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High-Spin Four- and Five-Coordinate Cobalt(II) and Nickel(II) Complexes with a Tridentate SNN Schiff Base

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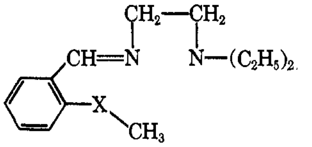
The Schiff base formed by *o*-methylthiobenzaldehyde and N,N-diethylethylenediamine (MSBen-N$(C_2H_5)_2$, set of donor atoms SNN) forms high-spin complexes with cobalt(II) and nickel(II) salts of the general formula M(MSBen-N$(C_2H_5)_2)X_2$. The stereochemistry of these complexes, both in the solid state and in solution, has been studied by magnetic and spectrophotometric measurements. The nickel halide complexes are five-coordinate in the solid state, whereas in solution in inert solvents they give rise to temperature-dependent equilibria between tetrahedral and five-coordinate species. The cobalt halide complexes are pseudo-tetrahedral both in the solid state and in solution. Nickel(II) iodide catalyzes demethylization of the sulfur atom of the ligand.

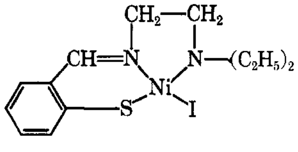
Introduction

It is well known that the electronic ground state of nickel(II) in five-coordinate complexes is influenced to a great extent by the nature of the donor atoms and bulkiness of the ligand. Ligands possessing donor atoms of low electronegativity and strong tendency to form π bonds (like P and As) form complexes of low-spin type, while the high-spin complexes so far described contain donor atoms of high electronegativity such as oxygen and nitrogen. Sulfur is intermediate on the scale of electronegativity and forms complexes of both low- and high-spin types.

In a systematic investigation to study the influence of the nature of the donor atoms on the stereochemistry and electronic configuration of the five-coordinate complexes of nickel(II), we have synthesized the potentially tridentate ligands derived from the condensation of N,N-diethylethylenediamine and *ortho*-substituted benzaldehydes of the general formula



When X = NH, the ligands are tridentate and form high-spin five-coordinate complexes with salts of nickel(II) and cobalt(II).[1] Now we have studied the ligand in which X = S, that is, the Schiff base formed from *o*-methylthiobenzaldehyde and N,N-diethylethylenediamine, possessing the potential set of donor atoms SNN. This ligand, which we will refer to as MSBen-N$(C_2H_5)_2$, forms complexes of the general formula M(MSBen-N$(C_2H_5)_2)X_2$, where X = Cl, Br, I, or NCS, with nickel(II) and cobalt(II) salts. The reaction of this ligand with nickel iodide may also result in the demethylization of the ligand with the formation of a complex of the general formula



which we will refer to in this article as Ni(SBen-N$(C_2H_5)_2$)I.

Experimental Section

Materials.—All solvents used were of purity grade RP. The 1-butanol was refluxed and distilled over BaO. The 1,2-dichloroethane was washed with a solution of 5% $NaHCO_3$ and dried over $CaCl_2$ and distilled.

Synthesis of the Ligand.—The *o*-methylthiobenzaldehyde (MSB) (bp 120° (1 torr)) was prepared starting with *o*-thiobenzoic acid by the general method described in the literature.[2] The Schiff base formed from MSB and N,N-diethylethylenediamine was obtained by mixing the stoichiometric quantities of the two components in the presence of anhydrous Na_2SO_4 and allowing them to remain overnight at room temperature. The product of this reaction was distilled under vacuum and the Schiff base was obtained as a straw-colored yellow oil with a boiling point of 120° at 0.5 torr.

Preparation of the M(MSBen-N$(C_2H_5)_2)X_2$ Complexes.—All of the complexes, except those of NiI_2, were prepared by the following general method. To a hot solution of 5 mmol of the appropriate metal salt in 20 ml of anhydrous 1-butanol was added a solution of 5 mmol (1.35 g) of the ligand in 20 ml of 1-butanol. The solution was concentrated and cyclohexane was added to aid precipitation of the complex. All of the complexes were recrystallized from 1-butanol and cyclohexane and collected on a porous filter and washed with a mixture of 1-butanol and petroleum ether in a 1:1 proportion. Finally they were dried in a vacuum oven at 75°. The crystalline complexes are slightly hygroscopic, and filtration and drying were performed in an inert atmosphere of dry nitrogen.

