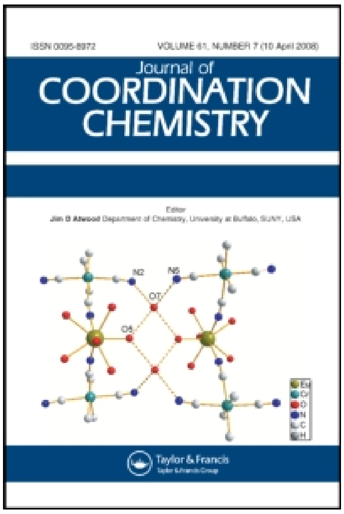

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X-RAY STRUCTURE ANALYSIS OF DIAQUOBIS(2-PYRAZINECARBOXYLATO) MANGANESE(II), COBALT(II), NICKEL(II), COPPER(II) AND ZINC(II) COMPLEXES

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X-RAY STRUCTURE ANALYSIS OF DIAQUOBIS (2-PYRAZINECARBOXYLATO) MANGANESE(II), COBALT(II), NICKEL(II), COPPER(II) AND ZINC(II) COMPLEXES

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The crystal structures of diaquobis (2-pyrazinecarboxylato) manganese(II) and isostructural diaquobis(2-pyrazinecarboxylato) cobalt(II), nickel(II), copper(II) and zinc(II) have been determined using single crystal X-ray intensity data. The former complex is orthorhombic (space group Fdd2), with unit cell dimensions $a = 15.418(1)$, $b = 23.537(3)$Å, $c = 6.940(4)$Å, the latter compounds are monoclinic (space group $P2_1/c$) with unit cell dimensions $a = 5.241(1)$Å, $b = 11.108(1)$Å, $c = 10.286(2)$Å, $\beta = 99.54(1)$deg for the cobalt complex. All structures show monomeric molecules consisting of a metal ion chelated by two oxygen atoms belonging to two monodentate carboxylic groups and two heteronitrogen atoms of two pyrazinic acid molecules and two water molecules. In the case of manganese dipyrazinate dihydrate the coordination polyhedron around the manganese ion is a distorted octahedron with the water molecules *cis*, while in the remaining compounds the octahedra are fairly regular with two water molecules above and below the plane defined by the metal ion and two pyrazinic acid molecules. The observed T-O and T-N (T-transition metal ion) distances are typical for complexes of the respective metals.

KEYWORDS: 2-pyrazinecarboxylic acid, manganese, cobalt, nickel, copper, zinc complex, X-ray structure analysis

INTRODUCTION

Complexation of metal ions by pyridine carboxylic acids reveals an interesting tendency: the chelating ability of the heteronitrogen seems to depend on its position relative to the carboxylic group. This feature is well illustrated by structures of uranyl complexes with 2,6-pyridine dicarboxylic (dipicolinic), 3-pyridine carboxylic (nicotinic) and 2-pyrazine carboxylic (pyrazinic) acids. In all three previously synthetized uranyl complexes with dipicolinic acid, the nitrogen atoms act as donors, jointly with carboxylic oxygens giving rise either to a

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three-dimensional polymeric structure[1] or monomeric molecules.[2,3] Uranyl dipyranizate dihydrate shows a monomeric structure with the UO_2^{2+} ion chelated by four oxygens from two carboxylic groups and two nitrogens resulting in a hexagonal equatorial coordination characteristic for a large number of uranyl complexes. On the other hand, in uranyl dinicotinate dihydrate, nitrogen atoms do not participate in bonding: the UO_2^{2+} ion in the equatorial plane interacts with four carboxylate oxygens from two nicotinic acid molecules and two water oxygens. Monomeric molecules have been observed in crystals of the latter two complexes.[4]

To collect more experimental evidence which could illustrate this tendency, the crystal structures of some divalent 3-*d* transition metal (T) complexes with pyrazinic acid have been determined.

