metrical and well defined than those of [Ni(triarsine)-Br_2]. A square-pyramid (with the L_{apex}–Ni–L_{base} angle probably >90°) is the easiest structure to visualize for the complexes containing two bidentates and one halide, with the bidentate ligands forming the square base and the halide in the apical position. The absorption spectra are consistent with a square-pyramidal structure. Obviously, the spectral and structural correlation will be definitive only when one or two of these structures are determined by X-ray crystallography and must be considered tentative until then.

In any case, a very significant conclusion from this investigation is that five-coordination with nickel(II) is quite general for ligands containing π-bonding atoms such as phosphorus, arsenic, sulfur, and selenium, and it does not depend on using a ligand with highly specific steric effects, such as a "tripod" tetradentate, at least in the diamagnetic series of nickel(II) complexes.[25,26]

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(25) A referee has pointed out that all of the ligands used in this study contain a phenyl–phosphorus linkage and that the *o*-hydrogen may be partially responsible for denying stereochemical access of a sixth ligand to the coordination sphere. Such an effect is important in the case of [Ru(P-$(C_6H_5)_3)_3Cl_2$].[26] The fact that we have prepared (this paper) paramagnetic, pseudo-octahedral [Ni(SP)$_2$Cl$_2$] and [Ni(SeP)$_2$Cl$_2$] complexes illustrates that the sixth coordination site is not blocked. Also, the electronic ground state of all these five-coordinate complexes is a singlet. If the *o*-hydrogen functioned to block access to one of the coordination positions, the electronic ground state should be a triplet due to the use of thiomethyl and selenomethyl donors.[20] Therefore, we believe the primary factor involved in formation of these diamagnetic, five-coordinate complexes is the use of the π-bonding donor atoms, which reduce the interelectronic repulsion parameters and create a favorable electronic state for five-coordination. In any case, the results of an X-ray investigation, currently underway, should settle this point.

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

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The tridentate Schiff base formed from N-methyl-*o*-aminobenzaldehyde and N,N-diethylethylenediamine (MABen-NEt_2, set of donor atoms NNN) forms high-spin complexes with Ni(II), Co(II), and Mn(II) salts of the general formula M(MABen-NEt_2)X_2. The stereochemistry of these complexes, both in the solid state and in solution, has been studied with magnetic and spectrophotometric measurements. The complexes of metal halides are five-coordinate; those with nickel(II) thiocyanate and nickel(II) nitrate are six-coordinate, the former through bridging linkages, the latter through bidentate and monodentate nitrate groups. In solution the Ni(II)–halide complexes give rise to a five-coordinate ⇄ tetrahedral equilibrium.

Introduction

The first examples of high-spin five-coordinate complexes of nickel(II) and cobalt(II) have recently been described and characterized.[1] The most favorable ligands appear to be those which have strongly electronegative donor atoms (oxygen, nitrogen, halogens) and have little tendency to form π bonds with the metal ion. Moreover, to obtain five-coordination the ligands should provide steric hindrance, so that six-coordination is prevented, and be polydentate, so that rigidity may be imparted to the complex.

Some Schiff bases, which are formed from ring-substituted salicylaldehydes and N,N-disubstituted ethylenediamines, having the general formula $XC_6H_3(OH)$-$CH{=}N(CH_2)_2N(R)R'$ (X–SALen–N(R)R′), appear to be able to form high-spin five-coordinate complexes.[1a,b] X-Ray structure analysis has shown that 5-Cl–SALen-NEt_2 forms nickel(II) and cobalt(II) complexes with a distorted square-pyramidal configuration in which one ligand molecule is bidentate while the other is tridentate.[2] The steric hindrance and the electronic effects caused by two ethyl groups on the β nitrogen seem to be critical. In fact, among a large number of ligands with different substituents on the β nitrogen, only the diethyl derivatives form five-coordinate complexes, while the others give four- or six-coordinate complexes.[1a,3] Other ligands such as those formed from polymethyl polyamines like $MeN(CH_2CH_2NMe_2)_2$ (Me_5dien) or $N(CH_2CH_2NMe_2)_3$ (Me_6tren) function as tri- or tetradentates with donor atom sets N_3 or N_4, to give five-coordinate complexes with the bivalent metals of the first transition series by coordination of

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(1) (a) L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *Inorg. Chem.*, **4**, 943 (1965); (b) L. Sacconi, M. Ciampolini, and G. P. Speroni, *ibid.*, **4**, 1116 (1965); (c) L. Sacconi, M. Ciampolini, and G. P. Speroni, *J. Am. Chem. Soc.*, **87**, 3102 (1965); (d) M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966); (e) M. Ciampolini and G. P. Speroni, *ibid.*, **5**, 45 (1966); (f) L. Sacconi and I. Bertini, *J. Am. Chem. Soc.*, **88**, 5180 (1966).

