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Octahedral Nickel(II) Complexes with the Tripod Ligand Tris(2-dimethylarsinoethyl)amine

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Nickel(II) complexes with the tripod tetradentate ligand tris(2-dimethylarsinoethyl)amine (Me_6nas_3) having the general formula [$NiX_2(Me_6nas_3)$], X = Cl, Br, I, NCS, were prepared and characterized. All the complexes have octahedral geometry: the chloride and bromide derivatives are monomeric; the iodide and thiocyanate compounds have a polymeric chain structure in which the ligand Me_6nas_3 is bridging between two nickel atoms.

Introduction

The tripod ligand tris(2-diphenylarsinoethyl)amine, $N(CH_2CH_2As(Ph)_2)_3$, nas_3, forms transition metal complexes with coordination numbers ranging from four to five with trigonal pyramidal [1] and trigonal bipyramidal geometries [2]. The congestion around the bonding face of the arsenic atoms, due to the two phenyl groups, does not permit metal complexes with coordination numbers greater than five.

It was observed recently with the tripod ligand tris(2-diphenylphosphinoethyl)amine, np_3, that reduction of the cone angle on the phosphorus atoms by substitution of phenyl with methyl groups induces drastic changes in the coordinating properties of the ligand [3].

To investigate further the changes of the coordinating properties of tripod ligands by reduction of the steric hindrance we have synthesized a ligand having the inner skeleton of nas_3, but methyl substituents in place of the phenyl groups, *i.e.* tris(2-dimethylarsinoethyl)amine, Me_6nas_3. This ligand reacts with nickel(II) halides and pseudohalides to give complexes of general formula [$NiX_2(Me_6nas_3)$], X = Cl, Br, I, NCS. The chloride and bromide derivatives are monomeric with octahedral geometry; the iodide and thiocyanate complexes have a polymeric chain structure in which the Me_6nas_3 ligand is bridging between two nickel atoms. The complexes have been characterized by the usual physical measurements.

Experimental

The solvents were purified and dried using standard methods. All the reactions were carried out under nitrogen due to air decomposition of the ligand. Electronic and infrared spectra, molar conductivities, and other physical measurements were car-

TABLE I. Analytical and Physical Data for the Complexes.

Compound	Colour	n[a]	% Calcd.				% Found				μ_{eff}/μ_B (293 K)
			C	H	N	Ni	C	H	N	Ni	
[$NiCl_2(Me_6nas_3)$][b]	green	0.99	26.55	5.57	2.58	10.82	26.50	5.60	2.61	10.80	3.06
[$NiBr_2(Me_6nas_3)$][c]	green	0.97	22.80	4.79	2.22	9.29	22.80	4.89	2.26	9.19	3.03
[$NiI_2(Me_6nas_3)$]$_n$[d]	brown		19.86	4.17	1.93	8.09	19.84	4.21	1.89	8.06	3.04
[$Ni(NCS)_2(Me_6nas_3)$]$_n$[e]	brown		28.60	5.14	7.15	9.98	28.57	4.32	7.13	9.95	3.06
[$NiI(Me_6nas_3)$]BPh_4[f]	violet		47.10	5.49	1.53	6.10	47.11	5.54	1.51	6.31	diam.

[a] Ratio of the observed to the theoretical monomeric molecular weight for *ca.* 3×10^{-3} *M* soln in 1,2-dichloroethane. [b] Calcd.: Cl, 13.06. Found: Cl, 13.00. [c] Calcd.: As, 35.58. Found: As, 35.44. [d] Calcd.: I, 34.98. Founo: I, 34.88. [e] Calcd.: As, 38.23; S, 10.90. Found: As, 38.12; S, 10.61. [f] Calcd.: I, 13.82. Found: I, 13.71.

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TABLE II. Electronic Spectra of the Complexes.

Compound		Absorption Max., kK (ε for soln., l mol^{-1} cm^{-1})
$[NiCl_2(Me_6nas_3)]$	a	8.5, 9.5, 11.4, 16.8, 25.0sh
	b	8.5(37), 9.5(43), 16.5(227)
	c	8.5(41), 9.5(45), 16.6(215)
$[NiBr_2(Me_6nas_3)]$	a	8.1, 8.9, 11.9, 16.7, 25.0sh
	b	8.4(35), 9.2(42), 16.2(210), 23.2sh
	c	8.4(39), 9.3(45), 16.3(220), 22.8sh
$[NiI_2(Me_6nas_3)]_n$	a	8.3sh, 10.8, 17.2sh, 20.7
	b	10.9, 14.2, 18.2, 20.8
$[Ni(NCS)_2(Me_6nas_3)]_n$	a	9.4sh, 11.3, 19.1, 26.3
	b	9.0, 13.8sh, 15.6sh, 19.2
$[NiI(Me_6nas_3)]BPh_4$	a	14.3, 18.5
	b	14.1(1610), 18.2(715), 24.5(1246)
	c	14.1(1503), 18.2(684), 24.4(1280)

^{a}Reflectance Spectra. ^{b}1,2-Dichloroethane solution. ^{c}Nitroethane solution.

ried out using methods already described [4].

