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Cobalt(II) and Nickel(II) Complexes with N,N,N'-Trimethylated and Triethylated Alkylenediamines[1]

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The ligands N,N,N'-trimethylethylenediamine (Me₃en), N,N,N'-triethylethylenediamine (Et₃en), N,N,N'-trimethyltrimethylenediamine (Me₃tn) form 1:1 adducts with cobalt(II) and nickel(II) halides having the general formulas $M(Me_3tn)X_2$, $M(Et_3en)X_2$ and $Ni(Me_3en)X_2$ ($M = Co, Ni$; $X = Cl, Br, I$). Adducts with a metal to ligand ratio of 1:2, $M(Me_3en)_2X_2$, are also obtained with the ligand Me₃en and they have a distorted octahedral structure. The $M(Me_3tn)X_2$ and $M(Et_3en)X_2$ complexes are pseudotetrahedral with the exception of $Ni(Me_3tn)Cl_2$ and $Ni(Et_3en)Cl_2$ which have a polymeric octahedral structure as do $Ni(Me_3en)X_2$. The cobalt(II) and nickel(II) octahedral complexes, in solution give rise to temperature dependent equilibria between octahedral and pseudotetrahedral species.

Introduction

It is well known that mono and bis N–substituted ethylenediamines such as N–methyl, N,N–dimethyl, N,N–diethyl, and N,N'–dimethylethylenediamine, form complexes with cobalt and nickel salts with a metal to ligand ratio 1:2 or 1:3.[2,3]

These complexes are mostly octahedral. More bulky ligands like N,N,N',N'–tetramethylalkylenediamines (ethylene or trimethylenediamine) form adducts with cobalt(II) and nickel(II) halides with a metal to ligand ratio of 1:1.[4] The steric requirements of the ligands favour the formation of pseudotetrahedral species. Now we report an investigation of the coordinating properties of ligands with intermediate bulkiness such as N,N,N'–trimethylethylenediamine, (Me₃en), N,N,N'–triethylethylenediamine (Et₃en) and N,N,N'–trimethyltrimethylenediamine (Me₃tn) towards cobalt and nickel halides. To our knowledge only the six-coordinated $Ni(Me_3en)_2(ClO_4)_2$ has already prepared with a ligand of this type.[3]

Experimental Section

Synthesis of the Ligands. The Me₃en ligand is available from Fluka A. G. and was employed without further purification. The ligand Me₃tn was prepared as follows:[5] 74 g (0.3 moles) of $(CH_3)_2N(CH_2)_3Br$. HBr[6] dissolved in 100 ml of alcohol-water solution was added to 85 g (0.9 moles) of CH_3NH_2 85% aqueous solution. The mixture was gently warmed (temp. max. = 50°C) for 12 hours with continuous stirring. Solid NaOH was then added to the cold solution and the free amine was extracted with diethyl ether, dried over $CaSO_4$ and NaOH and distilled. (B.p. = 140-145°C/760). The ligand Et₃en was prepared using an analogous procedure starting from $(C_2H_5)_2N(CH_2)_2$-Br . HBr (0.3 moles) and $C_2H_5NH_2$ (0.9 moles). (B.p. = 171-174°C/760).

Preparation of the Complexes. The stoichiometric amount of the diamine in 10 ml of butanol was added to a boiling solution of 10 mmoles of the appropriate nickel and cobalt halides in 50 ml of butanol. The solution was concentrated and cyclohexane added until crystals were obtained. These were collected by filtration and washed with butanol and petroleum ether (B.p. 40-70). The filtration was carried out in a dry nitrogen atmosphere in order to eliminate atmospheric moisture. The preparation of the cobalt complexes was carried out in a nitrogen atmosphere in order to prevent atmospheric oxidation. Some physical and analytical data are reported in Table I.

Physical Measurements. The absorption spectra were recorded in the range 4000-30,000 cm^{-1} with a Beckman DK2 spectrophotometer using 1 cm silica cells. The diffuse reflectance spectra were measured using the standard Beckman reflectance attachment with magnesium oxide as the reference. Details of the electronic spectra for some typical complexes are reported in Table II. The magnetic measurements were performed by the Gouy method with the apparatus already described.[7] The sample tube was calibrated with $Co[Hg(NCS)_4]$[8] and freshly distilled water. Diamagnetic corrections were calculated from Pascal's constants.[9] The magnetic data are reported in Table I.