The complex Ni(MSBen-N$(C_2H_5)_2)I_2$ was obtained using the following procedure. A 5-mmol amount of NiI_2 was dissolved in 15 ml of boiling 1-butanol, and the solution was filtered and then cooled in a desiccator over $CaCl_2$. When room temperature was reached, the solution was mixed with a solution of 5 mmol of ligand in 15 ml of 1-butanol and cyclohexane was added to aid the precipitation of the complex. Red-brown crystals were obtained.

Preparation of the Ni(SBen-N$(C_2H_5)_2$)I Complex.—This complex was prepared by the first method using NiI_2. Brown crystals were obtained. In a separate test the reaction was performed in dry nitrogen stream, and the vapors were bubbled into an ethanolic solution of $AgNO_3$. A pale yellow precipitate of $AgI \cdot AgNO_3$ was obtained which is indicative of the formation of CH_3I in the reaction.

Spectrophotometric Measurements.—The absorption spectra were recorded with a Beckman DK2 spectrophotometer using 1-

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[1] L. Sacconi, I. Bertini, and R. Morassi, *Inorg. Chem.*, **6**, 1548 (1967).
[2] B. Eistert, W. Schade, and H. Selzer, *Chem. Ber.*, **97**, 1470 (1964).

TABLE I

PHYSICAL AND ANALYTICAL DATA OF THE COMPLEXES

Compound	Color	Mp, °C	Molar conductance, cm^2/ohm mol^c	$\tilde{n}^d$	Analyses, %: N Calcd	N Found	Metal Calcd	Metal Found	Halogen Calcd	Halogen Found
$Ni(MSBen–N(C_2H_5)_2)Cl_2$	Light green	182–184	0.09	0.97	7.73	7.46			18.66	18.98
$Ni(MSBen–N(C_2H_5)_2)Br_2$[a]	Yellow-green	182–185	0.51	0.99	5.97	5.81	12.52	12.55	34.08	34.15
$Ni(MSBen–N(C_2H_5)_2)I_2$	Red-brown	155–156	1.07		4.95	5.18	10.43	10.44	45.09	45.01
$Ni(SBen–N(C_2H_5)_2)I$[b]	Brown	198–199	0.17	1.05	6.65	6.31	13.95	13.90	30.14	30.24
$Ni(MSBen–N(C_2H_5)_2)(NCS)_2$	Light green	185–188	0.29		13.17	13.22	13.80	13.50		
$Co(MSBen-N(C_2H_5)_2)Cl_2$	Blue	173–177	0.08	0.98	7.36	7.40			18.64	18.62
$Co(MSBen–N(C_2H_5)_2)Br_2$	Greenish blue	192–194	0.13	0.96	5.97	6.02			34.06	34.00
$Co(MSBen–N(C_2H_5)_2)I_2$	Green	192–194	0.38	0.97	4.97	5.14			45.07	45.77
$Co(MSBen–N(C_2H_5)_2)(NCS)_2$	Grayish violet	168–169	0.15	0.94	13.17	13.10	13.85	13.64		

[a] *Anal.* Calcd: C, 35.86; H, 4.73; S, 6.84. Found: C, 36.06; H, 4.73; S, 6.91. [b] *Anal.* Calcd: C, 37.08; H, 4.55; S, 7.62. Found: C, 38.01; H, 4.98; S, 7.83. [c] For *ca.* 10^{-3} *M* solutions in 1,2-dichloroethane at 25°. [d] Ratio of the found to the theoretical molecular weight.

cm quartz cells. The solutions were about 4–5 × 10^{-3} *M* in 1,2-dichloroethane. The absorption spectra at various temperatures were recorded in solutions of *o*-dichlorobenzene. The extinction coefficients were calculated using a graph of the variation of the density of the solution with increasing temperature. The reflectance spectra were measured with the standard reflectance attachment for the Beckman DK2 using MgO for a reference.

