

## Chromium(II) Complexes with Pyrazoles and Imidazoles as Ligands

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*Synthesis and characterization of six-coordinate chromium(II) complexes with the ligands pyrazole (pz), imidazole (iz), N-methylimidazole (Nmiz) having the general formula  $CrL_4X_2$  ( $X = Cl, Br, I$ ) and  $CrL_2Cl_2$  ( $L = pz, Nmiz$ ) are reported. With the ligands 3,5-dimethylpyrazole (dmpz)  $CrL_2Cl_2$  and  $CrL_3Br_2$  derivatives have been obtained. On the basis of spectral and magnetic data a trans octahedral structure is assigned to the above complexes. Those with a 2:1 ligand to metal ratio are weakly antiferromagnetic and possess a polymeric chlorine bridged structure.*

### Introduction

Despite considerable studies also recently devoted to imidazole and pyrazole complexes with most 3d metal ions,<sup>1</sup> chromium(II) ion has been so far neglected in these studies.

As a part of a more general investigation on chromium(II) coordination chemistry,<sup>2</sup> we extended to this ion the study of the coordination properties of pyrazole (pz), 3,5-dimethylpyrazole (dmpz), imidazole (iz) and N-methylimidazole (Nmiz).

### Experimental

Pyrazole, imidazole, and N-methylimidazole are available from Fluka A.G. and were employed without further purification. The ligand 3,5-dimethylpyrazole was prepared from acetylacetone and hydrazine hydrate as previously reported.<sup>3</sup> 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 chromium(II) halides<sup>4</sup> were dehydrated by heating to 120°C under vacuum.

The complexes have been prepared using ethyl alcohol as solvent (n-butanol in the case of the complexes  $[Cr(Nmiz)_4Cl_2]$  and  $[Cr(pz)_4Cl_2]$ ). The complexes with a 2:1 ligand to metal ratio and  $[Cr(dmpz)_3Br_2]$  have been readily obtained upon adding room tem-

perature solutions of the chromium(II) halides in excess to the appropriate ligand solutions. The complexes with a 4:1 ligand to metal ratio have been obtained by mixing boiling solutions of the reactants in the stoichiometric ratios and cooling (or evaporating, in a few cases) to room temperature the resulting mixtures. The crystalline products were collected by filtration, washed with ethyl alcohol and ether and dried in a stream of dry nitrogen at 80°C. The analytical data are reported in Table I.

Magnetic, spectrophotometric and conductivity measurements have been performed with the apparatus and the techniques already described.<sup>5</sup>

The conductivity data ( $\Lambda$ ,  $cm^2 \text{ ohm}^{-1} \text{ mol}^{-1}$ ) of N,N-dimethylformamide solutions of the complexes at various concentrations ( $\text{mol l}^{-1}$ ) are:  $[Cr(pz)_4Cl_2]$ , 12,  $3.1 \times 10^{-2}$ ; 22,  $1.0 \times 10^{-2}$ ; 47,  $1.2 \times 10^{-3}$ .  $[Cr(pz)_4Br_2]$ , 48,  $2.2 \times 10^{-2}$ ; 58,  $1.0 \times 10^{-2}$ ; 68,  $5.6 \times 10^{-3}$ .  $[Cr(pz)_4I_2]$ , 120,  $1.1 \times 10^{-3}$ .  $[Cr(iz)_4Cl_2]$ , 13,  $3.5 \times 10^{-2}$ ; 64,  $8.2 \times 10^{-4}$ .  $[Cr(iz)_4Br_2]$ , 57,  $1.2 \times 10^{-2}$ ; 67,  $5.9 \times 10^{-3}$ ; 126,  $4.4 \times 10^{-4}$ .

### Results and Discussion

Two series of chromium(II) complexes have been obtained: those having general formula  $CrL_4X_2$  ( $L = pz, Nmiz, X = Cl, Br, I$ ;  $L = iz, X = Cl, Br$ ) and those with the formula  $CrL_2Cl_2$  ( $L = pz, dmpz, Nmiz, X = Cl$ ). A compound with the formula  $[Cr(dmpz)_3Br_2]$  has been also obtained. In no case was it possible to obtain complexes with a ligand to metal ratio greater than four, irrespective of the ratios of the reactants.

