-thiahexa-1,3-dienyl)pyridine, $C_5H_4NCH=NN=C(SMe)_2$ *(N-N-SMe), forms stable, crystalline complexes with manganese(II), cobalt(II), nickel(II), and copper(II)*

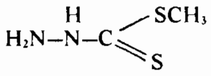
The complex $Mn(N\text{-}N\text{-}SMe)Cl_2$ *is probably halogen-bridged and six-coordinate. With cobalt the complexes* $Co(N\text{-}N\text{-}SMe)X_2$ *(X = Cl, Br, I),* $Co(N\text{-}N\text{-}SMe)_2(NCS)_2.H_2O$, $[Co(N\text{-}N\text{-}SMe)_2NO_3]NO_3$, $[Co(N\text{-}N\text{-}SMe)_2](ClO_4)_2.H_2O$ *and* $[Co(N\text{-}N\text{-}SMe)_2](BF_4)_2$ *were isolated. The halide complexes are tetrahedral, with bidentate NN-bonded ligand. The nitrato complex is probably five-cordinate, with NN-bonded ligand. The perchlorate and fluoborate complexes are low-spin.*

All nickel complexes isolated are six-coordinate. The complex $[Ni(N\text{-}N\text{-}SMe)_2NO_3]NO_3$ *probably has bidentate ligand and one bidentate nitrate. The other nickel complexes* $Ni(N\text{-}N\text{-}SMe)X_2$ *(X = Cl, Br, I, NCS) and* $[Ni(N\text{-}N\text{-}SMe)_2](ClO_4)_2$ *contain tridentate NNS bonded ligand, and the mono-ligand complexes are anion-bridged.*

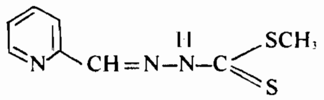
Thi structure of $Cu_2(N\text{-}N\text{-}SMe)Cl_4$ *is uncertain. The complexes* $Cu(N\text{-}N\text{-}SMe)X_2$ *(X =* NO_3*, NCS) have coordinated anion. Bidentate NN-bonded ligand is present in the thiocyanato complex. The complexes* $[Cu(N\text{-}N\text{-}SMe)_2](ClO_4)_2.4H_2O$, $[Cu(N\text{-}N\text{-}SMe)_2](BF_4)_2$ *and* $[Cu(N\text{-}N\text{-}SMe)_2I]BF_4$ *contain bidentate NN-bonded ligand and resemble the complexes of diimine ligands such as 1,10-phenanthroline. The reasons for the predominantly bidentate behaviour of N-N-SMe with cobalt(II) and copper(II), and tridentate behaviour with nickel(II) are discussed.*

Introduction

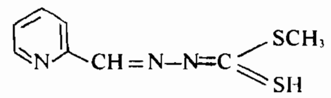
In Part II of this series the Schiff base formed by the condensation of S-methyldithiocarbazate(I) with pyridine-2-aldehyde was reported.[1] This compound exists in the solid state in the form (IIa) but in solution it exists as an equilibrium mixture of the tautomeric forms (IIa) and (IIb). The form (IIb), by loss of the proton from the thiol sulphur, acts as a singly charged tridentate ligand, forming complexes with bivalent manganese, iron, cobalt, nickel, and copper.[1] In Part III we reported the α-*N*-methyl derivative of the Schiff base (IIa), *viz.*, α-*N*-methyl-*S*-methyl-β-*N*-(2-pyridyl)methylendithiocarbazate(III,N-NMe-S), which cannot exhibit the same type of tautomerism as (II). With 3*d* metal ions it forms complexes in which it behaves as a neutral tridentate ligand.[2] The corresponding derivative formed by condensation with 6-methylpyridine-2-aldehyde, *viz*, α-*N*-methyl-*S*-methyl-β-*N*-(6-methylpyrid-2-yl)methylendithiocarbazate (IV, MeN-NMe-S) was reported in Part IV. This ligand also behaves as a neutral tridentate ligand but differs from N-NMe-S in giving five-coordinate complexes with bivalent nickel and copper.[3]



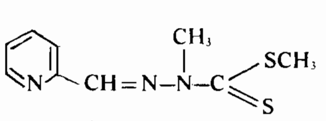
(I)



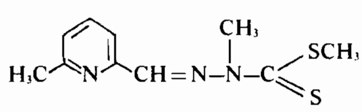
(IIa)



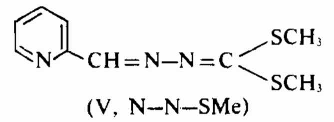
(IIb)



(III, N–NMe–S)



(IV, MeN–NMe–S)



(V, N–N–SMe)

In order to study the metal chelates of a derivative of dithiocarbazic acid having thioether sulphur as

---

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

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

(3) M. Akbar Ali, S. E. Livingstone and D. J. Phillips, *Inorg. Chim. Acta*, 6, 39 (1972).

