Synthesis and Characterization of Chromium(II) Complexes of Tris-(2-diphenylphosphinoethyl)phosphine and *o*-Phenylenebis(dimethylarsine)

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The preparation and properties of new high-spin five-co-ordinate and low-spin six-co-ordinate chromium(II) complexes are reported, $[Cr(tdpep)X][BPh_4]$ [X = Cl, Br, or I; tdpep = tris(2-diphenylphosphinoethyl)phosphine] and $[Cr(pdma)_2X_2]$ [X = Cl, Br, or I; pdma = *o*-phenylenebis(dimethylarsine)] respectively.

CHROMIUM(II) complexes so far reported are not very numerous and most are high-spin octahedral species.[1] Recently, rare examples of chromium(II) complexes with tetrahedral [2] and trigonal-bipyramidal [3] geometries have been described. Studies of chromium(II) chemistry have now been extended to include the complexing behaviour toward chromium(II) halides of ligands containing 'soft'-donor atoms, P and As, which have been shown to possess marked capacity for inducing spin pairing in some 3*d* metal ions.[4]

In this paper we report the preparation and characterization of chromium(II) complexes with the ligands tris(2-diphenylphosphinoethyl)phosphine (tdpep) and *o*-phenylenebis(dimethylarsine) (pdma).

RESULTS AND DISCUSSION

$[Cr(tdpep)X][BPh_4]$ *Complexes*.—Chromium(II) halides react with the ligand tdpep in the presence of sodium tetraphenylborate to give blue crystalline products of formula $[Cr(tdpep)X][BPh_4]$ (X = Cl, Br, or I). These complexes are high spin with effective magnetic moments at room temperature in the range 4·5—4·7 B.M., slightly below the spin-only value of 4·9 B.M. expected for four unpaired electrons.† The complexes are soluble in 1,2-dichloroethane and behave essentially as 1 : 1 electrolytes in this solvent. The electronic spectra of these complexes in 1,2-dichloroethane solution were all similar and did not differ from their solid-reflectance spectra. These spectra contain a maximum at *ca.* 14 000 cm^{-1} (Table 2 and Figure 1) and a less intense, poorly resolved, band in the range 18 000—19 000 cm^{-1}, and are strictly correlatable to the spectra of previously reported $[Cr(Me_6tren)Br]^+$ [Me_6tren = tris(2-dimethylaminoethyl)amine] and $[Cr(tdpea)X]^+$ [X = Cl, Br, or I and tdpea = tris(2-diphenylphosphinoethyl)amine], species to which a five-co-ordinate trigonal-bipyramidal geometry has been assigned.[3] On the basis of a one-electron splitting scheme of *d* orbitals in D_{3h} symmetry, two spin-allowed transitions are expected for a high-spin d^4 ion (^5D ground term),[5] and the two *d–d* bands in the spectra of the present five-co-ordinate chromium(II) complexes are assigned as in Figure 1. The lower intensity of the high-energy band agrees with the dipole-forbidden character of $^5A_1' \rightarrow {}^5E''$ transition in strictly D_{3h} symmetry.

A survey of the magnetic properties of five-co-ordinate chromium(II), iron(II), cobalt(II), and nickel(II) complexes with the ligands tdpep and tdpea (Table 3) shows that spin-pairing tendency decreases in the order Ni > Co > Fe > Cr. The high-spin state of all five-co-ordinate chromium(II) complexes so far reported, including $[Cr(tdpep)I]^+$ which contains one of the most nucleophilic donor-atom sets [6] P_4I, is therefore attributable to the *e''* and *e'* orbitals whose difference in energy is smaller than the spin-pairing energy. It has been noted that a low-spin configuration for a d^4 ion would be favoured more by a chromophore with C_{4v} symmetry than one with D_{3h} symmetry.[5] However all attempts to obtain chromium(II) complexes with ligands which, on the basis of their steric requirements, tend to promote square-pyramidal geometry, were unsuccessful.

