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Transition Metal Complexes of Pyrazine-2,3-dicarboxylic Acid

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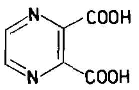
Complexes of empirical formula M(pyzDC)·nH$_2$O, where n = 4 for M = Mn, Fe, Co, Ni, Zn and n = ½ for M = Cu, were prepared. Six-coordination of the metal atoms are proposed after consideration of magnetic, thermal, visible and i.r. spectral data. The X-ray powder diffraction patterns indicated that Mn and Fe complexes are isostructural as are those of Co and Zn.

Introduction

Pyrazine-2,3-dicarboxylic acid, H$_2$pyzDC, (I) has six sites for potential coordination to a metal atom but without severe distortion it can only act as a mono- or bidentate chelating agent to a given metal atom.



(I)

Several studies of the 1:2 metal complexes have been reported [1–3] but only a brief thermal study of 1:1 complexes has appeared [4]. The crystal structures of the 1:1 complexes with bivalent Co [5] and Zn [6] have shown bridged polymeric structures: in the former the ligand remains essentially planar and coordination is via N and carboxylic groups; in the latter the second N remains uncoordinated and the carboxylic group next to it is rotated perpendicular to the plane of the pyrazine ring and both oxygen atoms of the group coordinate to other metal atoms. The octahedral coordination of these metal atoms is completed by water molecules.

We report here the properties of the 1:1 complexes of the bivalent metals Mn, Fe, Co, Ni, Cu and Zn.

Experimental

Synthesis

The ligand was prepared according to the method of Jones and McLaughlin [7]: m.p. 182 °C (dec.), ref. [7] m.p. 183–5 °C.

Complexes were prepared by adding a hot, concentrated aqueous solution of H$_2$pyzDC to a hot aqueous solution of metal acetate in excess. The resulting solution was filtered and allowed to stand for several hours. The resulting precipitate was filtered off, washed with water and air dried.

Physical Measurements

Magnetic moments were determined at room temperature using a Newport Single Temperature Gouy Balance (Model SM-12).

Visible spectra were recorded in the range 400–1000 nm on a Zeiss PMQ II spectrophotometer with RA3 reflectance attachment calibrated against MgO.

Infrared spectra were recorded in the range 4000–1200 cm^{-1} on a Perkin–Elmer 621 spectrometer in KBr discs.

Thermogravimetric studies were carried out on a Stanton–Redcroft balance (Model TG-750) in conjunction with a direct-readout recorder.

X-ray diffraction patterns were recorded on a Siemens Powder Diffractometer using CuK$_\alpha$ radiation with a $\theta/2\theta$ scan of 1 °/min.

Analyses

Mn, Ni, Cu and Zn were determined by titration with EDTA [8]. Fe and Co were determined spectrophotometrically using respectively 2,4,6-tris(2′-pyridyl)-1,3,5-triazine [9] and thiocyanate [10].

C, H and N were determined in the C.S.I.R.O. Microanalytical Laboratory, Melbourne, Australia.

Results and Discussion

Complexes of empirical formula M(pyzDC)·nH$_2$O, where n = 4 for M = Mn, Fe, Co, Ni, Zn and n = ½ for M = Cu, were prepared for which the analyses are given in Table I. Table II gives the magnetic moments of the complexes and their solid state reflectance spectra are shown in Figure 1. These data are typical for octahedral complexes of these metals [11]. Results of the thermogravimetric analyses are given in Table III. The compounds each show an initial loss of water followed by simultaneous decarboxylation and loss of base with the consequent formation of metal oxide. This pattern is consistent with the decomposition temperatures reported byAntinelli and Paris [4]

TABLE I. Analyses of Complexes.

Complex	% Required				% Found			
	C	H	N	M	C	H	N	M
Mn(pyzDC)·4H_2O	24.6	3.4	9.6	18.7	24.7	3.4	9.7	18.7
Fe(pyzDC)·4H_2O	24.5	3.4	9.5	19.0	24.7	3.3	9.8	19.2
Co(pyzDC)·4H_2O	24.3	3.4	9.4	19.8	24.3	3.3	9.7	19.7
Ni(pyzDC)·4H_2O	24.3	3.4	9.4	19.8	24.1	2.6	9.7	19.7
Zn(pyzDC)·4H_2O	23.7	3.3	9.2	21.5	23.8	2.7	9.4	21.6
Cu(pyzDC)·½H_2O	30.2	1.3	11.7	26.6	30.0	1.3	11.3	26.3
H_2pyzDC·2H_2O	35.3	2.9	13.8		35.0	2.8	13.8	

TABLE II. Magnetic Moments.