(2) L. Sacconi, P. L. Orioli, and M. Di Vaira, *ibid.*, **87**, 2059 (1965); P. L. Orioli, M. Di Vaira, and L. Sacconi, *ibid.*, **88**, 4383 (1966).

(3) L. Sacconi, P. Nannelli, and U. Campigli, *Inorg. Chem.*, **4**, 818 (1965).

TABLE I

PHYSICAL AND ANALYTICAL DATA FOR $M(MABen\text{-}NEt_2)X_2$ COMPLEXES

Complexes	Color	Molar conductance, cm^2/ohm M[a,b]	i[c]	N, %		Metal, %		Halogen, %	
				Calcd	Found	Calcd	Found	Calcd	Found
$Ni(MABen\text{-}NEt_2)Cl_2$	Amber-yellow	0.147	1.04	11.57	11.69	16.18	16.31	19.54	19.80
$Ni(MABen\text{-}NEt_2)Br_2$	Amber-yellow	0.319	1.00	9.30	9.34	13.00	13.07	35.37	35.14
$Ni(MABen\text{-}NEt_2)I_2$	Amber-yellow	1.947	1.06	7.70	7.84			46.49	45.73
$Ni(MABen\text{-}NEt_2)(NCS)_2$	Light green			17.15	16.95	14.38	14.48		
$Ni(MABen\text{-}NEt_2)(NO_3)_2$	Light green	0.135	1.06	16.84	17.01	14.11	14.28		
$Co(MABen\text{-}NEt_2)Cl_2$	Dark green	0.136	1.10	11.57	11.40			19.53	19.87
$Co(MABen\text{-}NEt_2)Br_2$	Dark green	0.202	1.02	9.30	9.25			35.35	35.84
$Mn(MABen\text{-}NEt_2)Br_2$	Yellow			9.36	9.55			35.66	35.25

[a] For *ca.* 10^{-3} M solutions in dichloroethane at 25°. [b] Reference value under the same conditions: $[(n\text{-}C_4H_9)_4N]Br$, 19. [c] van't Hoff coefficients for *ca.* 10^{-2} M solutions at 37°.

two or one anion groups to the metal.[1d,e] We have investigated a new ligand, the Schiff base formed by condensation of N,N-diethylethylenediamine and N-methyl-*o*-aminobenzaldehyde ($o\text{-}C_6H_4(NHCH_3)CH{=}N\text{-}(CH_2)_2NEt_2$), which differs from SALen–NEt_2 ligands in that it cannot be deprotonized, is potentially tridentate like Me_5dien, and possesses opportune steric hindrance on the β nitrogen. With nickel(II), cobalt(II), and manganese(II) salts this ligand, hereafter abbreviated MABen–NEt_2, forms complexes with the general formula $M(MABen\text{-}NEt_2)X_2$ where X = Cl, Br, I, NCS, or NO_3. The stereochemistry and the properties of such complexes have been studied by means of spectrophotometric, magnetic, and electric conductivity measurements, and the results are reported in this paper.

Experimental Section

Materials.—All the solvents were of reagent grade quality. Dichloroethane was washed with 5% sodium bicarbonate solution, dried over calcium chloride, and distilled. 1-Butanol was refluxed and distilled over barium oxide.

Synthesis of the Ligand.—N-Methylanthranilic acid, obtained by methylation of anthranilic acid with methyl sulfate,[4] was reduced with $LiAlH_4$ to N-methyl-*o*-aminobenzyl alcohol.[5] This was in turn oxidized to N-methyl-*o*-aminobenzaldehyde (MAB) with active manganese dioxide.[6] The aldehyde was distilled at 77–78° (1 torr) (lit.[7] 112° (10 torr); phenylhydrazone, mp 125°, lit.[7] 124°). To obtain the Schiff base, stoichiometric amounts of MAB and N,N-diethylethylenediamine were refluxed together in the presence of anhydrous sodium acetate, and the final product was distilled at 132–135° (1 torr).