The infrared spectra were recorded with a Perkin-Elmer Model 337 spectrophotometer using Nujol mulls or CsBr disks.

Magnetic Measurements.—The magnetic measurements were performed by the Gouy method with the apparatus and experimental technique described previously.[3] The sample tube was calibrated with $HgCo(NCS)_4$[4] and freshly distilled water.[4]

Conductivity Measurements.—The values of molar conductivity were measured with a WTW Model LBR/R conductivity bridge. The concentrations of the solutions were approximately 10^{-3} *M* in 1,2-dichloroethane.

Molecular Weight Measurements.—Molecular weight measurements were performed in 1,2-dichloroethane using a Mechrolab Model 301 A osmometer which was calibrated with benzil. The concentrations of the solutions used were about 10^{-3} *M*.

Results

The analytical and physical data of the complexes are reported in Table I. All of the complexes are crystalline and slightly hygroscopic, but are stable for long periods of time when stored in a dry atmosphere. They are moderately soluble in polar organic solvents like nitro and chloro derivatives, but the solutions become turbid upon standing. The cobalt(II) complexes do not oxidize appreciably in the solid state or in solution.

The room-temperature magnetic moments of the solid compound are reported in Table II and show that the complexes are all of the high-spin type.

The reflectance and absorption spectra, recorded in the region 3800–25,000 cm^{-1}, are reported in Figures 1, 3, and 4. In all cases the spectra of the complexes in the solid state and in solution are essentially identical. The positions of the absorption maxima and extinction coefficients for the electronic spectra of the complexes are reported in Table III. The spectra of the halogen complexes are all similar and the slight differences in the absorption maxima can be correlated with the position of the halogen in the spectrochemical series. Therefore, it can be concluded that the metal halides all possess essentially the same stereochemistry in the solid state and in solution. The spectra of the nickel and cobalt thiocyanate complexes differ substantially from those of the halogen, and thus it can be assumed that they possess a different stereochemistry. The absorption spectra of $Ni(MSBen–N(C_2H_5)_2)Cl_2$ and $Ni(MSBen–N(C_2H_5)_2)Br_2$ have been recorded in solutions of *o*-dichlorobenzene at various temperatures in the range 20–120° (Figure 2). With increasing temperature the peak heights of certain maxima in the range 13,000 cm^{-1} decrease while increasing temperature gives rise to new bands at about 10,000 and 12,000 cm^{-1}. The presence of two isosbestic points at about 11,000–12,000 and 14,000–15,000 cm^{-1} indicates the existence of two stereochemical forms in equilibrium.

TABLE II

MAGNETIC SUSCEPTIBILITY DATA OF THE COMPLEXES

Compound	Temp, °C	$10^6\chi_g$, cgs units	$10^6\chi_M$, cgs units	μ_{eff}, MB
$Ni(MSBen–N(C_2H_5)_2)Cl_2$	22	11.64	4626	3.32
$Ni(MSBen–N(C_2H_5)_2)Br_2$	22	9.01	4447	3.25
$Ni(MSBen–N(C_2H_5)_2)I_2$	19	6.91	4160	3.14
$Ni(SBen–N(C_2H_5)_2)I$	22		Diamagnetic	
$Ni(MSBen–N(C_2H_5)_2)(NCS)_2$	20	8.46	3823	3.00
$Co(MSBen–N(C_2H_5)_2)Cl_2$	22	23.54	9153	4.66
$Co(MSBen–N(C_2H_5)_2)Br_2$	22	19.49	9365	4.71
$Co(MSBen–N(C_2H_5)_2)I_2$	22	16.16	9352	4.72
$Co(MSBen–N(C_2H_5)_2)(NCS)_2$	18	20.54	8962	4.58

The molecular weight measurements were recorded

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(3) L. Sacconi, R. Cini, M. Ciampolini, and F. Maggio, *J. Am. Chem. Soc.*, **82**, 3487 (1960).

(4) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, p 415.