Complex	Colour	μ_{eff} (B.M.)
Mn(pyzDC)·4H_2O	Pale Yellow	5.92
Fe(pyzDC)·4H_2O	Dark Brown–Purple	5.17
Co(pyzDC)·4H_2O	Orange	4.84
Ni(pyzDC)·4H_2O	Light Blue–Green	3.27
Zn(pyzDC)·4H_2O	White	diamagnetic
Cu(pyzDC)·½H_2O	Green	1.82

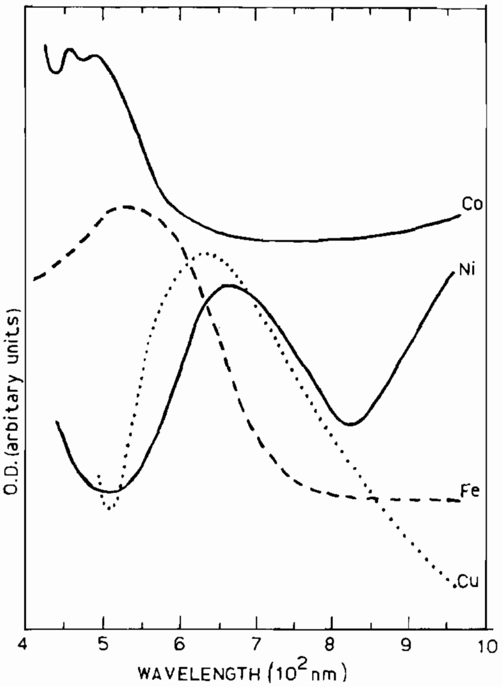


Figure 1. Diffuse reflectance spectra of the complexes.

for like compounds. The fact that decarboxylation occurred as a one step process and at fairly high temperatures indicates that both carboxylic acid groups are involved in coordination to the metal atoms [12].

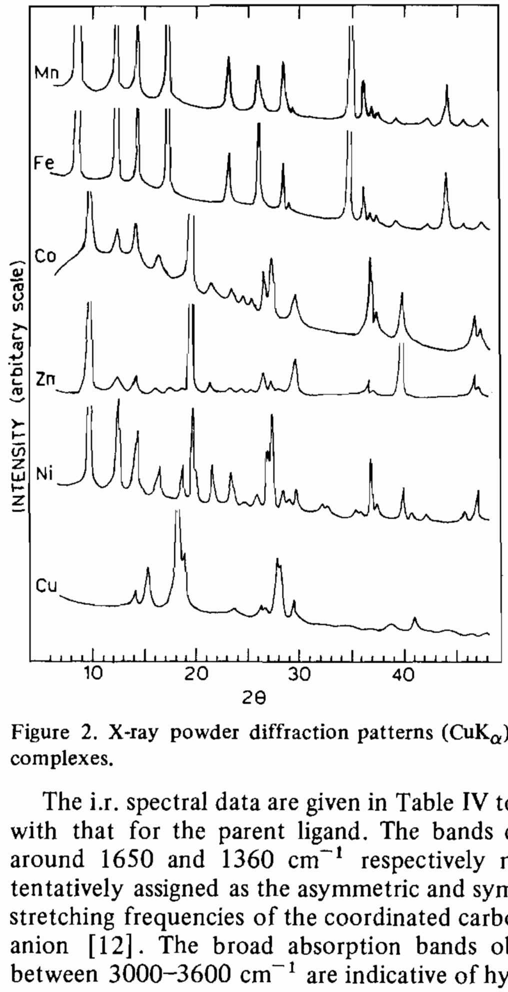


Figure 2. X-ray powder diffraction patterns (CuK_α) for the complexes.

The i.r. spectral data are given in Table IV together with that for the parent ligand. The bands centred around 1650 and 1360 cm^{-1} respectively may be tentatively assigned as the asymmetric and symmetric stretching frequencies of the coordinated carboxylate anion [12]. The broad absorption bands observed between 3000–3600 cm^{-1} are indicative of hydrogen bonding probably involving the water molecules.

Figure 2 shows the X-ray powder diffraction patterns for the complexes. From the patterns it is evident that the Mn and Fe complexes are isomorphous as are those of Co and Zn. Although the diffraction angles for the Ni complex closely parallel those of the Co and Zn complexes the intensities of the diffracted rays are considerably different. The results from i.r. and thermogravimetric studies are in accord with these isomorphous structural groupings.

TABLE III. Results of Thermogravimetric Studies.

