

The Crystal and Molecular Structures of Diaquabis(picolinato *N*-oxido) Complexes of Mn(II), Co(II), Ni(II) and Cu(II)

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The picolinato *N*-oxido complexes of Mn^{2+} , Co^{2+} and Ni^{2+} ions form an isostructural series belonging to the space group $P2_1/c$. The corresponding Cu^{2+} complex crystallizes in the space group $P1$.

All four complexes are octahedral, with picolinate *N*-oxide coordinating through the $N-O$ oxygen and one of the (COO) oxygens. The average bond distances between the metal ions and the organic ligand oxygens are 2.13, 2.07 and 2.03 Å for Mn^{2+} , Co^{2+} and Ni^{2+} complexes, respectively, and 1.94 Å for the copper(II) complex. The corresponding $M-O$ (aqua) distances are 2.23, 2.15, 2.09 and 2.49 Å. All structures were refined to final R -values of 0.030–0.049.

The present investigation is a continuation of the X-ray studies on $3d$ metal complexes of pyridine monocarboxylic acid *N*-oxides being carried out in this laboratory.^{1–3} Pyridine monocarboxylic acid *N*-oxides are interesting from a coordination point of view since they include two different coordinating groups, the carboxylate group and the *N*-oxide group. In all these complexes the picolinic acid *N*-oxide coordinates to the metal ion through the $N-O$ oxygen and one of the (COO) oxygens forming a stable six-membered chelate ring.

The coordination of pyridine monocarboxylic acids with $3d$ metals through the $N-O$ oxygen has been observed for these complexes and for diaquadi- μ -hydroxobis- μ -(nicotinato *N*-oxido)bis- μ -(nicotinato *N*-oxido)tricopper(II).¹ The study confirms the coordination of these complexes proposed earlier on the basis of IR-spectra and magnetic properties.^{4–8}

EXPERIMENTAL

Preparation of the compounds. All the metal complexes of picolinic acid *N*-oxide with metal salts were prepared according to instructions given in the literature^{4,8} except that solutions were more dilute.

Data collection. The crystal and intensity data were measured on a SYNTEX $P2_1$ automatic four-circle diffractometer using graphite monochromatized $MoK\alpha$ -radiation. The details of the data collection are seen in Table 1. The data were corrected for Lorentz and polarization factors but not for absorption effects.

Structure determination. The structure of triclinic diaquabis(picolinato *N*-oxido)copper(II) was solved by assuming the compound to be centrosymmetric

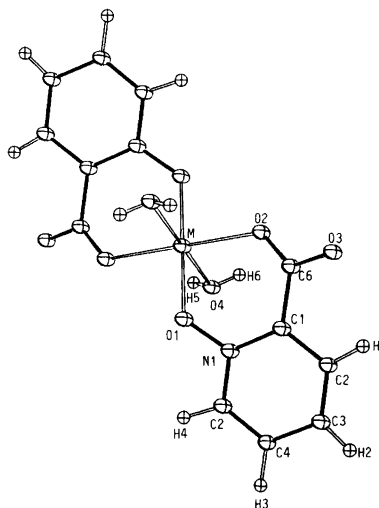


Fig. 1. The atomic labeling scheme of $[M(N\text{-picO})_2(H_2O)_2]$ complexes, $M = Mn^{2+}$, Co^{2+} , Ni^{2+} and Cu^{2+} .

Table 1. Details of the data collection for $[M(N\text{-picO})_2(\text{H}_2\text{O})_2]$ complexes, $M = \text{Mn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}$ and Cu^{2+} .

	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
(a) Crystal data				
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a (Å)	6.682(2)	6.673(3)	6.618(3)	6.634(11)
b	15.812(4)	15.729(13)	15.713(10)	7.302(14)
c	7.006(3)	6.993(2)	6.930(2)	7.968(9)
α (°)	90.0	90.0	90.0	80.5(1)
β	114.15(2)	115.29(3)	115.38(3)	89.4(1)
γ	90.0	90.0	90.0	61.4(1)
V (Å ³)	675.4	663.6	651.0	333.1
d_c (gcm ⁻³)		1.98		1.87
d_o		1.82		1.83
Z	2	2	2	1
$\mu\text{MoK}\alpha$ (cm ⁻¹)	8.35	14.20	15.63	17.78
M	363.14	367.14	366.91	371.75
(b) Intensity measurements				
$\theta - 2\theta$ Scan range		$4^\circ < 2\theta < 55^\circ$		
Scan rate		1° to $29.3^\circ \text{ min}^{-1}$		
Refl.meas.	1795	1768	1617	1636
Criteria		$I > 3\sigma(I)$		
Refl.obs.	1307	1324	1617	2636
$R\left(\frac{\sum F_o - F_c }{\sum F_o }\right)$	0.033	0.030	0.049	0.039

with the central metal ion occupying the special position $1a$ of the space group $P\bar{1}$. All other atoms, including hydrogen atoms, were located from the difference Fourier map.