TABLE III

SPECTROSCOPIC DATA OF THE COMPLEXES

Compound	State	Temp, °C	Absorption max, cm^{-1} (ϵ_{molar} for soln)
Ni(MSBen–N$(C_2H_5)_2$)Cl_2	Solid		<5000, 10,000 sh, 12,000 sh, 14,300, 22,500
	$(CH_2Cl)_2$	22	9000 sh, 10,500 sh, 12,800 (43), 18,200 sh, 22,500 (226), 24,500 sh
	o-$Cl_2C_6H_4$	22	9000 sh, 10,300 sh, 12,800 (35)
	o-$Cl_2C_6H_4$	120	10,000 (36), 11,800 (28), 14,300 (23), 20,500 (133)
Ni(MSBen-N$(C_2H_5)_2$)Br_2	Solid		<5000, 10,000 sh, 11,500 sh, 14,200, 22,000
	$(CH_2Cl)_2$	22	8500 sh, 10,300 sh, 13,000 (23), 22,500 (350)
	o-$Cl_2C_6H_4$	22	8700 sh, 10,400 (27), 12,800 (44)
	o-$Cl_2C_6H_4$	120	7000 sh, 9900 (53), 11,200 (39), 13,000 sh
Ni(MSBen–$(C_2H_5)_2$)I_2	Solid		4800, 9200 sh, 12,000 sh, 14,000, 18,000 sh, 21,500
Ni(MSBen–N$(C_2H_5)_2$)$(NCS)_2$	Solid		10,000, 16,500, 24,000 sh
	$(CH_2Cl)_2$	22	10,000, 16,000
Co(MSBen–N$(C_2H_5)_2$)Cl_2	Solid		6000, 7300, 10,100, 15,500, 17,200, 18,000 sh, 19,000 sh
	$(CH_2Cl)_2$	22	6000 (40), 7300 (51), 10,000 (30), 15,100 (348), 15,700 sh, 17,200 (358), 18,000 sh
Co(MSBen–N$(C_2H_5)_2$)Br_2	Solid		6000 sh, 7300, 10,000, 15,400, 16,500 sh, 17,500 sh, 18,800 sh
	$(CH_2Cl)_2$	22	5800 (24), 7000 (45), 9800 (25), 15,200 (460), 16,500 (360), 17,500 sh
Co(MSBen–N$(C_2H_5)_2$)I_2	Solid		5600 sh, 6800, 9700, 14,800, 15,700 sh, 17,500 sh
	$(CH_2Cl)_2$	22	5600 sh, 6800 (74), 9500 (53), 14,600 sh, 15,000 (668), 16,000 sh, 18,000 sh
Co(MSBen–N$(C_2H_5)_2$)$(NCS)_2$	Solid		5800, 13,000, 16,000 sh, 17,500, 18,500 sh
Ni($(CH_3)_5$dien)Br_2	Solid		≈5000, 9800 sh, 12,500, 15,400 sh, 18,200 sh, 21,600
Ni($(CH_3)_4$en)Br_2	Solid		7700 sh, 9800, 11,100 sh, 17,500 sh, 19,000
Co($(CH_3)_4$pn)$(NCS)_2$	CH_2Cl_2	22	6500 (42), 8200 (111), 10,900 (58), 15,450 (1207), 18,000 (265), 18,500 sh
Co($(CH_3)_5$dien)$(NCS)_2$[a]	Solid		5800, 13,500, 16,500, 20,000

[a] M. Ciampolini, private communication.

for all of the complexes, except that of $Ni(NCS)_2$, to determine the value of $\bar{n}$, the ratio of the found to the calculated molecular weight, and the results indicate that these complexes are monomeric (Table I).

The values of molar conductivity in dichloroethane, measured at 22°, were in the range of 0.80–1.07 ohm^{-1} cm^2 mole^{-1}. These values, which are less than 10% of those found for 1:1 electrolytes, indicate that the complexes are present as monomeric nonionic species in solution.

