Metal Complexes of 3-Pyridazinecarboxylic Acid (Hpdc). The X-ray Crystal Structure of $[Mn(pdc)_2(H_2O)_2]\cdot 2H_2O$ and a Structural Comparison between Equivalent Pyridine and Pyridazine Systems

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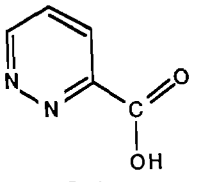
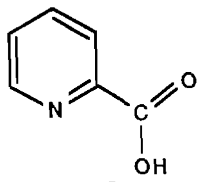
Abstract

An X-ray structure determination is reported for the complex $[Mn(pdc)_2(H_2O)_2]\cdot 2H_2O$ of 3-pyridazinecarboxylic acid (Hpdc). The complex is triclinic, $P\bar{1}$, with $a = 5.356(1)$, $b = 7.433(2)$, $c = 9.800(2)$ Å; $\alpha = 79.79(2)$, $\beta = 88.92(2)$, $\gamma = 71.74(2)^\circ$ and $Z = 1$. Centrosymmetric octahedral molecules of $[Mn(pdc)_2(H_2O)_2]$ are linked by hydrogen bonds involving the two lattice waters. The chelating 3-pyridazinecarboxylate ligands are present in a *trans*-planar arrangement, with each ligand coordinating via a carboxylate oxygen and the 2-nitrogen. Two water molecules coordinate in the axial positions. The structure differs from that of the corresponding 2-pyridinecarboxylic acid (Hpic) complexes $[M(pic)_2(H_2O)_2]\cdot 2H_2O$ (M = Co, Ni, Zn) only in terms of the hydrogen bonding network. This enables the first structural comparison between equivalent pyridine and pyridazine systems to be made. Magnetic susceptibility measurements to 89 K, and electronic, infrared and X-ray powder diffraction spectra are reported for the complexes $M(pdc)_2\cdot 4H_2O$ (M = Mn, Co, Ni, Zn) and $Cu(pdc)_2$. The Co and Ni complexes are isomorphous with $[Mn(pdc)_2(H_2O)_2]\cdot 2H_2O$. The Cu complex is probably six-coordinate with bridging carboxylate groups.

Introduction

There is considerable interest in metal complexes containing bridging pyridazine and phthalazine groups [1, 2]. To this end, many complexes of binucleating ligands based on 3,6-disubtituted pyridazines and 1,4-disubstituted phthalazines have been investigated [1, 2]. In contrast, metal complexes of chelating mono-substituted ligands appear to have been almost completely neglected. We recently reported [3] the X-ray structure of the dimeric complex aquacopper(II)-di-μ-[N,N'-bis(3'-pyridazinecarboxamido)-1,2-ethane]-copper(II) (3 + x)water. As part of an ongoing investigation of 3-substituted pyridazine ligands, we now report the manganese(II), cobalt(II), nickel(II), copper(II) and zinc(II) complexes of 3-pyridazinecarboxylic acid (Hpdc, I) and the X-ray structure of $[Mn(pdc)_2(H_2O)_2]\cdot 2H_2O$.


I, Hpdc


II, Hpic

Experimental

Metal complexes were prepared by the reaction of 3-pyridazinecarboxylic acid [4] with metal carbonates (Mn, Ni) or metal acetates (Co, Cu, Zn). Typical preparations are shown below. The complexes were dried in vacuum over phosphorus pentoxide.

$Mn(pdc)_2(H_2O)_4$

A hot aqueous solution (100 ml) of ligand (1.0 g) was added to a hot suspension of manganese(II) carbonate (0.46 g) in water (75 ml). The mixture was heated on a steam bath for 1 h and then allowed to cool. After 4 days yellow crystals were deposited.

$Zn(pdc)_2(H_2O)_4$

A hot solution of ligand (0.25 g) in water (20 ml) was slowly added to a hot solution of zinc acetate dihydrate (0.25 g) in water (20 ml). Very pale orange crystals were deposited after a few min.

Analyses and Physical Measurements

These were as previously described [5]. Analytical data are given in Table 1.