The ligand tris(2-dimethylarsinoethyl)amine, Me_6-nas_3, was prepared by the method previously described [1].

Synthesis of the Complexes

$[NiX_2(Me_6nas_3)]$, X = Cl, Br, I, NCS

The ligand (1 mmol) in boiling butanol (10 ml) and dimethylformamide (3 ml) was added to a hot solution of $NiX_2 \cdot 6H_2O$ (1 mmol) in butanol (20 ml). The crystalline compounds obtained by lowering the temperature of the solution to 80–90 °C, were filtered and washed with boiling butanol and light petroleum.

$[NiI(Me_6nas_3)]BPh_4$

A solution of sodium tetraphenylborate (1 mmol) in butanol (5 ml) was added to the solution obtained by mixing the ligand (1 mmol) in boiling butanol (10 ml) and dimethylformamide (4 ml) and nickel halide (1 mmol) in boiling butanol (10 ml). The crystalline product obtained by cooling the solution was filtered, washed with butanol and light petroleum.

Analytical data and physical properties of the complexes are reported in Table I.

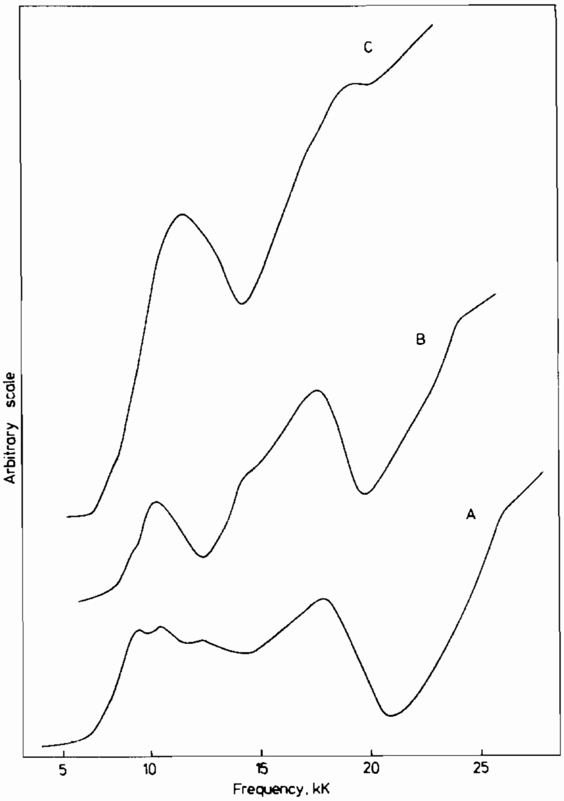

Fig. 1. Reflectance spectra of A, $[NiBr_2(Me_6\ nas_3)]$; B, $[NiBr_2(Vas_3)_2]$; C, $[Ni(NCS)_2(Me_6nas_3)]_n$.

Results and Discussion

All the compounds are air sensitive. The chloride and bromide complexes have effective magnetic moments at room temperature of 3.06 and 3.03 B.M., respectively, (Table I). Their diffuse reflectance spectra and 1,2-dichloroethane and nitroethane solution spectra, which are practically identical (Table II), show bands at *ca.* 8.3, 9.0, 11.5 and 16.7 kK and a shoulder at 25.0 kK in the d–d region. The two complexes are sparingly soluble in 1,2-dichloroethane and nitroethane where they are essentially non-electrolytes and monomeric. The spectral and magnetic data are consistent with a distorted octahedral geometry in which there is no center of symmetry [5], giving rise to bands in characteristic

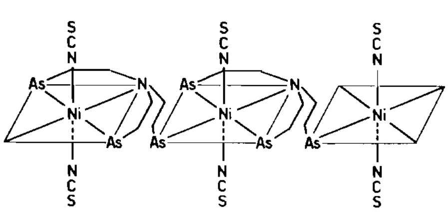

Fig. 2. Schematic inner skeleton of polymeric chain complex $[Ni(NCS)_2(Me_6nas_3)]_n$.

positions but with rather high intensities (ϵ 37–210 l mol^{-1} cm^{-1}) as found for other nickel(II) octahedral complexes having alkylated tritertiary arsines as donor atoms [6], (Fig. 1). Thus the available evidence and the geometric requirements of the ligand point to a *cis*-octahedral structure in which the tripod ligand spans two adjacent faces of the octahedron and the halides are mutually *cis*.

