$[Os(NH_3)_6]X_3$ complexes were stable in dry air but decomposed when moist. In aqueous solution they decomposed over a few hours, even under argon, to an intractable brown material, with no evidence of an osmium analog of "ruthenium red."[15]

The X-ray powder pattern of $[Os(NH_3)_6]I_3$ was similar to that reported by Watt and Vaska[2] and was indexed as face-centered cubic (probable space groups $Fm3m$, $F432$, or $F\bar{4}3m$) with $a = 11.04$ Å (seven lines observed, uncalibrated film). The iodide salt had a room-temperature magnetic moment of 1.6 BM, similar to that reported previously.[2] The electronic spectrum (aqueous solution, ClO_4^- or Cl^- salts) showed absorption bands at 221 nm (ϵ 760), 229 nm (ϵ 759) and 261 nm (ϵ 78). The ir spectra were similar to those of $[Ru(NH_3)_6]X_3$,[7] but with NH_3 vibrations approximately 25 cm^{-1} higher in energy.

In acid solution $[Os(NH_3)_6]I_3$ and nitric oxide gave $[Os(NH_3)_5NO]I_3 \cdot H_2O$. This preparation is more convenient than our earlier procedure[13] but gives a much lower overall yield. In 0.01 M hydroxide ion $[Ru(NH_3)_6]^{3+}$ and nitric oxide gave $[Ru(NH_3)_5N_2]^{2+}$ in 97% yield.[8] $[Os(NH_3)_6]^{3+}$ gave only $[OsNH_2(NH_3)_4NO]^{2+}$ [13] under the same conditions. In 1-4 M hydroxide a mixture of $[Os(NH_3)_5N_2]^{2+}$ [16] and $[OsNH_2(NH_3)NO]^{2+}$ was obtained; the percentage of dinitrogen complex increased with hydroxide ion concentration to approximately 100% at 4 M. However, the total yield was only 30% of the expected. Since no other product could be isolated, we cannot decide whether the low yield was due to decomposition of $[Os(NH_3)_6]^{3+}$ in solution or to other reactions of $[Os(NH_3)_6]^{3+}$ with NO.

Experimental Section

Hexaammineosmium(III) Salts, $[Os(NH_3)_6]X_3$ (X = Cl, Br, I, ClO_4). A mixture of $(NH_4)_2OsCl_6$ (0.50 g), Zn dust (0.5 g), and NH_3 (0.880 g cm^{-3}; 15 ml) was refluxed under argon for 5 hr. To the resultant mixture was added NH_3 (0.880 g cm^{-3}; 3 ml), the mixture was filtered, and KI (2 g) was added to the filtrate. The resultant yellow precipitate was purified by reprecipitation from cold water with HI; yield 0.244 g (32%). A further quantity (approximately 9%) was obtained by evaporating the filtrate under argon and recycling. *Anal.* Calcd for $H_{18}I_3N_6Os$: H, 2.70; I, 56.56; N, 12.49. Found: H, 2.57; I, 56.91; N, 12.45.

Cl^-, Br^-, and ClO_4^- salts were prepared metathetically from the iodide; yields 60, 78, and 65%, respectively. *Anal.* Calcd for $Br_3H_{18}N_6Os$: Br, 45.05; H, 3.41; N, 15.79. Found: Br, 44.89; H, 3.53; N, 15.89. Calcd for $Cl_3H_{18}N_6Os$: Cl, 26.67; H, 4.55; N, 21.08. Found: Cl, 26.88; H, 4.46; N, 21.39. Calcd for $Cl_3H_{18}N_6O_{12}Os$: N, 14.23. Found: N, 14.02.

Nitrosylpentaammineosmium Triodide Hydrate, $[Os(NH_3)_5NO]I_3 \cdot H_2O$. To a deoxygenated slurry of $[Os(NH_3)_6]I_3$ (0.096 g) in water (9 ml) was added 5 drops of concentrated HI, and NO was passed through for 24 hr. The orange solution was filtered and the product was precipitated with concentrated HI; yield 0.079 g (79%). The properties of the product were identical with those of $[Os(NH_3)_5NO]I_3 \cdot H_2O$ prepared by the literature method.[13]

Reaction of Hexaammineosmium with Nitric Oxide in Alkaline Solution. Nitric oxide was passed through a deoxygenated solution of $[Os(NH_3)_6]I_3$ (0.098 g) in NaOH (1-4 M; 4 ml) for 23 hr. The product was precipitated from the ice-cold orange-red solution with KI; yield 0.020 g (29%). The percentages of $[OsNH_2(NH_3)_4NO]^{2+}$ and $[Os(NH_3)_5N_2]^{2+}$ were estimated from the infrared and electronic spectra of the mixture.[13,16]

Acknowledgments. We thank Johnson, Matthey and Mallory, Montreal, for the generous loan of osmium salts and the National Research Council and University of New Brunswick Research Fund for financial support.