Table I. Metal Complexes of 2-(2,3-Diaza-4-methylthio-5-thiahexa-1,3-dienyl)pyridine

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 % Calc. Found		
				C	H	N	S	M
$Mn(N-N-SMe)Cl_2$	orange	5.95	insol	30.8	3.2	12.0	18.3	
				31.1	3.1	11.5	18.1	
$Co(N-N-SMe)Cl_2$	green	4.97	24	30.4	3.1	11.8	18.05	16.6
				30.3	3.2	11.7	17.8	16.4
$Co(N-N-SMe)Br_2$	green	4.90	29	24.3	2.5	9.5	14.4	13.3
				24.45	2.7	9.6	13.6	13.0
$Co(N-N-SMe)I_2$	brown	4.97	28	20.1	2.1	7.8	11.9	10.95
				20.2	2.1	7.5	11.4	10.8
$Co(N-N-SMe)_2(NCS)_2 . H_2O$	green	4.80	38	37.3	3.8	17.4	30.0	9.15
				37.3	3.75	17.1	30.1	10.25
$[Co(N-N-SMe)_2NO_3]NO_2$	yellowish-orange	4.88	76	34.1	3.5	17.7	20.2	9.3
				34.3	3.7	17.3	19.9	9.0
$[Co(N-N-SMe)_2](ClO_4)_2 . H_2O$	brown	2.03	179	29.8	3.3	11.6	17.65	8.1
				29.8	3.2	10.8	17.2	7.9
$[Co(N-N-SMe)_2](BF_4)_2$	brown	2.08	184	31.6	3.2	12.3	18.8	8.6
				31.7	3.3	12.45	18.1	9.0
$Ni(N-N-SMe)Cl_2$	yellow	3.10	insol.	30.4	3.1	11.8	18.1	16.5
				30.75	3.2	11.75	17.0	16.3
$Ni(N-N-SMe)Br_2$	deep yellow	3.14	insol.	24.4	2.5	9.5	14.45	13.2
				24.0	2.4	9.45	14.0	13.15
$Ni(N-N-SMe)I_2$	brown	2.90	insol.	20.1	2.1	7.8	11.9	10.9
				21.1	2.2	8.5	12.1	10.4
$Ni(N-N-SMe)(NCS)_2$	brownish-green	3.04	insol.	33.0	2.8	17.5	32.0	14.7
				33.0	2.7	17.2	32.1	14.6
$[Ni(N-N-SMe)_2(NO_3)]NO_3$	yellow	3.10	75	34.1	3.5	17.7	20.25	9.3
				33.9	3.3	17.4	19.8	9.15
$[Ni(N-N-SMe)_2](ClO_4)_2$	dark red	3.13	157	30.5	3.1	11.9	18.1	8.3
				30.9	3.5	10.9	17.6	7.85
$Cu_2(N-N-SMe)Cl_4$	brown	1.72	insol.	21.9	2.2	8.5	13.0	25.7
				22.15	2.6	8.5	12.5	25.0
$Cu(N-N-SMe)(NO_3)_2$	green	1.89	24	26.2	2.7	17.0	15.5	15.4
				26.1	2.7	16.4	15.0	15.2
$Cu(N-N-SMe)(NCS)_2$	dark green	1.88	8	32.6	2.7	17.3		
				32.8	2.7	15.8		
$[Cu(N-N-SMe)_2](ClO_4)_2 . 4H_2O$	green	2.06	169	[a]	[a]	10.7	16.3	8.1
						11.4	15.4	8.2
$[Cu(N-N-SMe)_2](BF_4)_2$	green	1.86	152	31.4	3.2	12.2	18.6	9.2
				31.5	3.1	12.9	18.4	9.0
$[Cu(N-N-SMe)_2I]BF_4$	light brown	1.76	77	29.7	3.0	11.5		
				28.9	3.1	11.2		

[a] C and H analyses could not be performed because of the explosive nature of the compounds.

one of the donor atoms, we have prepared the S-methyl derivative of (IIb), viz. 2-(2,3-diaza-4-methylthio-5-thiahexa-1,3-dienyl)pyridine (V, N-N-SMe). With (b) class metal ions the Schiff base (V) might be expected to behave as a tridentate ligand, coordinating through the pyridine nitrogen, the 2-aza nitrogen, and one of the thioether sulphur atoms. On the other hand, with (a) class or borderline metal ions, which have a low affinity for sulphur, it might be expected to act as a bidentate, coordinating through the pyridine and 2-aza nitrogen atoms only. Our results suggest that the ligand (V) does, in fact, behave both as a tridentate and a bidentate, depending on the metal ion and the anions present.