General Preparation of Complexes.—Hot solutions of the appropriate metal salt (0.025 mole) in 1-butanol (20 ml) and MABen–NEt_2 (0.6 g, 0.026 mole) in 1-butanol (10 ml) were mixed. The solution was filtered, concentrated until crystals began to precipitate, and cooled. In some cases, cyclohexane was added in order to promote crystallizaton. The crystalline compounds were filtered on a sintered glass plate, washed with cyclohexane, and dried in a vacuum oven at 70°. They were recrystallized from 1-butanol. The cobalt and manganese complexes were prepared, filtered, and recrystallized under dry nitrogen atmosphere in order to avoid oxidation. Attempts to prepare the CoI_2, $Co(NCS)_2$, and $Co(NO_3)_2$ complexes were unsuccessful.

Spectrophotometric Measurements.—The absorption spectra were recorded with a Beckman DK2 spectrophotometer using 1-cm silica cells. Concentrations of the solutions were about 5 × 10^{-3} M in dichloroethane. The absorption spectra at various temperatures were recorded using *o*-dichlorobenzene as solvent. Temperatures from 20 to 110° were obtained by circulating paraffin oil from a thermostat regulated to ±0.5° through a cell housing designed and constructed in this institute. Allowance was made for the temperature variation of solution density when calculating extinction coefficients. The reflectance spectra were measured with the standard Beckman attachment using magnesium oxide as reference. The infrared spectra were recorded with a Perkin-Elmer Model 337 spectrophotometer using Nujol mulls supported on CsBr plates.

Conductivity Measurements.—The molar conductivity values were measured on a WTW Model LBR/B conductance bridge. Concentrations of the solutions were approximately 10^{-3} M.

Molecular Weight Measurements.—Molecular weights were determined in dichloroethane at 37° with a Mechrolab Model 301 A vapor pressure osmometer calibrated with benzyl. Scale readings were made 4.5 min after the drop of the solution was placed on the thermistor. Concentrations of the solutions were about 10^{-2} M.

Magnetic Measurements.—The magnetic susceptibility measurements were performed by the Faraday method, using a Sartorius electrobalance and an electromagnet with specially shaped pole tips.[8] The calibration was made with $Hg[Co(NCS)_4]$.[9] Diamagnetic corrections were calculated from the Pascal constants.[10]

Results

All the complexes are crystalline, slightly hygroscopic, and decompose in water. The cobalt(II) and manganese(II) complexes are not oxidized appreciably in dry air or in solution. Analytical data, molar conductivity values, and measurements of molecular weights in dichloroethane are reported in Table I. All the complexes, except $Ni(MABen\text{-}NEt_2)(NCS)_2$, are soluble in common polar organic solvents, such as nitro and chloro derivatives. On standing in air these solutions become turbid.

The magnetic moments at room temperature are listed in Table II. The complexes are all of the high-spin type, and in each case the orbital contributions are relatively small. The magnetic moments of the nickel(II) complexes range from 3.12 to 3.32 BM. Those of the cobalt(II) complexes range from 4.75 to 4.85 BM

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[10] Reference 9, p 403.

Table II

Magnetic Data for M(MABen–NEt$_2$)X$_2$ Complexes

Compound	T, °C	$\chi_g \times 10^6$	$\chi_{Me} \times 10^6$	μ_{eff}, BM
Ni(MABen–NEt$_2$)Cl$_2$	20	12.29	4671	3.32
Ni(MABen–NEt$_2$)Br$_2$	20	9.44	4501	3.26
Ni(MABen–NEt$_2$)I$_2$	20	7.01	4115	3.12
Ni(MABen–NEt$_2$)(NCS)$_2$	20	10.11	4358	3.21
Ni(MABen–NEt$_2$)(NO$_3$)$_2$	20	9.57	4232	3.16
Co(MABen–NEt$_2$)Cl$_2$	20	26.44	9814	4.82
Co(MABen–NEt$_2$)Br$_2$	20	20.08	9310	4.70
Mn(MABen–NEt$_2$)Br$_2$	20	31.81	14488	5.86

and are intermediate between those found for tetrahedral and octahedral complexes.

The values of molar conductivity, measured at 25° in *ca.* 10^{-3} M solutions in dichloroethane, all fall within the range 0.14–1.9 ohm^{-1} cm^2 mole^{-1} and are less than 10% of those found for 1:1 electrolytes (17–20 ohm^{-1} cm^2 mole^{-1} under the same conditions). This indicates that the complexes are only dissociated to a small extent as is also indicated by the values of molecular weights determined in the same solvent, which are slightly less than those calculated for the monomeric formula (Table I). It may therefore be concluded that in solution all the complexes are largely present as nonionic monomeric species.

