(II) complexes derived from diimine ligands of salicylaldehyde (structure III), observed the following order of ligand field strength for R bridging groups: $-CH_2CH_2- > -CH_2CH_2CH_2- > -CH_2(CH_2)_2CH_2-$. The trend agrees with the order in this work in that chain lengthening in the central ring lowers the ligand field strength of the ligand. At the only two points of comparison, the tri- and tetramethylene bridges, the pyrrole-derivative ligands are stronger than the corresponding salicylaldiimine ones by about 3800 cm^{-1}. If this value is applied to the complexes reported here, the ligand field transition of ligands with a two-carbon chain would be extrapolated to near 460 mμ and would consequently be covered by a more intense band.

Conclusions.—It has been possible to synthesize and characterize planar nickel(II) complexes of tetradentate ligands which have the unusual central ring sizes of seven and eight. From ligand field spectra it has been shown that the ligand field decreases in the monomeric planar complexes as the size of the central ring increases. These tetradentate ligands containing four nitrogen donor atoms are stronger than the bidentate pyrrole-2-methylenimine ligands and are stronger than ligands in the salicylaldehyde system containing two oxygen and two nitrogen donor atoms.

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Metal Complexes of N,N,N′,N′-Tetramethyldiamines. I. Nickel(II) and Cobalt(II) Complexes

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Complexes of N,N,N′,N′-tetramethylated ethylenediamine (Me_4en), 1,2-propylenediamine (Me_4pn), and trimethylenediamine (Me_4tn) with nickel(II) and cobalt(II) salts have been prepared and investigated. Compounds of the type M(diamine)X_2 (M = Co, Ni and X = Cl, Br, I, NO_3, NCS) with tetrahedral and octahedral structures were obtained. The stereochemistry of the complexes, both in the solid state and in solution, is discussed on the basis of their magnetic and spectral properties. The tendency of the diamines to form tetrahedral complexes is found to increase in the order $Me_4en < Me_4pn < Me_4tn$.

Introduction

Many compounds of nickel(II) with N- and C-substituted ethylenediamines have been described and studied.[1,2] These have been found to have a planar or an octahedral structure. The latter configuration has also been assigned to some nickel(II) derivatives of C-substituted ethylenediamines (phenylethylenediamine, stilbenediamine) which were originally considered to be tetrahedral.[3] To our knowledge, however, no systematic investigation has been made on the ability of N,N,N′,N′-tetramethylated ethylenediamine (Me_4en), 1,2-propylenediamine (Me_4pn), and trimethylenediamine (Me_4tn) to form complexes with nickel(II) and cobalt(II) salts. Only the complex Ni(Me_4en)$(NO_2)_2$ has recently been prepared[4] and it has been found to have hexacoordinate structure with two bidentate nitro groups.[5]

We have found that, in anhydrous and noncoordinating solvents, nickel(II) and cobalt(II) halides, nitrates, and thiocyanates react with Me_4en, Me_4pn, and Me_4tn to give complexes of the general formula M(diamine)X_2.[6] The stereochemistry and the properties of these complexes have been studied, and the results are reported in this paper.

Experimental Section

Preparation of the Compounds.—The diamines were methylated, with a mixture of formic acid and formaldehyde, using standard methods. All of the complexes were prepared by the same general method. A solution of 10 mmoles of the diamine ligand in 20 ml of dry butanol was added slowly to a hot solution of 10 mmoles of the appropriate metal salt in 50 ml of butyl alcohol, which had previously been distilled over BaO. After boiling for some minutes, the solution was filtered and concentrated, and a precipitate was generally obtained. In some cases cyclohexane was added to promote precipitation. The crystals were collected by filtration and dried in a stream of dry nitrogen. The analytical data are reported in Table I.