Results and Discussion

The schiff base (V) forms stable crystalline complexes with the 3*d* metal ions manganese(II), cobalt(II), nickel(II), and copper(II); the complexes are listed in Table I.

The insolubility of the manganese complex $Mn(N-N-SMe)Cl_2$ suggests that it is not monomeric and it seems likely that it has a polymeric octahedral structure with chloro-bridges but otherwise its structure is uncertain.

With iron(II) idenfinite products were obtained; these were not characterized.

The cobalt halide complexes $Co(N-N-SMe)Hal_2$ have electronic absorption bands whose positions and intensities indicate the presence of tetrahedral cobalt(II) (Table II). The complexes $Co(N-NMe-S)Hal_2$ (N-NMe-S; III) have absorption typical of tetrahedral cobalt(II) and were assigned structures of the type $[Co(N-NMe-S)_2][Co(Hal)_4]$.[2] They exhibited additional electronic absorption bands associated with the octahedral cobalt(II) in the cation (Figure 1). Such ionic structures are not thought to occur with the $Co(N-N-SMe)Hal_2$ complexes reported here. These complexes are essentially non-electrolytes in nitromethane and show no electronic absorptions attributable to octahedral cobalt(II) (Tables I and II, Figure 1). They are considered to be complexes of the type $[Co(N-N-SMe)Hal_2]$, containing an NN bidentate ligand.

The complex $Co(N-N-SMe)_2(NO_3)_2$ is a uni-univalent electrolyte in nitromethane solution. In the solid state it has infrared absorptions at 1480, 1340, and 1282 cm^{-1}, indicating the presence of both coordinated and ionic nitrate.[4] It is formulated as $[Co(N-N-SMe)_2NO_3]NO_3$. The electronic spectrum does not resem-

---

(4) K. Nakamoto, « Infrared Spectra of Inorganic and Coordination Compounds », John Wiley and Sons New York, (1970).

Table II. Electronic Spectra of Cobalt Complexes.

Compound	Solid ν_{max} (cm^{-1})	In $MeNO_2$ solution ν_{max} (cm^{-1})	ε
$Co(N-N-SMe)Cl_2$	4600	4500	20
	7000sh		
	7600	7600	24
	16000	14800	180
	17500	15500	175
	18400	16000sh	
	19200	16800	180
$Co(N-N-NSMe)Br_2$	4200	4200	37
	6700		
	7600	7100	37
	15600	14700	304
	17000	16000	211
	18000		
	18700sh		
$Co(N-N-SMe)I_2$	4600	4400	37
	6500	6800	32
	7600	8200	25
		13800sh	
	14400	14300	220
		15000	210
	16300	16200	230
	19000sh	19000	1200
$Co(N-N-SMe)_2(NCS)_2 . H_2O$	8000	8000	70
	16000	16000	460
	17100	17000sh	
$[Co(N-N-SMe)_2NO_3]NO_3$	7600	9000	15
	11500	11500	15
	c. 16500sh	15000	22
$[Co(N-N-SMe)_2](ClO_4)_2 . H_2O$	7800	7800	46
	14400	14400	120
	19500sh	*c.* 19500sh	
$[Co(N-N-SMe)_2](BF_4)_2$	7800	7800	45
	14400	14400	120
	c. 19000sh	*c.* 19000sh	

Table III. Solid State Reflectace Spectra of Nickel and Copper Complexes.