EXPERIMENTAL

The title compounds were obtained by reacting hot aqueous solutions of pyrazinic acid with the corresponding carbonates in the molar ratio 1:2. Subsequently the solutions were boiled for a few hours and left for crystallization. Upon evaporation at room temperature, single crystals separated over a few days. The crystals had the form of rectangular plates. Their colours as well as the dimensions of crystals used for data collection, are listed in Table 1. Reflections were measured at room temperature using either KUMA KM4 (CuKα radiation) or SIEMENS R3m (MoKα radiation) four circle diffractometers operating in the ω-2θ mode. Maximum sin θ/λ values are given in Table 1. The scan-range was ± 0.65 (ω) around Kα_1-Kα_2 angles, scan speed 5–15(ω)min^{-1} depending on the intensity of a pre-scan; backgrounds were measured at each end of the scan for 0.3 of the scan time. Three standard reflections were monitored every 200 reflections. They remained constant throughout every data collection process. Unit cell dimensions and standard deviations were obtained by least-squares fit to 25 reflections ($20° < 2\theta < 40°$). Reflections were processed using profile analysis in each case and were corrected for Lorentz, polarization and absorption effects; those with ($I/\sigma^2(I) > 4.0$) were used in the refinement. Absorption corrections were introduced using a semiempirical procedure;[5] computing was performed with the ABSORB program.[6] Systematic absences defined the respective space groups unambigously. Metal ions were located by the Patterson method (SHELXS).[7] and light atoms including hydrogens then found by successive Fourier syntheses. Final refinement was done on positional parameters of all atoms and anisotropic temperature factors for all non H-atoms and isotropic temperature factors for hydrogen atoms. Final refinement was on F^2 by least squares methods. A weighting scheme was used in the form: $w = 1/[\sigma^2(Fo^2) + (A*P)^2 + B*P]$, where $P = (Max(Fo^2) + 2Fc^2)/3$ and A, B are refined parameters listed in Table 1. Computing was carried out with SHELXL93.[8] In the case of the Mn complex it was possible to determine the absolute structure, since the Flack parameter was calculated to be 0.0016 with esd. = 0.0181. This parameter is expected to be zero (within 3 esd's) for a correct and 1.0 for an inverted absolute structure.[9] Final atomic coordinates and equivalent isotropic displacements are listed in Table 2.

Table 1. Crystal data, X-ray refinement details.

compound	I	II	III	IV	V
formula	$C_{10}H_{10}N_4O_6Mn$	$C_{10}H_{10}N_4O_6Co$	$C_{10}H_{10}N_4O_6Ni$	$C_{10}H_{10}N_4O_6Cu$	$C_{10}H_{10}N_4O_6Zn$
M	337.2	341.2	340.9	345.8	347.6
system	orthorhombic	monoclinic	monoclinic	monoclinic	monoclinic
systematic absence	hkl(h + k, h + l, k + l2n) 0kl(k + 14n, k,12n) h01(h, + 14n), h,12n) hk0(h,k2n), 001(14n) h00(h4n), 0k0(k4n)	h01(12n) 0k0(k(2n)	h01(12n) 0k0(k2n)	h01(12n) 0k0(k2n)	h01(12n) 0k0(k2n)
space group	*Fdd*2	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$
a[A]	15.418(1)	5.241(1)	5.224(1)	5.439(1)	5.271(1)
b[A]	23.537(3)	11.108(1)	10.972(2)	10.872(2)	11.089(2)
c[A]	6.940(4)	10.286(2)	10.258(3)	10.364(3)	10.304(3)
β[DEG]		99.54(1)	100.37(3)	98.29(3)	99.38(3)
V[A^3]	2518.5	590.5	578.4	606.5	594.2
Z	8	2	2	2	2
D_c[g cm^{-3}]	1.778	1.919	1.957	1.893	1.943
(sin σ/λ)max	0.757	0.726	0.646	0.642	0.642
index ranges	-23/23, -35/35 -10/10	0/7,0/16, -14/14	-6/5,0/13, 0/13	-6/6,0/13, 0/13	-6/5,0/14, 0/13
μ[mm^{-1}]	(Mo-Kα)1.08	(Mo-Kα)1.49	(Cu-Kα)2.95	(Cu-Kα)2.93	(Cu-Kα)3.27
crystal size[mm]	0.28 × 0.12 × 0.10	0.26 × 0.06 × 0.10	0.3 × 0.1 × 0.1	0.2 × 0.1 × 0.1	0.20 × 0.10 × 0.05
absorp. corr. range	0.919–1.041	0.841 - 1 -045	0.888–1.210	0.909–1.248	0.858–1.281
refls. unique	1375	1538	1114	1273	1234
with I/σ^{2}4.0	1152	1366	1048	1228	1220
R_{int}	0.009	0.018	0.041	0.023	0.081
parameters refined	117	118	118	118	118
weight parameters	0.044, 1.73	0.044, 0.06	0.144, 0.63	0.072, 0.25	0.135,1.73
max shift/esd	0.001	-0.031	-0.373	0.001	-0.287
final $R1$	0.029	0.032	0.039	0.030	0.056
final $wR2$	0.072	0.072	0.134	0.095	0.179
(Fo-Fc)max[el/A^{-3}]	0.21/ -0.28	0.34/ -0.40	0.80/ -0.56	0.39/ -0.47	1.31–1.38
S(gof)	1.026	1.016	0.840	1.046	1.157