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TABLE I

ANALYTICAL DATA FOR THE N,N,N′,N′-TETRAMETHYLDIAMINE NICKEL(II) AND COBALT(II) COMPLEXES

Compound	Mp, °C	% nitrogen Calcd	% nitrogen Found	% halogen Calcd	% halogen Found	% metal Calcd	% metal Found
$Ni(Me_4en)Cl_2$	>300	11.40	11.30	28.85	28.85		
$Ni(Me_4en)Br_2$	198–202	8.35	8.44	47.85	48.05		
$Ni(Me_4en)I_2$	212–218	6.54	6.33	59.30	59.09		
$Ni(Me_4en)(NCS)_2$	>300	19.24	19.53			20.17	19.86
$Ni(Me_4en)(NO_3)_2$	181–183	18.70	18.54			19.64	19.69
$Ni(Me_4pn)Cl_2$	300 dec	10.76	10.45	27.32	27.12		
$Ni(Me_4pn)Br_2$	222–225	8.02	7.73	45.80	46.10		
$Ni(Me_4pn)I_2$	226–232	6.33	6.68	57.32	56.96		
$Ni(Me_4pn)(NCS)_2$	>300	18.46	18.70			19.25	18.96
$Ni(Me_4pn)(NO_3)_2$	164–168	17.91	17.88			18.76	19.00
$Ni(Me_4tn)Cl_2$	222–228	10.76	11.10	27.32	27.15		
$Ni(Me_4tn)Br_2$	265–272	8.02	8.13	45.80	45.94		
$Ni(Me_4tn)I_2$	258–264	6.33	6.89	57.32	57.14		
$Ni(Me_4tn)(NCS)_2$	>300	18.46	18.40			19.25	19.33
$Ni(Me_4tn)(NO_3)_2$	177–180	17.91	18.11			18.76	18.95
$Co(Me_4en)Cl_2$	176–180	11.40	11.46	28.85	29.40		
$Co(Me_4en)Br_2$	186–189	8.35	8.45	47.85	47.85		
$Co(Me_4en)I_2$	213–222	6.54	6.48	59.30	58.91		
$Co(Me_4en)(NCS)_2$	192–197	18.24	19.27			20.23	19.96
$Co(Me_4en)(NO_3)_2$	176–178	18.70	18.73			19.69	19.68
$Co(Me_4pn)Cl_2$	208–214	10.76	10.80	27.39	27.56		
$Co(Me_4pn)Br_2$	221–226	8.02	7.93	45.80	46.02		
$Co(Me_4pn)I_2$	227–233	6.33	6.35	57.28	57.50		
$Co(Me_4pn)(NCS)_2$	181–183	18.46	18.43			19.30	19.23
$Co(Me_4pn)(NO_3)_2$	154–155	17.91	17.85			18.80	18.62
$Co(Me_4tn)Cl_2$	232–241	10.76	10.88	27.31	27.80		
$Co(Me_4tn)Br_2$	262–270	8.02	8.20	45.80	45.90		
$Co(Me_4tn)I_2$	270–284	6.33	6.34	57.31	57.59		
$Co(Me_4tn)(NCS)_2$	188–201	18.46	18.23			19.30	19.35
$Co(Me_4tn)(NO_3)_2$	185–188	17.91	17.86			18.80	18.62

TABLE II

MAGNETIC DATA FOR THE N,N,N′,N′-TETRAMETHYLDIAMINE NICKEL(II) AND COBALT(II) COMPLEXES

Compound	Temp, °C	$10^6\chi_g$	$10^6\chi_{Me}$	μ_{eff}, BM
$Ni(Me_4en)Cl_2$	18	20.16	5078	3.45
$Ni(Me_4en)Br_2$	20	13.02	4514	3.26
$Ni(Me_4en)I_2$	18	9.99	4465	3.24
$Ni(Me_4en)(NCS)_2$	20	14.78	4453	3.24
$Ni(Me_4en)(NO_3)_2$	20	14.31	4410	3.23
$Ni(Me_4pn)Cl_2$	20	18.84	5039	3.45
$Ni(Me_4pn)Br_2$	20	13.58	4904	3.40
$Ni(Me_4pn)I_2$	20	10.42	4823	3.37
$Ni(Me_4pn)(NCS)_2$	21	13.65	4326	3.20
$Ni(Me_4pn)(NO_3)_2$	20	13.50	4367	3.22
$Ni(Me_4tn)Cl_2$	18	18.00	4822	3.37
$Ni(Me_4tn)Br_2$	18	12.98	4695	3.32
$Ni(Me_4tn)I_2$	17	10.13	4695	3.32
$Ni(Me_4tn)(NCS)_2$	17	13.86	4389	3.20
$Ni(Me_4tn)(NO_3)_2$	17	12.52	4148	3.12
$Co(Me_4en)Cl_2$	18	36.95	9227	4.65
$Co(Me_4en)Br_2$	18	28.45	9685	4.76
$Co(Me_4en)I_2$	20	21.07	9221	4.66
$Co(Me_4en)(NCS)_2$	20	37.07	10952	5.08
$Co(Me_4en)(NO_3)_2$	17	30.25	9182	4.65
$Co(Me_4pn)Cl_2$	19	35.46	9367	4.70
$Co(Me_4pn)Br_2$	19	24.12	8586	4.50
$Co(Me_4pn)I_2$	16	20.16	9139	4.61
$Co(Me_4pn)(NCS)_2$	21	36.43	11248	5.16
$Co(Me_4pn)(NO_3)_2$	18	29.97	9529	4.73
$Co(Me_4tn)Cl_2$	19	34.21	9041	4.60
$Co(Me_4tn)Br_2$	17	25.25	8980	4.58
$Co(Me_4tn)I_2$	19	20.78	9414	4.70
$Co(Me_4tn)(NCS)_2$	19	25.58	7970	4.34
$Co(Me_4tn)(NO_3)_2$	19	30.16	9800	4.80