Registry No. $[Os(NH_3)_6]Cl_3$, 42055-53-8; $[Os(NH_3)_6]Br_3$, 42055-54-9; $[Os(NH_3)_6]I_3$, 42055-55-0; $[Os(NH_3)_6](ClO_4)_3$, 42055-56-1; $(NH_4)_2OsCl_6$, 12125-08-5.

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Nickel(II) and Cobalt(II) Complexes Containing Bis(diphenylphosphino)-*o*-carborane

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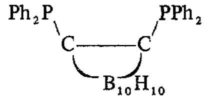
Received June 12, 1973

In recent years there have been a number of reports of the preparation of metal complexes containing ligands in which the *o*-carborane nucleus functions as a ligand backbone.[2,3] In particular we were intrigued by the results obtained in the reactions between bis(diphenylphosphino)-*o*-carborane, dpc,



dpc

L, and divalent salts of the first transition series.[2] Although Smith obtained planar complexes of the type $[Ni(dpc)Cl_2]$ and $[Ni(dpc)_2]Cl_2$ he could obtain no reaction between this diphosphine and cobalt(II) salts. Recent work by some of us has involved studies of the stereochemical and spectrochemical aspects of altering chelate chain linkages,[4-6] and we were thus interested in the apparent effect of the *o*-carborane backbone in making bis(diphenylphosphino)-*o*-carborane unreactive toward cobalt(II) salts. Previous work by Sacco and Gorieri[7] and by Horrocks, *et al.*,[8] in the characterization of the pseudotetrahedral $[Co(dpe)X_2]$ (X = Cl, Br, I) and pentacoordinate, square-pyramidal $[Co(dpe)_2X]X$ (X = Cl, Br, I) (dpe = 1,2-bis(diphenylphosphino)ethane) has shown that bisphosphines form very stable complexes with cobalt(II). We here wish to report the isolation of tetrahedral cobalt(II) and trigonal-pyramidal nickel(II) and cobalt(II) complexes with dpc.

Experimental Section

Bis(diphenylphosphino)-*o*-carborane (I) was synthesized according to the method of Alexander and Schroeder.[9]

Diiodobis[bis(diphenylphosphino)-*o*-carborane]nickel(II). Nickel(II) iodide (0.31 g, 1.0 mmol) in ethanol (7 ml) was added dropwise to a stirred solution of the ligand (1.02 g, 2.0 mmol) in dichloromethane (50 ml). An immediate deep blue-black color developed and stirring was continued for 15 min, the solution was filtered, and diethyl ether (100 ml) was added dropwise to the stirred filtrate. After

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Table I. Some Physical Properties of the Complexes

Complex	Color	μ_{eff}, BM	Analyses, % found (calcd) C	H	B	Halogen
$[NiL_2I]I$	Blue-black	0.43	46.0 (46.6)	4.5 (4.5)	15.7 (16.1)	19.2 (19.0)
$[CoLCl_2]$	Blue	4.31	48.4 (48.2)	4.8 (4.7)	17.2 (16.9)	11.0 (10.8)
$[CoL(NCS)_2]$	Blue	4.42	48.3 (48.7)	4.5 (4.4)	16.0 (15.7)	4.3 (4.1)[a]
$[CoL_2Br]Br$	Green	2.19	51.0 (50.3)	5.0 (4.8)	17.7 (17.4)	13.2 (12.9)
$[CoL_2I]I$	Deep green	2.23	46.3 (46.6)	4.6 (4.4)	16.0 (16.1)	19.6 (19.0)
$[CoL_2(NCS)]CNS$	Green	2.23	53.7 (54.0)	5.3 (5.0)	18.4 (18.0)	2.1 (2.3)[a]

[a] Nitrogen.

Table II. Electronic Spectra of the Complexes

Compd	E_{max},[a] cm^{-1}	ϵ_{max}, M^{-1} cm^{-1}	E_{max},[b] cm^{-1}
$[NiL_2I]I$	16,835	2,390	16,870
	26,316 sh	4,530	26,700
	33,898	47,890	33,490
$[CoLCl_2]$	6,849	103	
	7,463	101	7,300
	13,624	665	13,710
	15,220	591	14,990
	16,949	638	16,885
	19,417	480	19,480
	23,697	512	23,610
$[CoL(NCS)_2]$	7,692	87	7,905
	16,080	579	16,200
	17,420	593	17,470
	18,730	489	18,710
	20,408 sh	331	
	23,256 sh	306	23,100
	29,240	457	29,380
$[CoL_2Br]Br$	6,536	137	
	7,813	152	7,400
	13,263	230	13,310
	14,599	202	14,605
	16,077	189	16,090
	26,525	324	26,070
$[CoL_2I]I$	5,950	184	
	7,250	193	7,400
	12,370	340	12,400
	13,420	370	13,280
	14,540	385	14,590
	18,020	sh	
	18,760	490	18,810
	29,410	sh	

[a] In dichloromethane. [b] Solid reflectance.

the addition, a fine microcrystalline precipitate was obtained. This was dissolved in CH_2Cl_2, filtered, and again precipitated by the addition of ether. The blue-black microcrystalline solid was obtained in 81% yield.