	Temperature Range (°C)	Volatile Products	Weight Loss (%)		Metal (%)^b	
			Calc^a	Found	Calc	Found
Mn(pyzDC)$\cdot$4H_2O	60–120	3H_2O	18.4	17.5		
	120–350	H_2O	6.1	5.9		
	350–400	pyzDC	49.4	50.1		
		Total loss:	74.0	73.5	18.7	19.1
Fe(pyzDC)$\cdot$4H_2O	50–145	3H_2O	18.4	18.5		
	190–380	H_2O	6.1	54.0		
		pyzDC	49.3			
		Total loss:	73.8	72.5	19.0	19.9
Co(pyzDC)$\cdot$4H_2O	35–240	4H_2O	24.3	24.5		
	335–350	pyzDC	48.8	48.0		
		Total loss:	73.1	72.5	19.8	20.2
Ni(pyzDC)$\cdot$4H_2O	25–235	4H_2O	24.3	24.4		
	255–360	pyzDC	50.6	52.5		
		Total loss:	74.8	76.9	19.8	18.2
Zn(pyzDC)$\cdot$4H_2O	40–260	4H_2O	23.7	23.5		
	270–470	pyzDC	49.5	49.6		
		Total loss:	73.2	73.1	21.5	21.6
Cu(pyzDC)$\cdot$½H_2O	30–140	½H_2O	3.8	4.0		
	245–350	pyzDC	62.9	64.3		
		Total loss:	66.7	68.3	26.6	25.3

^{a}Gain of oxygen taken into account when calculating final step loss and total loss in weight. ^{b}Assuming the following metal oxides to be the final products for the complexes of the respective metal: Mn_3O_4, Fe_3O_4, Co_3O_4, NiO, ZnO and CuO.

TABLE IV. Infrared Spectral Data^a.

Mn(pyzDC)$\cdot$4H_2O	3290(sbr), 1635(ms), 1590(ss), 1460(w), 1430(w), 1390(ms), 1360(ss)
Fe(pyzDC)$\cdot$4H_2O	3220(sbr), 1630(sh), 1590(ss), 1460(w), 1430(w), 1390(ms), 1360(ss)
Co(pyzDC)$\cdot$4H_2O	3560(ms), 3185(sbr), 1640(ss), 1595(sh), 1465(ms), 1435(w), 1395(ss), 1365(ss)
Ni(pyzDC)$\cdot$4H_2O	3560(ms), 3190(sbr), 1640(ss), 1595(sh), 1460(ms), 1435(w), 1395(ss), 1360(ss)
Zn(pyzDC)$\cdot$4H_2O	3560(ms), 3180(sbr), 1665(ss), 1590(sh), 1460(ms), 1430(w), 1390(ss), 1360(ss)
Cu(pyzDC)$\cdot$½H_2O	3420(wbr), 3080(ms), 1640(ss), 1575(m), 1420(ms), 1315(ss)
H_2pyzDC$\cdot$2H_2O	3300(mbr), 2850(wbr), 2520(wbr), 1720(ss), 1560(mbr), 1430(wbr), 1340(sh), 1290(mss)

^{a}s, strong; ss, strong and sharp; m, medium; w, weak; br, broad; sh, shoulder; ms, medium–strong; mss, medium–strong and sharp.

The X-ray powder diagrams do not correlate with either of the known structures [5, 6]. Although the diffraction angles observed for the Zn complex are consistent with the cell parameters of the Zn trihydrate complex [6] the intensity distribution is at variance with the given data (*e.g.* maximum F_o = 129.6 for 200, whose $2\theta\,(CuK_\alpha)$ = 28.2°). The cell parameters for the reported Co dihydrate structure [5] do not correlate with any of the powder diffraction patterns. A possible explanation for the above inconsistencies may be the different degree of hydration observed in this work. Attempts to obtain analogous complexes of lower hydration were unsuccessful.

The properties of the Cu complex, and its ability to lose water readily, agree with work previously reported for the anhydrous complex [2]. Matthews and Walton [2] proposed a polymeric structure involving both N atoms and with square-planar coordination about Cu. This arrangement of ligand molecules would require rotation of the carboxylic acid groups with respect to the pyrazine ring to lessen adjacent O ... O interactions. Such rotation would facilitate carbonyl bridging with consequent increase in coordination number. In the structure of the Co dihydrate complex [5], where the ligand molecules have this arrangement, this form of rotation is apparent. From data given by those authors rotation angles of 28.7 and 29.0° may be calculated. It is of interest that a similar twist (34°) is evident in the structure of the parent acid [13].

From a consideration of the above results it may be concluded that several structural possibilities exist for the 1:1 complexes discussed, each allowing 6-coordination of the respective metal atom.

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