Table 2 Fractional atomic coordinates and equivalent isotropic displacement (A^2); $Ueq = (U_{11} + U_{22} + U_{33})/3$.

	x	*y*	*z*	Ueq
Mn	0	0	.3298(1)	.0237(1)
Ow	-.0734(1)	.0350(1)	.0884(3)	.0327(3)
O1	-.2235(1)	.0790(1)	.1933(2)	.0311(3)
O2	.0587(1)	.0801(1)	.3875(2)	.0290(3)
N1	-.0959(1)	.0474(1)	.5288(5)	.0247(3)
N2	.0408(1)	.1230(1)	-.0647(3)	.0332(3)
C1	-.1718(1)	.0320(1)	.6046(3)	.0322(4)
C2	-.2276(1)	.0718(1)	.6838(3)	.0342(4)
C3	-.1331(1)	.1419(1)	.6114(3)	.0280(4)
C4	-.0759(1)	.1027(1)	.5332(3)	.0216(3)
C5	.0103(1)	.1197(1)	.4472(3)	.0223(3)
H1	-.189(1)	-.007(1)	.596(5)	.04(1)
H2	-.281(2)	.058(1)	.742(4)	.04(1)
H3	-.117(2)	.180(1)	.601(5)	.04(1)
H4	-.049(2)	.061(1)	.038(6)	.07(1)
H5	-.116(2)	.051(1)	.118(4)	.04(1)
Co	0	0	0	.0169(1)
Ni	0	0	0	.0154(3)
Cu	0	0	0	.0243(2)
Zn	0	0	0	.0259(4)
Ow	.2953(3)	-.0261(2)	.1644(2)	.0252(4)
	.2892(4)	-.0253(2)	.1657(2)	.0224(4)
	.3102(3)	-.0225(2)	.1865(2)	.0348(3)
	.2970(8)	-.0245(3)	.1691(3)	.0323(7)
O1	-.3015(3)	.2404(1)	.2355(1)	.0294(4)
	-.3009(4)	.2382(2)	.2351(2)	.0277(5)
	-.2987(3)	.2321(1)	.2290(1)	.0388(4)
	-.3021(6)	.2413(3)	.2340(3)	.0356(7)
O2	-.2311(3)	.0727(1)	.1273(1)	.0213(3)
	-.2336(3)	.0694(1)	.1250(2)	.0298(4)
	-.2205(2)	.0633(1)	.1207(1)	.0277(3)
	-.2329(6)	.0722(2)	.1275(3)	.0286(6)
N1	-.1115(4)	-.1812(2)	-.0030(2)	.0175(3)
	-.1088(4)	-.1780(2)	-.0028(2)	.0167(5)
	-.1115(2)	-.1742(1)	-.0024(1)	.0228(3)
	-.1094(6)	-.1803(2)	-.0027(3)	.0233(7)
N2	-.2483(5)	-.4206(2)	-.0504(2)	.0323(5)
	-.2474(5)	-.4204(2)	-.0485(3)	.0291(6)
	-.2471(3)	-.4175(1)	-.0478(2)	.0352(4)
	-.2465(8)	-.4201(3)	-.0494(4)	.0386(9)
C1	-.2809(4)	-.2357(2)	.0606(2)	.0214(4)
	-.2787(5)	-.2317(2)	.0615(3)	.0206(6)
	-.2820(3)	-.2263(1)	.0602(2)	.0278(4)
	-.2798(8)	-.2339(3)	.0610(4)	.0290(9)
C2	-.3487(5)	-.3548(2)	.0366(2)	.0264(5)
	-.3477(6)	-.3531(2)	.0377(3)	.0243(6)
	-.3487(4)	-.3485(2)	.0365(2)	.0310(4)
	-.3475(9)	-.3542(4)	.0368(4)	.0326(9)
C3	.0784(5)	.3664(2)	.1117(2)	.0263(5)
	.0734(6)	.3661(2)	.1111(3)	.0251(6)
	.0743(4)	.3639(2)	.1083(2)	0310(4)
	.0739(9)	.3658(3)	.1107(4)	.0319(9)