Dichlorobis[bis(diphenylphosphino)-*o*-carborane]cobalt(II). Anhydrous cobalt(II) chloride (0.26 g, 2.0 mmol) in ethanol (7 ml) was added dropwise to a solution of the ligand (1.02 g, 2.0 mmol) in dichloromethane (50 ml) and the resulting green solution was stirred overnight, during which time the color became light blue. Dropwise addition of ether (30 ml) resulted in the precipitation of a light blue microcrystalline powder. The isothiocyanato derivative was synthesized in an analogous manner; yields ~78%.

Dibromobis[bis(diphenylphosphino)-*o*-carborane]cobalt(II) and the analogous iodo and isothiocyanato derivatives were made in a manner similar to that used to prepare the nickel(II) iodide complex. Yields were in the 72-79% range.

Physical Measurements. Conductivities were measured on a Cambridge Instruments Ltd. conductivity bridge. Infrared spectra were measured in Nujol or hexachlorobutadiene mulls on a Perkin-Elmer 621 spectrophotometer, and electronic spectra on a Beckman DK2 spectrophotometer.

Results and Discussion

This study would seem to indicate that the complexing ability of dpc toward cobalt(II) is not as great as that of dpe but that, nonetheless, if care is taken, stable solid derivatives can be isolated. Appreciable concentrations of hydroxylic solvents decompose the complexes. The complexes isolated together with physical properties and analytical data are contained in Table I. Table II contains electronic spectral data.

The blue $[Co(dpc)X_2]$ (X = Cl, NCS) complexes appear to be quite typical CoP_2X_2 tetrahedral species; they are essentially nonconducting in nitromethane. The room-temperature magnetic moments are similar to other tetrahedrally coordinated Co(II) species.[8,10] Similarly, the electronic spectra in the solid state and in dichloromethane are readily assignable as tetrahedral complexes, the observed splittings being due to a combination of the C_{2v} component and the spin-orbit coupling. The multiplets which appear at *ca.* 7 and 16 kK can be assigned to the transitions $^4A_2 \rightarrow {}^4T_1(F)$ and $^4A_2 \rightarrow {}^4T_1(P)$ of rigorous T_d symmetry. The infrared spectrum of $[Co(dpc)(NCS)_2]$ in Nujol exhibits a broad absorption at 2080 cm^{-1}, assignable to the ν(CN) of Co-NCS bonds. This conclusion may be contrasted with the deduction of S bonding in $[Co(PPh_3)_2(SCN)_2]$.[11]

Reaction of $CoBr_2$ and CoI_2 with a 2 molar equiv of dpc was carried out in a solvent mixture containing mainly dichloromethane. Deep green $[Co(dpc)_2X]X$ was obtained; attempts to exchange the free halide group by large counteranions such as BPh_4^- led to rapid decomposition of the complexes. Nonetheless, the complexes are 1:1 electrolytes in fresh nitromethane solutions [Λ_0 = 87 (Br), 81 (I) ohm^2 cm^{-1} mol^{-1}], and so it must be assumed that the stability of the complexes in the solid state is to a certain degree dependent on packing forces and cation and/or anion size.

The electronic spectral absorptions of the $[Co(dpc)_2X]^+$ species are almost identical with those of the $[Co(dpe)_2X]^+$ complexes[8] and thus the former complexes can be assigned a similar pentacoordinate square-pyramidal structure. The magnetic moments are also consistent with this assignment. That the band positions in the two series of complexes are so alike indicates that dpc exerts a somewhat similar ligand field strength to that of dpe. The reflectance spectra are very similar to the solution spectra, and thus the complexes have a similar structure in both physical states.

We made a number of attempts to isolate $[Ni(dpc)_2X]^+$ species but were only successful in the case of $[Ni(dpc)I]I$. This blue-black diamagnetic complex does not appear to be square pyramidal, as are many pentacoordinate nickel(II) complexes of bidentate ligands.[4,10] The energy of the main visible absorption at 16,835 cm^{-1} is much lower than that found in the majority of square-pyramidal complexes but is in the range found for $[Ni(L_4)I]^+$ complexes which are essentially trigonal bipyramidal.[12]

Registry No. $[NiL_2I]I$, 42505-90-8; $[CoLCl_2]$, 42425-78-5; $[CoL(NCS)_2]$, 42425-79-6; $[CoL_2Br]Br$, 42425-80-9; $[CoL_2I]I$, 42505-91-9; $[CoL_2(NCS)]CNS$, 42505-92-0.

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