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Synthesis and Characterization of Chromium(II) Complexes with Poly(1-pyrazolyl)methane Ligands

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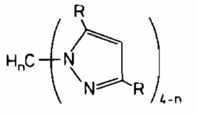
The preparation and properties of six- and five-co-ordinate chromium(II) complexes with the ligands 1,1′-methylenedipyrazole (H_2Cpz_2), 1,1′-methylenebis(3,5-dimethylpyrazole) (H_2Cdmpz_2), and tris(1-pyrazolyl)methane ($HCpz_3$) are reported. The complexes with formula $[Cr(HCpz_3)_2](BPh_4)_2$, $[Cr(H_2Cpz_2)Cl_2]$, $[Cr(H_2Cpz_2)_2X_2]$ (X = Br, I) and $[Cr(H_2Cpz_2)_2X]BPh_4$ (X = Cl, Br) are assigned a six-co-ordinate structure on the basis of their spectral and magnetic properties. Spectral, magnetic and conductivity data for the complexes $[Cr(H_2Cdmpz_2)_2Cl]BF_4$, $[Cr(H_2Cdmpz_2)_2X]BPh_4$ (X = Br, I) and $[Cr(H_2Cdmpz_2)_2X]X$ (X = Br, I) are consistent with a five-co-ordinate structure both in the solid state and in solution.

Introduction

The coordination chemistry of chromium(II) ion has been under investigation in this laboratory for a number of years [1, 2]. Recently the anionic ligands poly(1-pyrazolyl)borates were found to give stable complexes with this metal ion [2]. In this connection it seemed of interest to investigate the coordinating behaviour of the neutral ligands poly(1-pyrazolyl)alkanes, which are isoelectronic and isostructural with poly(1-pyrazolyl)borates, towards chromium(II).

This paper reports the synthesis and characterization of some complexes obtained from chromium(II) salts and the ligands 1,1′-methylenedipyrazole (H_2Cpz_2; I, n = 2, R = H), 1,1′-methylenebis(3,5-dimethylpyrazole) (H_2Cdmpz_2; I, n = 2, R = CH_3), and tris(1-pyrazolyl)methane ($HCpz_3$; I, n = 3, R = H). Complexes with formula CrL_2X_2 (L = H_2Cpz_2, H_2Cdmpz_2, X = Br, I), $Cr(H_2Cpz_2)Cl_2$, CrL_2XY (L = H_2Cpz_2, X = Cl, Br; Y = BPh_4; L = H_2Cdmpz_2, X = Cl, Y = BF_4; X = Br, I, Y = BPh_4), and $Cr(HCpz_3)_2(BPh_4)_2$ have been isolated.



(I)
n=2, R=H, H_2Cpz_2
n=2, R=CH_3, H_2Cdmpz_2
n=1, R=H, $HCpz_3$

Experimental

The ligands 1,1′-methylenedipyrazole and 1,1′-methylenebis(3,5-dimethylpyrazole) were prepared by the reaction of methylene iodide with potassium pyrazolide and potassium 3,5-dimethylpyrazolide, respectively [3]. The ligand tris(1-pyrazolyl)methane was purchased from Columbia Organic Chemicals and was employed without further purification.

Hydrated chromium(II) halides [4] were dissolved in CH_3OH or C_2H_5OH, evaporated to dryness several times, and finally dried at 100 °C under reduced pressure.

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

The complexes were prepared in n-butanol or absolute ethanol as follows. A warm solution of the anhydrous chromium(II) halide (1 mmol in 20 ml) was added to a warm solution of the ligand in slight excess to the stoicheiometric ratio. Crystalline products formed readily upon heating the resulting solutions. In some cases the solutions were concentrated to effect crystallization. The tetraphenylborate derivatives were obtained upon addition of a stoicheiometric amount of sodium tetraphenylborate, dissolved in absolute ethanol, to a boiling solution of the chromium(II) halide and the appropriate ligand in the same solvent. The fluoroborate derivative was similarly obtained by addition of a methanol solution of sodium tetrafluoroborate and cooling of the resulting solution to room temperature. In all cases the solid complexes were washed by decantation with a mixture of ethanol or n-butanol and diethyl ether, then filtered off, washed with diethyl ether and finally dried in a stream of dry nitrogen at 100 °C. The tetraphenylborate and tetra-

TABLE I. Analytical Data for the Complexes.