Table 2 — (Continued)

C4	.0058(4)	.2465(2)	.0898(2)	.0182(4)
	.0038(5)	.2450(2)	.0891(2)	.0172(5)
	.0055(3)	.2418(1)	.0864(2)	.0227(3)
	.0043(7)	.2458(3)	.0886(3)	.0230(7)
C5	.1918(4)	-.1831(2)	-.1584(2)	.0192(4)
	.1942(5)	-.1806(2)	-.1577(2)	-.0178(5)
	.1868(3)	-.1764(2)	-.1531(2)	.0242(4)
	.1926(8)	-.1827(3)	-.1575(4)	.0247(8)
H1	-.340(5)	-.188(2)	.126(2)	.02(1)
	-.349(7)	-.191(3)	.120(4)	.03(1)
	-.351(5)	-.181(2)	.116(2)	.04(1)
	-.337(9)	-.190(4)	.128(5)	.03(1)
H2	-.477(6)	-.390(2)	.078(2)	.03(1)
	-.453(7)	-.382(3)	.091(3)	.02(1)
	-.462(5)	-.379(2)	.078(2)	.04(1)
	-.493(9)	-.388(5)	.080(5)	.03(2)
H3	.001(6)	.410(2)	.169(3)	.03(1)
	-.005(8)	.409(3)	.173(4)	.03(1)
	.007(5)	.409(3)	.162(2)	.04(1)
	.006(11)	.417(6)	.164(6)	.06(2)
H4	.314(7)	-.084(3)	.196(3)	.04(1)
	.305(9)	-.093(4)	.190(4)	.02(1)
	.328(7)	-.080(3)	.207(4)	.06(1)
	.310(13)	-.089(6)	.201(7)	.06(2)
H5	.428(7)	.007(3)	.165(3)	.04(1)
	.421(10)	.005(4)	.171(5)	.04(1)
	.409(7)	.011(3)	.183(3)	.05(1)
	.409(13)	-.001(5)	.166(7)	.03(2)