The spectra of these complexes in the crystal field region have been measured in both the solid state and in solution up to 20,000–23,000 cm^{-1}, where an intense band appears which is probably due to charge transfer. Frequencies of the maxima and their molar absorbances are given in Table III, while the spectra of nickel complexes are illustrated in Figures 1, 4, and 5 and those of cobalt complexes in Figure 6. In each case the reflectance spectra do not differ appreciably from those in solution in inert solvents like dichloroethane and *o*-dichlorobenzene. Furthermore, the spectra of the chloro and bromo complexes for a given metal are very similar. Small displacements of the frequencies of the maxima can be correlated with the respective positions of the halogens in the spectrochemical series. Essentially the same stereochemistry may therefore be assigned to these complexes. The spectrum of the nickel iodide complex shows differences in both the form and frequency which cannot be attributed to the difference in field strength between iodine and the other halogens. The spectra of the nickel nitrate and nickel thiocyanate complexes, although they are almost identical, are completely different from those of the halide complexes. The absorption spectra of the complexes Ni(MABen–NEt$_2$)Br$_2$ and Ni(MABen–NEt$_2$)I$_2$ have been measured in *o*-dichlorobenzene solution at various temperatures ranging from 18 to 110° (Figures 2 and 3). In this range the decreasing intensity and disappearance of some maxima and the appearance of new maxima, with the presence of two isosbestic points, is indicative of the presence of two forms in equilibrium.

Infrared spectra have been measured in the 4000–400 cm^{-1} range. N–H stretching vibration frequencies are generally lowered by 80–120 cm^{-1} with respect to the value of 3350 cm^{-1} found for the free ligand. This shift in frequency indicates metal–nitrogen bonding. Only the nickel chloride complex shows a lowering of 190 cm^{-1}, which is presumably also caused by stronger hydrogen bonding. The frequencies assigned to vibrations of the nitrate and thiocyanate groups are discussed later.

Table III

Spectroscopic Data for M(MABen–NEt$_2$)X$_2$ Complexes

Compound	State	Absorption max, cm^{-1} (ϵ_{molar} for soln)
Ni(MABen–NEt$_2$)Cl$_2$	Solid	8300, 12,800, 19,200 sh
	(CH$_2$Cl)$_2$	8700 (18), 13,300 (40), 19,400 (35.6)
Ni(MABen–NEt$_3$)Br$_2$	Solid	8160, 12,400, 18,100 sh
	o-Cl$_2$C$_6$H$_4$	8600 (18.6), 13,100 (47.6), 18,100 sh
Ni(MABen–NEt$_2$)I$_2$	Solid	<5000, 8700 sh, 9700 sh, 11,100 sh, 14,300, 18,000 sh
	(CH$_2$Cl)$_2$	<5000, 9700 sh, 11,100 sh, 13,700 (68), 18,000 sh
Ni(MABen–NEt$_2$)(NCS)$_2$	Solid	10,300, 16,130
Ni(MABen–NEt$_2$)(NO$_3$)$_2$	Solid	10,750, 16,600
	(CH$_2$Cl)$_2$	10,750 (21), 16,600 (24)
Co(MABen–NEt$_2$)Cl$_2$	Solid	5200, 9500, 11,100 sh, 15,600, 16,700 sh, 17,800 sh
	(CH$_2$Cl)$_2$	9500 (23), 11,700 sh, 15,800 (187), 16,700 sh, 17,800 sh
Co(MABen–NEt$_2$)Br$_2$	Solid	≈5000, 9300, 11,100 sh, 15,800, 16,700 sh, 17,400 sh
	(CH$_2$Cl)$_2$	9100 (29.2), 11,600 sh, 15,400 (220), 16,300 sh, 17,200 sh

The X-ray diffraction powder photograms of the M(MABen–NEt$_2$)Br$_2$ complexes are indistinguishable, which indicates that the same stereochemistry may be attributed to all the complexes of this type.

Discussion

Nickel Chloride and Bromide.—Spectral data in the crystal field region indicate that the same stereochemistry may be assigned to both of these complexes in the solid state and in solution. As the complexes are monomeric and undissociated in solution and the ligand is potentially tridentate, the coordination number of nickel cannot be greater than five. Since the complexes are of the high-spin type, a square-planar structure is not possible. Furthermore, the spectral data in the 5000–20,000 cm^{-1} region cannot be consistently interpreted on the basis of a pseudo-tetrahedral structure, which would be derived by coordination of only two nitrogen atoms. On the other hand, these spectra appear to be similar to those of other high-spin complexes to which a five-coordinate structure has been attributed. In particular, the bands at 8300, 12,800, and 19,200 cm^{-1} for Ni(MABen–NEt$_2$)Cl$_2$ can be correlated with those at 9600, 12,700, and 18,900 cm^{-1} for the five-coordinate Ni(Me$_5$dien)Cl$_2$,[1e] which also has a N$_3$Cl$_2$ set of donor atoms (Figure 1). The bands of Ni(Me$_5$dien)Cl$_2$ are displaced by 1500–2000 cm^{-1}