Molecular weights were determined in nitroethane and dichloroethane at 37°C with an Hitachi Perkin-Elmer Model 115 molecular weight apparatus. The

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Table I. Analytical and Physical Data for the Cobalt(II) and Nickel(II) Complexes

Compound	Color	Mp, °C	Λ, cm²/ohm M	%N		%Halogens		%Metal		μ_{eff} (B.M.)
				Calcd.	Found	Calcd.	Found	Calcd.	Found.	298°K
$Co(Me_3en)_2Cl_2$	pink	>130 dec	0.12	16.76	16.80	21.22	21.08			5.12
$Co(Me_3en)_2Br_2$	pink	>140 dec	0.30	13.24	13.10	37.77	37.35			5.05
$Co(Me_3en)_2I_2$	violet	>150 dec	0.70	10.38	10.85	49.09	48.80			4.70
$Co(Et_3en)Cl_2$	blue	117-120	0.05	10.22	10.45			21.50	21.20	4.60
$Co(Et_3en)Br_2$	blue	144-146	0.27	7.71	7.85			16.23	16.05	4.60
$Co(Et_3en)I_2$	blue	145-147	0.10	6.13	6.18			12.89	12.67	4.48
$Co(Me_3tn)Cl_2$	blue	178-183	0.08	11.39	11.65	28.81	28.80			4.56
$Co(Me_3tn)Br_2$	blue	185-187	0.08	8.36	8.55	47.71	47.80			4.65
$Co(Me_3tn)I_2$	turquoise	187-190	0.30	6.53	6.50	59.17	58.80			4.62
$Ni(Me_3en)Cl_2$	green	>330	0.08	12.09	11.80	30.17	30.37			3.14
$Ni(Me_3en)Br_2$	yellow	222-226	0.04	8.73	7.75	49.83	49.73			3.07
$Ni(Me_3en)_2Cl_2$	green	>150 dec	0.18	16.78	16.45	21.23	21.05			3.22
$Ni(Me_3en)_2Br_2$	green	>150 dec	0.16	13.25	13.60	37.79	37.50			3.22
$Ni(Me_3en)_2I_2$	green	>140 dec	0.13	10.84	10.70	49.11	48.90			3.32
$Ni(Et_3en)Cl_2$	yellow	180-183	0.19	10.23	10.25			21.43	20.95	3.32
$Ni(Et_3en)Br_2$	purple	164-166	0.21	7.72	7.80			16.17	16.55	3.30
$Ni(Et_3en)I_2$	purple	145-147	0.23	6.13	6.25			18.84	18.43	3.24
$Ni(Me_3tn)Cl_2$	yellow	171-174	0.35	11.40	11.45	28.85	28.65			3.29
$Ni(Me_3tn)Br_2$	violet	181-185	0.18	8.35	8.40	47.75	47.65			3.35
$Ni(Me_3tn)I_2$	dark green	180-187	0.20	6.54	6.50	59.21	58.90			3.35

Table II. The Maxima and Extinction Coefficients for the Electronic Spectra of the Complexes

