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High-Spin Five-Coordinate Nickel(II) Complexes of a Tridentate Aliphatic Amine Containing Primary Amino Groups[1a]

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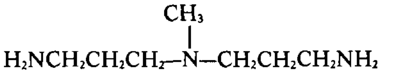
Examples of five-coordinate high-spin nickel(II) halide complexes of a tridentate aliphatic amine containing primary amino groups have been prepared. The stereochemistry of complexes of the type Ni[$H_2N(CH_2)_3N(CH_3)(CH_2)_3NH_2$]$X_2$, X = Cl, Br, I is deduced from spectral, magnetic, molecular weight and conductivity data.

Introduction

Many five-coordinate high-spin complexes of nickel(II) have been described since they were first discovered in 1965.[2,3] The occurrence of high-spin five-coordinate complexes is apparently related to the character of the donor atoms and the steric requirements of the ligands.[3,4] The range and occurrence of this new type of coordination has been investigated *via* synthetic studies employing polydentate Schiff bases[2,3,5] and aliphatic polyamines containing dialkylamino groups.[6]

In the course of the preparation and study of nickel halide complexes of Schiff bases derived from benzaldehydes and aliphatic triamines,[7] compounds of the formula Ni(triamine)X_2 were obtained when the triamine was bis(3-aminopropyl)methylamine, MeDPT.



$$H_2NCH_2CH_2CH_2\text{—}\underset{}{\overset{CH_3}{\overset{|}{N}}}\text{—}CH_2CH_2CH_2NH_2$$

Apparently hydrolysis of the Schiff base occurs in n-butanol solution in the presence of nickel halides in the case of this triamine.

These complexes, the analyses of which are reported in Table I are soluble in polar organic solvents such as chloroform, 1,2-dichloroethane and nitrobenzene. The chloro and bromo derivatives are essentially monomeric in 1,2-dichloroethane and the bromo complex does not conduct in this solvent. All are paramagnetic with magnetic moments of *ca.* 3.3 BM (see Table I). Their solution electronic spectra in chloroform, 1,2-dichloroethane, or ethanol are very similar to one another, each exhibiting three principal bands at *ca.* 9000, 16000, and 25000 cm^{-1}. The band positions depend on the halogen in the manner expected from the spectrochemical series. The spectra are shown in Figure 1. Although the band frequencies are strongly reminiscent of hexacoordinate nickel(II) complexes,[8] the molecular weight data eliminate this possibility since only five donor atoms are present in the monomeric unit. Moreover, the high molar extinction coefficients, especially of the third band (ε = 200-400 l cm^{-1} mole^{-1}), cannot be explained on the basis of a six-coordinate structure.[9]

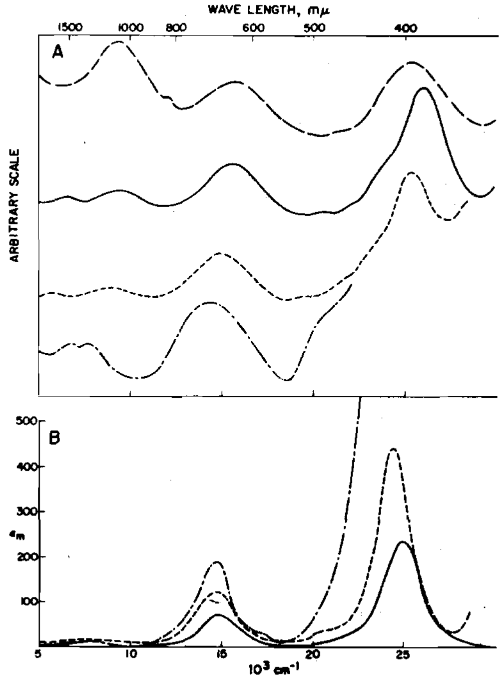


Figure 1. Electronic spectra of Ni[MeDPT]$_2X_2$ complexes. A: Nujol mull spectra; B: Solution spectra in 1,2-dichlorotehane. Ni[MeDPT]Cl_2 ———; Ni[MeDPT]Br_2 - - - -; Ni[MeDPT]I_2 - — - — - — —; Ni[DEN]Cl_2 — — — —.

