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Five-Coordinate Chromium(II) Complexes with Nitrogen-Phosphorus Tetradentate Ligands

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Preparation and properties of new five-coordinate complexes of chromium(II) are reported. The ligands tris(2-diphenylphosphinoethyl)amine (NP_3) and bis(2-diethylaminoethyl) - (2-diphenylphosphinoethyl) amine (N_3P) form chromium(II) complexes with the general formula [CrLX]BPh_4 ($L=NP_3$, $X=Cl$, Br, I; $L=N_3P$, $X=Br$; BPh_4 = tetraphenylborate). Spectral and conductivity data show that the complexes are five-coordinate both in the solid state and in solution.

Introduction

Although many five-coordinate 3d metal complexes have been reported, the $[Cr(Me_6tren)Br]^+$ cation[1] is the only documented example in which chromium(II) has been found to posses this coordination number.[2]

In this laboratory tripod ligands with mixed donor atoms are being investigated. It has been shown that these ligands form five-coordinate complexes with Ni^{II} and Co^{II} salts.[3] We have now extended this investigation to include the coordination properties of some of these ligands, containing N, P, and As as donor atoms, towards the Cr^{II} ion.

In this paper we report the complexes of Cr^{II} halides with the ligands tris(2-diphenylphosphinoethyl)-amino (NP_3) and bis(2-diethylaminoethyl)-(2-diphenylphosphinoethyl)amine (N_3P).

Experimental Section

In order to prevent oxidation all reactions and operations were carried out under moisture free nitrogen. The solvents were carefully deoxygenated by boiling and flushing with nitrogen before use. Hydrated Cr^{II} halides[4] were dehydrated by heating to 120°C under vacuum. The synthesis of the ligands was already reported.[3] A solution in *n*-butanol of the appropriate anhydrous Cr^{II} halide was added to the stoichiometric amount of the ligand in *n*-butanol. The complexes are readily obtained upon addition of a solution of sodium tetraphenylborate. The crystalline products were collected by filtration, washed with *n*-butanol and petroleum ether, and dried in a stream of dry nitrogen. All complexes quickly decompose when exposed to the air. Attempts to prepare the analogous complexes with the ligand tris(2-diphenylarsinoethyl)amine (NAs_3) have been unsuccessful. The analytical data are reported in Table I. Magnetic, spectrophotometric and conductivity measurements have been performed with the apparatus already described.[5]

Results and Discussion

The complexes obtained as tetraphenylborates have the general formula [CrLX]BPh_4 ($L=NP_3$, $X=Cl$, Br, I; $L=N_3P$, $X=Br$; BPh_4=tetraphenylborate). Attempts to prepare the dihalo derivatives were unsuccessful.

All of the complexes are of the high-spin type. The magnetic moments of the complexes $[Cr(N_3P)Br]BPh_4$ and $[Cr(NP_3)I]BPh_4$ are close to the spin-only value (Table I). Those of the complexes $[Cr(NP_3)X]BPh_4$ ($X=Cl$, Br) are 0.2-0.3 B.M. below this value. The magnetic susceptibility of the $[Cr(NP_3)Br]BPh_4$ complex has been determined as a function of the temperature between 77.5 and 293°K. The Curie law is obeyed with a Weiss constant of 0°K. It is interesting to note that the donor properties of the NP_3I donor set, which is sufficient to induce spin pairing in five-coordinate nickel(II) and cobalt(II) complexes,[3] are not sufficient to produce a spin paired configuration in the corresponding chromium(II) complexes.

The N_3P complex decomposes in common organic solvents and therefore the solution properties of this species could not be studied. The NP_3 derivatives are soluble in 1,2-dichloroethane and behave as 1:1 electrolytes in this solvent. The reflectance spectra of these complexes are all similar and do not differ substantially from their solution spectra in 1,2-dichloroethane. They show an intense band around 13,000 cm^{-1} and a weaker one in the region 16,000-17,000 cm^{-1} (Table II). The frequencies of these absorption maxima shift toward high energies in the order $Cl > Br > I$ according to the relative position of the halogen in the spectrochemical series. A weak band is also present at *ca.* 22,000 cm^{-1} and is attribu-

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[1] (Me_6tren)=tris(2-dimethylaminoethyl)amine.

[2] M. Ciampolini, *Chem. Comm.*, 1966, 47. M. Ciampolini and N. Nardi, *Inorg. Chem.*, *5*, 1150, (1966).