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0020-1693/89/$3.50

TABLE 1. Analytical data

Compound		Analyses (%)				Colour
		C	H	N	M	
$Mn(pdc)_2(H_2O)_4$	calc.	32.2	3.8	15.0	14.6	yellow
	found	32.5	3.6	14.9	14.7	
$Co(pdc)_2(H_2O)_4$	calc.	31.8	3.7	14.9	15.5	reddish-brown
	found	32.2	3.5	15.0	15.7	
$Ni(pdc)_2(H_2O)_4$	calc.	31.9	3.7	14.9	15.5	green
	found	32.0	3.6	15.0	15.3	
$Cu(pdc)_2$	calc.	38.8	2.0	18.1	20.4	grey
	found	38.5	2.0	17.9	20.7	
$Zn(pdc)_2(H_2O)_4$	calc.	31.3	3.7	14.6	17.0	very pale orange
	found	31.6	3.3	14.7	17.3	

Crystallography

Crystal data

$Mn(C_5H_3N_2O_2)_2(H_2O)_2 \cdot 2H_2O$, M 373.2, triclinic, space group $P\bar{1}$, $a = 5.356(1)$, $b = 7.433(2)$, $c = 9.800(2)$ Å, $\alpha = 79.79(2)$, $\beta = 88.92(2)$, $\gamma = 71.74(2)°$, $V = 364.3(2)$ Å^3, $Z = 1$, D_c 1.70 g cm^{-3}, μMo 9.16 cm^{-1}. Crystal had 14 faces of the pinacoids {100}, {010}, {001}, {011}, {012}, {110} and {111} developed, with min. and max. dimensions 0.10 and 0.25 mm. Number of reflections was 1201 considered observed out of 1280 measured, with $2\theta_{max}$ 50°. Final residuals R, R_w were 0.021, 0.033.

Structure determination

Reflection data for a multi-faceted yellow crystal were measured with an Enraf-Nonius CAD-4 diffractometer in $\theta/2\theta$ scan mode using graphite monochromatized molybdenum radiation (λ 0.7107 Å). Data were corrected for absorption. Reflections with $I > 3\sigma(I)$ were considered unobserved. The Mn atom was arbitrarily placed at $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$ and the remaining non-hydrogen atoms were located using Fourier syntheses. Hydrogen atoms were located in difference Fouriers after partial refinement of the heavier atoms, and were assigned isotropic thermal parameters equivalent to those of the atom to which they were bonded. Positional parameters for all atoms and anisotropic thermal parameters for non-hydrogen atoms were refined using full-matrix least-squares.

Reflection weights used were $1/\sigma^2(F_o)$, with $\sigma(F_o)$ being derived from $\sigma(I_o) = [\sigma^2(I_o) + (0.04I_o)^2]^{1/2}$. The weighted residual is defined as $R_w = (\Sigma w(\Delta F)^2/\Sigma w F_o^2)^{1/2}$. Atomic scattering factors and anomalous dispersion parameters were from the International Tables for X-ray Crystallography [6]. Refinement used BLOCKLS, a local version of ORFLS [7], and ORTEP-II [8] was used for the structure diagrams. Cyber 171 and IBM 3090 computers were used for all calculations. Atomic parameters for the non-hydrogen atoms are given in Table 2, and bond lengths and angles are in Table 3.

TABLE 2. Final atomic parameters and the isotropic equivalent of the anisotropic temperature factor[a]

	x	y	z	B_{eq} (Å^2)
Mn	0.5000	0.5000	0.5000	2.22(1)
O(1)	0.2921(2)	0.4641(2)	0.6860(1)	2.73(3)
O(2)	0.2955(3)	0.2848(2)	0.8938(1)	3.40(4)
OW(1)	0.3215(2)	0.3121(2)	0.4115(1)	2.94(3)
OW(2)	0.2350(3)	0.4726(2)	1.1329(1)	4.10(4)
N(1)	0.7697(2)	0.2427(2)	0.6386(1)	2.17(3)
N(2)	1.0104(3)	0.1396(2)	0.6066(1)	2.59(1)
C(1)	1.1365(3)	−0.0212(2)	0.6925(2)	3.11(3)
C(2)	1.0327(4)	−0.0883(3)	0.8140(2)	3.49(4)
C(3)	0.7910(3)	0.0203(2)	0.8480(2)	3.04(3)
C(4)	0.6638(3)	0.1883(2)	0.7561(1)	2.18(4)
C(5)	0.3942(3)	0.3244(2)	0.7808(2)	2.35(3)

[a] e.s.d.s are given in parentheses.

Results and Discussion

The complexes are shown in Table 1 with the analytical data.