TABLE 1

Analytical data for the complexes

		Found (%)				Calc. (%)			
Complex	Colour	C	H	P	Cr	C	H	P	Cr
$[Cr(tdpep)Cl][BPh_4]$	Blue	72·4	6·5	11·3		73·55	5·80	11·5	
$[Cr(tdpep)Br][BPh_4]$	Blue	69·5	6·4	11·0		70·65	5·60	11·05	
$[Cr(tdpep)I][BPh_4]$	Blue	67·0	5·5	10·4		67·8	5·35	10·6	
$[Cr(pdma)_2Cl_2]$	Red-brown	34·6	4·7		7·4	34·55	4·65		7·50
$[Cr(pdma)_2Br_2]$	Red-brown	30·9	3·9		6·5	30·65	4·10		6·65
$[Cr(pdma)_2I_2]$	Brown	27·5	3·6		5·7	27·35	3·65		5·90

$[Cr(pdma)_2X_2]$ *Complexes*.—Complexes of most 3*d* metals have long been known with this ligand, but to

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† 1 B.M. ≃ $9·27 \times 10^{-24}$ A m^2.

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[3] (*a*) M. Ciampolini, *Chem. Comm.*, 1966, 47; (*b*) F. Mani and L. Sacconi, *Inorg. Chim. Acta*, 1970, **4**, 365.

[4] (*a*) R. B. King, R. N. Kapoor, M. S. Singh Saran, and P. N. Kapoor, *Inorg. Chem.*, 1971, **10**, 1851; (*b*) R. S. Nyholm and G. J. Sutton, *J. Chem. Soc.*, 1958, 560, and ref. therein; C. H. Harris, R. S. Nyholm, and D. J. Phillips, *ibid.*, 1960, 4379.

[5] C. Furlani, *Co-ordination Chem. Rev.*, 1968, **3**, 141; M. Ciampolini, *Structure and Bonding*, 1969, **6**, 52.

[6] L. Sacconi, *Co-ordination Chem. Rev.*, 1972, **7**, 352.

TABLE 2

Physical data for the complexes

	$\mu_{eff.}$/B.M. (298 K)	$\mu_{eff.}$/B.M. (84 K)	θ [a]	λ [b]/ S cm^2 mol^{-1}	State [c]	$10^{-3}\bar{\nu}$/cm^{-1} (ε/l mol^{-1} cm^{-1})
[Cr(tdpep)Cl][BPh$_4$]	4·49			14	R	14·7, 19·0 (sh)
					D	15·1 (560)
[Cr(tdpep)Br][BPh$_4$]	4·70			14	R	14·3, 18·1 (sh)
					D	14·8 (585), 18·1 (sh)
[Cr(tdpep)I][BPh$_4$]	4·70			16	R	14·3, 18·7
					D	14·4 (440), 18·7 (sh)
[Cr(pdma)$_2$Cl$_2$]	2·85	2·85	0		R	7·4, 8·8, 15·4 (sh), >20
[Cr(pdma)$_2$Br$_2$]	2·94	2·90	0		R	6·4, 7·9, 14·3, >20
[Cr(pdma)$_2$I$_2$]	2·99	2·98	0		R	6·7, 13·3, >20
[Mo(pdma)$_2$Cl$_2$]	2·85 [d]				R	8·5, 10·9, (15·4), >17

[a] Weiss constant. [b] For *ca.* 10^{-3}M solutions at 20 °C. The reference value in 1,2-dichloroethane was 19 S cm^2 mol^{-1} for Bu$^n{}_4$NBr. [c] R = Solid-state reflectance spectra, D = absorption spectra in 1,2-dichloroethane. [d] Ref. 8.

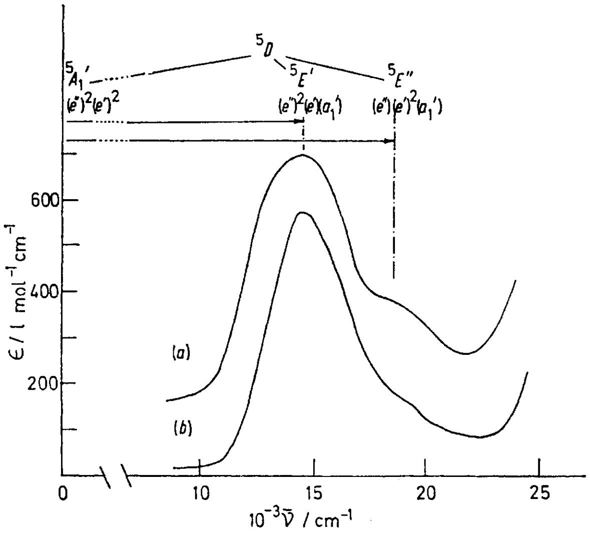

FIGURE 1 Spectra of the complex [Cr(tdpep)Br][BPh$_4$]: (*a*), reflectance; (*b*), absorption in 1,2-dichloroethane