DISCUSSION

The crystals of all compounds described in this study contain monomeric molecules composed of a metal ion, two pyrazinic acid and two water molecules. In the case of manganese pyrazinate dihydrate the coordination polyhedron around the metal ion consists of atoms contributed by two pyrazinic acid molecules and two molecules of water. The planes of the pyrazinic acid molecules make a dihedral angle of 52.56(6) deg. Maximum and minimum atomic shifts from the mean plane defined by these molecules are, respectively, 0.050(2) and 0.001(2) Å. Two oxygen atoms from two monodentate carboxylic groups, a nitrogen and an oxygen atom from a water molecule are situated at apexes of a distorted square. The other nitrogen and oxygen atoms of the second water molecule are located above and below the plane of this square giving rise to a strongly distorted octahedron. This follows also from Table 3 which lists the respective interbond angles. The characteristic feature of this coordination is the position of water molecules which are situated *cis*. Fig. 1 obtained using the MOVIEMOL program[10] shows the monomeric molecule with atom numbering. The determined Mn-O bond lengths are in good agreement with those reported earlier for manganese pyrazinates.[11] The monomeric molecules are held together by fairly short hydrogen bonds operating between water molecules and the unbonded oxygen atoms belonging to the carboxylic groups of the adjacent monomers. Much longer than Ow-H4...O1 hydrogen bonds are the bonds linking the water oxygens with the unbonded

Table 3 Selected bond lengths (in Å) and angles (in deg.).

	Mn	Co	Ni	Cu	Zn
distances:					
covalent bonds					
T-Ow	2.183(2)	2.115(2)	2.079(1)	2.388(1)	2.162(1)
-O2	2.130(2)	2.087(1)	2.068(1)	1.977(1)	2.097(1)
-N1	2.310(2)	2.094(1)	2.033(1)	1.987(1)	2.080(1)
N1-C4	1.336(2)	1.340(2)	1.341(2)	1.333(1)	1.333(1)
-C1	1.333(3)	1.333(2)	1.334(3)	1.332(1)	1.335(1)
N2-C2	1.329(3)	1.329(3)	1.330(2)	1.330(2)	1.327(2)
-C3	1.329(3)	1.334(3)	1.343(3)	1.336(2)	1.333(2)
C1-C2	1,285(4)	1.382(3)	1.390(2)	1.389(3)	1.394(3)
C3-C4	1.387(3)	1.388(3)	1.385(2)	1.389(3)	1.389(3)
C4-C5	1.512(2)	1.517(3)	1.525(2)	1.512(1)	1.520(1)
C5-O1	1.236(2)	1.231(2)	1.225(2)	1.223(2)	1.235(2)
-O2	1.262(2)	1.276(2)	1.272(2)	1.280(2)	1.273(2)
H1-C1	0.93(4)	0.95(4)	0.88(4)	0.88(4)	0.93(4)
H2-C2	0.96(4)	0.95(4)	0.90(4)	0.86(4)	1.01(4)
H3-C3	0.93(4)	0.89(4)	0.94(4)	0.86(4)	0.90(6)
H4-Ow	0.78(4)	0.70(4)	0.78(4)	0.66(4)	0.79(6)
H5-Ow	0.79(4)	0.80(4)	0.75(4)	0.65(4)	0.66(6)
angles:					
covalent bonds					
Ow-T-Ow'	79.7(1)	180.0	180.0	180.0	180.0
O2-T-O2'	158.3(1)	180.0	180.0	180.0	180.0
N1-T-N1'	106.6(1)	180.0	180.0	180.0	180.0
N1'-T-Ow'	86.8(1)				
Ow	166.5(1)	87.3(1)	87.5(1)	84.8(1)′	87.0(1)
N1'-T-O2	92.4(1)	78.9(1)	80.3(1)	82.7(1)	79.3(1)
O2'	74.4(1)				
Ow'-T-O2	104.9(1)	91.4(1)	92.0(1)	93.1(1)	92.1(1)
O2'	91.8(1)				
H4-Ow-H5	103(2)	112(3)	110(2)	117(3)	112(7)

Operators for generating equivalent atoms: for Mn (') = − x + 1, −y, z and for Co, Ni, Cu, Zn, (') = −x, −y, −z.