X-ray Crystal Structure of $[Mn(pdc)_2(H_2O)_2] \cdot 2H_2O$

The structure is illustrated [8] in Fig. 1 and crystallographic data are given in Tables 2 and 3. Centrosymmetric octahedral molecules of $[Mn(pdc)_2(H_2O)_2]$ are linked by hydrogen bonds involving two lattice waters (oxygen atoms OW(2) and OW(2)′). Two chelating pyridazinecarboxylate ligands coordinate in a *trans*-planar arrangement via the N(1) and O(1) atoms. Two water molecules (oxygen atoms OW(1) and OW(1)′) coordinate in the axial positions. Bond distances are all normal.

TABLE 3. Selected bond length (Å) and bond angle (°) data[a]

Mn–O(1)	2.138(1)	O(1)–Mn–OW(1)	90.00(4)
Mn–N(1)	2.239(1)	O(1)–Mn–N(1)	74.68(4)
Mn–OW(1)	2.217(1)	OW(1)–Mn–N(1)	90.42(4)
Mn–O(1)'	2.138(1)	O(1)–Mn–OW(1)'	90.00(4)
Mn–N(1)'	2.239(1)	N(1)–Mn–OW(1)'	89.58(4)
Mn–OW(1)'	2.217(1)	O(1)–Mn–N(1)'	105.32(4)
N(1)–N(2)	1.341(2)	N(2)–N(1)–C(4)	120.8(1)
N(2)–C(1)	1.324(2)	N(1)–N(2)–C(1)	118.5(1)
C(1)–C(2)	1.383(3)	N(2)–C(1)–C(2)	123.3(1)
C(2)–C(3)	1.365(2)	C(1)–C(2)–C(3)	117.9(1)
C(3)–C(4)	1.388(2)	C(2)–C(3)–C(4)	117.5(1)
C(4)–N(1)	1.328(2)	N(1)–C(4)–C(3)	122.0(1)
C(4)–C(5)	1.525(2)	N(1)–C(4)–C(5)	114.7(1)
C(5)–O(1)	1.250(2)	C(3)–C(4)–C(5)	123.3(1)
C(5)–O(2)	1.245(2)	O(1)–C(5)–O(2)	126.1(1)
		O(1)–C(5)–C(4)	117.2(1)
		O(2)–C(5)–C(4)	116.7(1)

[a]Primes indicate the symmetry transformation 1 – *x*, 1 – *y*, 1 – *z*.

The pyridazinecarboxylate ligand is almost planar, with the maximum deviations, from its least-squares plane, being –0.0637 and +0.0748 Å (for the carboxylate oxygens O(1) and O(2), respectively). The C(4), C(5), O(1), O(2) carboxylate entity is rotated by 5.2° from the pyridazine plane.

Structural comparisons with other pyridazinecarboxylate complexes are not possible because no previous complexes have been reported. The structures are known, however, of the isomorphous complexes $[M(pic)_2(H_2O)_2]\cdot 2H_2O$ (M = Co, Ni, Zn) with 2-pyridinecarboxylic acid (Hpic, II) [9–12]. The general geometry of coordinated 3-pyridazinecarboxylate resembles that of the analogous pyridine ligand. The structures of the above pyridinecarboxylate complexes and of $[Mn(pdc)_2(H_2O)_2]\cdot 2H_2O$ appear to be the first examples of structures of equivalent pyridine and pyridazine systems. They may therefore be examined for the influence of replacing a CH in the pyridine in order to produce an N in the pyridazine system. The molecular geometries of the $[ML_2(H_2O)_2]$ species are equivalent and the only structural differences in the complexes involve the hydrogen bonds, of which there are three types in $[Mn(pdc)_2(H_2O)_2]\cdot 2H_2O$ and four types in the pyridinecarboxylate system.