Physical Measurements.—The absorption spectra were recorded in the range 5000–30,000 cm^{-1} with a Beckman DK-2 spectrophotometer and 1-cm silica cells. The diffuse reflectance spectra were measured using the standard Beckman reflectance attachment and magnesium oxide as the reference. Infrared spectra were recorded on a Perkin-Elmer Model 337 spectrophotometer employing mulls in Nujol supported on CsBr plates. Some magnetic susceptibilities were measured with the Gouy balance already described,[7] and others, by the Faraday method using a sensitive Sartorius electrobalance and an electromagnet with specially shaped pole tips.[8] With this latter apparatus small samples of substances (10–15 mg) can be used. The apparatus were calibrated with $Co[Hg(SCN)_4]$.[9]

Results

Nickel(II) Bromides and Iodides.—The bromide compounds are violet, and the iodide compounds are dark green. They are all very sensitive to moisture and are soluble without dissociation or decomposition only in dry organic solvents. These compounds are of the high-spin type, the values of their magnetic moments at room temperature ranging between 3.20 and 3.40 BM (*cf.* Table II). Their diffuse reflectance spectra (Figure 1) are all similar and are not significantly different from their absorption spectra in solution in inert solvents. The frequencies of the absorption maxima are reported in Table III. Measurements of molecular weight and conductivity in solution, taken on $Ni(Me_4pn)Br_2$, indicate that these complexes are monomeric. These results and the similarity of the spectra with those observed for pseudotetrahedral complexes of the type NiL_2X_2[10–13] lead us to assign a pseudotetrahedral structure of these compounds. On this basis[14] the bands at 7100–8000 cm^{-1} are assigned to one of the three components of the ν_1 transition $^3T_1(F) \rightarrow {}^3T_2(F)$, the band at 9500–11,000 cm^{-1} as the ν_2 $^3T_1(F) \rightarrow {}^3A_2(F)$, and the bands at 14,500–19,000 cm^{-1} as ν_3 $^3Ti(F) \rightarrow {}^3T_1(P)$. The two peaks at 10,400–11,600 cm^{-1} which, if they are not resolved, appear as a shoulder on the short-wavelength side of ν_2, are assigned to a spin-forbidden transition to an upper state arising from the ^1D state of the free ion. The intensity of these bands is abnormally large for a spin-forbidden transition. In some cases, *e.g.*, for $Ni(Me_4tn)Br_2$ it is scarcely less than that of ν_2. This has been explained[12] by assuming that the upper singlet state mixes with the nearby triplet state *via* spin–orbit coupling.

The relative intensity of ν_2 also merits comment. In regular tetrahedral complexes the intensity ratios show that ν_3 is generally 10–20 times stronger than ν_2.[12] When low-symmetry components of the ligand field are pronounced, the intensity of ν_2 increases appreciably relative to that of ν_3 (see Table III and Figure 1). The operation of the low-symmetry component of the ligand field is also shown by the values of the magnetic mo-

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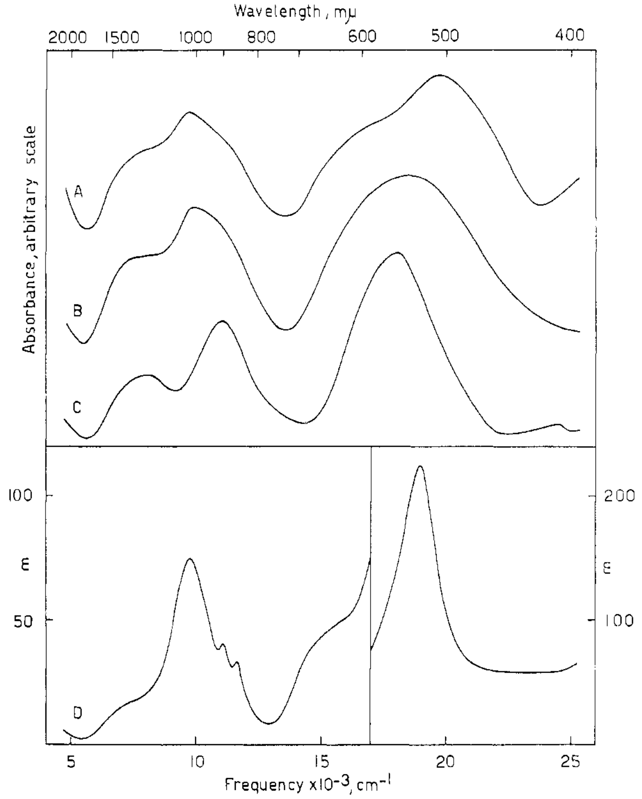

Figure 1.—Reflectance spectra of: $Ni(Me_4en)Br_2$, curve A; $Ni(Me_4pn)Br_2$, curve B; $Ni(Me_4tn)Br_2$, curve C. Absorption spectrum of $Ni(Me_4pn)Br_2$ in benzene, curve D.