All the complexes are high-spin. The magnetic moment values of  $CrL_4X_2$  and  $[Cr(dmpz)_3Br_2]$  complexes are normal for spin free chromium(II); those of  $CrL_2Cl_2$  derivatives are below the spin-only value for four unpaired electrons, and temperature dependent (Table II).

The complexes are insoluble in those organic solvents which do not cause oxydation or at least partial decomposition.

Solid-reflectance spectra of the  $CrL_4X_2$  complexes

TABLE I. Analytical Data for the Complexes.

Compound	Found %				Calcd %			
	C	H	N	Cr	C	H	N	Cr
[Cr(pz) <sub>4</sub> Cl <sub>2</sub> ]	36.4	4.16	28.4	13.1	36.47	4.08	28.35	13.16
[Cr(pz) <sub>4</sub> Br <sub>2</sub> ]	29.8	3.33	23.0	10.9	29.77	3.33	23.14	10.74
[Cr(pz) <sub>4</sub> I <sub>2</sub> ]	25.1	2.93	19.3	8.99	24.93	2.79	19.38	8.99
[Cr(iz) <sub>4</sub> Cl <sub>2</sub> ]	36.2	3.98	28.3	13.0	36.47	4.08	28.35	13.16
[Cr(iz) <sub>4</sub> Br <sub>2</sub> ]	30.1	3.43	22.8	10.9	29.77	3.33	23.14	10.74
[Cr(Nmiz) <sub>4</sub> Cl <sub>2</sub> ]	42.1	5.11	24.6		42.58	5.60	24.83	
[Cr(Nmiz) <sub>4</sub> Br <sub>2</sub> ]	35.1	4.52	20.7	9.39	35.57	4.47	20.74	9.62
[Cr(Nmiz) <sub>4</sub> I <sub>2</sub> ]	30.0	3.89	17.5		30.30	3.81	17.67	
[Cr(Nmiz) <sub>2</sub> Cl <sub>2</sub> ]	32.9	4.39	19.1		33.40	4.21	19.51	
[Cr(dmpz) <sub>2</sub> Cl <sub>2</sub> ]	38.1	5.14	17.5		38.11	5.11	17.77	
[Cr(dmpz) <sub>3</sub> Br <sub>2</sub> ]	36.3	5.04	16.8	10.1	36.01	4.83	16.80	10.39
[Cr(pz) <sub>2</sub> Cl <sub>2</sub> ]	28.0	3.11	21.2	20.1	27.81	3.11	21.62	20.07

TABLE II. Some Physical Data for the Complexes.

Compound	$\mu_{\text{eff}}$ (BM)		State <sup>a</sup>	Absorption Max. (kK) of the Electronic Spectra, with $C_{\text{molar}}$ (mol l <sup>-1</sup> ) and $\epsilon_{\text{molar}}$ (l mol <sup>-1</sup> cm <sup>-1</sup> ) in Parentheses
	(298 K)	(84 K)		
[Cr(pz) <sub>4</sub> Cl <sub>2</sub> ]	4.93	4.90	R	12.5 sh, 18.2
			D	12.5 (3.1 × 10 <sup>-2</sup> ; 49)
[Cr(pz) <sub>4</sub> Br <sub>2</sub> ]	4.93		R	13.3 sh, 18.5
			D	13.3 (2.2 × 10 <sup>-2</sup> ; 20)
[Cr(pz) <sub>4</sub> I <sub>2</sub> ]	4.93		R	15.4 sh, 18.3
[Cr(iz) <sub>4</sub> Cl <sub>2</sub> ]	4.87	4.86	R	13.3 sh, 17.5
			D	14.0 (3.5 × 10 <sup>-2</sup> ; 40)
[Cr(iz) <sub>4</sub> Br <sub>2</sub> ]	4.85		R	16.6 sh, 19.2
			D	17.4 (1.2 × 10 <sup>-2</sup> ; 30)
[Cr(Nmiz) <sub>4</sub> Cl <sub>2</sub> ]	4.90		R	13.3 sh, 17.7
[Cr(Nmiz) <sub>4</sub> Br <sub>2</sub> ]	4.90	4.88	R	14.0 sh, 17.7
[Cr(Nmiz) <sub>4</sub> I <sub>2</sub> ]	4.90		R	15.5 sh, 17.7
[Cr(Nmiz) <sub>2</sub> Cl <sub>2</sub> ]	4.69	4.30	R	13.95
[Cr(dmpz) <sub>2</sub> Cl <sub>2</sub> ]	4.48	3.65	R	8.35 sh, 15.0
[Cr(dmpz) <sub>3</sub> Br <sub>2</sub> ]	4.95	4.95	R	15.0
[Cr(pz) <sub>2</sub> Cl <sub>2</sub> ]	4.62	4.06	R	11.1 sh, 14.7