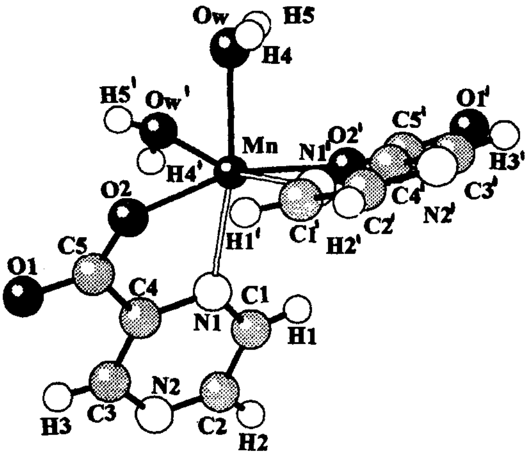

Figure 1 MOVIEMOL[10] picture of the Mn dipyrazinate dihydrate molecule showing atomic numbering.

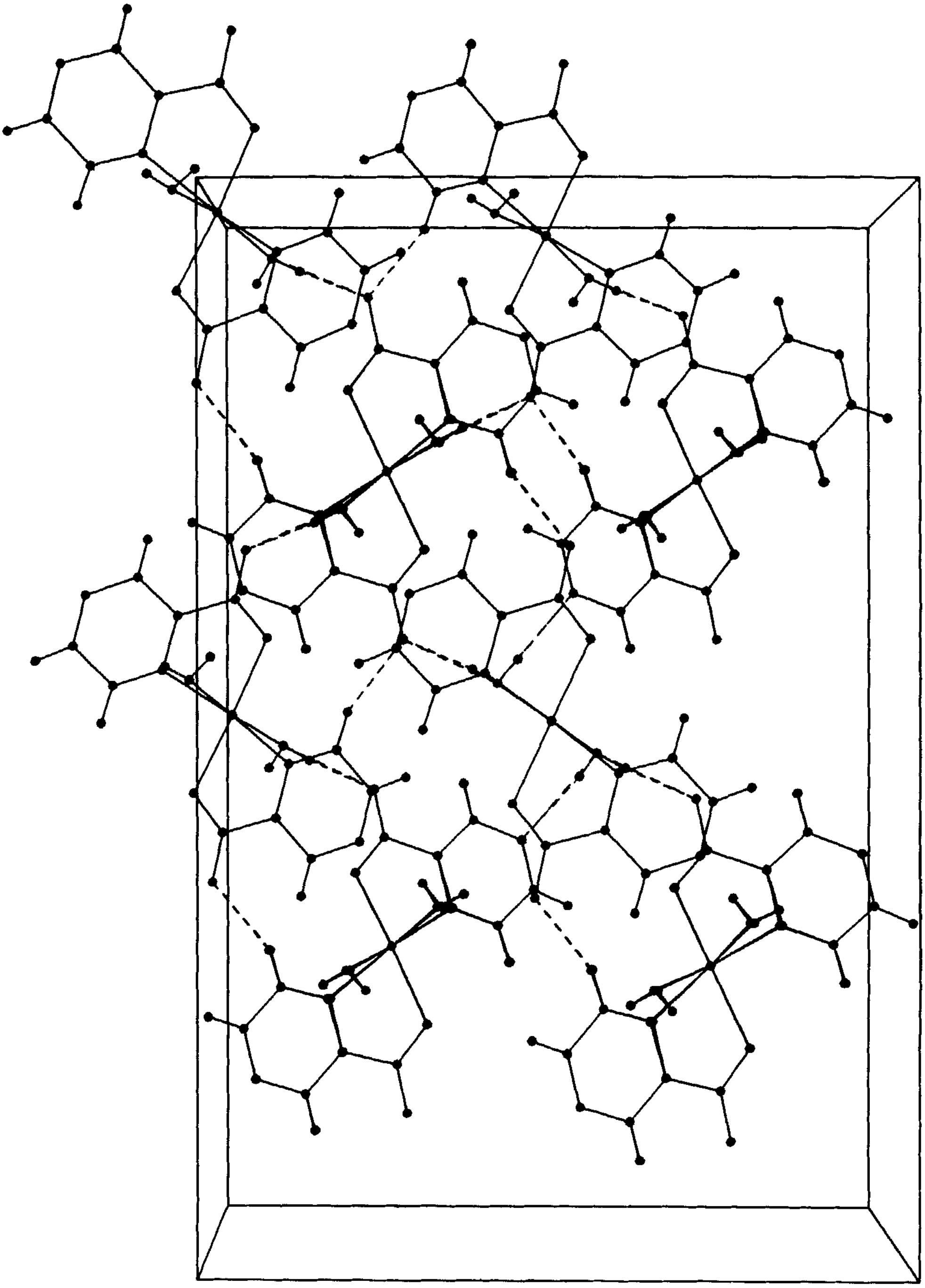

Figure 2 Packing of the Mn complex molecules in the crystal.

nitrogens Ow-H5...N2. The molecule packing of this complex is displayed with Fig. 2.

Fairly regular coordination octahedra were found in cobalt, nickel, copper and zinc dipyrinizates. Two pyrazinic acid molecules and the metal ion constitute a plane with atomic shifts from the mean plane ranging from 0.004(2) to 0.095(2)Å. The metal ion is bonded to two nitrogens and two oxygens from two monodentate carboxylic groups with T-N and T-O distances listed in Table 3. The water molecules are situated above and below the plane with the Ow-T-Ow' angle of 180 deg.(Table 3). The T-Ow bond lengths in Co, Ni, Zn compounds do not differ much from T-O bonds in the plane (see Table 3), however, in the case of the copper compound a distinct elongation of the octahedron along the Ow-Cu-Ow' axis is observed, resulting from the Jahn-Teller effect. The molecule is displayed in Fig. 3, and a packing diagram in Fig. 4.