Table III

Spectroscopic Data for the N,N,N′,N′-Tetramethyldiamine Nickel(II) and Cobalt(II) Complexes

Complexes	Solvent	Absorption max, cm^{-1} (ϵ_{molar} for soln)
$Ni(Me_4en)Cl_2$		7400, 9090, 13,300 sh, 14920, 25,000
	o-$Cl_2C_6H_4$	7200 sh, 9100 (5.6), 13,300 sh, 14,700 (10.3), 23,500 sh, 25,000 (25)
$Ni(Me_4en)Br_2$		7700 sh, 9800, 11,100 sh, 17,500 sh, 19,000
$Ni(Me_4en)I_2$		8000 sh, 10,000, 14,500 sh, 17,550
	o-$Cl_2C_6H_4$	7800 sh, 9500 (144), 10,400 sh, 14,300 sh, 17,400 (375)
$Ni(Me_4en)(NCS)_2$		8300 sh, 9550, 15,650, 25,000 sh
$Ni(Me_4en)(NO_3)_2$		10,200, 15,500, 26,300
	CH_2Cl_2	9700 (10.6), 12,500 (4.80), 15,900 (26), 26,100 (43.2)
$Ni(Me_4pn)Cl_2$		7400, 9100 sh, 12,000 sh, 14,300, 23,800
	o-$Cl_2C_6H_4$	8000 (7.2), 10,000 (11.8), 11,500 (7.3), 12,000 (7.4), 14,100 (14), 15,000 sh, 20,000 (20), 23,800 (22)
$Ni(Me_4pn)Br_2$		7900 sh, 9850, 11,100 sh, 19,050
	C_6H_6	7150 sh, 9700 (75), 11,100 (40.5), 11,600 (32.4), 15,600 sh, 19,000 (210)
$Ni(Me_4pn)I_2$		4300, 7700 sh, 10,000, 14,700 sh, 17,400
	CH_2Cl_2	7400 sh, 9520 (118), 10,600 sh, 14,500 sh, 17,500 (359)
$Ni(Me_4pn)(NCS)_2$		8100 sh, 9520, 15,400, 25,000 sh
$Ni(Me_4pn)(NO_3)_2$		10,000, 15,900, 26,300
	CH_2Cl_2	9520 (10), 12,500 (4.3), 15,600 (27), 26,300 (48)
$Ni(Me_4tn)Cl_2$		9100 sh, 10,700, 11,500 sh, 18,900
	i-$C_5H_{11}OH$	9090 sh, 10,700 (40), 11,500 (34), 12,000 (35), 18,880 sh, 19,550 (84)
$Ni(Me_4tn)Br_2$		8400, 11,100, 18,200
	i-$C_5H_{11}OH$	9090 sh, 10,380 (65), 11,380 (61.5), 11,690 (62), 17,880, sh, 18,600 (176)
$Ni(Me_4tn)I_2$		4400, 8000, 10,000 sh, 11,600, 16,400
	C_6H_6	8000 sh, 10,000 sh, 11,550 (109), 17,000 (366)
$Ni(Me_4tn)(NCS)_2$		8690, 13,000 sh, 15,100, 24,400
$Ni(Me_4tn)(NO_3)_2$		8690, 13,000 sh, 15,100, 24,400
$Co(Me_4en)Cl_2$		6000 sh, 7250, 10,000, 15,400, 17,200
	CH_2Cl_2	5950 sh, 7250 (56.7), 10,000 (18.2), 15,200 (447), 17,300 (214), 18,000 sh
$Co(Me_4en)Br_2$		5900 sh, 6900, 9600, 15,400, 16,250
	CH_2Cl_2	5900 sh, 6900 (73.2), 9600 (27.3), 15,200 (270), 16,670 (310), 17,540 sh
$Co(Me_4en)I_2$		5700 sh, 6620, 9150, 15,150, 15,900 sh
$Co(Me_4en)(NCS)_2$		7400, 9100, 17,200 sh, 19,200
$Co(Me_4en)(NO_3)_2$		9300, 15,900 sh, 19,400
	CH_2Cl_2	9100 (16), 15,400 sh, 19,000 (93), 20,500 sh
$Co(Me_4pn)Cl_2$		5950, 7300, 10,000, 15,700, 16,700 sh
	C_6H_6	6000 (26), 7300 (65), 10,000 (18), 15,300 (466), 17,300 (236), 18,000 sh
$Co(Me_4pn)Br_2$		6000, 7250, 9900, 15,500, 16,600 sh
	C_6H_6	5900 sh, 6850 (68), 9600 (21), 15,950 (57), 16,600 (251), 17,550 sh
$Co(Me_4pn)I_2$		5700 sh, 6600, 9300, 15,000
	CH_2Cl_2	5700 sh, 6600 (103), 9260 (44), 14,300 sh, 15,050 (74), 15,750 sh
$Co(Me_4pn)(NCS)_2$		7460, 9300 sh, 17,200 sh, 19,200
	CH_2Cl_2	6500 (42), 8200 (111), 10,900 (58), 15,450 (1207), 18,000 (265), 18,500 sh
$Co(Me_4pn)(NO_3)_2$		9200, 15,600 sh, 19,000
	o-$Cl_2C_6H_4$	9100 (14), 19,050 (85), 20,400 sh
$Co(Me_4tn)Cl_2$		6400, 7700, 10,500, 16,800
	CH_2Cl_2	6450 (35), 7700 (63), 10,500 (49), 16,130 (430), 17,250 sh
$Co(Me_4tn)Br_2$		6300 sh, 7400, 10,000, 16,800
	CH_2Cl_2	6450 sh, 7400 (76), 10,000 (70), 15,750 (645), 16,700 sh, 17,850 sh
$Co(Me_4tn)I_2$		6300, 7100, 9600, 15,600,
	CH_2Cl_2	6200 sh, 7100 (109), 9530 (121), 14,700 (675), 15,500 (680), 16,130 (610)
$Co(Me_4tn)(NCS)_2$		7400 sh, 8700, 11,400, 17,300
	CH_2Cl_2	7400 sh, 8700 (132), 11,250 (168), 16,130 (1055), 17,850 sh
$Co(Me_4tn)NO_3)_2$		7400 sh, 8300, 13,900 sh, 16,400 sh, 19,200