<sup>a</sup> R = diffuse reflectance; D = DMF soln.

are substantially similar to each other: they show an absorption maximum in the range 17.5–19.0 kK with a less intense, sometimes not well resolved, shoulder in the range 12.5–16.5 kK. The spectra of the complexes with 2:1 ligand to metal ratio are similar to those of the above complexes except for the position of the bands which are moved to the lower frequencies.

These reflectance spectra are typical of tetragonally distorted six-coordinate chromium(II) complexes.<sup>6</sup> The splitting of the ground term <sup>5</sup>D (*d*<sup>4</sup> free ion) in an octahedral ligand field axially elongated (symmetry D<sub>4h</sub>) is depicted in Figure 1. Such tetragonal distortions

have been usually found in chromium(II) six-coordinate complexes whose structures are known.<sup>7</sup>

Assuming this scheme to be qualitatively correct, the lower energy band in the spectra of the complexes is assigned to the transition between the components of the <sup>5</sup>E ground term (<sup>5</sup>A<sub>1g</sub> ← <sup>5</sup>B<sub>1g</sub>), whilst the more intense band at higher energy is assigned to the unresolved transitions to the components of the <sup>5</sup>T<sub>2</sub> ex-

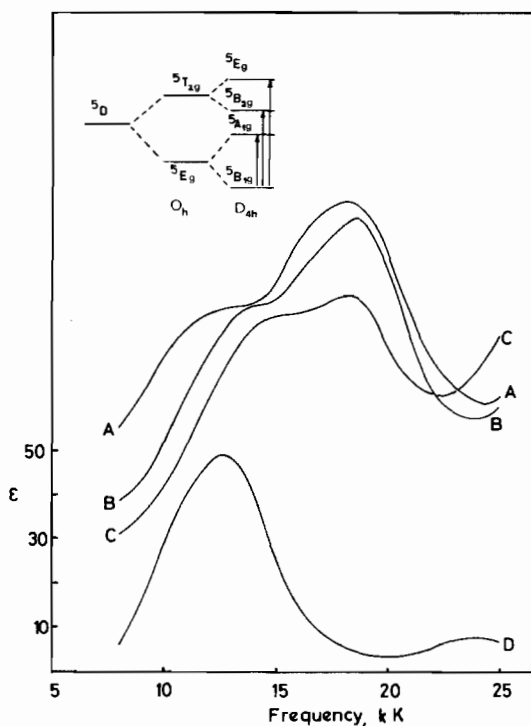


Figure 1. Reflectance spectra of [Cr(pz)<sub>4</sub>Cl<sub>2</sub>], curve A; [Cr(pz)<sub>4</sub>Br<sub>2</sub>], curve B; [Cr(pz)<sub>4</sub>I<sub>2</sub>], curve C. Absorption spectrum in N,N-dimethylformamide of [Cr(pz)<sub>4</sub>Cl<sub>2</sub>], curve D.

cited term ( ${}^5B_{2g} \leftarrow {}^5B_{1g}$ ;  ${}^5E_g \leftarrow {}^5B_{1g}$ ). The position of the main band in the spectra of the  $CrL_4X_2$  derivatives is practically unaffected as the halogens are changed from Cl to Br and I, whilst the frequency of the lower energy band is greatly halogen dependent. This band is shifted to the higher energies in the order Cl, Br, I which is the opposite of the increasing ligand field strength of the halogens. This spectral behaviour suggests that tetragonal distortion of the  $CrN_4X_2$  chromophores increases as the ligand field strength of the axial donor atoms (the halogens) becomes weaker in comparison to that of in-plane donor atoms (the nitrogen atoms).

