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Five-coordinate Chromium(II) Complexes with the Ligands Tris(*o*-diphenylphosphinophenyl)phosphine and Tris(2-dicyclohexylphosphinoethyl)amine

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Synthesis and characterization of new five-coordinate chromium(II) complexes are reported. These complexes have the general formula $[CrLX]Y$ *where* L = *tris(o-diphenylphosphinophenyl)phosphine (QP),* X = *Cl, Br, I,* Y = *tetraphenylborate* (BPh_4)*;* L = *tris (2-dicyclohexylphosphinoethyl)amine* (np_3cy)*,* X = *Cl, Br, and* Y = *hexafluophosphate* (PF_6)*. Spectral, magnetic and conductivity data are consistent with a five-coordinate essentially trigonal bipyramidal structure of these complexes both in the solid state and in solution.*

Introduction

Of the very few known chromium(II) complexes most have high-spin octahedral coordination geometries. Recently some examples of chromium(II) complexes with different coordination geometry (tetrahedral or trigonal bipyramidal) or spin state (low-spin hexacoordinate) have been reported.[1] As a part of a general investigation of chromium(II) chemistry we now include this study on the coordination ability toward this ion of the potentially tetradentate tripod-like ligands tris(*o*-diphenylphosphinophenyl)phosphine (QP) and tris(2-dicyclohexylphosphinoethyl)amine (np_3cy).

The ligand QP has been previously shown to form low-spin five-coordinate complexes with some 3*d* metal ions;[2] the ligand np_3cy has been prepared for the first time.

Experimental

In order to prevent oxidation, all reactions and operations were carried out under moisture free nitrogen or argon. The solvents were carefully deoxygenated by boiling and flushing with nitrogen before use.

Hydrated chromium(II) halides[3] were dehydrated by heating to 100° C under vacuum.

The synthesis of the ligand QP has been reported.[2] The ligand np_3cy was prepared as follows: $N(CH_2CH_2Cl)_3$[4] (0.04 mol) in dry tetrahydrofuran (50 ml) was slowly added with continuous stirring to $(C_6H_{11})_2PLi$[5] (0.12 mol) dissolved in dry tetrahydrofuran (400 ml).

The solution was heated under reflux for one hour and then concentrated to a small volume on a steam bath. The residue was treated with light petroleum; the resulting solution was filtered, concentrated and the ligand precipitated as white crystals by the addition of ethyl alcohol; yield 90%. Calcd. for $C_{42}H_{78}NP_3$: C, 73.1; H, 11.4; N, 2.0; P, 13.4. Found: C, 73.1; H, 11.4; N, 2.0; P, 13.3.

Synthesis of the Complexes

A solution in ethyl alcohol of the appropriate anhydrous chromium(II) halide was added to the stoichiometric amount of the ligand QP dissolved in 1,2-dichloromethane; the compounds are readily obtained as green crystals upon addition of a solution of sodium tetraphenylborate. The complexes with the ligand np_3cy are obtained as blue crystals with the same procedure using absolute ethanol as solvent and sodium hexafluophosphate. The products were collected by filtration, washed with absolute alcohol and light petroleum and dried in a stream of dry nitrogen. All complexes decompose when exposed to the air.

The analytical data are reported in Table I. Magnetic, spectrophotometric and conductivity data have been obtained with the apparatus already described.[6]

Results and Discussion

The complexes here reported have the general formula $[CrLX]Y$ where $L = QP$, $X = Cl, Br, I$, $Y = BPh_4$ and $L = np_3cy$, $X = Cl, Br$, $Y = PF_6$. All the complexes are high-spin with an effective magnetic moment at room temperature in the range expected for four unpaired electrons (Table I).

The complexes are readily soluble in 1,2-dichloroethane and behave as 1:1 electrolytes in this solvent. The electronic spectra of these derivatives dissolved in 1,2-dichloroethane are similar and do not differ from the solid reflectance spectra. All show an absorption

TABLE I. Physical Constants and Analytical Data.