Compound	Bands (cm^{-1})		
$Ni(N-N-SMe)Cl_2$	9400	14500	19300
$Ni(N-N-SMe)Br_2$	9200	14500	21600
$Ni(N-N-SMe)I_2$	8800	*c.* 15000sh	*c.* 20000sh
$Ni(N-N-SMe)(NCS)_2$	10400	17700	*c.* 22000sh
$[Ni(N-N-SMe)_2NO_3]NO_3$	11200	17800	23000sh
$[Ni(N-N-SMe)_2](ClO_4)_2$	12800	19300	
$Cu_2(N-N-SMe)Cl_4$	12500	*c.* 22000sh,hr	
$[Cu(N-N-SMe)NO_3)_2]$	14200	*c.* 22000sh	
$[Cu(N-N-SMe)(NCS)_2]$	14000	*c.* 22000sh	
$[Cu(N-N-SMe)_2](ClO_4)_2 . 4H_2O$	13000	*c.* 15000sh	*c.* 22000sh
$[Cu(N-N-SMe)_2](BF_4)_2$	13000	*c.* 15500sh	*c.* 22000sh
$[Cu(N-N-SMe)_2I]BF_4$	11700	*c.* 22000sh	
$[Ni(mepic)_2NO_3]NO_3$ [a]	10400	17100	27500

[a] From ref. 7, mepic = 6-methyl-2-aminomethylpyridine.

ble that of six-coordinate cobalt(II), as it has two bands in the 7,000-12,000 cm^{-1} region (Table II, Figure 1) but is similar to those for five-coordinate cobalt(II).[5,6] We therefore suggest a structure containing two bidentate NN-bonded ligands and one unidentate nitrate.

The complexes $[Co(N-N-SMe)_2](ClO_4)_2 . H_2O$ and $[Co(N-N-SMe)_2](BF_4)_2$ are low-spin bi-univalent electrolytes in nitromethane. Four- or five-coordination is usual for low-spin cobalt(II). The spectra of these complexes are richer than the few reported for four-coordinate cobalt(II) and are closer to the spectra of five-coordinate low-spin cobalt(II) complexes.[5,6] If the complexes are five-coordinate, then one bidentate and one tridentate ligand per cobalt ion would be expected. These N-N-SMe complexes contrast with $[Co(N-NMe-S)_2](ClO_4)_2$ and $[Co(MeN-NMe-S)_2]$-

(5) M. Ciampolini, *Structure and Bonding*, 6, 53 (1969).
(6) A. B. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Amsterdam, (1968).

$(ClO_4)_2 \cdot 2H_2O$ (N-NMe-S = III, MeN-NMe?S = IV), which are high-spin and six-coordinate, with two tridentate ligand molecules per cobalt ion.[2,3]

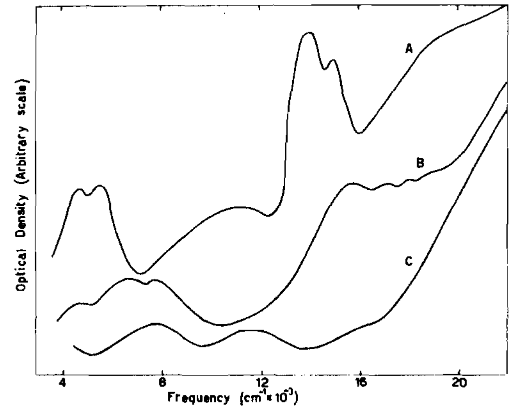


Figure 1. Diffuse reflectance spectra: (A), $[Co(N{-}NMe{-}S)_2][CoBr_4]$; (B), $[Co(N{-}N{-}SMe)Br_2]$; (C), $[Co(N{-}N{-}SMe)_2NO_3]NO_3$.

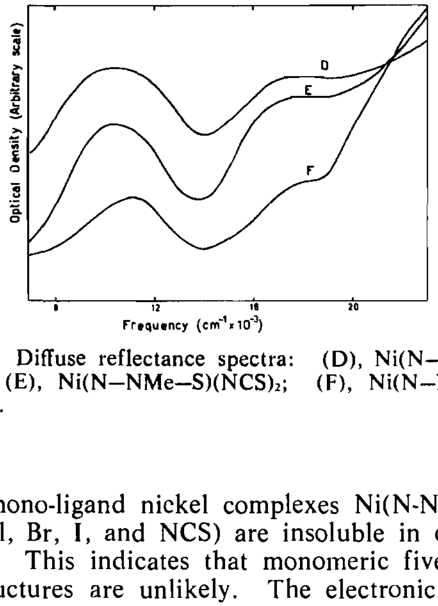


Figure 2. Diffuse reflectance spectra: (D), $Ni(N{-}N{-}SMe)(NCS)_2$; (E), $Ni(N{-}NMe{-}S)(NCS)_2$; (F), $Ni(N{-}N{-}SMe)_2NO_3]NO_3$.