Hydrogen bonding in $[Mn(pdc)_2(H_2O)_2]\cdot 2H_2O$ is illustrated in Fig. 2. In $[Mn(pdc)_2(H_2O)_2]\cdot 2H_2O$, each lattice water (oxygen OW(2)) is hydrogen-bonded to a coordinated water molecule (oxygen OW(1)) in a neighbouring metal complex (O–O distance 2.76 Å, van der Waals distance 2.8 Å [13]) and also to an uncoordinated carboxylate oxygen, O(2), in each of two further complex molecules (O–O distances 2.84 and 2.90 Å). Interactions of these types are also present in the pyridinecarboxylate complexes. In addition, however, there is hydrogen bonding in $[Mn(pdc)_2(H_2O)_2]\cdot 2H_2O$ between each coordinated water and the uncoordinated nitrogen, N(2), of a pyridazine ring in an adjacent metal

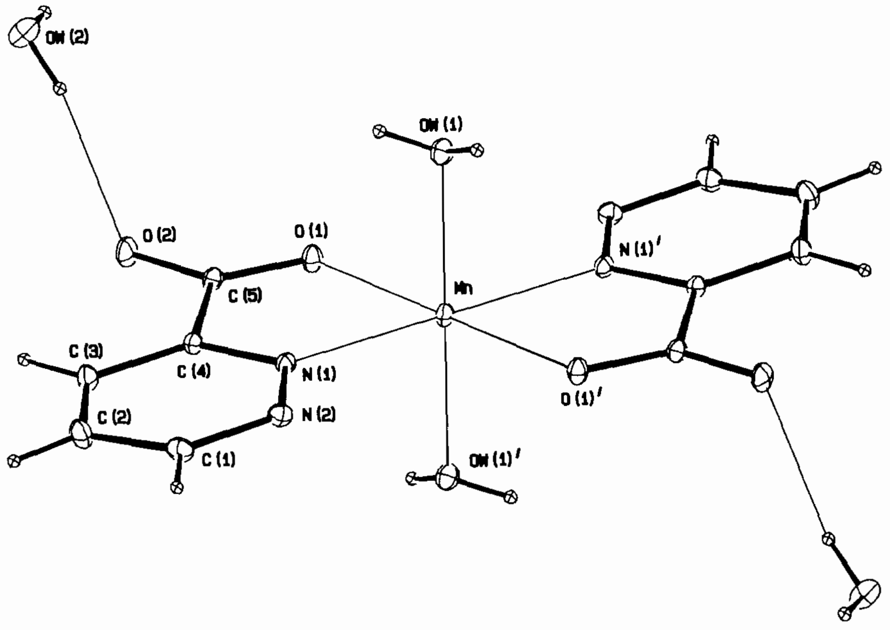

Fig. 1. A perspective drawing of the complex $[Mn(pdc)_2(H_2O)_2]\cdot 2H_2O$ (X' represents the atom X at 1 – *x*, 1 – *y*, 1 – *z*).

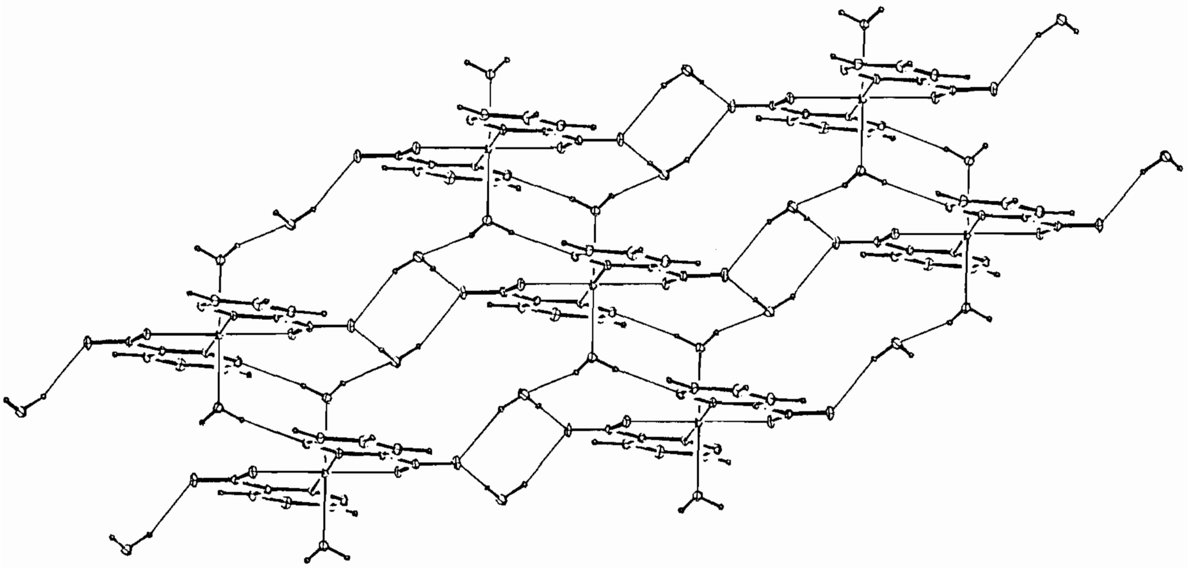

Fig. 2. The hydrogen bonding network in the $[Mn(pdc)_2(H_2O)_2] \cdot 2H_2O$ system.