The structures of diaquabis(picolinato N -oxido) $\text{Mn}(\text{II})$, $\text{Co}(\text{II})$ and $\text{Ni}(\text{II})$ were solved with the MULTAN 78 program.⁹ The central metal ions were located at the special position $2a$ of the space group $P2_1/c$.

Block-diagonal refinements was carried out with programs of the X-Ray System.¹⁰ The scattering factors for the metal ions and O, N and C atoms were those of Cromer and Mann¹¹ and for H atoms those of Stewart, Davidson and Simpson.¹²

In the final least-squares refinement, non-hydrogen atoms were assigned anisotropic and hydrogen atoms isotropic thermal parameters. Unit weights were used. The final difference Fourier

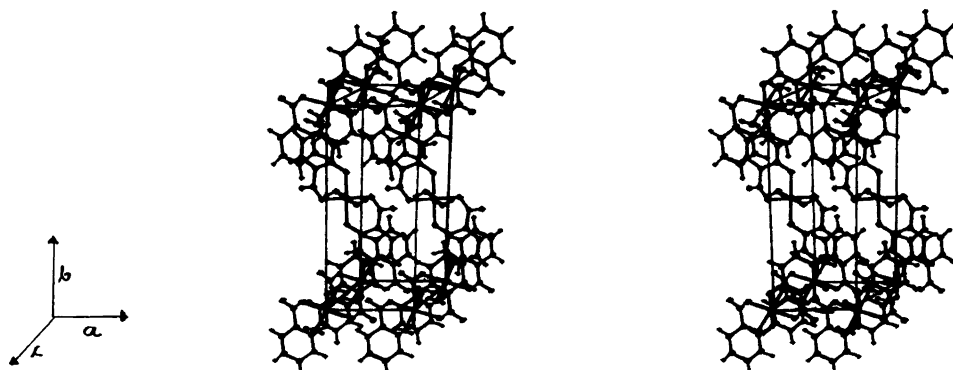


Fig. 2. A stereoview of the packing of the $[M(N\text{-picO}_2)(\text{H}_2\text{O})_2]$ molecules in the unit cell, $M = \text{Mn}^{2+}, \text{Co}^{2+}$ and Ni^{2+} .

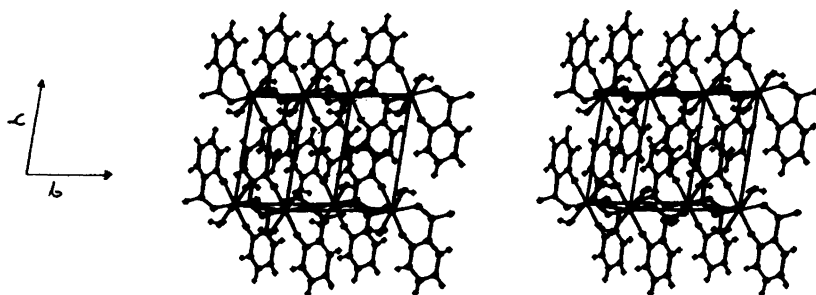


Fig. 3. A stereoview of the packing of the $[\text{Cu}(\text{N-picO})_2(\text{H}_2\text{O})_2]$ molecules in the unit cell.

Table 2. Selected bond distances (Å) and bond angles ($^\circ$) with their standard deviations for $[\text{M}(\text{N-picO})_2(\text{H}_2\text{O})_2]$, $\text{M} = \text{Mn}^{2+}$, Co^{2+} , Ni^{2+} and Cu^{2+} .

	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
M—O1	2.154(1)	2.061(1)	2.035(3)	1.947(4)
M—O2	2.113(1)	2.079(1)	2.015(3)	1.922(3)
M—O4	2.226(1)	2.148(1)	2.094(3)	2.488(5)
O1—N1	1.322(1)	1.341(1)	1.329(5)	1.330(2)
O2—C6	1.252(1)	1.274(1)	1.249(4)	1.266(2)
O3—C6	1.246(1)	1.271(1)	1.232(4)	1.229(2)
C6—C1	1.512(1)	1.507(2)	1.510(6)	1.500(2)
O1—M—O2	97.17(3)	94.03(3)	92.3(1)	90.19(9)
O1—M—O4	89.50(4)	89.99(5)	90.1(1)	87.1(2)
O2—M—O4	88.79(3)	87.43(3)	88.1(1)	92.8(1)
N1—O1—M	120.88(6)	120.18(6)	118.6(3)	116.1(1)
C6—O2—M	128.43(6)	125.94(7)	126.2(3)	124.93(6)
O2—C6—O3	125.31(8)	124.41(9)	123.1(4)	124.77(9)

Table 3. Hydrogen bonding data for $[\text{M}(\text{N-picO})_2(\text{H}_2\text{O})_2]$ complexes, $\text{M} = \text{Mn}^{2+}$, Co^{2+} , Ni^{2+} and Cu^{2+} .