TABLE 3

Spin state (H = high spin, L = low spin) of the [M(ligand)X]Y complexes (ligand = tdpep or tdpea; X = Cl, Br, or I; Y = BPh$_4$ or PF$_6$)

Set	Cr	Fe	Co	Ni
NP$_3$X	H[3b]	H *	H + L †	L †
PP$_3$X	H	L[4a]	L[4a]	L ‡

* P. Stoppioni, F. Mani, and L. Sacconi, *Inorg. Chim. Acta*, 1974, **11**, 227. † L. Sacconi and I. Bertini, *J. Amer. Chem. Soc.*, 1968, **90**, 5443. ‡ The complex [Ni(tdpep)Cl][PF$_6$], first reported by King *et al.*,[4a] is said to possess a magnetic moment of 2·23 B.M.; however, a complex corresponding to the above formula prepared in this laboratory was found to be diamagnetic.

date only those having the formula [Cr(pdma)$_2$X$_3$][4] and [Cr(pdma)$_2$(CO)$_2$X$_2$][7] have been described for chromium. Chromium(II) halides react with the ligand pdma to give brown crystalline products of formula [Cr(pdma)$_2$X$_2$] (X = Cl, Br, or I). These complexes are low spin with magnetic moments at room temperature ranging between 2·85 and 2·99 B.M., close to the spin-only value of 2·83 B.M. expected for two unpaired electrons. The magnetic moments of the complexes measured between 84 and 298 K were constant within experimental error, with a Weiss constant of 0 K. The complexes are insoluble in the common organic solvents (C$_6$H$_6$, CHCl$_3$, CH$_2$Cl$_2$, ClCH$_2$CH$_2$Cl, MeOH, and EtOH were tried) but soluble in MeNO$_2$ and EtNO$_2$. Absorption spectra in the latter two solvents exhibit two intense bands at *ca.* 15 000 and 21 000 cm^{-1}, indicating almost complete oxidation of the chromium(II) species. Reflectance spectra of the [Cr(pdma)$_2$X$_2$] complexes (X = Cl or Br) exhibit two maxima at *ca.* 7 000 and 8 000 cm^{-1} and a poorly resolved band at *ca.* 15 000 and above 20 000 cm^{-1} (Figure 2 and Table 2). The spectrum of the iodo-derivative does not differ substantially from the former spectra, but one asymmetric band appears at *ca.* 7 000 cm^{-1} and the band at *ca.* 13 000 cm^{-1} is better resolved. The positions of the absorption maxima shift toward higher frequencies in the order I < Br < Cl, in accordance with the relative positions of the halogens in the spectrochemical series.

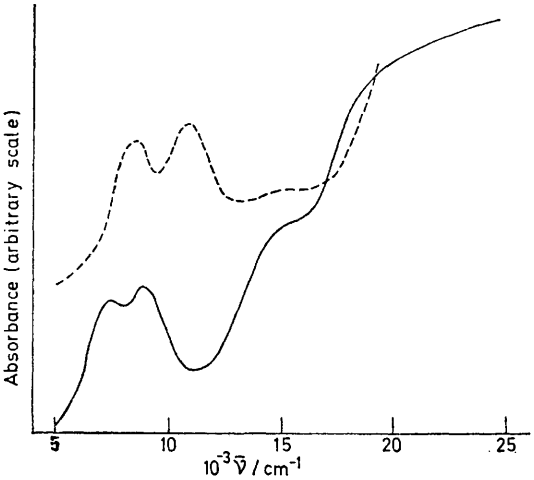

FIGURE 2 Reflectance spectra of [Cr(pdma)$_2$Cl$_2$], (——) and [Mo(pdma)$_2$Cl$_2$] (— — —)