Discussion

Nickel(II) Chloride, Bromide, and Iodide.—On the basis of spectral data, the same stereochemistry may be assigned to these complexes in the solid state and in solution. The complexes, whose magnetic moments are in the range 3.00–3.32 BM, are monomeric and undissociated. Since the ligand is potentially tridentate, a planar or octahedral configuration may be excluded. Also a tetrahedral structure must be excluded because the crystal field spectra of the complexes cannot be consistently interpreted on the basis of this configuration. The complexes exhibit bands at about 5000, 8500–10,000, 12,500–14,000, and 21,000–22,000 cm^{-1} (Figure 1) which correspond to the absorption bands of the complexes Ni($(CH_3)_5$dien)Cl_2, -Br_2, and -I_2,[5] occurring at about 5000, 9800, 12,500, 15,400, 18,200, and 21,600 cm^{-1}. These complexes are five-coordinate since they are isomorphous with the corresponding cobalt complexes which have been shown to be five-coordinate by X-ray analysis.[6] On this basis, to the Ni(MSBen–N$(C_2H_5)_2$)Cl_2, -Br_2, and -I_2 complexes may be assigned a five-coordinate stereochemistry with the set of donor atoms SN_2X_2.

A final proof of the five-coordinate stereochemistry is the fact that the two complexes Ni(MSBen–N$(C_2H_5)_2$)Cl_2 and Ni(MSBen–N$(C_2H_5)_2$)Br_2 give rise to a temperature-dependent reversible equilibrium in solutions of o-dichlorobenzene. At 120° the band at 12,800 cm^{-1}, attributable to a five-coordinate stereochemistry, disappears and two new bands, at 10,000 and 11,200 cm^{-1} (Figure 2) appear and are almost identical in form and frequency with those of the pseudo-tetrahedral complexes Ni($(CH_3)_4$en)Br_2[7] in which $(CH_3)_4$en is N,N,N′,N′-tetramethylethylenediamine. These bands have been assigned, respectively, to a spin-allowed ν_2 transition, $^3T_1(F) \rightarrow {}^3A_2(F)$ in a symmetry field T_d, and to a spin-forbidden transition to a higher state derived from the ^1D state of the free

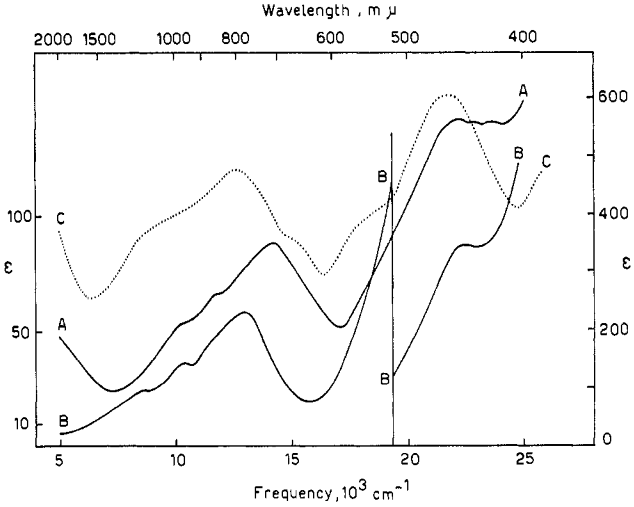

Figure 1.—Electronic spectra of some nickel(II) complexes: A, reflectance spectrum of Ni(MSBen–N$(C_2H_5)_2$)Br_2; B, absorption spectrum of Ni(MSBen–N$(C_2H_5)_2$)Br_2 in 1,2-dichloroethane solution; C, reflectance spectrum of Ni($(CH_3)_5$dien)Br_2.

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(5) M. Ciampolini and G. P. Speroni, *Inorg. Chem.*, **5**, 45 (1966).

(6) M. Di Vaira and P. L. Orioli, *Chem. Commun.*, 590 (1965).

(7) L. Sacconi, I. Bertini, and F. Mani, *Inorg. Chem.*, **6**, 262 (1967).