Electronic spectra of  $CrL_2Cl_2$  derivatives are similar in shape and comparable in frequencies of absorption maxima to those of the complexes with a 4:1 ligand to metal ratio. Therefore the compounds of stoichiometry  $CrL_2Cl_2$  can be formulated as  $CrCl_4L_2$  six-coordinate species with a polymeric chlorine bridged structure. Displacement of absorption maxima to the lower frequencies in the spectra of the  $CrL_2Cl_2$  derivatives in comparison to those of  $CrL_4Cl_2$  is consistent with the weaker ligand field strength of chlorine as compared to that of nitrogen atoms.

Owing to the substantial similarity of the spectra, a six-coordinate, presumably polymeric structure, could be also assigned to  $[Cr(dmpz)_3Br_2]$ . Nevertheless the magnetic behaviour of this compound does not agree with this hypothesis.

#### Magnetic Results

The  $CrL_4X_2$  complexes obey the Curie law with room temperature magnetic moment values very close

to the spin only value (4.90 B.M.) as expected for spin free six-coordinate chromium(II) complexes.

The  $CrL_2X_2$  compounds have room temperature magnetic moment values below 4.90 B.M. (Table II) which decrease even more with temperature. This magnetic behaviour is typical of compounds where appreciable antiferromagnetic interactions occur between metal ions. A superexchange mechanism involving chlorine bridges between chromium(II) ions accounts for partial spin coupling and is consistent with the proposed polymeric structure of the complexes.

The  $[Cr(dmpz)_3Br_2]$  complex has a temperature independent magnetic moment close to the spin only value. This magnetic behaviour seems to rule out for this complex a six-coordinate bromine bridged structure, which would lead to an at least partial magnetic interaction between chromium(II) ions as found in the  $CrL_2Cl_2$  derivatives and in the previously reported  $[Cr(den)Br_2]$ <sup>8</sup> complex which possesses the same donor set. The stoichiometry of the compound seems to suggest a five-coordinate structure for the  $[Cr(dmpz)_3Br_2]$  derivative, even though its spectrum is not typical of a trigonal bipyramidal chromium(II) complex.<sup>2,9</sup>

#### Infrared Spectra and Coordinating Behaviour of the Ligands

It is well ascertained that pyrazole and imidazole type ligands which contain both  $-N=$  and  $-N(H)-$  groups, usually utilize pyridine (or iminic) nitrogens as donor atoms and pyrrole (or aminic) nitrogens in intermolecular or intramolecular hydrogen bonding.<sup>1,10,11</sup> The lone pair of aminic nitrogen in pyrazole and imidazole rings is part of the aromatic sextet, therefore coordination through this atom is expected to be very unfavorable since it would interrupt the system of  $\pi$  conjugated bonds. Coordination through iminic nitrogen leaves this  $\pi$  system unchanged and therefore is favoured.

As the existence of hydrogen bonding markedly influences the N-H stretching frequency, we recorded infrared spectra in the range  $4000-250\text{ cm}^{-1}$  of some chromium(II) pyrazole and imidazole complexes. The position of the N-H stretching frequencies (Table III) is in the range usually found for other 3d metal complexes with the same ligands where hydrogen bonding between N-H groups and halogen atoms has been verified.<sup>12</sup> In the spectra of all the complexes the N-H stretching frequency is at higher energy than in the solid free ligand, thus indicating that hydrogen bonding is reduced upon coordination, but is always at lower energy than in the gaseous free ligand where hydrogen bonding is negligible.