For comparison purposes the previously reported octahedral complex [Mo(pdma)$_2$Cl$_2$][8] was prepared. The *X*-ray powder photograph of this complex is practically indistinguishable from that of [Cr(pdma)$_2$Cl$_2$]. Moreover the reflectance spectrum of the molybdenum(II) derivative in the region 5 000—25 000 cm^{-1} is similar to the spectrum of the analogous chromium(II) complex, apart from the absorption maxima being shifted toward higher frequencies in the molybdenum(II) complex. This shift is expected in the spectrum of a 4*d* metal complex when compared to that of a 3*d* metal. The

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[7] J. Lewis, R. S. Nyholm, C. S. Pande, S. S. Sandhu, and M. H. B. Stiddard, *J. Chem. Soc.*, 1964, 3009.

[8] J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 1962, 2592.

low-intensity band which appeared at *ca.* 15 000 cm^{-1} in the $[Mo(pdma)_2Cl_2]$ spectrum is presumably due to the presence of traces of oxidation products of molybdenum {yellow $[Mo(pdma)_2Cl_2]$ quickly becomes dark brown when exposed to air and strongly absorbs at *ca.* 15 000 cm^{-1}}, while the third band, which appeared in the region of 13 000—15 000 cm^{-1} in the chromium(II) spectrum, is very likely masked in the molybdenum(II) spectrum by a charge-transfer band which starts at *ca.* 17 000 cm^{-1}. On the basis of these spectral and *X*-ray data, we conclude that $[Cr(pdma)_2Cl_2]$ and $[Mo(pdma)_2Cl_2]$ have similar octahedral geometries. Magnetic and spectral data of the $[Cr(pdma)_2Br_2]$ and $[Cr(pdma)_2I_2]$ complexes were very similar to those of the chloro-derivative and indicate also an octahedral geometry for these derivatives. The $[Cr(pdma)_2X_2]$ complexes described here are among the few examples so far reported of octahedral low-spin chromium(II) complexes.[9]

EXPERIMENTAL

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. Anhydrous chromium(II) halides [3b] and *o*-phenylenebis(dimethylarsine) (pdma) [10] were prepared as already described. The ligand tris(2-diphenylphosphinoethyl)phosphine (tdpep) was obtained from Pressure Chemical Co.

Halogeno[tris(2-diphenylphosphinoethyl)phosphine]-chromium Tetraphenylborates.—A solution in n-butanol (20 cm^3) of the appropriate anhydrous chromium(II) halide (10^{-3} mol) was added to the stoicheiometric amount of the ligand dissolved in methylene chloride (30 cm^3). The complexes were readily obtained after sodium tetraphenylborate (10^{-3} mol) dissolved in n-butanol (15 cm^3) had been added to the solution. The crystalline *products* were collected by filtration, washed several times with n-butanol–light petroleum, and dried in a stream of dry nitrogen. Attempts to prepare analogous complexes with the open-chain tetradentate ligand 3,6-diphenyl-3,6-diphosphaoctane-1,8-bis(diphenylphosphine) were unsuccessful.

*Dihalogenobis[*o*-phenylenebis(dimethylarsine)]chromium Complexes.*—A saturated solution in n-butanol of the appropriate anhydrous chromium(II) halide (2×10^{-3} mol) was added to the stoicheiometric amount of the ligand (4×10^{-3} mol) in n-butanol (5 cm^3). The resulting blue solution was cooled in ice and after a little time red-brown crystals separated. The *products* were filtered off, washed with n-butanol–light petroleum, then light petroleum, and finally dried in a stream of nitrogen.

Analytical data for the complexes are reported in Table 1. The complex $[Mo(pdma)_2Cl_2]$ was prepared for comparative purposes as described by Nyholm and his co-workers.[8] All the complexes quickly decompose when exposed to air. Magnetic, spectrophotometric, conductivity, and *X*-ray measurements were carried out using methods already described.[11]

We thank Mr. P. Innocenti for technical assistance, Mr. F. Nuzzi for the analyses, and the Italian C.N.R. for financial support.

[4/1086 *Received, 4th June,* 1974]

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[11] I. Bertini and F. Mani, *Inorg. Chem.*, 1967, **6**, 2032.