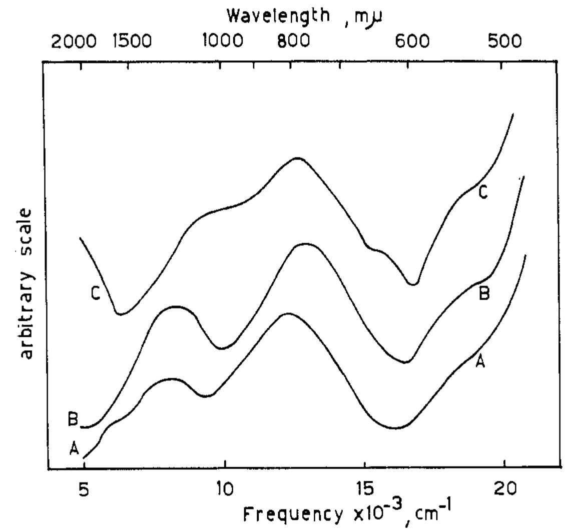

Figure 1.—Reflectance spectra of: Ni(MABen–NEt$_2$)Br$_2$, curve A; Ni(MABen–NEt$_2$)Cl$_2$, curve B; Ni(Me$_5$dien)Cl$_2$, curve C.

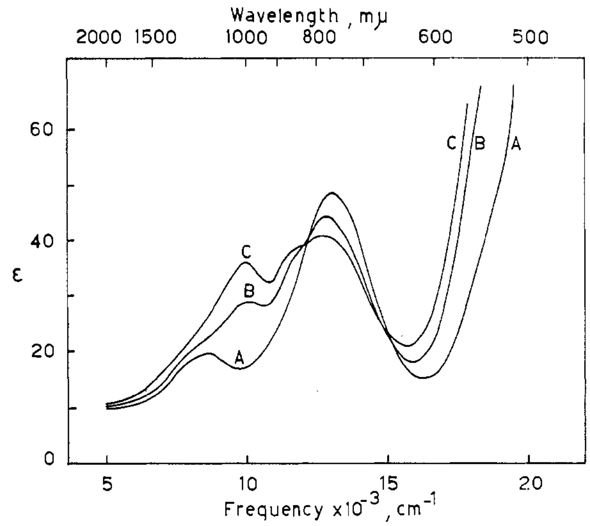

Figure 2.—Absorption spectra of Ni(MABen–NEt$_2$)Br$_2$ in *o*-Cl$_2$-C$_6$H$_4$ solution: (A) at 18.5°; (B) at 80°; (C) at 110°.

toward lower frequencies with respect to those for [Ni(Me$_6$tren)Cl]Cl with an N$_4$Cl set of donor atoms.[1d] The latter are in reasonable agreement with those calculated for a regular trigonal bipyramidal configuration.[11]

Further evidence for a five-coordinate structure is indicated by the absorption spectra of a solution of Ni(MABen–NEt$_2$)Br$_2$ at various temperatures (Figure 2). Increasing the temperature gradually to 110° causes a decrease in intensity of the band at 13,100 cm^{-1} and the appearance of two new bands at *ca.* 9800 and 11,000 cm^{-1}. The new bands are identical with those which appear in the spectra of the pseudo-tetrahedral Ni(Me$_4$tn)X$_2$ complexes,[12] where Me$_4$tn is N,N,N′,N′-tetramethyltrimethylenediamine, and have been assigned to a spin-allowed ν_2 $^3T_1(F) \rightarrow {}^3A_2(F)$ transition in fields with T$_d$ symmetry and to a spin-forbidden transition to a higher state derived from the ^1D state of the free ion.[13,14] The equilibrium, which is reversible, can be explained by considering the strain in the bonds of the tridentate ligand. When the temperature is increased one of the atoms which is coordinated to the metal ion is detached, forming a pseudo-tetrahedral structure. Presumably this atom is either the terminal nitrogen of the ethylenediamine group or the nitrogen attached to the benzene ring. This hypothesis is confirmed by conductivity measurements, which indicate that neither of the halide atoms is dissociated at 80°.