Complex	Colour	Found (%)			Calcd (%)		
		C	H	N	C	H	N
$[Cr(HCpz_3)_2](BPh_4)_2$	Greenish-gray	73.6	5.88	15.2	72.99	5.41	15.02
$[Cr(H_2Cpz_2)Cl_2]$	Greenish-blue	31.0	3.29	20.5	31.02	2.99	20.66
$[Cr(H_2Cpz_2)_2Br_2]$	Green	33.0	3.19	21.8	33.10	3.17	22.05
$[Cr(H_2Cpz_2)_2I_2]$	Lilac-gray	27.7	2.61	18.3	27.93	2.67	18.61
$[Cr(H_2Cpz_2)_2Cl]BPh_4$	Green	64.7	5.47	15.8	64.90	5.16	15.94
$[Cr(H_2Cpz_2)_2Br]BPh_4$	Greenish-gray	60.4	5.29	15.3	61.06	4.86	14.99
$[Cr(H_2Cdmpz_2)_2Br]Br$	Light-blue	41.9	5.04	17.7	42.59	5.21	18.05
$[Cr(H_2Cdmpz_2)_2I]I$	Light-blue	37.1	5.08	15.4	36.99	4.52	15.70
$[Cr(H_2Cdmpz_2)_2Cl]BF_4{}^a$	Blue	45.8	6.07	18.7	45.34	5.54	19.22
$[Cr(H_2Cdmpz_2)_2Br]BPh_4{}^b$	Blue	63.7	6.05	13.3	64.27	6.10	13.03
$[Cr(H_2Cdmpz_2)_2I]BPh_4{}^c$	Blue	61.1	6.08	12.7	60.94	5.78	12.35

[a] Cl: calcd 6.08; found 6.20%. [b] Br: calcd 9.30; found 9.62. [c] I: calcd 14.00; found 13.8.

TABLE II. Physical Data for the Complexes.

	μ_{eff}/B.M.		λ^a/S cm^2 mol^{-1}	State^b	10^{-3} $\tilde{\nu}$/cm^{-1} (ϵ/l mol^{-1} cm^{-1})
	(298 K)	(84 K)			
$[Cr(HCpz_3)_2](BPh_4)_2$	4.82			R	10.2(w), 18.9
$[Cr(H_2Cpz_2)Cl_2]$	4.45	3.60		R	10.5(sh), 13.2
$[Cr(H_2Cpz_2)_2Br_2]$	4.80			R	8.2(w), 14.1
$[Cr(H_2Cpz_2)_2I_2]$	4.80			R	13.2(sh), 17.4
$[Cr(H_2Cpz_2)_2Cl]BPh_4$	4.42	3.80		R	8.6(w), 14.7
$[Cr(H_2Cpz_2)_2Br]BPh_4$	4.14	3.15		R	11.6(sh), 17.2
$[Cr(H_2Cdmpz_2)_2Br]Br$	4.93		132	R	11.3, 15.4
				A	11.7(37), 16.0(53)
$[Cr(H_2Cdmpz_2)_2I]I$	4.83		195	R	11.1, 15.3
				A	11.5(46), 15.5(75)
$[Cr(H_2Cdmpz_2)_2Cl]BF_4$	4.80	4.85	150	R	12.5, 17.0
				A	12.2(sh), 16.6(50)
$[Cr(H_2Cdmpz_2)_2Br]BPh_4$	4.85	4.85	122	R	12.5, 16.0
				A	12.0(40), 16.1(58)
$[Cr(H_2Cdmpz_2)_2I]BPh_4$	4.88	4.80	181	R	11.1, 14.7
				A	11.4(48), 15.4(72)

[a] For *ca.* 10^{-3} *M* solutions at 20 °C. The reference values in acetonitrile are 160 S cm^2 mol^{-1} for Bu_4^nNBr, 120 S cm^2 mol^{-1} for $Bu_4^nNBPh_4$ and 250 S cm^2 mol^{-1} for $(Bu_4^nN)_2CoBr_4$. [b] R = Solid-state reflectance spectra; A = absorption spectra in acetonitrile.

fluoroborate derivatives were also washed with water to eliminate the sodium halide.

The analytical data for the complexes are reported in Table I.