Compound		Absorption max., cm^{-1} (ε_{molar} for the soln.)
$Co(Me_3en)_2Cl_2$		8500, 16,200 sh, 18,000 sh, 19,200, 19,800.
	$(CH_2Cl)_2$	7150 (3.5), 9400 sh, 15,200 (17.8), 15,600 sh, 17,400 (13.2), 18,200 sh, 18,700 sh, 20,000 sh.
$Co(Me_3en)_2Br_2$		8700, 16,600, 18,000 sh, 19,200, 20,400.
	$(CH_2Cl)_2$	7150 (5), 9400 sh, 14,900 sh, 15,250 (41), 16,650 (27), 17,550 (20), 18,900 (16.5), 20,000 sh.
$Co(Me_3en)_2I_2$		5500, 12,000, 19,000.
	$(CH_2Cl)_2$	6650 (16), 7520 (12), 14,300 sh, 14,900 (123), 15,750 (100), 16,500 sh, 17,700 sh, 20,400 sh, 21,000 (30).
$Co(Et_3en)Cl_2$		6100, 7460, 10,360, 15,400, 17,100, 17,800 sh, 18,900 sh.
	$(CH_2Cl)_2$	6050 (29), 7300 (56), 10,100 (17), 15,150 (550), 17,250 (243), 18,200 sh.
$Co(Et_3en)Br_2$		5900 sh, 6950, 9900, 15,500, 16,400 sh, 17,250 sh, 18,200.
	$(CH_2Cl)_2$	5800 sh, 7000 (65), 9850 (27), 15,150 (525), 16,650 (288), 17,700 sh.
$Co(Et_3en)I_2$		5550 sh, 6780, 9460, 15,600, 17,100 sh.
	$(CH_2Cl)_2$	5600 sh, 6650 (89), 9380 (51), 14,400 sh, 15,950 (658), 15,760 sh, 16,670 sh, 17,800 sh.
$Co(Me_3tn)Cl_2$		6550 sh, 7850 , 10,630, 16,260, 17,100 sh, 17,900 sh.
	$(CH_2Cl)_2$	6450 (41.5), 7780 (73), 10,500 (51), 15,750 sh, 16,100 (396).
$Co(Me_3tn)Br_2$		6450 sh, 7650, 10,250, 15,900, 16,950 sh, 17,700 sh.
	$(CH_2Cl)_2$	6400 sh, 7500 (74), 10,250 (59), 13,500 sh, 15,650 (539), 16,700 sh, 17,500 sh.
$Co(Me_3tn)I_2$		6250, 7300, 9750, 15,400, 16,700 sh, 19,300 sh.
	$o-C_6H_4Cl_2$	7150 (91.8), 9800 (86.7), 14,900 sh, 15,400 (625), 16,150 (517), 16,700 sh, 19,600 sh.
$Ni(Me_3en)Cl_2$		8550, 13,900, 23,800.
	$o-C_6H_4Cl_2$	8650 (5.5), 12,000 sh, 14,100 (11.1), 19,000 sh, 23,800 (27.8).
$Ni(Me_3en)Br_2$		8350, 13,500, 22,800.
	$o-C_6H_4Cl_2$	7400 sh, 10,000 (14.6), 11,100 sh, 11,500 sh, 13,100 sh, 14,100 (25), 19,700 (38), 24,400 (73).
$Ni(Me_3en)_2Cl_2$		8250, 10,250, 15,400, 20,000 sh, 25,000.
	$(CH_2Cl)_2$	8200 (5.4), 12,100 sh, 14,900 (5.7), 24,700 (14).
$Ni(Me_3en)_2Br_2$		7500, 10,620, 15,200, 19,400 sh, 25,000.
	$(CH_2Cl)_2$	7250 (7.4), 10,400 (2.4), 14,700 (8.2), 19,200 sh, 24,400 (24).
$Ni(Me_3en)_2I_2$		8200, 14,600.
	$(CH_2Cl)_2$	6450 (2.7), 10,500 (2), 14,700 (4.5), 18,200 (4.5).
$Ni(Et_3en)Cl_2$		8250, 13,300, 23,000.
	$(CH_2Cl)_2$	7400 sh, 10,700 (64), 11,550 (37), 12,000 (31), 16,500 sh, 19,800 (119).
$Ni(Et_3en)Br_2$		8000 sh, 10,400, 11,200 sh, 17,500 sh, 19,400.
	$(CH_2Cl)_2$	7400 sh, 10,200 (87), 11,250 (61), 11,560 (53), 17,400 sh, 19,250 (198).
$Ni(Et_3en)I_2$		8000 sh, 10,400, 11,750 sh, 16,400 sh, 18,200.
	$(CH_2Cl)_2$	8800 sh, 9750 (135), 10,500 (131), 16,000 sh, 17,850 (392).
$Ni(Me_3tn)Cl_2$		7100, 11,100 sh, 13,250, 20,000 sh, 23,000.
	$o-C_6H_4Cl_2$	8000 sh, 10,600 (16.9), 11,600 (14), 12,000 (16.5), 14,400 (9), 18,200 sh, 19,800 (33.8), 25,000 (39).
$Ni(Me_3tn)Br_2$		8200, 10,500 sh, 11,600, 17,700 sh, 18,700.
	$o-C_6H_4Cl_2$	7700 sh, 10,500 (86.2), 11,300 (85), 11,700 (88), 19,050 (212), 24,000 (75).
$Ni(Me_3tn)I_2$		8000, 11,100, 16,150 sh, 17,700, 22,800.

conductivity measurements on 1,2–dichloroethane solutions were performed using a WTW Model LBR/B conductance bridge. The conductivity values for *ca.* 10^{-3} *M* solutions at 20°C are reported in Table I. Reference value in 1,2–dichloroethane is: $[(n-C_4H_9)_4N]Br$, 19 cm^2 ohm^{-1} $mole^{-1}$.