Nickel Iodide.—The spectrum of this complex is slightly different from that of the previous ones in both the solid state and in solution. There is a broad asymmetrical band at higher frequencies (8000–15,000 cm^{-1}) instead of the two bands in the near-infrared region. This displacement cannot be correlated with the respective position of the halogen in the spectrochemical series. However, the solution spectrum of this complex at 80° can be interpreted as pseudo-tetrahedral as in the case of Ni(MABen–NEt$_2$)Br$_2$ (Figure 3). The solution spectrum at room temperature is similar (Figure 4) to that of Ni(Me$_4$daeo)X$_2$ complexes (Me$_4$daeo = O(CH$_2$CH$_2$NMe$_2$)$_2$) to which a five-coordinate structure has been attributed.[15] When the symmetry decreases, the spectrum of five-coordinate complexes in the near-infrared region changes from four bands, attributable to the splitting of the ^3F term for complexes with D$_{3h}$ symmetry, to one very broad band with several weak shoulders (6000–15,000 cm^{-1}).[15] It is therefore not unreasonable to assume that the nickel iodide complex also has a five-coordinate structure but with a lower symmetry than in the case of the previous complexes. Furthermore, as has already been observed, the lower symmetry of the five-coordinate structure, when compared with that of tetrahedral or octahedral structure, causes the splitting of the nickel(II) terms into a relatively large number of levels and, thus, small geometrical distortions can invert the order of these levels resulting in marked variations in the spectrum. In this case it has been shown by using Stuart models that the greater steric hindrance of the iodide ion may cause a larger distortion than in the analogous chloride and bromide complexes. The fact that at 80° the five-coordinate ⇄ tetrahedral equilibrium is strongly displaced toward the second species for the iodide complex in contrast to its bromide analog (see Figures 2 and 3) confirms that the former must overcome a stronger internal strain to achieve five-coordination.

Nickel Nitrate and Thiocyanate.—The crystal field spectra of these complexes show two diffuse bands at *ca.* 10,000 and 16,000 cm^{-1} which can be assigned to the transitions ν_1 $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$ and ν_2 $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ in fields with O$_h$ symmetry (Figure 5).[13]

The nickel nitrate complex is soluble in inert organic solvents like dichloroethane and chloroform, and in these solutions it is monomeric and nonionic. It is

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[15] M. Ciampolini and N. Nardi, *Inorg. Chem.*, **6**, 445 (1967).

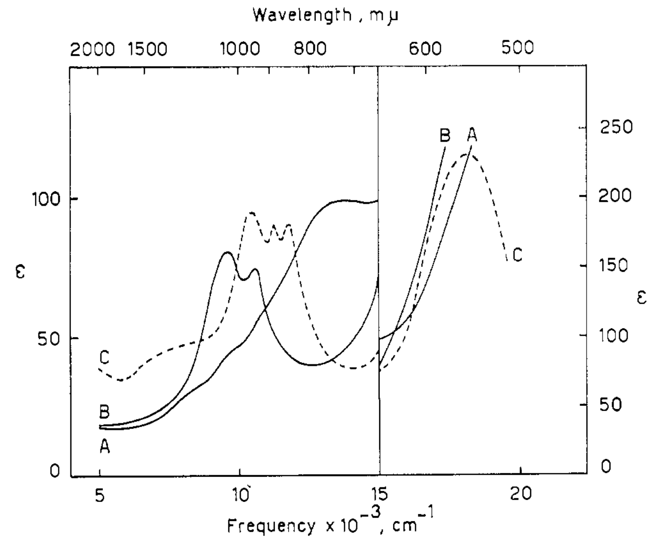

Figure 3.—Absorption spectra of Ni(MABen–NEt$_2$)I$_2$ in *o*-Cl$_2$C$_6$H$_4$ solution: (A) at 20°; (B) at 80°. Absorption spectrum of Ni(Me$_4$tn)I$_2$ in C$_6$H$_6$ solution at 25° (C, dashed line).

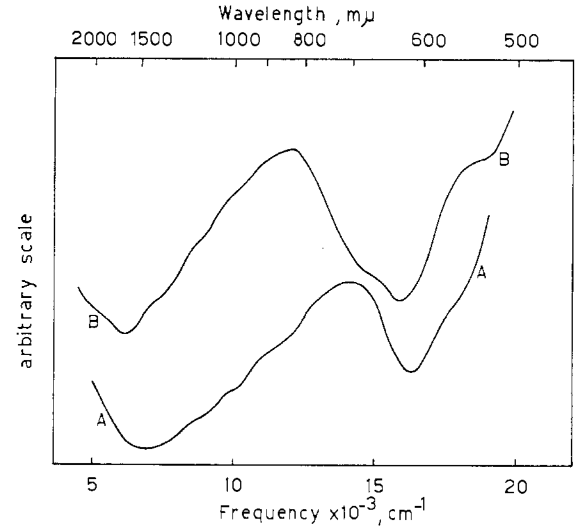

Figure 4.—Reflectance spectra of: Ni(MABen–NEt$_2$)I$_2$, curve A; Ni(Me$_4$daeo)Br$_2$, curve B.