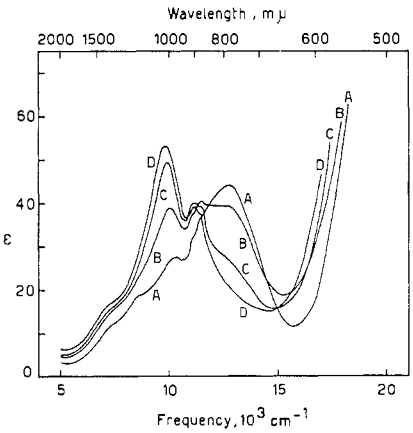
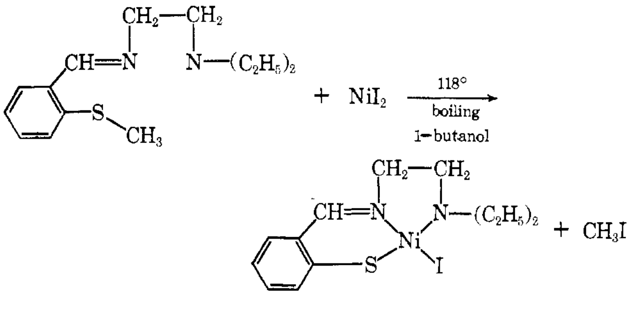


Figure 2.—Absorption spectra of $Ni(MSBen{-}N(C_2H_5)_2)Br_2$ in *o*-dichlorobenzene solution: (A) at 20°; (B) at 55°; (C) at 89°; (D) at 120°.

ion.[8,9] Since the two complexes, even at 85°, in *o*-dichlorobenzene, remain nonconducting, the tetrahedral configuration must be formed by the bond cleavage of a donor atom of the Schiff base, probably the sulfur atom. This hypothesis is favored by the fact that the complexes in which X = NH (MAB; set NNN)[1] in the same solvent and at the same temperature give rise to a small percentage of tetrahedral species. This hypothesis is also strengthened by the behavior of the complexes of cobalt(II) (see next sections).

The $Ni(MSBen{-}N(C_2H_5)_2)I_2$ complex in *o*-dichlorobenzene solution undergoes an irreversible structural transformation when the temperature is increased. At 90° the spectrum is similar to that of the tetrahedral complexes of nickel(II), with maxima at 9500 and 10,300 cm^{-1} and a shoulder at 14,300 cm^{-1}. Finally, at 150°, a spectrum is obtained which is characteristic of the planar compounds, since it does not show any peaks below 12,000 cm^{-1}. This spectrum does not change when the temperature of the solution is decreased.

The diamagnetic complex $Ni(SBen{-}N(C_2H_5)_2)I$, which has been assigned a square-planar configuration, is formed by the demethylization of the Schiff base in the reaction



This dealkylization reaction of the ligand is a new example of sulfur demethylization catalyzed by the presence of nickel(II) which can be added to those previously described.[10] We were not able to obtain the compound $Ni(MSBen{-}N(C_2H_5)_2)I_2$ by addition of CH_3I to solutions of the $Ni(SBen{-}N(C_2H_5)_2)I$ complex in butanol, dimethylformamide, or benzene.

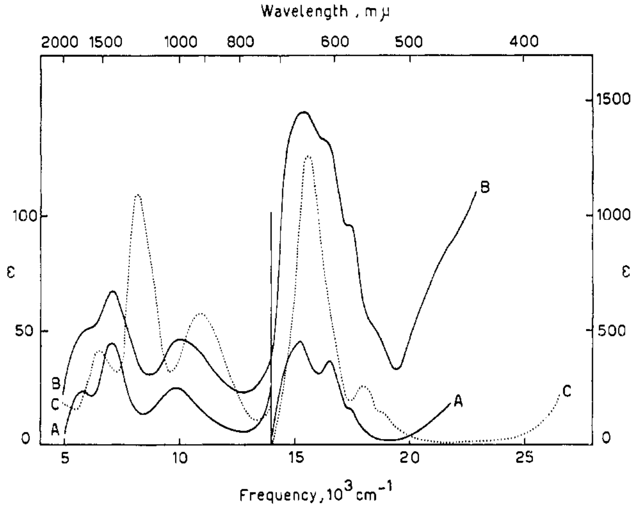


Figure 3.—Electronic spectra of some cobalt(II) complexes: A, absorption spectrum of $Co(MSBen{-}N(C_2H_5)_2)Br_2$ in 1,2-dichloroethane solution; B, reflectance spectrum of $Co(MSBen{-}N(C_2H_5)_2)Br_2$; C, absorption spectrum of $Co((CH_3)_4pn)(NCS)_2$ in dichloromethane solution.