Results and Discussion

Cobalt(II) Complexes. The complexes obtained with the ligand Me_3en have the general formula $Co(Me_3en)_2X_2$ (X = Cl, Br, I). Those obtained with the ligand Me_3tn and Et_3en have the general formula

Co(Ligand)X_2. We are unable to prepare complexes with different metal to diamine ratios even by changing the relative proportions of the reagent compounds. All of the complexes are of the high-spin type, (Table I). The reflectance spectra of the Co(Me_3tn)X_2 and Co(Et_3en)X_2 complexes are similar and are practically identical to the absorption spectra in inert polar solvents such as 1,2-dichloroethane or *o*-dichlorobenzene (Figure 1). The compounds are non-electrolytes in dichloroethane solution. The electronic spectra with bands at *ca.* 6000, 7000, 10,000, 15,000-17,000 cm^{-1} (Table II) differ from those of octahedral complexes particularly for the significantly greater intensity of the bands. These spectra instead closely resemble those observed for pseudotetrahedral complexes of the type CoL_2X_2 (L = Triphenylphosphine, triphenylarsine oxide, etc.)[10] and in particular those of the Co(Me_4tn)X_2 complexes,[4] which have been assigned a pseudotetrahedral structure. On this basis an analogous assignment of the bands can be made.

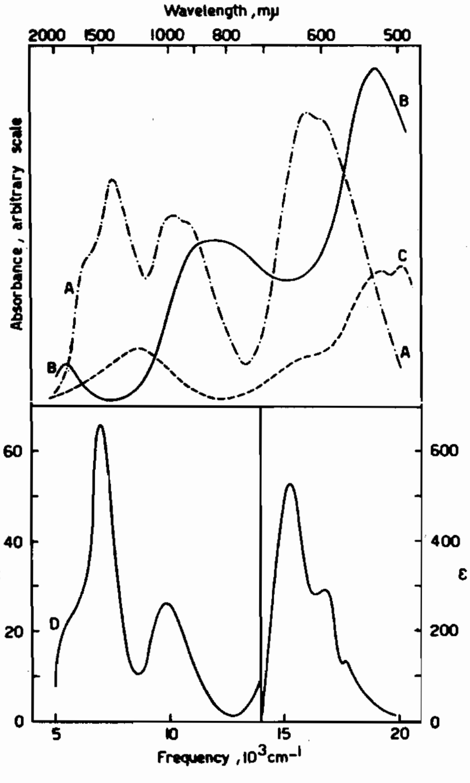

Figure 1. Reflectance spectra of: Co(Me_3tn)Br_2, curve A; Co(Me_3en)$_2I_2$, curve B; Co(Me_3en)$_2Cl_2$, curve C. Absorption spectrum of Co(Et_3en)Br_2 in $(CH_2Cl)_2$, curve D.

The complexes Co(Me_3en)$_2X_2$ (X = Cl, Br) are pink in color. Both the chloro and bromo derivatives of the bis diamine complexes have reflectance spectra with maxima at *ca.* 8500 cm^{-1} and one broad band with several peaks at *ca.* 20,000 cm^{-1} (Figure 1). These spectra and the magnetic moment values are typical of hexa-coordinated cobalt(II) complexes.[11]

The absorption spectra are different from the reflectance spectra: three bands are present in the 5000-10,000 cm^{-1} region and two system of bands are present at *ca.* 15,000 and 17,500-20,000 cm^{-1}. On heating the color of the solutions changes from violet to blue and the bands at 6000, 7000, 10,000, 15,000 and 17,000 cm^{-1} increase in intensity (Figure 2).