The bond lengths and bond angles within the pyrazinic acid molecules in all complexes reported in this study are in fair agreement with those previously reported.[12]

Our results confirm the data previously published for pyrazinic acid complexes with manganese[13] as well as with cobalt[14] and copper.[15] The same coordination of pyrazinic acid ligands and water has been observed in the calcium compound.[16]

The 3-*d* transition metal dipyrazinates, similar to uranyl dipyrizinate, exhibit the same feature: only one nitrogen acts as a ligand to the central ion, the second remaining unbonded. The chelating nitrogen is that one which is situated close to the carboxylic group of the pyrazinic acid ligand. It is interesting to note, that in the structure of the cobalt complex with 2,3-pyrazine-dicarboxylic acid both nitrogens of the pyrazinic ring are involved in the bonding together with oxygens of monodentate carboxylic groups giving rise to planar chains propagating in the [010] direction and held together by a network of hydrogen bonds.[17] However, in its zinc

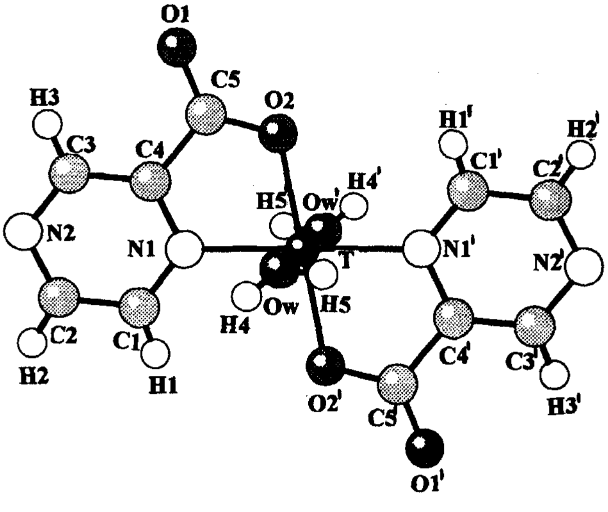

Figure 3 MOVIEMOL[10] picture of the T (T = Co, Ni, Cu, Zn) dipyrazinate dihydrate molecule showing atomic numbering.