[3] L. Sacconi and I. Bertini, *J. Am. Chem. Soc.*, *90*, 5443 (1968). L. Sacconi, I. Bertini, and F. Mani, *Inorg. Chem.*, *7*, 1417 (1968). L. Sacconi and R. Morassi, *J. Chem. Soc.*, 2904 (1969).

[4] H. Lux and G. Illman, *Chem. Ber.*, *91*, 2143 (1958).

[5] I. Bertini and F. Mani, *Inorg. Chem.*, *6*, 2032 (1967).

Table I. Analytical and Some Physical Data for the Chromium(II) Complexes

Compound	%C Calcd.	%C Found	%H Calcd.	%H Found	%P Calcd.	%P Found	Λ, cm²/ohm M [a] $(CH_2Cl)_2$	μ_{eff} (BM)
$[Cr(NP_3)Cl]BPh_4$	74.96	74.40	5.91	6.10	8.78	8.77	15	4.62
$[Cr(NP_3)Br]BPh_4$ [b]	71.94	71.78	5.67	5.78	8.43	8.69	19	4.55
$[Cr(NP_3)I]BPh_4$	69.00	69.38	5.43	5.70	8.09	8.19	21	4.95
$[Cr(N_3P)Br]BPh_4$	69.00	69.70	7.13	7.16	5.48	5.40		4.97

[a] Conductivity values for *ca.* 10^{-3} M solutions at 20°C. Reference value in 1,2-dichloroethane is: $[(n\text{—}C_4H_9)_4N]Br$, 19. [b] Cr (%), Calcd. 4.72; Found 4.81.

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

Compound		Absorption max., cm^{-1} (ε_{molar} for the soln.)
$[Cr(NP_3)Cl]BPh_4$		13,500; 16,700
	$(CH_2Cl)_2$	13,800(510); 17,000(470)
$[Cr(NP_3)Br]BPh_4$		13,000; 16,100
	$(CH_2Cl)_2$	13,300(530); 16,000(415)
$[Cr(NP_3)O]BPh_4$		12,730; 15,400
	$(CH_2Cl)_2$	13,150(520); 15,600(380)
$[Cr(N_3P)Br]BPh_4$		11,600; 14,100

ted to the presence of Cr^{III} impurities which absorbs in this region (Figure 1). The spectra of these Cr^{II} complexes are similar in shape and comparable in frequency to the spectrum of $[Cr(Me_6tren)Br]Br$ complex which has been shown to have a trigonal bipyramidal structure.[1] The two bands of the NP_3 complexes occur at higher frequencies (*ca.* 2000 cm^{-1}) than those of the chromium(II) Me_6tren complex and are five times more intense. Both of these features are typical of complexes containing donor atoms of low electronegativity such as P and As which can form extensive covalent bonds with the metal atom.[6] On this basis the two d–d bands at 13,000 and 17,000 cm^{-1} are tentatively assigned to the two $^5A_1 \rightarrow {}^5E$ transitions in C_{3v} symmetry.

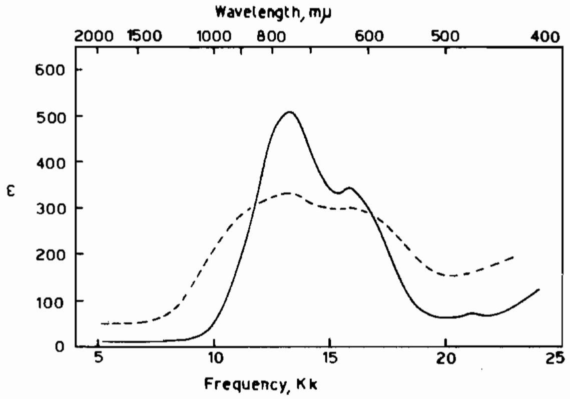

Figure 1. Reflectance spectrum of $[Cr(NP_3)I]BPh_4$ (dotted line) and absorption spectrum in $(CH_2Cl)_2$ (solid line).

Substantially the same spectrum in the solid state is shown by the $[Cr(N_3P)Br]BPh_4$ complex and therefore the same five-coordinate configuration can be presumably assigned to this complex.

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(6) G. Dyer, J. G. Hartley, and L. M. Venanzi, *J. Chem. Soc.*, 1293 (1965).