The complex $[NiI(Me_6nas_3)]BPh_4$, obtained from nickel(II) iodide and the ligand in presence of sodium tetraphenylborate, is diamagnetic in the solid state and a 1:1 electrolyte in 1,2-dichloroethane and nitroethane solution. Visible spectra both in the solid state and in solution show two bands at 14.3 and 18.5 kK (ϵ 1503 and 684 l mol^{-1} cm^{-1}, respectively) (Table II). These spectra are characteristic of low spin trigonal bipyramidal nickel(II) complexes with tripod ligands [7]; the two bands may be assigned to be $(a_1')^2 \rightarrow a_1'e'$ and $(a_1)^2 \rightarrow a_1'e''$ transition, respectively [8].

The two isomorphous complexes $[NiX_2(Me_6nas_3)]$, X = I, NCS, have effective magnetic moments of 3.04 and 3.06 B.M. The reflectance spectra of the two complexes are similar (Table II) and show bands at *ca.* 9.0, 11.0 and 20.0 kK, the iodo derivative also shows a shoulder at 17.24 kK. The infrared spectrum of the thiocyanate derivative in the 2000 cm^{-1} region shows an intense ν(CN) band at 2065 cm^{-1} indicative of N-bonded, equivalent non-bridging thiocyanate groups [9]. The equivalence of the two thiocyanate ions is not consistent with a monomeric compound considering the geometric requirements of the tripod ligand; furthermore the reflectance spectra of the two compounds are not comparable to the spectra of other nickel(II) complexes with known geometry [10]. In order to obtain information about the coordination geometry of these complexes an X-ray structural analysis has been carried out on the complex $[Ni(NCS)_2(Me_6nas_3)]$.

Preliminary results of the diffraction analysis have shown that the chromophore $[Ni(NCS)_2(Me_6nas_3)]$ has a polymeric chain structure consisting of a sequence of six-coordinate metal ions with distorted octahedral geometry, (Fig. 2). Three equatorial positions of each octahedron are occupied by the nitrogen and two arsenic atoms of one Me_6nas_3 ligand, the other equatorial site is occupied by an arsenic atom of an adjacent Me_6nas_3 ligand which bridges the chain of octahedra. The two thiocyanate ions are bound *trans* to the metal in the apical positions of the octahedron. In order to hold together the metal atoms the ligands Me_6nas_3 are almost completely flattened.

The two polymeric complexes are slightly soluble in 1,2-dichloroethane and nitroethane with decomposition; these solutions show some conductivity [11]. The absorption spectrum of the iodo derivative shows bands at the same frequency as those found in the solid state and two other bands characteristic of the chromophore $[NiI(Me_6nas_3)]^+$ (Table II). These data are consistent with the following solution equilibrium:

$$[NiI_2(Me_6nas_3)]_n \rightleftarrows n[NiI(Me_6nas_3)]^+ + nI^-$$

By comparing the complexes reported here with the five-coordinate derivatives of the nas_3 ligand it appears that the smaller cone angle of the arsenic donor atoms of the Me_6nas_3 ligand reduces the steric hindrance around the metal atom so that it may coordinate two halides or pseudohalides and adopt an octahedral geometry; when the two halides have a small size (Cl, Br) the complexes are monomeric; with larger ions (I, NCS) these complexes are polymeric and the metal has a geometry in which these ions are in *trans* position.

The complexes $[NiX(TAP)]^+$ [12], where TAP is tris(2-dimethylarsinopropyl)phosphine which differs from $Menas_3$ only in the major length of the chains between the apex and the arsenic donor atoms, have a trigonal bipyramidal geometry. The different coordination of the complexes with TAP may be explained by the fact that the six member ring pushes the plane of the three arsenic atoms below [13] the nickel atom which is enclosed into the tripod skeleton of the ligand; in this way reduction of the steric hindrance on the arsenic face is not enough to give compounds with higher coordination number.

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