TABLE 4. Major lines in X-ray powder diffraction patterns (d spacings, Å)

$Ni(pdc)_2(H_2O)_4$	$Co(pdc)_2(H_2O)_4$	$Mn(pdc)_2(H_2O)_4$	$Zn(pdc)_2(H_2O)_4$
9.94s	9.51vs	9.56s	9.46w
7.17s	6.89w	6.94w	7.47vs
6.39vs	6.19s	6.17vs	6.61w
5.01w	4.90w	4.93w	5.14m
4.83w	4.75w	4.82w	4.82m
4.62w	4.51w	4.56m	4.58w
4.27m	4.29w	4.34w	4.44w
3.63m	3.60w	3.60w	3.61w
3.49w	3.39w	3.39w	3.43w
3.15w	3.15w	3.21w	3.20w
3.05m	3.00m	3.01s	3.10s

complex (O–N distance 2.90 Å, van der Waals distance 2.9 Å [13]). This type of hydrogen bonding is, of course, impossible in the pyridinecarboxylate system.

Two further hydrogen bonding modes are present only in the pyridinecarboxylate system. For example, each coordinated water is hydrogen-bonded to a coordinated carboxylate oxygen in an adjacent $[M(pic)_2(H_2O)_2]$ molecule, (O–O distance *c.* 2.75 Å). Also, in the pyridinecarboxylate system, lattice waters occur in hydrogen-bonded pairs with O–O distances of *c.* 2.9 Å [9–12]. With $[Mn(pdc)_2(H_2O)_2] \cdot 2H_2O$, the lattice waters also occur in pairs, but the disposition of the hydrogen atoms and the O–O distance of 3.54 Å, indicate that hydrogen bonding does not occur within each pair of waters.

Spectroscopic and Magnetic Properties of the Complexes

X-ray powder diffraction patterns of the pyridazinecarboxylate complexes are given in Table 4. These show that the cobalt(II) and nickel(II) complexes are isostructural with $[Mn(pdc)_2(H_2O)_2] \cdot 2H_2O$. Magnetic properties of the complexes are given in Table 5. There is no evidence for significant magnetic interaction. This indicates that diimine bridges are absent [1, 2], in keeping with the monomeric structures established for the manganese(II), cobalt(II) and nickel(II) complexes. The room temperature μ_{eff} for the cobalt(II) complex is at the bottom end of the range for octahedral cobalt(II) complexes [14]. This may be because the low symmetry of the *trans*-N_2O_4 donor grouping partially lifts the orbital degeneracy of the $^4T_{1g}$ ground state.

TABLE 5. Magnetic data

Compound	μ_{eff} (BM)		θ (K)[a]
	303 K	89 K	
$Mn(pdc)_2(H_2O)_4$	5.91	5.94	0
$Co(pdc)_2(H_2O)_4$	4.67	4.48	−7
$Ni(pdc)_2(H_2O)_4$	3.17	3.13	−4
$Cu(pdc)_2$	1.83	1.82	−2
$Zn(pdc)_2(H_2O)_4$	diamagnetic		

[a] Curie–Weiss law taken as $\chi_A^{-1} \alpha (T - \theta)$.

TABLE 6. Diffuse reflectance spectra[a]

Compound	Absorption maxima ($cm^{-1} \times 10^{-3}$)[a]
$Co(pdc)_2(H_2O)_4$	
Room temperature	9.2; *c.* 19.5sh
90 K	9.6; *c.* 19.5sh
$Ni(pdc)_2(H_2O)_4$	
Room temperature	*c.* 8.5sh, 11.4; 16.4, *c.* 18.5sh
90 K	*c.* 9.0sh, 11.7; 16.4, 18.7
$Cu(pdc)_2$	16.8

[a] Strong charge-transfer/ligand absorption commences at *c.* 23 000 cm^{-1} and extends through the higher frequency region.