Nickel(II) Thiocyanate.—The reflectance spectrum of this complex exhibits two maxima at 10,000 and 16,000 cm^{-1} and a shoulder at 24,000 cm^{-1} attributable to transitions ν_1 [$^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$], ν_2 [$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$], and ν_3 [$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$] in a symmetry field O_h.[7] The octahedral configuration is probably attained by means of polymeric thiocyanate bridges. In fact, the infrared spectra exhibit two bands at 2090 and 2120 cm^{-1}, which can be assigned to C–N stretching. These values are much higher than those found for monomeric nickel thiocyanate complexes, which must be presumably attributed to the thiocyanate groups acting as bridging linkages.[11,12]

Cobalt(II) Complexes.—The magnetic moments of the complexes $Co(MSBen{-}N(C_2H_5)_2)X_2$ where X = Cl, Br, or I have values in the range 4.66–4.72 BM. The solid and solution spectra (Figure 3) exhibit an absorption band in the region 6000–10,500 cm^{-1} with three peaks and two other strong absorption bands at 15,000 and 18,000 cm^{-1}. These bands are very similar to those observed for the distorted tetrahedral complexes of cobalt(II) of the type $Co((CH_3)_4pn)X_2$.[6] In accordance with other authors[13] the three bands in the range 6000–10,500 cm^{-1} have been assigned to the ν_2 transition $^4A_2(F) \rightarrow {}^4T_1(F)$ and the bands at 15,000 and 18,000 cm^{-1} to the ν_3 transition $^4A_2(F) \rightarrow {}^4T_1(P)$ for T_d symmetry. The large splitting of the components of the frequencies ν_2 and ν_3 can be attributed to large distortions from ideal tetrahedral symmetry.

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(8) A. D. Liehr and C. J. Ballhausen, *Ann. Phys.* (N. Y.), **6**, 134 (1959).

(9) F. A. Cotton and D. M. L. Goodgame, *J. Am. Chem. Soc.*, **82**, 5771 (1960); D. M. L. Goodgame and F. A. Cotton, *ibid.*, **82**, 5774 (1960); D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *ibid.*, **83**, 4161 (1961).

(10) S. E. Livingstone and T. N. Lockyer, *Inorg. Nucl. Chem. Letters*, **3**, 35 (1967); L. F. Lindoy, S. E. Livingstone, and T. N. Lockyer, *Inorg. Chem.*, **6**, 652 (1976), and references therein.

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

(12) R. J. H. Clark and C. S. Williams, *Spectrochim. Acta*, **22**, 1081 (1966), and references therein.

(13) D. L. M. Goodgame and M. Goodgame, *J. Am. Chem. Soc.*, **83**, 4690 (1961); *cf.* A. D. Liehr, *J. Phys. Chem.*, **67**, 1314 (1963).

Since these complexes are undissociated in solution, the tetrahedral configuration can be achieved only if one of the potential donor atoms of the Schiff base does not form a bond to the metal ion. The sulfur atom is probably the unbonded atom because of its low donor power with respect to that of the nitrogen atoms. The complexes of $Co(MABen\text{-}N(C_2H_5)_2)X_2$ (X = Cl, Br, I),[1] which have an $NH\text{-}CH_3$ group in the place of the $S\text{-}CH_3$ group studied here, form five-coordinate complexes which suggests that the previous suggestion is correct.

The high-spin complex $Co(MSBen\text{-}N(C_2H_5)_2)(NCS)_2$, which is monomeric and undissociated in dichloroethane solution, exhibits a spectrum different from that of the preceding complexes (Figure 4). The absorption bands, which occur at 5800, 13,000, 16,000, 17,500, and 18,500 cm^{-1}, can be correlated with those of $Co((CH_3)_5\text{-}dien)X_2$[5] which have been shown to possess a five-coordinate structure by X-ray crystal structure analysis.[6] The first two bands have been assigned[14] as transitions from the ground state to the $^4E''(F)$ and $^4E'(F)$ states in a D_{3h} symmetry field, respectively, and the other bands are derived from transitions to the levels which originate from the splitting of the ^4P level of the free ion.