Infrared spectra in the region  $300-330\text{ cm}^{-1}$  show one strong absorption (sometimes split in two components) whose frequency is substantially anion and ligand independent and which is absent in the free

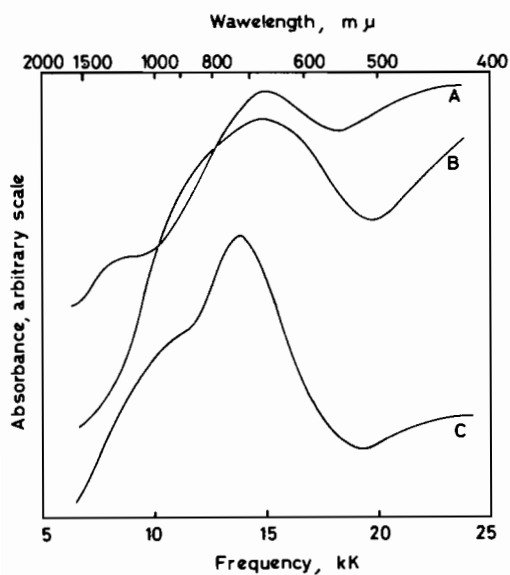


Figure 2. Reflectance spectra of  $[Cr(dmpz)_2Cl_2]$ , curve A;  $[Cr(dmpz)_3Br_2]$ , curve B;  $[Cr(pz)_2Cl_2]$ , curve C.

TABLE III. Infrared Data for Some Complexes (Frequencies in  $\text{cm}^{-1}$ ).<sup>a</sup>

Compound	(N-H)	(Cr-N)
Solid pz	2900 s,br	
Gaseous pz <sup>13</sup>	3541 s	
[Cr(pz) <sub>4</sub> Cl <sub>2</sub> ]	3230 s	320–310 s
[Cr(pz) <sub>4</sub> Br <sub>2</sub> ]	3220 s	315–300 s
[Cr(pz) <sub>4</sub> I <sub>2</sub> ]	3230 s,br	310 s
Solid iz	2800 s,br	
Gaseous iz <sup>14</sup>	3518 s	
[Cr(iz) <sub>4</sub> Cl <sub>2</sub> ]	3220 s,br	320–310 s
[Cr(iz) <sub>4</sub> Br <sub>2</sub> ]	3180 s,br	325 s
[Cr(dmpz) <sub>2</sub> Cl <sub>2</sub> ]	3260–3210 s	315 s
[Cr(dmpz) <sub>3</sub> Br <sub>2</sub> ]	3280–3230 s	310–295 s

<sup>a</sup> S = strong; br = broad.

ligands. Moreover this absorption is the only one present in the range  $650\text{--}250\text{ cm}^{-1}$  in the spectra of the  $\text{CrL}_4\text{X}_2$  derivatives; therefore it seems reasonable to us to assign these bands to the Cr–N stretching modes. In the case of the chloro derivatives one of the components of the band could also be attributed to the Cr–Cl stretching mode.

#### Behaviour in Solution

All the complexes here reported are insoluble in the common organic solvents with the exception of N,N-dimethylformamide where indeed an extensive solvolysis of the compounds occurs as shown by the marked change of absorption spectra as compared to the solid-reflectance spectra. The absorption maxima of the spectra of chromium(II) complexes dissolved in N,N-dimethylformamide are shifted to the lower frequencies (Table II) thus indicating that a ligand exchange occurs between pyrazole or imidazole and N,N-dimethylformamide molecules, while displacement of the halogens must occur to a less extent. In fact the position of N,N-dimethylformamide in the spectrochemical series is intermediate between halogens and pyrazole or imidazole, *i.e.* N,N-dimethylformamide has a ligand field strength greater than halogens but weaker than pyrazole or imidazole.<sup>12</sup>

This behaviour is also confirmed by conductivity

measurements of solutions of chromium(II) complexes dissolved in N,N-dimethylformamide at various concentrations. The obtained values (see Experimental) show that molar conductivity increases in the order Cl, Br, I and with increasing dilution. Chloro derivative solutions at the same concentration as those used for absorption spectra are essentially non-electrolytes, whilst Br and I derivatives have molar conductivity values lower than those usually respectively for 1:1 and 2:1 electrolytes.<sup>15</sup>

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