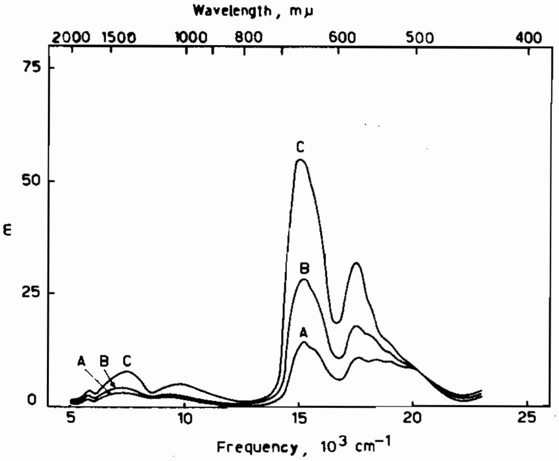

Figure 2. Absorption spectra of Co(Me_3en)$_2Cl_2$ in $(CH_2Cl)_2$ at: (A) 20°C, (B) 40°C, (C) 60°C.

This is indicative of an equilibrium between octahedral form Co(Me_3en)$_2X_2$ and a pseudotetrahedral form probabily Co(Me_3en)X_2. In fact molecular weight measurements show that the Co(Me_3en)$_2Cl_2$ complex dissociates in nitroethane solution (M_{found}/M_{calcd} = 0.5). Moreover in the solid state the complex loses one molecule of the ligand when warmed at 80°C *in vacuo* for 24 hours. The iodo derivative behaves in the same manner in solution in inert solvents, but the reflectance spectrum with bands at 5000, 11,500 and 19,000 cm^{-1} is quite different from those of bromo and chloro analogs (Figure 1). The 11,500 cm^{-1} band seems to exclude both the tetrahedral and octahedral stereochemistries. No conclusion however can be drawn on the basis of the reflectance spectrum only.

Nickel(II) Complexes. With nickel halides, complexes of the general formula Ni(diamine)X_2 with the ligand Me_3en, Et_3en and Me_3tn and Ni(Me_3en)$_2X_2$ have been obtained. All of the complexes are paramagnetic (Table I). The reflectance spectra of the complexes Ni(Me_3tn)X_2 and Ni(Et_3en)X_2 (X = Br, I) are not significantly different from their absorption spectra in inert solvents and show bands at *ca.* 8000, 11,500 and 20,000 cm^{-1} (Figure 3). These frequencies as well as the shape of the spectra are typical of distorted tetrahedral complexes as particularly exemplified by Ni(Me_4tn)X_2.[4] The Ni(Me_3en)$_2X_2$ complexes are green in color and non-conducting in solution in inert solvents. Their spectra in the solid state show bands at *ca.* 8000, 10,500 and 25,000 cm^{-1} (Figure 3) which are characteristic of octahedral nickel complexes.[4-2] Molecular weight measure-

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(10) D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *Inorg. Chem.*, *1*, 239 (1962) and reference therein.

(11) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 338 (1959). R. L. Carlin, in « Transition Metal Chemistry », Marcel Dekker, Ink., New York, N. Y., 1965, Vol. 1, pages 12 and 21.

ments on the $Ni(Me_3en)_2Cl_2$ complex in 1,2-dichloroethane solution indicates that the complex is monomeric (n = 1.05). It is interesting to note that the analogous complex with the ligand en, $Ni(en)_2Cl_2$, is dimeric octahedral with chlorine bridges.[12] The absorption spectrum of the $Ni(Me_3en)_2I_2$ complex in 1,2-dichloroethane shows two new bands at 10,000 and 18,500 cm^{-1} whose intensities increase with the temperature. This indicates the presence of an equilibrium between hexa-coordinated and tetrahedral species. Since the solution is non-conducting and the new peaks very closely resemble those of the tetrahedral $Ni(Et_3en)I_2$ complex, the equilibrium must take place through the displacement of one molecule of ligand. This is also supported by the degree of association of the complex in nitroethane solution which is 0.5 at 38°C. The absorption spectra of the chloride and bromide complexes are practically identical to the reflectance spectra but the peaks characteristic of the tetrahedral form become visible at temperature greater than 120 and 50°C respectively.