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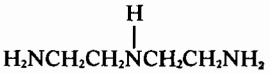
Table I. Analytical and Magnetic Data

	C %		H %		N %		
	Calcd.	Found	Calcd.	Found	Calcd.	Found	μ_{eff}, BM [d]
$Ni(MeDPT)Cl_2$ [a]	30.59	30.55	6.97	7.43	15.28	14.97	3.29
$Ni(MeDPT)Br_2$ [b, c]	23.11	23.18	5.25	5.45	11.57	11.71	3.28
$Ni(MeDPT)I_2$	18.36	18.55	4.18	3.90	9.18	9.01	3.30

[a] Association degree in 1,2-dichloroethane n = 1.02. [b] Association degree in 1,2-dichloroethane n = 1.07. [c] Molar conductivity in 1,2-dichloroethane = 0.15 ohm^{-1} cm^2 mol^{-1}. [d] Measured at room temperature 23-25° and corrected for diamagnetic contributions as calculated from B. N. Figgis and J. Lewis in « Modern Coordination Chemistry », Interscience Publishers, Inc., New York, N. Y., 1960, p. 403.

The foregoing results indicate that the complexes $Ni(MeDPT)X_2$ are five-coordinate at least in solution. On this basis the bands at 9000 and 16000 cm^{-1} may be assigned to F→F transitions and that at 25000 cm^{-1} to F→P transitions.[10] The relatively high energies of these transitions, which are in the range typical of octahedral complexes, may be attributed to the strong ligand field provided by the primary amino nitrogen donor atoms.

The mull spectra are quite similar to the solution spectra, however the band intensities cannot be used as a criterion and the band positions are not diagnostic of five-coordination as mentioned earlier. The mass spectra of the chloro and bromo derivatives show parent peaks corresponding to monomers as well as fragment peaks, but no peaks at higher mass numbers. Nickel halide complexes of the related ligand bis-(2-aminoethyl)amine, DEN, which are associated in the solid state to



$$\mathrm{H_2NCH_2CH_2\overset{\displaystyle H}{\overset{|}{N}}CH_2CH_2NH_2}$$

yield six-coordination at the nickel,[11] are insoluble in chlorinated organic solvents and do not exhibit a mass spectrum under similar conditions. The mass spectral results on the present MeDPT complexes are consistent with a monomeric five-coordinate formulation, but they do not represent absolute proof since reorganization may take place in going from the solid to the vapor phase.

The present MeDPT complexes represent the first examples wherein a tridentate polyamine ligand containing primary amino groups gives rise to five-coordination. Apparently the presence of the three carbon aliphatic chains and perhaps the presence of the central N–CH_3 group plays a decisive role. These are the two features which distinguish MeDPT from DEN, the latter ligand gives rise to associated octahedral species.

Experimental Section

The ligand MeDPT was kindly supplied by the Union Carbide Corp. The complexes were prepared by adding 5 mmoles of MeDPT dissolved in 10 ml of *n*-butanol to a solution of 5 mmoles of anhydrous nickel halide salt dissolved in 20 ml of the same solvent. After boiling for several minutes the solution was filtered, concentrated and crystals obtained. These were collected on a filter-frit under dry nitrogen and dried at 100° *in vacuo*. The analyses were performed by Baron Consulting Co., Orange, Conn.

Magnetic moments were determined by the Gouy method calibrated with distilled water and $Hg[Co(NCS)_4]$.[12] The electronic spectra were recorded in the range 5000-30000 cm^{-1} with a Cary 14 spectrophotometer using 1 cm quartz cells. Molecular weights were determined in 1,2-dichloroethane at 37° using a Mechrolab model 301A vapor pressure osmometer calibrated with benzil. The conductivity value was measured on an ESI Universal Jmpedance Bridge, Model 250DA, using solutions of *ca* 10^{-3} M concentration.

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