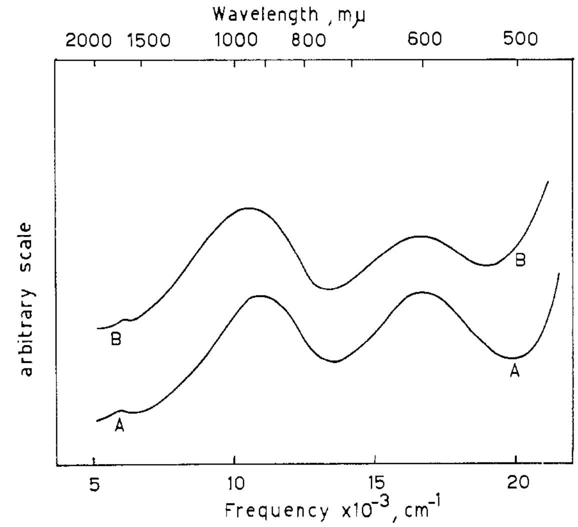

Figure 5.—Reflectance spectra of: Ni(MABen–NEt$_2$)(NO$_3$)$_2$, curve A; Ni(MABen–NEt$_2$)(NCS)$_2$, curve B.

therefore impossible that the coordination number six is reached *via* polymerization. The infrared spectrum of this complex shows four strong bands in the 1200–1500 cm^{-1} region which are attributable to the nitrate ion. The free nitrate ion (D$_{3h}$ symmetry) shows a single band of the species E′ at *ca.* 1370 cm^{-1}. In the case of both monodentate and bidentate (C$_{2v}$ symmetry) coordinate nitrate ions this band is split into two components (A$_1$ + B$_2$).[16,17] The magnitude of this splitting is greater for the bidentate than for the monodentate nitrate group.[17] On this basis the two bands at 1260 and 1500 cm^{-1}, with a splitting of 240 cm^{-1}, have been assigned to a bidentate nitrate group and those at 1310 and 1450 cm^{-1}, with a splitting of 140 cm^{-1}, to a monodentate nitrate group, both of which are present in the molecule. Other bands expected for the nitrate group, which are generally rather weak, have not been assigned, as they are probably masked by those of the organic ligand. On this basis it may be concluded that the octahedral structure of this complex is achieved *via* a monodentate nitrate group and a bidentate nitrate group.

The infrared spectrum of the thiocyanate complex shows two bands (2090, 2130 cm^{-1}), in the C–N stretching region. The values of these frequencies are higher than those found for monomeric complexes of nickel thiocyanate.[18,19] This is presumably due to the thiocyanate groups acting as bridging linkages. The value of the C–S stretching frequency (790 cm^{-1}) is also in the range of those found for polymeric octahedral complexes of nickel thiocyanate.[19] The insolubility of this complex in inert organic solvents, like dichloroethane, is in accordance with the hypothesis that six-coordination is achieved *via* intermolecular bridge bonds (Ni–NCS–Ni) of the thiocyanate groups, which give rise to a polymeric structure.

Cobalt Chloride and Bromide.—The spectra of these complexes are shown in Figure 6. They are very similar to those of other high-spin cobalt complexes, like Co(Me$_5$dien)Cl$_2$,[1e] for which a distorted five-coordinate structure has been shown by means of X-ray crystallography.[20] This complex and the analogous bromide and iodide complexes show bands at *ca.* 4000, 8800, 10,500, and 16,200 cm^{-1} which can be correlated with those at 5000, 9500, 11,000, and 15,600 cm^{-1} for Co(MABen–NEt$_2$)X$_2$ (Figure 6). The first three bands are assignable to transitions between levels originating from splitting of the ^{4}F term. As for other five-coordinate complexes the first band is assignable to a $^4A_2'(F) \rightarrow {}^4E''(F)$ transition and the other two to the two components of the $^4A_2'(F) \rightarrow {}^4E'(F)$ transition in D$_{3h}$ symmetry.[15] The fact that the latter tran-