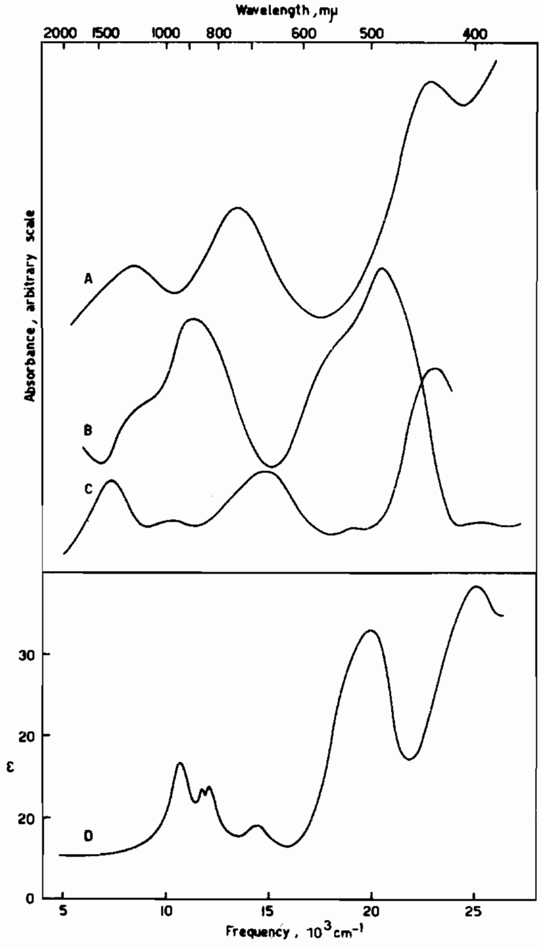

Figure 3. Reflectance spectra of: $Ni(Me_3en)Br_2$, curve A; $Ni(Et_3en)Br_2$ curve B; $Ni(Me_3en)_2Br_2$, curve C. Absorption spectrum of $Ni(Me_3tn)Cl_2$ in $(CH_2Cl)_2$, curve D.

The $Ni(Me_3en)X_2$, $Ni(Et_3en)Cl_2$ and $Ni(Me_3tn)Cl_2$ complexes are yellow green in color. Their reflectance spectra (Figure 3) are very similar in form and frequencies to those reported for $Ni(Amine)_2Cl_2$ complexes with a polymeric hexa-coordinated configuration achieved via halogen bridges.[13] Their solutions in *o*-dichlorobenzene are thermochroic, changing from green to violet as the temperature rises. The absorption spectra show two new bands at 11,000-12,000 and 20,000 cm^{-1} whose intensity increases with the temperature while those of the bands at 15,000 and 25,000 cm^{-1} decrease. This is indicative of an equilibrium between hexa-coordinate octahedral and tetrahedral forms. This equilibrium is displaced towards the tetrahedral form as the temperature increases.

Conclusions. The coordinating properties towards cobalt(II) and nickel(II) halides of the ligand Me_3en are different from these of the ligand Me_4en. In fact Me_4en forms only 1:1 complexes and they are pseudotetrahedral when X = Br, I. In this respect the coordinating properties of the ligand Me_4en are similar to those of Et_3en and Me_3tn. In fact with the ligands Me_4en Et_3en, and Me_3tn only 1:1 complexes are obtained and they have the same stereochemistry for a given metal and halide. Me_4tn also forms only 1:1 complexes, strongly favouring a tetrahedral structure. The order of increasing bulkiness amongst these ligands is presumably $Me_3en < Me_4en \simeq Et_3en \simeq Me_3tn < Me_4tn$. The coordinating number of the metal ions tend to decrease in this order and the tetrahedral structure is increasingly favored. The stereochemistry of the nickel complexes is also determined by the bulkiness of the halogens. The tetrahedral form is favored by the halogens in the order $I > Br > Cl$. In general these results show that the steric requirements of these ligands are the most important factor in determining the stereochemistry of these metal complexes.

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[12] A. S. Antsyshkina and M. A. Poray-Koshits, *Dokl. Akad. Nauk., SSSR, 143,* 105 (1962).

[13] A. B. P. Lever, S. M. Nelson, and T. M. Shepard, *Inorg. Chem., 4,* 810 (1965). A. B. P. Lever, *ibid., 4,* 753 (1965).