Magnetic and spectrophotometric measurements have been performed with an apparatus already described [5] using suitable airtight containers (Gouy tube and uv cells) filled in dry-box under inert atmosphere.

Results and Discussion

Complexes with the Ligands H_2Cpz_2 and $HCpz_3$

The potentially bidentate ligand H_2Cpz_2 reacts with chromium(II) halides to give complexes with 1:1 (halide = Cl) and 1:2 (halide = Br, I) metal-to-ligand ratios. Upon addition of tetraphenylborate, compounds of general formula $[CrL_2X]BPh_4$ (X = Cl, Br) are obtained. Addition of tetraphenylborate

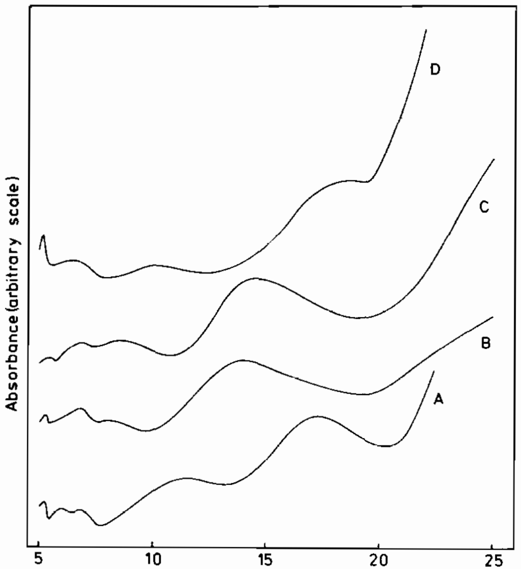


Fig. 1. Reflectance spectra of: A, $[Cr(H_2Cpz_2)_2Br]BPh_4$; B, $[Cr(H_2Cpz_2)_2Br_2]$; C, $[Cr(H_2Cpz_2)_2Cl]BPh_4$; D, $[Cr(HCpz_3)_2](BPh_4)_2$.

to a solution of chromium(II) halide and the potentially tridentate ligand $HCpz_3$ invariably yields a complex with formula $[Cr(HCpz_3)_2](BPh_4)_2$. The solid complexes are moderately air stable with the exception of the iodide derivatives which are readily oxidised by air. All the complexes are high-spin. The magnetic moment values of the $[Cr(H_2Cpz_2)_2X_2]$ derivatives and of $[Cr(HCpz_3)_2](BPh_4)_2$ are close to the spin-only value of 4.90 B.M. for spin-free chromium(II) (Table II) and are temperature independent. Those of the $[Cr(H_2Cpz_2)Cl_2]$ and $[Cr(H_2Cpz_2)_2X]$ BPh_4 derivatives are appreciably below the spin-only value and decrease with temperature (Table II).

The reflectance spectrum of $[Cr(HCpz_3)_2](BPh_4)_2$ (Table II and Fig. 1) shows two well separated bands which can be assigned as d–d transitions, a strong one at 18 900 cm^{-1} (on the low frequency side of a more intense charge-transfer band) and a weaker one at 10 200 cm^{-1}. These spectral features are typical of six-co-ordinate chromium(II) complexes little distorted from O_h symmetry [2, 6] as exemplified by those formed by pyrazolylborate ligands, *i.e.* $[Cr(HBpz_3)_2]$ and $[Cr(Bpz_4)_2]$. A distortion is expected in six-co-ordinate chromium(II) complexes as a result of the Jahn–Teller effect inherent in the high-spin d^4 configuration. In addition to this, the steric requirements of the H_2Cpz_2 ligand may also lower the O_h symmetry of the ligand field around chromium(II) thus causing the splitting of the $^5E_g \rightarrow {}^5T_{2g}$ transition.

The reflectance spectra of the complexes with the bidentate ligand H_2Cpz_2 show a strong band in the range 13 200–17 400 cm^{-1} and a weaker band or shoulder in the range 8200–13 200 cm^{-1} as usually found in six-co-ordinate chromium(II) complexes with comparable ligands [1]. For the $[Cr(H_2Cpz_2)_2X_2]$ complexes all six donors are assumed to be co-ordinated in a neutral monomeric structure, whereas the stoicheiometry of $[Cr(H_2Cpz_2)_2X]BPh_4$ complexes suggests that six-co-ordination is achieved in a polymeric structure, possibly with halide bridges, as confirmed by their antiferromagnetic behaviour (Table II).