Compound	Λ_M^a (cm^2 ohm^{-1} mol^{-1})	Anal%										μ_{eff}(BM)
		Calcd.					Found					
		C	H	N	P	Cr	C	H	N	P	Cr	
$[CrCl(QP)]BPh_4$	18	76.7	5.1		10.1	4.3	76.9	5.3		10.3	4.2	4.85
$[CrBr(QP)]BPh_4$	20	74.0	4.9		9.8	4.1	73.3	5.3		9.8	4.0	4.82
$[CrI(QP)]BPh_4$	20	71.4	4.8		9.4	4.0	71.5	5.0		9.4	4.0	4.89
$[CrCl(np_3cy)]PF_6$	20	54.7	8.5	1.5		5.6	54.3	8.4	1.4		5.5	4.84
$[CrBr(np_3cy)]PF_6$	21	52.0	8.1	1.4			51.7	8.2	1.4			4.88

[a] Molar conductance of *ca.* 10^{-3}M soln. in 1,2-dichloroethane; reference value in this solvent is: $[(n\text{-}C_4H_9)_4N]Br$, 19.

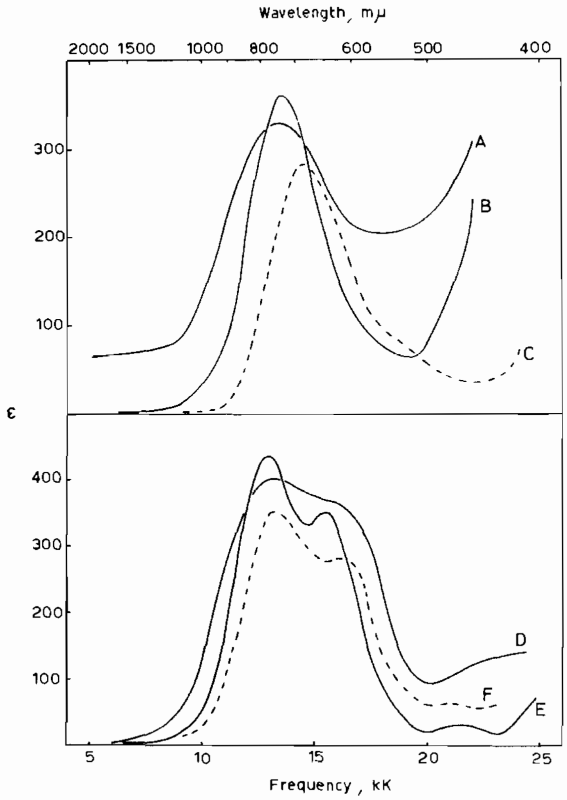

Figure 1. Reflectance spectrum of $[CrBr(QP)]BPh_4$, A; absorption spectra in $(CH_2Cl)_2$ of $[CrBr(QP)]BPh_4$, B, and $[CrBr(pp_3)]BPh_4$, C (ref. 1b); reflectance spectrum of $[CrBr(np_3cy)]PF_6$, D; absorption spectra in $(CH_2Cl)_2$ of $[CrBr(np_3cy)]PF_6$, E, and $[CrBr(np_3)]BPh_4$, F (ref. 1a).

maximum at *ca.* 13 kK (Figure 1 and Table II); however a less intense peak is present at *ca.* 16 kK in the spectra of np_3cy derivatives. The frequencies of these absorption maxima shift towards high energies in the order I, Br, Cl, according to the relative positions of the halogens in the spectrochemical series.

TABLE II. Spectroscopic Data for the Complexes.