ments at room temperature, which range from 3.24 to 3.40 BM.

Nickel(II) Chlorides.—The Me_4en and Me_4pn derivatives are green. Their solutions in o-$Cl_2C_6H_4$ are thermochroic, changing from green to violet as the temperature rises. The Me_4tn derivative is violet both in the solid state and in solution and does not show thermochromism. Reflectance spectra (Figure 2) of the former complexes show peaks at *ca.* 7400, 9100, 14,500, and 25,000 cm^{-1}. Their shape and frequency are very similar to that reported for $Ni(amine)_2Cl_2$ complexes with polymeric hexacoordinated configurations achieved *via* chlorine bridges.[15] The high value of the magnetic moments (μ_{eff} = 3.37–3.45 BM) is of the same order of magnitude as that observed for other nickel(II) complexes with similar polymeric structure.[16] The absorption spectrum of the complex $Ni(Me_4pn)Cl_2$ in solution in o-$Cl_2C_6H_4$ shows two new peaks at *ca.* 10,000 and 17,000 cm^{-1}, which indicate the presence of tetrahedral forms in equilibrium with the octahedral forms. This equilibrium is displaced toward the tetrahedral form when the temperature increases. Also the spectra of the $Ni(Me_4en)Cl_2$ compound, at temperatures higher than room temperature, show an analogous octahedral $\rightleftarrows$ tetrahedral equilibrium. The relative intensities of the bands indicate that, for a given temperature, the proportion in the tetrahedral form is greater for the Me_4pn derivative than for the Me_4en analog. The visible spectra of $Ni(Me_4tn)Cl_2$ are indicative of a tetrahedral configuration both in the solid state and in solution (Figure 2).

Cobalt(II) Halides.—All the complexes are blue and are not very sensitive to moisture, although they decompose in aqueous solution. They are soluble in

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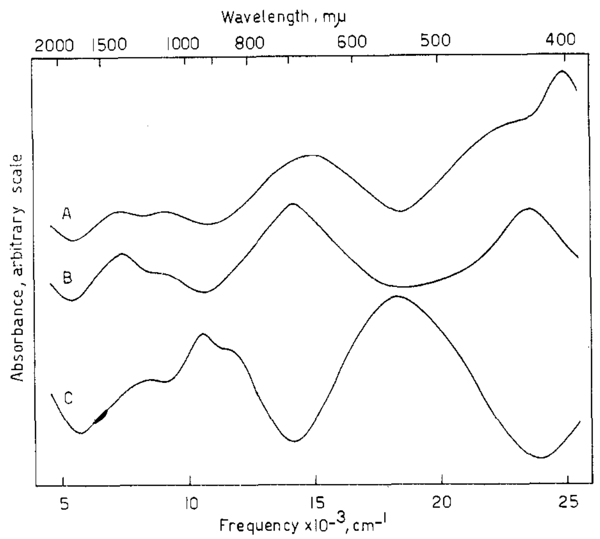

Figure 2.—Reflectance spectra of: $Ni(Me_4en)Cl_2$, curve A; $Ni(Me_4pn)Cl_2$, curve B; $Ni(Me_4tn)Cl_2$, curve C.

ordinary organic solvents. Their magnetic moments range from 4.50 to 4.70 BM indicating a high-spin configuration with three unpaired electrons. The orbital contribution is small, as is generally found for tetrahedral complexes.[17] Their diffuse reflectance spectra and their absorption spectra are similar to those observed for distorted tetrahedral complexes.[18] The spectrophotometric data are reported in Table III. In accordance with the assignment made by other authors,[19] the three bands between 7000 and 10,000 cm^{-1} are assigned to the components of the $^4A_2(F) \rightarrow {}^4T_1(F)$ (ν_2) transition for T_d symmetry, and the bands at 15,000–20,000 cm^{-1} are assigned to the components of the $^4A_2(F) \rightarrow {}^4T_1(P)$ (ν_3) transition. The large splittings of the components of the ν_2 and ν_3 frequencies are presumably due to a large distortion from true tetrahedral symmetry.