It must be observed that the absorption frequencies in the spectra of these complexes do not shift according to the spectrochemical series. For example the two bands in the spectrum of $[Cr(H_2Cpz_2)_2Cl]$ BPh_4 are at lower frequencies (about 3000 cm^{-1}) than those of the bromide analog, and the same is true in the $[Cr(H_2Cpz_2)_2X_2]$ series. This behaviour suggests that the degree of distortion from regular octahedral symmetry brought about by different halide donors is a major effect in determining the absorption frequencies, as it causes the splitting of both the ^5E_g ground term and the $^5T_{2g}$ excited term [1, 6]. There is, however, no obvious relationship between the degree of distortion of the chromophore and the donor strength of the halides. As a matter of fact the spectra of $[Cr(H_2Cpz_2)_2I_2]$ and $[Cr(H_2Cpz_2)_2Br]BPh_4$ (Table II and Fig. 1) are similar to each other and indicative of a strong tetragonal distortion, whereas those of $[Cr(H_2Cpz_2)_2Br_2]$ and $[Cr(H_2Cpz_2)_2Cl]BPh_4$ (Table II and Fig. 1) are nearly identical to each other and similar in shape to that of $[Cr(HCpz_3)_2](BPh_4)_2$, *i.e.* typical of a slightly distorted octahedral geometry as shown by the low-energy of the first d–d transition.

All the above complexes are sparingly soluble in the common organic solvents. They are dissolved by N,N′-dimethylformamide, but, in spite of the care employed to prevent oxidation, the solutions decompose so rapidly that physical measurements are practically precluded.

The spectral and magnetic properties of the complex $[Cr(H_2Cpz_2)Cl_2]$ can be accounted for on the basis of a distorted *cis*-octahedral geometry achieved by means of four bridging chlorine atoms in a polymeric structure.

Complexes with the Ligand H_2Cdmpz_2

This ligand forms chromium(II) complexes with the same stoicheiometry as those obtained with the ligand H_2Cpz_2, but with different spectral and magnetic properties.

The magnetic moment values of the complexes $[Cr(H_2Cdmpz_2)_2X]Y$ ($X = Cl$, $Y = BF_4$; $X = Br, I$, $Y = BPh_4$) are in the range 4.80–4.88 B.M. at room temperature and do not vary appreciably in the temperature range investigated (Table II). This magnetic behaviour rules out a halide-bridged structure which would lead to a magnetic interaction between chromium(II) atoms as found for the $[Cr(H_2Cpz_2)_2X]$-

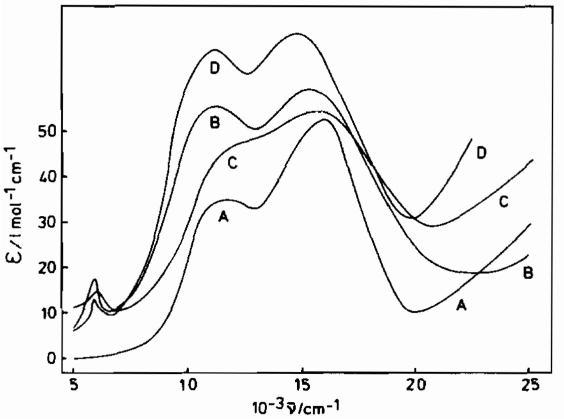
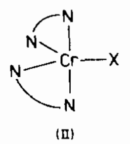


Fig. 2. Spectra of the complex $[Cr(H_2Cdmpz_2)_2Br]Br$: A, absorption in acetonitrile; B, reflectance. Reflectance spectra of: C, $[Cr(H_2Cdmpz_2)_2Br]BPh_4$; D, $[Cr(H_2Cdmpz_2)_2I]$-BPh_4.