The mono-ligand nickel complexes $Ni(N\text{-}N\text{-}SMe)X_2$ (X = Cl, Br, I, and NCS) are insoluble in common solvents. This indicates that monomeric five-coordinate structures are unlikely. The electronic spectra of the complexes suggest six-coordinate structures (Table III, Figure 2). The thiocyanate complex has infrared ν(C-N) absorptions at 2120 and 2075 cm^{-1}, indicating the presence of both bridging and terminal N-bonded thiocyanate.[4] This supports a polymeric octahedral structure with one of the thiocyanate groups acting as a bridging group between each pair of adjacent nickel ions, and with tridentate ligand molecules. Similar structures with bridging halogens, seem likely for the halide complexes.

Such structures were earlier proposed[2] for the complexes $Ni(N\text{-}NMe\text{-}S)X_2$ (N-NMe-S = III, X = Cl, Br, I, and NCS). In keeping with this the electronic spectra of the corresponding nickel halide and thiocyanate complexes with N-NMe-S and N-N-SMe are generally similar (Figure 2).

The nickel nitrate complex $Ni(N\text{-}N\text{-}SMe)_2(NO_3)_2$, like the analogous cobalt compound, is a uni-univalent electrolyte in nitromethane solution and has infrared absorption at 1480, 1340, and 1275 cm^{-1}, showing the presence of both coordinated and ionic nitrate in the solid state.[4] Formulation as $[Ni(N\text{-}N\text{-}SMe)_2NO_3]NO_3$ is therefore indicated. The electronic spectrum, in contrast to that of the cobalt complex, suggests a six-coordinate structure. The electronic spectrum resembles that of $[Ni(6\text{-methyl-2-aminomethylpyridine})_2NO_3]NO_3$ which contains two NN chelates and one bidentate nitrate (Table III).[7] In view of this, we suggest an analogous structure for $[Ni(N\text{-}N\text{-}SMe)_2NO_3]NO_3$ involving two bidentate NN-bonded ligands and one bidentate nitrate. Because of ligand absorption, it was impossible to detect the presence or absence of ν(M-S) in the infrared spectra of any of the complexes.

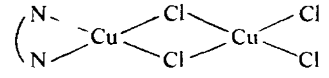
Since the ν_1 and ν_4 infrared absorptions for nitrate cannot be reliably used to distinguish between unidentate or bidentate coordination,[4,8] we are unable to confirm the mode of bonding of nitrate in the cations $[M(N\text{-}N\text{-}SMe)_2NO_3]^+$ (M = Co, Ni). X-ray diffraction patterns for $[Co(N\text{-}N\text{-}SMe)_2NO_3]NO_3$ and $[Ni(N\text{-}N\text{-}SMe)_2NO_3]NO_3$ are quite different, consistent with the proposed difference in structures.

The bis-ligand perchlorate complex $[Ni(N\text{-}N\text{-}SMe)_2](ClO_4)_2$ is high-spin and a bi-univalent electrolyte in nitromethane solution. Its electronic spectrum indicates a six-coordinate structure and resembles those[2,3] for $[Ni(N\text{-}NMe\text{-}S)_2](ClO_4)_2$ and $Ni(MeN\text{-}NMe\text{-}S)_2](ClO_4)_2H_2O$.

There are therefore two tridentate ligand molecules coordinate to each nickel ion.

The results given above for the cobalt and nickel complexes show that, as expected, the thioether sulphur in N-N-SMe has a lower tendency to coordinate than the thioketone sulphur in N-NMe-S. For the nickel and cobalt complexes isolated, wherever N-N-SMe is tridentate then the structures of its complexes are analogous to the structures of the corresponding complexes of N-NMe-S. Wherever structures of corresponding complexes of N-N-SMe and N-NMe-S are different, then N-N-SMe is bidentate.

The simplest molecular formulation for the copper chloride complex is $Cu_2(N{-}N{-}SMe)Cl_4$, in contrast to the formulation $Cu(N{-}NMe{-}S)Cl_2$ found[2] with N–NMe–S. This suggests that the N–N–SMe chelate may be bidentate in this case. Since the insolubility of the complex suggests that it is non-ionic, the simplest structure appears to be as in VI. Magnetic data



(VI)

do not provide confirmation for this halogen - bridged structure since the complex obeys the Curie-Weiss law down to liquid nitrogen temperature with a θ value of +10° (Table IV).

The complex $Cu(N{-}N{-}SMe)(NO_3)_2$ has infrared absorptions at 1480 and 1280 cm^{-1} which indicate that both nitrate groups are coordinated[4]. The thiocyanate compound $Cu(N{-}N{-}SMe)(NCS)_2$ is a non-electrolyte in nitromethane. The ν(C–N) infrared absorption appears as a single band at 2080 cm^{-1} which

(7) S. Utsuno, *J. Inorg. Nucl. Chem.*, 32, 1631 (1970).