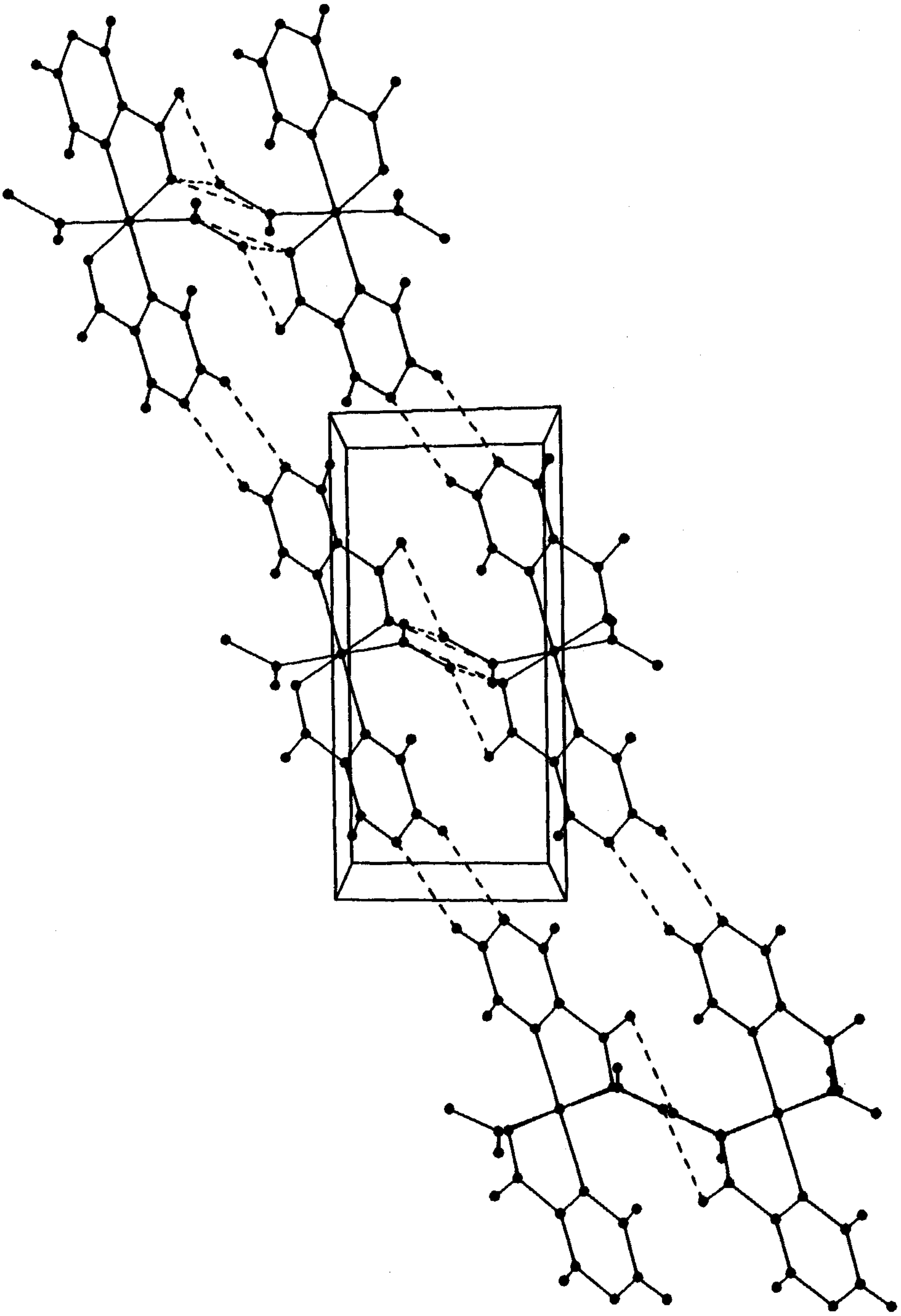

Figure 4 Packing of T (T = Co, Ni, Cu, Zn) complex molecules in the crystal.

analogue only one carboxylic group and nitrogen of the pyrazine molecule act as donors to the Zn^{2+} ion.[18] Monomeric molecules are formed in all cases.

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