Nickel(II) and Cobalt(II) Thiocyanates.—The nickel complexes are all green and are insoluble in organic solvents. The complexes of cobalt with Me₄en and Me₄pn are both purple. Only the latter compound, however, dissolves in organic solvents, changing from purple to blue. The diffuse reflectance spectra of the nickel complexes (Figure 3) show two bands in the visible and ultraviolet region, at *ca.* 15,000 and at *ca.* 24,500 cm^{-1}, which must be assigned as the ν_2 $^3A_{2g}$ (F) $\rightarrow$ $^3T_{1g}$ (F) and ν_3 $^3A_{2g}(F) \rightarrow {}^3T_{1g}$ (P) transitions of O_h symmetry. The hexacoordinate configuration is probably achieved through Ni–NCS–Ni bridges. The $Co(Me_4en)(NCS)_2$ and $Co(Me_4pn)(NCS)_2$ complexes give reflectance spectra with two peaks in the near-infrared region and, with respect to the halogen complexes, the system of bands in the visible region is displaced to even higher energies than would be expected for the increase in field strength due to the introduction of the thiocyanates group. Furthermore, the orbital contribution to the magnetic moment is relatively high, since the magnetic moments are higher than 5 BM, values peculiar of octahedral cobalt(II) complexes.[17a] The purple Me₄pn derivative dissolves in CH_2Cl_2 giving a blue solution with an absorption spectrum which is different from the reflectance spectrum but which is similar to that of the halide analogs. This compound, then, which is polymeric octahedral in the solid state, becomes pseudotetrahedral in solution. The distortion of such a polymeric configuration and the fact that the ligand atoms are not equivalent explain why two bands appear in the reflectance spectrum at *ca.* 9000 cm^{-1} (Figure 3) instead of the single band found in regular or weakly distorted octahedral cobalt(II) complexes. In a cubic field this band corresponds to the transition $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ and both states are split in fields of lower symmetry.[20] An analogous splitting is observed in the ν_1 transition $^3A_{2g}$ (F) $\rightarrow$ $^3T_{2g}$(F) of the corresponding nickel complexes (Figure 3). The infrared spectra of these compounds show two bands in the C–N stretching region (Table IV). The values of these frequencies are higher than those found for monomeric nickel and cobalt thiocyanate complexes.[21] This is presumably due to the thiocyanate groups acting as bridges.[21] Also the C–S stretching frequen-

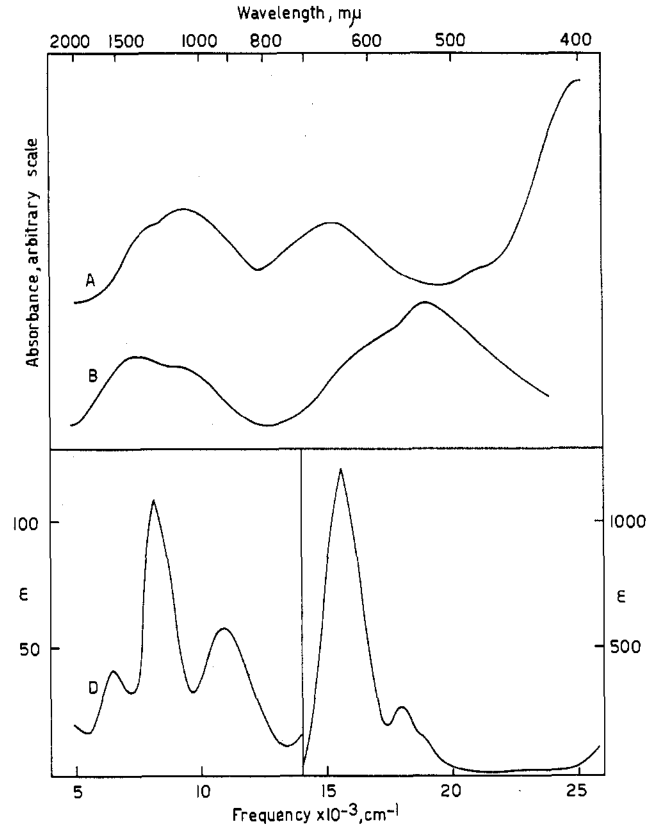

Figure 3.—Reflectance spectra of: $Ni(Me_4pn)(NCS)_2$, curve A; $Co(Me_4pn)(NCS)_2$, curve B. Absorption spectrum of $Co(Me_4pn)(NCS)_2$ in CH_2Cl_2, curve C.