	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}
O4—H5(i)	0.51(1)	0.78(2)	1.0(1)	0.74(1) (viii)
O4—H6(ii)	0.93(1)	0.86(1)	0.95(4)	0.66(1) (viii)
O4 \cdots O3 (iii)	2.729(1)	2.788(1)	2.737(3)	2.768(5) (viii)
O4 \cdots O3 (ii)	2.751(1)	2.745(1)	2.736(5)	2.834(6) (ix)
O3 \cdots H6 (iv)	2.361(1)	1.97(1)	1.80(4)	2.215(8) (x)
O3 \cdots H5 (i)	2.26(1)	1.97(2)	1.71(7)	2.051(8)
(v)O4—H5—O3 (v)	167(2)	175(1)	172(5)	163.5(6) (viii)
(vi)O4—H6—O3 (vii)	165(1)	160(1)	165(6)	156.9(7) (x),(viii)

Symmetry code:

(i) $2-x, y, -\frac{1}{2}, \frac{1}{2}+z$

(ii) x, y, z

(iii) $-x, 1-y, -z$

(iv) $2-x, \frac{1}{2}-y, -z$

(v) $1-x, \frac{1}{2}+y, \frac{1}{2}-z$

(vi) $1-x, 1-y, -z$

(vii) $1+x, y, z$

(viii) $1-x, -y, -z$

(ix) $x, y-1, z$

(x) $1-x, 1-y, -z$

Table 4. Final positional parameters for non-hydrogen atoms with *e.s.d.*'s in parentheses and U_{eq}^a ($\text{\AA}^2 \times 10^3$).

	x	y	z	U_{eq}^a
Mn	0.0000	0.5000	0.5000	18.13(7)
O1	0.90919(9)	0.61570(4)	0.32255(10)	27.5(3)
O2	1.34338(9)	0.51779(3)	0.62314(9)	24.8(3)
O3	0.32470(9)	0.50704(4)	0.13018(9)	25.9(3)
O4	0.00425(10)	0.43197(4)	0.22350(9)	28.3(3)
N1	0.73912(11)	0.66063(4)	0.31496(10)	20.2(3)
C1	0.54090(13)	0.62508(5)	0.27754(12)	20.7(4)
C2	0.36646(14)	0.67665(6)	0.25875(14)	27.8(4)
C3	0.39042(16)	0.76344(6)	0.27607(15)	33.5(5)
C4	0.59428(17)	0.79760(5)	0.31644(15)	34.0(5)
C5	0.76534(15)	0.74594(5)	0.33407(14)	27.9(5)
C6	0.50856(13)	0.53026(5)	0.25941(13)	21.0(4)
Co	0.0000	0.5000	0.5000	17.7(1)
O1	0.92226(9)	0.61084(4)	0.32999(9)	26.2(3)
O2	1.33588(9)	0.52275(4)	0.62530(9)	24.3(3)
O3	0.32515(9)	0.50590(4)	0.13252(9)	26.0(3)
O4	0.00775(10)	0.43432(4)	0.23461(9)	26.5(3)
N1	0.75281(10)	0.65806(5)	0.32331(10)	20.2(4)
C1	0.55210(12)	0.62254(6)	0.28404(12)	19.7(4)
C2	0.37864(13)	0.67638(6)	0.26505(13)	26.1(5)
C3	0.40743(15)	0.76336(7)	0.28360(14)	32.1(5)
C4	0.61465(16)	0.79700(6)	0.32587(14)	32.9(5)
C5	0.78353(15)	0.74283(6)	0.34480(13)	25.7(4)
C6	0.51522(12)	0.52834(6)	0.26183(12)	21.1(4)
Ni	0.0000	0.5000	0.5000	18.5(3)
O1	0.9296(4)	0.6108(2)	0.3319(4)	27.3(2)
O2	1.3317(5)	0.5224(2)	0.6275(4)	26.3(1)
O3	0.3268(4)	0.5067(2)	0.1338(4)	26.0(1)
O4	0.0091(5)	0.4362(2)	0.2386(4)	27.0(2)
N1	0.7589(5)	0.6577(2)	0.3241(4)	18.7(2)
C1	0.5554(6)	0.6227(3)	0.2821(6)	23.0(2)
C2	0.3831(6)	0.6767(3)	0.2618(6)	26.0(2)
C3	0.4108(7)	0.7629(3)	0.2785(6)	32.3(2)
C4	0.6212(7)	0.7964(3)	0.3255(6)	31.3(2)
C5	0.7874(6)	0.7429(3)	0.3427(6)	23.7(2)
C6	0.5180(6)	0.5277(2)	0.2584(6)	20.7(2)
Cu	0.0000	0.0000	0.0000	27.28(3)
O1	-0.11135(5)	0.20219(5)	-0.21436(4)	32.1(2)
O2	0.20304(6)	0.10617(5)	0.05112(3)	35.0(2)
O3	0.30192(6)	0.35767(5)	-0.00766(4)	40.8(2)
O4	0.28714(6)	-0.25767(5)	-0.16340(4)	39.1(2)
N1	-0.04880(6)	0.78083(5)	0.30683(4)	24.4(1)
C1	0.21757(7)	0.24269(6)	-0.23912(5)	24.2(2)
C2	0.62610(8)	0.73226(7)	0.34171(5)	31.6(2)
C3	0.35644(9)	0.26986(8)	-0.51541(6)	37.0(2)
C4	0.18179(10)	0.24704(7)	-0.57980(5)	37.1(2)
C5	0.97055(9)	0.77794(7)	0.47536(5)	31.8(2)