BPh_4 series. The stoicheiometry of the $[Cr(H_2Cdmpz_2)_2X]Y$ complexes thus suggests a monomeric five-co-ordinate structure for the $[Cr(H_2Cdmpz_2)_2X]^+$ ion. The reflectance spectra of these complexes are substantially similar (Table II and Fig. 2): they show an absorption maximum in the range 14,700–17,000 cm^{-1} whose frequency increases in the order of increasing ligand field strength ($I < Br < Cl$) and a slightly weaker band in the range 11,100 - 12,500 cm^{-1} whose intensity increases in the order $Cl < Br < I$. These spectral features are distinctly different from those of the six-co-ordinate $[Cr(H_2Cpz_2)_2X]BPh_4$ complexes, but on the other hand they are not typical of either trigonal-bipyramidal [7] or square-pyramidal [8] five-co-ordinate chromium(II) complexes. The relative intensity of the two d–d bands in the spectra of the former type of complexes is in fact reversed with respect to that found for the present complexes. However it must be observed that all the trigonal-bipyramidal chromium(II) complexes so far reported are formed by tetradentate tripod-like ligands whose geometry imposes a strict trigonal symmetry to the chromophore [9]: under these conditions two d–d bands are expected as a result of transitions between the states $^5A_1 \rightarrow {}^5E'$ and $^5A_1 \rightarrow {}^5E''$, the latter being lower in intensity on account of its dipole-forbidden character.

If we assume a five-co-ordinate stereochemistry for the $[Cr(H_2Cdmpz_2)_2X]Y$ complexes, this is expected to deviate from trigonal symmetry because of the bidentate nature of the ligand. A molecular structure with an approximate C_{2v} symmetry of the chromophore (II) can be reasonably suggested: on this basis the two d–d bands can be tentatively assigned as unresolved transitions to the components $^5A_1 + {}^5B_2$ and $^5A_2 + {}^5B_1$ of the two excited states $^5E'$ and $^5E''$. Both transitions are allowed in C_{2v} symmetry, in agreement with their comparable relative intensity (Table II and Fig. 2).



(II)

The spectral features of these five-co-ordinate chromium(II) complexes are closely related to those of several copper(II) complexes to which a five-co-ordinate distorted trigonal-bipyramidal structure has been assigned or found by X-ray diffraction methods [10].

The reflectance spectra of $Cr(H_2Cdmpz_2)_2X_2$ (X = Br, I) are quite similar to each other and to the reflectance spectrum of the $[Cr(H_2Cdmpz_2)_2I]BPh_4$ derivative (Table II and Fig. 2). While this comparison suggests for these complexes a five-co-ordinate ionic $[Cr(H_2Cdmpz_2)_2X]X$ structure, it does not definitely rule out the possibility of a *cis*-octahedral six-co-ordinate structure. As already reported for some copper(II) complexes with formulas $[Cu(NN)_2X]Y_2$ (NN = bidentate ligand with nitrogen donor atoms, X = neutral monodentate ligand, Y = PF_6, ClO_4) and $[Cu(NN)_2X]Z$ (X = halide, Z = halide, pseudohalide, perchlorate) [11] it is sometimes impossible to distinguish between trigonal-bipyramid and *cis*-octahedral geometries on the basis of reflectance spectra alone, when the complexes are largely distorted from these limiting geometries.

Further evidence in favour of a five-co-ordinate structure for all these complexes is given by their conductivity and spectral data in N,N'-dimethylformamide and acetonitrile solutions. The chloro- and bromo-derivatives behave essentially as 1:1 electrolytes (Table II). Intermediate molar conductivity values between those expected for 1:1 and 2:1 electrolytes are found for the iodo-derivatives, thus indicating that iodide ions are replaced by solvent molecules to some extent. In addition, the electronic spectra of all the complexes dissolved in N,N'-dimethylformamide and acetonitrile are similar in shape and band frequency to the solid reflectance spectra of the $[Cr(H_2Cdmpz_2)_2X]Y$ derivatives (Table II and Fig. 2). All these data suggest that five-co-ordinate $[Cr(H_2Cdmpz_2)_2X]^+$ species are present in solution.

Conclusions

The results reported here, together with those previously reported [1, 7] indicate that severe distortions from the regular geometry in five-co-ordinate and six-co-ordinate chromium(II) complexes affect the electronic levels to such an extent that clear-cut types of spectra, which might, by themselves, be taken as diagnostic of a specific stereochemistry, are hardly obtained. As a general trend, however, it can be observed that the absorption bands of *cis*-octahedral or trigonal-bipyramidal complexes generally occur at lower frequencies and exhibit a smaller separation than those of *trans* octahedral with a similar donor set. In the latter case an increasing tetragonal-type distortion has the effect of increasing the absorption frequencies and decreasing the separation of the d–d bands.

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