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TABLE IV

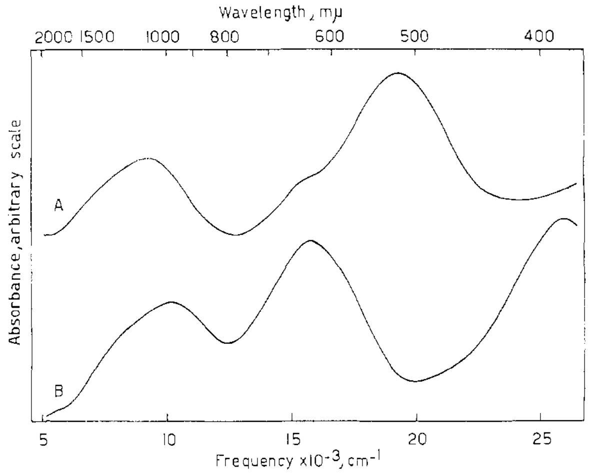
INFRARED ABSORPTION FREQUENCIES (CM^{-1}) OF THE ANIONS IN THE COMPLEXES

Compounds	Absorption bands[a]
$Ni(Me_4en)(NCS)_2$	2120, 2090, vs, C–N str, 815 (?) m, C–S str
$Ni(Me_4pn)(NCS)_2$	2135, 2115, vs, C–N str, 780 m, C–S str
$Ni(Me_4tn)(NCS)_2$	2135, 2080, vs, C–N str, 775 m, C–S str
$Co(Me_4en)(NCS)_2$	2130 sh, 2115 vs, C–N str, 779 m, C–S str
$Co(Me_4pn)(NCS)_2$	2130, 2115, vs, C–N str, 783 m, C–S str
$Co(Me_4tn)(NCS)_2$	2060, 2070 vs, C–N str, 845 m, 850 m, C–S str
$Ni(Me_4en)(NO_3)_2$	1540, 1510, 1280, 1260, vs, br, N–O str, 808 m, out-of-plane def
$Ni(Me_4pn)(NO_3)_2$	1530, 1510, 1265, vs, br, N–O str, 802 m, out-of-plane def
$Ni(Me_4tn)(NO_3)_2$	1530, 1500, 1270, vs, br, N–O str, 807 m, out-of-plane def
$Co(Me_4en)(NO_3)_2$	1510, 1285, vs, br, N–O str, 808 sh, 802 m, out-of-plane def
$Co(Me_4pn)(NO_3)_2$	1530, 1510, 1270, vs, br, N–O str, 806 mw, out-of-plane def
$Co(Me_4tn)(NO_3)_2$	1530, 1500, 1300 sh, 1270, vs, br, N–O str

[a] s, strong; m, medium; w, weak; br, broad; sh, shoulder; v, very.

cies fall in the range expected for NCS bridging groups.[21b] The $Co(Me_4tn)(NCS)_2$ complex, which is blue, has a magnetic moment (4.34 BM) and reflectance and absorption spectra which are indicative of a pseudotetrahedral structure. The infrared spectrum shows two C–N stretching and two C–S stretching frequencies in the range expected for thiocyanate complexes, in which the NCS group is linked to the metal only by the nitrogen.[21]

Nickel and Cobalt Nitrates.—The nickel complexes are turquoise; those of cobalt are purple. They are all soluble in polar organic solvents. The diffuse reflectance spectra and the absorption spectra of the nickel compounds (Figure 4) are easy to assign on the basis of octahedral symmetry. The bands at 9000, 15,000, and 25,000 cm^{-1} are assigned to the $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions, respectively. The weak band or shoulder at 12,500 cm^{-1} is probably due to a spin-forbidden transition to the singlet state $^1T_2(D)$.[11] This implies that the two nitrate groups act as bidentate ligands. Various authors have discussed the infrared spectrum of coordinated nitrate compared with that of the nitrate ion.[22–24] In going from D_{3h} symmetry (ionic nitrate) the doubly degenerate vibrations ν_3 (symmetrical stretching) and ν_4 (deformation in the plane) lose their degeneracy and are both split into two components. There is moreover a lowering of the vibration frequency ν_2 (deformation outside the plane) while the symmetric stretching ν_1 becomes active in the infrared. These characteristics are, however, the same for both the monodentate and the bidentate nitrate group. Recently Curtis and Curtis,[24] for a series of ionic, monodentate, and bidentate nitrates, have shown that the lowering of the frequencies and the magnitude of the splittings increase going from the monodentate to the bidentate nitrate group. The values of the frequencies assigned as vibrational modes of the nitrate group reported in Table IV are strongly indicative of the bidentate nitrate group, for both the nickel and cobalt complexes. The N–O stretching frequencies are largely split in the range 1270–1530 cm^{-1} and the out-of-plane deformation is lowered until *ca.* 805 cm^{-1}.



Figur 4.—Reflectance spectra of: $Co(Me_4en)(NO_3)_2$, curve A; $Ni(Me_4en)(NO_3)_2$, curve B.