TABLE 7. Infrared spectra (cm^{-1}) of Hpdc and metal complexes[a]

Compound	$\nu_{asy}(CO_2)$	$\nu_{sym}(CO_2)$	$\Delta\nu(CO_2)$ [b]
Hpdc	1735s,b	1308s,b	427
$Mn(pdc)_2(H_2O)_4$	1630s,b	1385s	245
$Co(pdc)_2(H_2O)_4$	1630s,b	1390s	240
$Ni(pdc)_2(H_2O)_4$	1630s,b	1390s	240
$Cu(pdc)_2$	1640s,b	1360s	280
$Zn(pdc)_2(H_2O)_4$	1635s,b	1389s	246

[a] s, strong; m, medium; w, weak; b, broad. [b] $\Delta\nu(CO_2) = \nu_{asy}(CO_2) - \nu_{sym}(CO_2)$.

The reflectance electronic spectra are summarized in Table 6. No d–d absorptions were detectable in the reflectance spectrum of the manganese(II) complex. The spectra of the cobalt(II) and nickel(II) complexes are typical of six-coordinate complexes [15], the $\nu_3(^4T_{1g}(P) \leftarrow {}^4T_{1g})$ absorption in the cobalt(II) complex occurring as a shoulder on charge-transfer absorption and the $\nu_3(^3T_{1g}(P) \leftarrow {}^3A_{2g})$ absorption in the nickel(II) complex being obscured. The spectrum of the nickel(II) complex is in keeping with the low symmetry of the *trans*-N_2O_4 coordination in that the $\nu_1(^3T_{2g} \leftarrow {}^3A_{2g})$ and $\nu_2(^3T_{1g}(F) \leftarrow {}^3A_{2g})$ bands at *c.* 11 000 and *c.* 16 000 cm^{-1} are asymmetric at room temperature, with the shoulder on ν_2 at *c.* 18 500 cm^{-1} becoming resolved at liquid nitrogen temperature [15].

The infrared spectrum of the anhydrous complex $Cu(pdc)_2$ resembles those of the other complexes and so a bidentate ligand is likely. Bis-chelate complexes of this type, involving no steric hindrance from the ligand molecules, usually involve planar coordination by the ligands, frequently with five- or six-coordinate structures produced by axial coordination due to bridging interactions or additional ligand [16, 17]. The complex could have N_2O_2 square-planar coordination or, alternatively, carboxylate bridging could produce five- or six-coordination. Square-planar bis-chelate CuN_2O_2 complexes usually have electronic spectra [16, 18–20] with a band at *c.* 19 000–21 000 cm^{-1} (which may sometimes be partly obscured by ligand or charge-transfer absorption) and a second band or shoulder at *c.* 15 000–17 000 cm^{-1}. Formation of a five- or six-coordinate structure by axial coordination usually leads to a single electronic spectral band whose frequency decreases as the strength of the axial interaction increases, and a single band in the approximate region 15 000–17 000 cm^{-1} is common [16, 20].

The reflectance electronic spectrum of $Cu(pdc)_2$ contains a single band at 16 800 cm^{-1}. There is no evidence for a second band in the 19 000–21 000 cm^{-1} region and so a square-planar structure is unlikely. The spectrum resembles that of $Cu(pic)_2 \cdot 2H_2O$, which has a single band at 16 900 cm^{-1} [21]; this compound has a six-coordinate carboxylate-bridged structure, with axial Cu–O bonds of 2.75 Å and with lattice water molecules [22]. Similar carboxylate bridging is likely for $Cu(pdc)_2$.

Infrared spectral data for the complexes are given in Table 7. Bands attributed to $\nu(OH_2)$ occur at *c.* 3300–3200 cm^{-1} in the hydrated complexes. The $\nu(CO_2)$ values of the hydrates are in the ranges found for other metal complexes in which hydrogen bonding occurs to the uncoordinated carboxylate oxygens [23]. This is considered to reduce the difference in bond order between the coordinated and uncoordinated oxygens, and to result in $\Delta\nu(CO_2)$ (the difference between the asymmetric and symmetric frequencies) being somewhat smaller than for anhydrous complexes [23]. In our system, the $\Delta\nu(CO_2)$ value for anhydrous $Cu(pdc)_2$ is, in fact, only moderately larger than for the hydrated complexes and this could be due to the proposed carboxylate bridging, which might have an effect similar to that of hydrogen bonding to the uncoordinated carboxylate oxygen [23].

Supplementary Material

All atom and thermal parameters and all interatomic angles and torsional angles, as well as structure factor listings, are available from the authors on request.

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