(8) C. C.Addison and N. Logan, *Advan. Inorg. Chem. Radiochem.*, 6, 71 (1964).

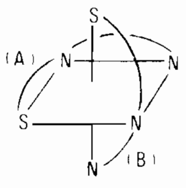
indicates the presence of unidentate N—bonded thiocyanate.[4] The reflectance spectrum is in accord with a four-coordinate structure with the ligand bidentate.

With copper perchlorate and fluoborate the bis-ligand complexes $Cu(N-N-SMe)_2X_2$ ($X = ClO_4, BF_4$) were readily obtained by reaction in ethanol. This is in marked contrast to N—NMe—S (III) which gives no complexes with copper perchlorate or copper fluoborate.[2]

Table IV. Magnetic Data for $Cu_2(N-N-SMe)Cl_4$

T(°K)	313	283	253	223	193	163	123	83
$10^6\chi'_M$	1138	1293	1406	1573	1806	2120	2739	3939
μ(B.M.)	1.69	1.72	1.69	1.68	1.68	1.67	1.65	1.62

This reluctance by N—NMe—S to form a bis-ligand complex with copper(II) was attributed[2] to the Jahn-Teller effect which elongates the bonds in the apical sites about copper(II). This may place too great a strain on the planar tridentate ligand (B) which has to ocupy both apical sites in (VII).



(VII)

The different behaviour with copper(II) by N—N—SMe is readily explained if it acts as a bidentate ligand. Bidentate coordination by N—N—SMe in the copper perchlorate and fluoborate complexes is supported by the similarity of their reflectance spectra (Table III, Figure 3) to those of $Cu(diimine)_2X_2$ complexes (diimine = 1,10-phenanthroline, 2,2'-bipyridine; $X = ClO_4, BF_4$).[10-12] It has been suggested that some of the latter diimine complexes are five-coordinate in the solid state with one cordinated anion.[10,11,13] In nitrobenzene solution there is also evidence[10] for species of the type [$Cu(diimine)_2X$]X. Our complexes $Cu(N-N-SMe)_2X_2$ ($X = ClO_4, BF_4$) are bi-univalent electrolytes in nitrobenzene and nitromethane, but five-coordination cannot be ruled out in the solid state.

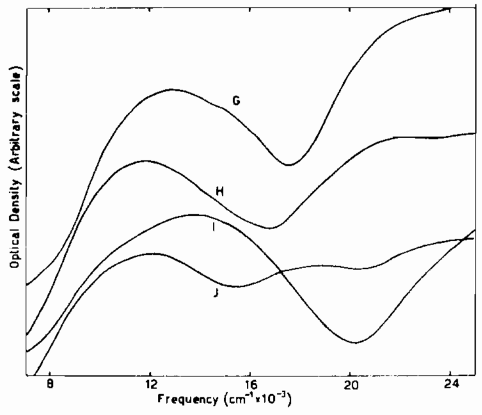


Figure 3. Diffuse reflectance spectra: (G), $Cu(N-N-SMe)_2(BF_4)_2$; (H), $[Cu(N-N-SMe)_2I]BF_4$; (I), $Cu(1,10\text{-phenanthroline})_2(BF_4)_2$; (J), $[Cu(1,10\text{-phenanthroline})_2I](BF_4)$.

The analogy between the behaviour of N—N—SMe and diimine ligands is greatly strengthened by the isolation of the mono-iodo adduct $[Cu(N-N-SMe)_2I]BF_4$, which we believe is five coordinate. This is a uni-univalent electrolyte in nitromethane and its electronic spectrum (Table III, Figure 3) resembles those of complexes containing the five coordinate cation $[Cu(diimine)_2]^+$ (diimine = 1,10-phenanthroline, 2,2'-bipyridine).[12-15]

Conclusions

Our results show that the thioether sulphur in N—N—SMe is a poorer donor than the thioketone sulphurs in N—NMe—S and MeN—NMe—S. The thioketone ligands always coordinate as tridentates, whereas N—N—SMe is almost exclusively bidentate with cobalt(II) and copper(II), and tridentate with nickel(II).

Since the steric requirements of cobalt(II) and nickel(II) are similar, the greater extent of thioether coordination with nickel(II) is attributed to greater softness or class (b) character with nickel(II) than with cobalt(II). This is borne out by the relative values for cobalt(II) and nickel(II), of the softness parameters σ_P and σ_A given in Table V.[16] The reluctance of N—N—SMe to act as a tridentate in the copper complexes is attributed to the steric restriction placed upon a planar tridentate ligand by Jahn-Teller distortion.