The absorption spectra of the cobalt complexes (Figure 4) show a single band in the near-infrared region which can be assigned to the $^4T_{1g} \rightarrow {}^4T_{2g}(F)$ transition in an octahedral field. The values of the magnetic moments ranging from 4.65 to 4.80 BM are rather low with respect to those found for octahedral cobalt complexes. This magnetic behavior, which has been found also for other nitrate complexes of cobalt(II),[23] has been explained by postulating that the six-coordinated complex can be regarded as having pseudotetrahedral symmetry.[23] Indeed, if the nitrate ions are simply considered as large, diffuse, uninegative anions centered at the nitrogen atom positions, the coordination of the cobalt ion may be regarded as having a distorted tetrahedral symmetry.[23]

Conclusions

Tetrahedral complexes of nickel(II) are still scarce in comparison with the more common octahedral or planar complexes. It has been shown[25] that tetrahedral complexes of nickel(II) are usually produced when steric and electronic requirements of the ligands make a planar or an octahedral configuration unfavorable. The alkylenediamines and the N- and C-substituted alkylenediamines, except those reported in this paper, give, with nickel(II), complexes in the ratio $^3/_1$ or $^2/_1$ with structures preferably octahedral. On the other hand, as the ligand becomes more and more bulky by successive substitutions on the carbon of the aliphatic chain (*e.g.*, 1,2-propylenediamine,[2c] 2,3-butylenediamine,[2c], C-phenylethylenediamine,[3] stilbenediamine[3]), the planar diamagnetic configuration becomes more stable. As a matter of fact, C,C,C′,C′-tetramethylethylenediamine gives only square-planar complexes of the formula $Ni(diamine)_2{}^{2+}$.[2a] In the present study the steric influence of the methylated N-atoms of these

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N,N,N',N'-tetramethylated diamines and the small size of the nickel(II) and cobalt(II) ions lead to two effects: (a) the diamine to metal ratio in the complexes is $^1/_1$;[26] (b) the tetrahedral configuration is favored over the planar. All of the cobalt halide complexes and the $Co(Me_4tn)(NCS)_2$ compound are tetrahedral. Only the thiocyanate derivatives with Me_4en and Me_4pn are octahedral in the solid state by polymerization. Of the nickel(II) compounds, the complex $Ni(Me_4tn)Cl_2$ and the bromo and iodo complexes with Me_4en, Me_4pn, and Me_4tn are pseudotetrahedral. All of the other chlorides and the thiocyanates are polymerized octahedral. From these results it appears that the formation of pseudotetrahedral structures is increasingly favored in the order: $Ni < Co$, $SCN < Cl < Br < I$, and $Me_4en < Me_4pn < Me_4tn$. It is now well established that nickel(II) shows a marked preference for an octahedral as compared with a tetrahedral environment, in contrast to cobalt(II), for which tetrahedral complexes are very common. The second sequence corresponds to that found by other workers[10,27] for complexes of the type NiL_2X_2, with the difference that when L is a substituted picoline[11] or phosphine[10] the nontetrahedral complexes are planar and diamagnetic, while in the present case the nontetrahedral complexes are octahedral and paramagnetic. This difference in behavior may be due to the low donor power of the tertiary nitrogen (which gives generally high-spin complexes) compared with phosphorus (which has a greater tendency to give low-spin complexes). With regard to the third sequence, the greater length of the Me_4tn chain, compared with Me_4en and Me_4pn, certainly accounts for the greater capacity of Me_4tn to form pseudotetrahedral complexes. As a matter of fact, although the diamine Me_4en has been found[28] to give N–Ni–N angles of 85.5°, the $N-(CH_2)_3-N$ chain permits the formation of N–Ni–N angles[29] of 92–94°, which are closer to the tetrahedral angle. The trimethylene chain will, furthermore, cause greater crowding around the central atom than the other two diamines and thus inhibit six-coordination. This is particularly well demonstrated in the two series of complexes of nickel(II) chloride and cobalt(II) thiocyanate, in which only the complexes with Me_4tn are tetrahedral. The reasons for the greater tendency of Me_4pn, compared with Me_4en, to form pseudotetrahedral complexes are less obvious. Although the N–Ni–N angle is probably about 85°, the additional methyl group will cause crowding as for the trimethylene chain. It is interesting to note that nitrate groups have a marked tendency to act in a bidentate manner in these metal complexes. The smaller bulkiness of one bidentate nitrate group compared with two monodentate ligands makes it easier to reach the six-coordinated configuration. In fact, all of the nitrate complexes reported in this paper are six-coordinated. The nickel complexes have magnetic moments and absorption spectra typical of octahedral structures. The ratio between the Racach interelectronic repulsion integral which is effective in the ion complex and that for free ion is 0.83, 0.86, and 0.83 for Me_4en, Me_4pn, and Me_4tn nickel complexes, respectively. These values are comparable to those obtained for other octahedral nickel complexes.[30] Using the simple matrices of Tanabe and Sugano, values of the ν_2 and ν_3 frequencies have been obtained which are in satisfactory agreement with the observed frequencies. This indicates that, although the configuration of the complex is far from O_h symmetry, the effects of the crystal field on the nickel(II) ion can be regarded, with reasonable approximation, as being due to a cubic field. On the other hand the octahedral cobalt nitrate complexes have magnetic moments close to those of tetrahedral configurations and do not always have characteristic absorption spectra.[23]

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