Compound		Absorption max. (kK), (ε_{molar} for soln. in parentheses)
$[CrCl(QP)]BPh_4$	a	13.4
	$(CH_2Cl)_2$	14.1 (762)
$[CrBr(QP)]BPh_4$	a	13.6
	$(CH_2Cl)_2$	13.7 (360)
$[CrI(QP)]BPh_4$	a	13.3
	$(CH_2Cl)_2$	13.4 (830)
$[CrCl(np_3cy)]PF_6$	a	13.3; 16.4
	$(CH_2Cl)_2$	13.3 (546); 16.4 (370)
$[CrBr(np_3cy)]PF_6$	a	13.2; 15.6
	$(CH_2Cl)_2$	13.2 (415); 15.8 (340)

[a] Diffuse reflectance spectrum.

On the basis of the steric requirements of the potentially tetradentate ligands QP and np_3cy, the stoichiometry of the derivatives and their electrolytic behaviour, it is assumed that the complexes here reported are five-coordinate both in the solid state and in solution.

A ligand field of D_{3h} symmetry splits the cubic ^5D term into a singly degenerate $^5A_1'$ ground term and two doubly degenerate excited states $^5E'$, $^5E''$.[7] On this basis the absorption maximum in the spectra of the chromium complexes at *ca.* 13 kK can be assigned to the $^5A_1' \rightarrow {}^5E'$ transition. The low intensity of the peak on the high energy side of the main band shown by np_3cy derivative spectra is consistent with the dipole forbidden character of the $^5A_1' \rightarrow {}^5E''$ transition in D_{3h} symmetry. An absorption attributable to the latter transition appears in the spectra of the QP derivatives as an ill defined shoulder in the tail of the main band, at higher energy than np_3cy derivatives (presumably in the region at 17–19 kK) and with much lower intensity. It is interesting to note that the differences in spectral behaviour between QP and np_3cy chromium(II) complexes can also be found in the spectra of five-coordinate chromium(II) complexes with the ligands pp_3[1b] and np_3[1a] previously reported (see Figure 1).

Lacking structural data on the actual geometry of these five-coordinate chromium(II) complexes it is not possible to relate the detailed spectral behaviour to factors such as a slightly different coordination geometry for the $[CrX(np_3)]^+$ and $[CrX(P_4)]^+$ chromophores or to the different electronic properties of the N and P apical donor atoms. Moreover the energy separation of the two spin allowed bands in the spectra of five-coordinate chromium(II) complexes so far reported increases in the order I, Br, Cl, which is opposite to that expected on the basis of a model of point charges of C_{3v} symmetry.[8] This fact indicates that a crystal field splitting scheme is adequate to explain the main features of chromium(II) five-coordinate spectra but is not necessarily in agreement with the details of these spectra.

The $^5A_1'$ term which is the ground state for the chromium(II) ion in a ligand field of D_{3h} symmetry is orbitally non degenerate and therefore the magnetic moment of trigonal bipyramidal chromium(II) complexes should have, to a first approximation, the spin only value (4.90 BM) for four unpaired electrons. The magnetic moments of the chromium(II) complexes here reported are in the range 4.85–4.89 BM at room temperature (Table I). These fall consistently just below the value cxpected for spin only contribution. Theoretically on orbital contribution due to a mixing of ground (non magnetic) and excited states (with an orbital contribution to the magnetic moment) via spin–orbit coupling would reduce the magnetic moment of a d^4 ion below the spin only value. Furthermore this reduction is expected to be small owing to the small value of the spin orbit constant, λ, for the chromium(II) ion.[9]

The high-spin state of all five-coordinate chromium (II) complexes so far reported, which persists even with ligands which are able to induce spin pairing in analogous five-coordinate iron(II), cobalt(II) and nickel (II) complexes, seems to be attributable to the e″ (xz, yz) and e′ (x^2–y^2, xy) orbitals having similar energy. A low spin configuration for a d^4 ion would be favoured by a chromophore with a C_{4v} symmetry rather than one with a D_{3h} symmetry.[2]

However all attempts to obtain chromium(II) complexes with ligands which tend to promote, on the basis of their steric requirements, square-pyramidal geometry, were unsuccessful.

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