Table V. Softness Parameters* for Some Metal Ions

Metal ion:		Ba^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Hg^{2+}
Softness	σ_P	0.184	0.130	0.126	0.104	0.06
Parameters *	σ_A	0.5	1.8	2.0	3.1	4.6

* The smaller the values of σ_P and the greater the value of σ_A, then the greater the degree of softness which is indicated (S. Ahrland, *Structure and Bonding*, 5, 118 (1968)).

Experimental Section

2-(2,3-Diaza-4-methylthio-5-thiahexa-1,3-dienyl)pyridine. S-Methyl-N-(2-pyridyl)methylendithiocarbazate[1] (15 g) was added to a solution of potassium hydroxide (4.5 g) in alcohol (500 ml) and the mixture

---

(9) J. P. Beale, private communication.

(10) N. T. Barker, C. M. Harris, and E.D. McKenzie, *Proc. Chem. Soc.*, 335 (1961).

(11) G. H. Faye, *Can. J. Chem.*, *44*, 2165 (1966).

(12) M. Akbar Ali, S. E. Livingstone, and D. J. Phillips, unpublished results.

(13) E. D. McKenzie, *Coord. Chem. Rev*, 6, 187 (1971).

(14) H. Elliot, B. J. Hathaway, and R. C. Slade, *J. Chem. Soc.* (A), 1443 (1966).

(15) C. M. Harris, T. N. Lockyer, and H. Waterman. *Nature*, *192*, 424 (1961).

(16) S. Ahrland, *Structure and Bonding*, 5, 118 (1968).

was stirred for 30 min. Methyl iodide (50 g) was added and the mixture was stirred for a further 4 hr. The deposit of potassium iodide was filtered off and the filtrate was concentrated in a rotary exaporator. Chloroform (300 ml) was then added and the mixture was shaken vigorously and filtered. The chloroform was then removed from the filtrate under reduced pressure to give the crude compound as a red oil. Attempts to induce crystallization of the oil were unsuccessful.

The crude product was dissolved in alcohol (100 ml) and this solution (*c.* 15% w/v) was used for the preparation of the metal complexes.

Preparation of the 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-2-(2,3-diaza-4-methylthio-5-thiahexa-1,3-dienyl)pyridine Complexes of Manganese(II), Cobalt(II), and Nickel-(II). The metal halide (0.01 mole) in alcohol (50 ml) was added to the Schiff base solution (10 ml, *c.* 0.006 mole). The mixture was heated on the steam bath for 2 min and then allowed to cool, whereupon the crystalline complex, which had deposited, was separated; yield 0.3-0.5 g.

Diiodo-2-(2,3-diaza-4-methylthio-5-thiahexa-1,3-dienyl)pyridinecobalt(II). A solution of cobalt nitrate hexahydrate (2 g) and lithium iodide (3 g) in alcohol (50 ml) containing 2,2-dimethoxypropane (10 ml) after being heated on the steam bath for 5 min, was treated with the Schiff base solution (10 ml) and heated for a further 2 min and cooled. Ligroin (5 ml) was added and crystallization was induced by scratching the inside of the container. The brown crystals of the complex were separated by filtration; yield, 0.4 g.

Dithiocyanatobis{2-(2,3-diaza-4-methylthio-5-thiahexa-1,3-dienyl)pyridine}cobalt(II) Monohydrate. The Schiff base solution (10 ml) was added to a hot solution of cobalt thiocyanate (1 g) in alcohol (40 ml). The compound was deposited as deep green crystals; yield, 0.4 g.

Nitratobis{2-(2,3-diaza-4-methylthio-5-thiahexa-1,3-dienyl)pyridine}cobalt(II) Nitrate. The Schiff base solution (10 ml) was added to a solution of cobalt nitrate hexahydrate (3 g) in 2: 1 alcohol: 2,2-dimethoxypropane (50 ml). The mixture, after being heated on the steam bath for 3 min and cooled, yielded the crystalline complex; yield, 1.0 g.

Bis{2-(2,3-diaza-4-methylthio-5-thiahexa-1,3-dienyl)-pyridine}cobalt(II) Perchlorate. Cobalt perchlorate hexahydrate (1.5 g) in 2: 1 alcohol-dimethoxypropane (30 ml) was added to the Schiff base solution (20 ml). The mixture, after being heated on the steam bath for 3 min and cooled, yielded the crystalline complex; yield, 0.3 g.