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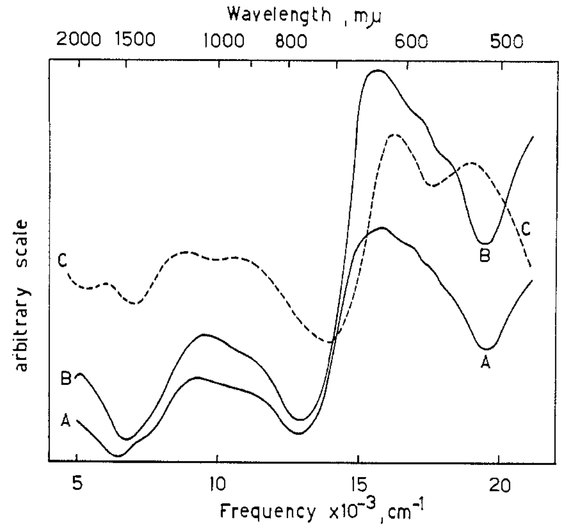

Figure 6.—Reflectance spectra of: $Co(MABen\text{-}NEt_2)Br_2$, curve A; $Co(MABen\text{-}NEt_2)Cl_2$, curve B; $Co(Me_5dien)Cl_2$, curve C.

sition is split into two components with an energy difference of *ca.* 1500 cm^{-1} is indicative of a high distortion in these complexes. The final band, which is due to a $^4A_2'(F) \rightarrow {}^4A_2'(P)$ transition, is expected to be almost independent of the ligand field strength and the geometry of the complex and is, as anticipated, around 16,000 cm^{-1}.

The magnetic moments are also in the same range as those found for other five-coordinate cobalt complexes (4.7–4.8 BM). All the physical measurements therefore suggest that a five-coordinate structure may also be assigned to the cobalt complexes, as is confirmed by the isomorphism between $Co(MABen\text{-}NEt_2)Br_2$ and the corresponding nickel complex.

Manganese Bromide.—The crystal field spectra of manganese complexes, as is well known, are of little use in determining the stereochemistry. The only useful correlation is therefore given by X-ray diffraction powder photograms which show the complex to be isomorphous with its cobalt and nickel analogs. This suggests that it may also be assigned a similar five-coordinate structure.

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The Crystal Structure of *trans*-Bis(phenylethynyl)bis(triethylphosphine)nickel(II), $[P(C_2H_5)_3]_2Ni(C{\equiv}CC_6H_5)_2$

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The crystal structure of *trans*-bis(phenylethynyl)bis(triethylphosphine)nickel(II), $[P(C_2H_5)_3]_2Ni(C{\equiv}CC_6H_5)_2$, has been determined from three-dimensional counter data at room temperature. The crystals are monoclinic ($P2_1/a$), with $a = 15.31$, $b = 10.88$, $c = 9.08$ A (all ±0.01 A), and $\beta = 105° \ 30' \pm 10'$. The structure consists of discrete molecules separated by ordinary van der Waals distances. Space group symmetry demands that the Ni atom and its four nearest neighbors be coplanar. The Ni–P bond length was found to be 2.220 ± 0.003 A, while the Ni–C distance is 1.879 ± 0.011 A. Both are significantly shorter than what is expected for "single" bonds and indicate substantial $d\pi\text{–}d\pi$ and $d\pi\text{–}p\pi$ interaction. The acetylenic and benzene C–C distances appear normal, as do the bond distances in the triethylphosphine groups. The benzene ring is tilted by 43.6 ± 0.5° to the Ni–P–C plane.

Introduction

In general, transition metal to alkyl or aryl M–C σ bonds are unstable at room temperature as well as air and water sensitive. However, if strongly π-bonding ligands such as CO, $\pi\text{-}C_5H_5$, phosphines, or arsines are also present in the molecule, then stable alkyls and aryls can be prepared, *e.g.*, *cis*-$(PR_3)_2Pt(CH_3)_2$.[1] If, in addition to the presence of one of the π-bonding ligands in the molecule, the carbon σ bonded to the transition metal is involved in an acetylenic bond, then the metal–carbon bond is still further stabilized.[2] This increase in stability of the metal–carbon bond by the above ligands is generally attributed to the fact that these ligands tend to increase the separation between the highest filled and lowest empty MO's.[1-3] Similar reasoning can be used to explain the increasing M–C stability with increasing atomic number in the series Pt > Pd > Ni as observed by Chatt and Shaw. The transition metal–carbon σ bond can also be stabilized by making the carbon part of a highly fluorinated alkyl

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