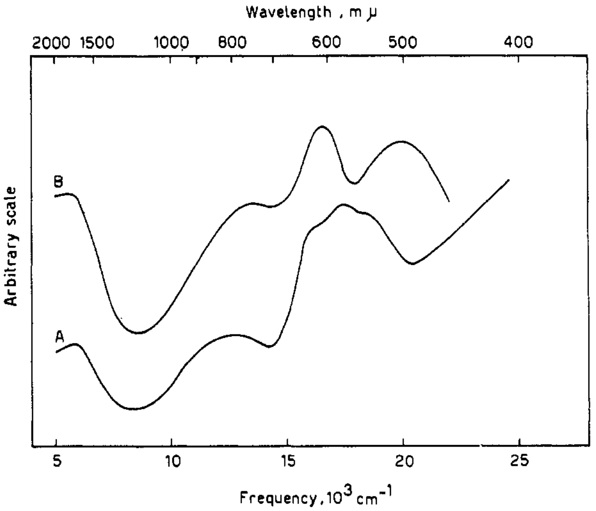

Figure 4.—Reflectance spectra of: A, $Co(MSBen\text{-}N(C_2H_5)_2)(NCS)_2$; B, $Co((CH_3)_5dien)(NCS)_2$ (M. Ciampolini, private communication).

The infrared spectrum of the complex $Co(MSBen\text{-}N(C_2H_5)_2)(NCS)_2$ exhibits two bands at 2060 and 2075 cm^{-1} assignable to the C–N stretching vibrations of the two thiocyanate groups. The values of the frequencies are in the range of those found for nitrogen-bonded thiocyanate complexes.[10]

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[14] M. Ciampolini, N. Nardi, and G. P. Speroni, *Coord. Chem. Rev.*, **1**, 222 (1966); M. Ciampolini and N. Nardi, *Inorg. Chem.*, **6**, 445 (1967).

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Multidentate Ligand Kinetics. XII. Ethylenediaminetetraacetate Ion Reaction with Mono- and Bis(diethylenetriamine)nickel(II) Complexes

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The stepwise process by which one multidentate ligand displaces another from a metal ion is observed in the reactions of $Ni(dien)_2^{2+}$ and $Ni(dien)^{2+}$ with EDTA. The bis-dien complex does not react directly with EDTA but must completely lose one dien first. The mono-dien complex reacts rapidly with EDTA to give $Ni(dien)EDTA^{2-}$ and this complex undergoes successive unwrapping of dien and increasing coordination to EDTA. Two successive first-order steps are observed before $NiEDTA^{2-}$ and dien are produced. Excess $Ni(dien)^{2+}$ can slow the reaction with EDTA owing to the formation of a bridged EDTA species, [Ni(dien)EDTA(dien)Ni]. Difference spectral studies indicate another possible bridged species, $[Ni(dien)(EDTA)Ni(EDTA)(dien)Ni]^{2-}$.

Introduction

The mechanism by which one multidentate ligand displaces another from a metal ion depends on the ability of both ligands to coordinate the metal simultaneously. It may be necessary to replace segments of the initially bound ligand by solvent before an incoming ligand can gain a coordination foothold. The more segments which must be unwrapped from the metal the slower the reaction. Thus, the EDTA[1] reaction with nickel–trien is faster than its reaction with nickel–tetren[2] and both are much faster than the EDTA reaction with nickel–CyDTA.[3] In the latter case complete dissociation of CyDTA from nickel occurs before EDTA reacts. In the present study the tridentate

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[1] Abbreviations used are: dien, diethylenetriamine; trien, triethylenetetramine; tetren, tetraethylenepentamine; EDTA, ethylenediaminetetraacetate ion; CyDTA, cyclohexylenediaminetetraacetate ion.

[2] D. B. Rorabacher and D. W. Margerum, *Inorg. Chem.*, **3**, 382 (1964).

[3] W. J. Huber, M.S. Thesis, Purdue University, 1964.