Bis{2-(2,3-diaza-4-methylthio-5-thiahexa-1,3-dienyl)-pyridine}cobalt(II) Tetrafluoborate. This compound was prepared from cobalt tetrafluoborate hexahydrate (3 g) by the same method as used for the perchlorate; yield, 0.3 g.

Bis{2-(2,3-diaza-4-methylthio-5-thiahexa-1,3-dienyl)-pyridine}nickel(II) Perchlorate. This compound was prepared from nickel perchlorate hexahydrate by the same method as used for the analogous cobalt complex; yield, 0.4 g.

Diiodo- and Dithiocyanato-2-(2,3-diaza-4-methythio-5-thiahexa-1,3-dienyl)pyridinenickel(II). The Schiff base solution (10 ml) was added to a solution of nickel nitrate hexahydrate (2 g) and lithium iodide or thiocyanate (3 g) in alcohol (100 ml), containing 2,2-dimethoxypropane (20 ml). The mixture, after being heated on the steam bath for 3 min and cooled, yielded crystals of the metal complex; yield, 0.5-0.6 g.

Nitratobis{2-(2,3-diaza-4-methylthio-5-thiahexa-1,3-dienyl)pyridine}nickel(II) Nitrate. This compound was prepared by the same method as that used for the corresponding cobalt complex; yield, 1.1 g.

Di-μ-chlorodichloro-2-(2,3-diaza-4-methylthio-5-thiahexa-1,3-dienyl)pyridinedicopper(II). The Schiff base solution (10 ml) was added to a solution of copper(II) chloride dihydrate (2.0 g) in alcohol (100 ml). The mixture, after being heated on the steam bath for 3 min, gave brown crystals of the complex; yield, 0.5 g.

Dinitrato-2-(2,3-diaza-4-methylthio-5-thiahexa-1,3-dienyl)pyridinecopper(II). The Schiff base solution (10 ml) was added to a solution of copper nitrate hexahydrate (2 g) in 1: 1 alcohol: dimethoxypropane (30 ml). The mixture after being heated on the steam bath for 3 min, deposited green crystals of the complex on cooling; vield, 0.45 g.

Dithiocyanato-2-(2,3-diaza-4-methylthio-5-thiahexa-1,3-dienyl)pyridinecopper(II). The Schiff base solution (10 ml) was added to a solution of copper nitrate tetrahydrate (1.0 g) in absolute alcohol (20 ml). The solution, on being heated, yielded green crystals. A solution of lithium thiocyanate (2.0 g) in absolute alcohol (10 ml) was added to the mixture, which was then heated for 10 min. Dark green crystals resulted, yield, 1.0 g.

Bis{2-(2,3-diaza-4-methylthio-5-thiahexa-1,3-dienyl)-pyridine}copper(II) Perchlorate Tetrahydrate. The Schiff base solution (40 ml) was added to a solution of copper perchlorate hexahydrate (1.0 g) in absolute alcohol (50 ml). The solution was heated for 5 min. Green crystals resulted; yield, 0.7 g.

Bis{2-(2,3-diaza-4-methylthio-5-thiahexa-1,3-dienyl)-pyridine}copper(II) Fluoborate. The Schiff base solution (30 ml) was added to a hot solution of copper fluoborate hexahydrate (1.0 g) in hot absolute alcohol (15 ml). The solution was heated on a steam bath for 10 min and then allowed to cool. Green crystals of the complex were deposited; yield, 0.7 g.

Iodobis{2-(2,3-diaza-4-methythio-5-thiahexa-1,3-dienyl)pyridine}copper(II) Fluoborate. The Schiff base solution (30 ml) was added to a boiling solution of copper fluoborate hexahydrate (1.0 g) in absolute alcohol. The mixture was heated on a steam bath for 0.5 min and then a solution of lithium iodide (2.0 g) in absolute alcohol (20 ml) was added. The mixture was heated on the steam bath for 10 min and then allowed to cool, producing a yellowish-brown precipitate, yield, 1.4 g.

Spectral Measurements. The electronic spectra were measured on a Zeiss PMQ II spectrophotometer. The diffuse reflectance spectra were obtained 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: measurements below 400 cm^{-1} were obtained on a Perkin-Elmer 521 spectrophotometer.

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

X-ray Diffraction Patterns. These were obtained with CuK_α radiation using a Philips PW1010 X-ray generator and powder diffractometer.

Acknowledgment. The authors are grateful to Dr. J.P. Beale of the School of Chemistry, University of New South Wales, for measuring the X-ray diffraction patterns.