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Nature of Bonding in Pyrazine-2,3-dicarboxamide Complexes of Copper(II), Cobalt(II), and Nickel(II)

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Synopsis. Pyrazine-2,3-dicarboxamide complexes with the perchlorates of copper(II), cobalt(II), and nickel(II) have been prepared and characterised, copper having a square planar configuration and cobalt and nickel an octahedral geometry. Bonding takes place through a ring nitrogen and the oxygen atom of the adjacent amide group.

Heterocyclic carboxamides are known to possess powerful antitubercular activity.[1] During the course of the investigation on metal ion-assisted hydrolysis of pyrazine-2,3-dicarboxamide (pzda), a paper[2] was published on several cobalt and nickel(II) complexes with both ring nitrogens of the ligand bonded to the same metal without participation of the amide groups. The structure seemed untenable to us. Since delineation of the above mentioned reaction requires knowledge of the bonding in metal complexes, this problem has been reinvestigated. In this study perchlorate has been chosen as the anion since the stereochemistry will not be affected by the anion participation.

Experimental

Preparation. To the ligand (0.2 g) dissolved in water (30 ml) on a steambath, was added the metal perchlorate (1 g). The copper compound which separated as bluish violet crystals when cooled to room temperature, was washed with cold water and recrystallised from hot water. Large orange-red crystals of the cobalt(II) complex and greenish crystals of the nickel(II) complex, however, separated on slow evaporation of the solution over concentrated H_2SO_4. The crystals were filtered, washed with dry ethanol, dried in air. The analytical data (Table 1) confirms the complexes to be $[Cu(pzda)_2](ClO_4)_2$ (I), $[Co(pzda)_2(H_2O)_2](ClO_4)_2$ (II), and $[Ni(pzda)_2(H_2O)_2](ClO_4)_2$ (III) respectively.

Results and Discussion

The preparation of pyrazine-2,3-dicarboxamide complexes possessed difficulties because of the poor solubility of the ligand in common organic solvents including 1-butanol used by Singh *et al.*,[2] consequently an aqueous solution of the ligand was used for preparation of the complexes. Since the copper(II) complex, cobalt(II) and nickel(II) compounds decomposed on dissolution in water, an excess of the metal perchlorates which consumed the ligand totally and hindered any dissociation was used.

Table 2 shows the important IR bands of the ligand, its deuterated form, and the metal complexes. The assignments of these bands can readily be made by comparing them with the 2-pyridine carboxamide (pya) and 2-pyrazine carboxamide (pza) complexes,[3,4] and by taking into considerations the pyrazine ring vibrations.[5] In all the complexes the asymmetric and symmetric OCN stretching bands are shifted to lower and higher frequencies respectively relative to the free ligand, indicating that coordination takes place through the oxygen atom of the amide group. Similar shifts describing coordination through amide oxygen have been observed for complexes of 2-pyridine carboxamide,[3,6,7] 2-pyridine acetamide,[8] 2-pyrazine carboxamide[9] and 8-quinoline carboxamide.[10]

The room temperature magnetic moments and electronic spectra (Table 1) are indicative of the square planar configuration of the copper complex and the octahedral geometry of the cobalt(II) and nickel(II) complexes.[11] In an aqueous solution the copper(II) complex shows only a single broad band (10520—

TABLE 1. ELEMENTAL ANALYSIS,[a] MAGNETIC MOMENTS, AND ELECTRONIC SPECTRA OF METAL COMPLEXES OF PYRAZINE-2,3-DICARBOXAMIDE

Compound	%C	%H	%N	%M	$\%ClO_4$	μ_{eff} in B. M. (27 °C)	ν_{max}/cm^{-1}	Transition	10 *Dq*/cm^{-1}
I	24.42	1.95	18.64	10.61	33.42	2.01	12100[b]	${}^2B_{1g}$-${}^2A_{1g}$	
	(24.23)	(2.02)	(18.64)	(10.69)	(33.46)		18180 sh	${}^2B_{1g}$-${}^2E_g$	
II	23.14	2.54	17.74	9.53	31.70	3.48	10100	${}^4T_{1g}$-${}^4T_{2g}$	11120
	(23.00)	(2.55)	(17.88)	(9.39)	(31.79)		17530	?	
							20850	${}^4T_{1g}$-${}^4T_{1g}^{(P)}$	
III	23.32	2.53	17.76	9.28	31.68	4.74	10160	${}^3A_{2g}$-${}^3T_{2g}$	10160
	(23.00)	(2.55)	(17.88)	(9.41)	(31.78)		11770 sh	${}^3A_{2g}$-${}^1E_g$	
							17400	${}^3A_{2g}$-${}^3T_{1g}$	

a) Calculated values in parenthesis. Electronic spectra in Nujol mulls. b) This band is observed both in aqueous solutions and in Nujol mulls.

Table 2. Infrared spectra of pyrazine-2,3-dicarboxamide and of its metal complexes in KBr discs, cm^{-1}

pzda		Cu	Ni	Co	Assignment
H	D[a]				
3430(s)	2580(s)	3440(m)	3420(s, b)[b]	3430(s, b)[b]	NH_2 antisym. stretch
3310(s)	2540(s)	3380(w)	3320(m)	3320(m)	NH_2 sym. stretch
3205(m)	2410(m)	3290(m)			
1695(sh)	1660(s)	1690(sh)	1670(s)	1695(s)	OCN antisym. stretch
1680(sh)		1660(s)		1670(sh)	(mainly C=O stretch)
1615(m)	1170(m)				NH_2 scissoring
	1140(m)				
1565(m)	1565(m)	1565(m)	1565(m)	1560(m)	Pyrazine ring
1445(w)	1440(m)	1530(w)	1535(sh)	1540(sh)	vibration
		1425(m)	1425(w)	1420(w)	
1395(m)	1410(m)	1405(w)	1400(w)	1400(w)	OCN sym. stretch
1348(m)	1355(m)	1365(m)	1365(w)	1360(w)	(mainly C-N stretch)

a) D stands for the deuterated ligand. Bands occuring at lower frequencies are not shown. b) Broadening of this band indicates its merger with OH stretching of water molecules.

14300 cm^{-1}). The mull spectrum, however, shows the presence of a shoulder in addition to that observed in solution. It is expected that due to the absence of Jahn-Teller distortion more bands should appear in the visible range,[12] Ferguson has shown[13] that distinct bands observed in the polarised spectra of square planar copper(II) complexes are considerably broadened in solution. It has therefore been concluded that the square planar geometry of the copper(II) complex is retained in solution.

Regarding the nature of bonding in pyrazine-2,3-dicarboxamide complexes support is given by the X-ray crystallographic study of $[Cu(pzda)_2]\ (ClO_4)_2$.[14]

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