$$^a U_{\text{eq}} = \frac{1}{3} \sum_i U_{ii}$$

maps showed no peaks above $0.5 \text{ e} \text{ \AA}^{-3}$. All calculations were carried out on a UNIVAC 1100/60 computer.

RESULTS AND DISCUSSION

The atomic labeling is shown in Fig. 1 and the packing of the molecules in Figs. 2 and 3. Final atomic coordinates and thermal parameters with their standard deviations are presented in Tables 4 and 5. Tables of observed and calculated structure factors and anisotropic temperature factors are available from the author on request.

The octahedral coordination geometry about the central metal atom in the Mn^{2+} , Co^{2+} and Ni^{2+} complexes is not very much distorted, but in the Cu complex clearly elongated. In the latter case, the Jahn-Teller effect causes an extension of the Cu–O4(aqua) bond to 2.488(5) Å, which in the other complexes is between 2.09(1) and 2.26(1) Å. The most important bond distances and bond angles of the complexes are presented in Table 2. The bond distances between the metal atoms and the picolinato *N*-oxido ligand oxygens range from 2.154(1) to 1.922(3) Å in order of decreasing metal ion radius. The M–O4 bond distance becomes shorter, too, on moving from the Mn^{2+} complex to the Ni^{2+} complex [2.226(1)–2.094(3)].

The change of the central metal ion has only a slight influence on the bond distances in the picolinato *N*-oxide ligand. The bond distances N1–O1 vary from 1.337(1) to 1.322(1) Å, whereas the same distance is 1.329(1) Å in the "free" nicotinic acid *N*-oxide.¹³ The bond distance between the coordinated oxygen and the carbon atom, O2–C6, varies between 1.252(1) and 1.266(1) Å, and the uncoordinated oxygen carbon distance O3–C6 varies between 1.229(1) and 1.247(1) Å in the carboxylato group of the complexes. The corresponding distances in the free acid are 1.301(1) and 1.198(1) Å.¹³ The angle of the carboxylato group, O2–C6–O3, is 125.3(1)–123.1(4)°, compared with 125.15(4)° in the free acid.¹³ Thus coordination does not cause any noticeable opening of the carboxylato group angle.

The hydrogen bonds connecting the molecules with each other through the aqua oxygen atom, O4, and the uncoordinated carboxylate oxygen atom, O3, are shown in Table 3. The hydrogen bonds are so oriented that one connects the molecules in the direction of the *a* axis and the other in the direction of the *b* axis. In the Mn–Ni complex series there is

Table 5. $[\text{M}(\text{N-picO})_2(\text{H}_2\text{O})_2]$, M = Mn^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+} . Final positional parameters and isotropic thermal parameters ($\times 10^2$) for hydrogen atoms with their standard deviations.

	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}
[Mn(<i>N</i>-picO)₂(H₂O)₂]				
H1	0.264(2)	0.798(1)	0.275(2)	5.3(4)
H2	0.225(2)	0.649(1)	0.347(1)	3.2(3)
H3	0.374(2)	0.359(1)	0.134(2)	8.9(5)
H4	0.908(2)	0.764(1)	0.343(2)	5.0(3)
H5	0.928(2)	0.941(1)	0.284(2)	7.1(4)
H6	0.874(2)	0.448(1)	0.109(2)	4.8(3)
[Co(<i>N</i>-picO)₂(H₂O)₂]				
H1	0.245(2)	0.647(1)	0.233(2)	5.1(3)
H2	0.296(2)	0.805(1)	0.264(2)	5.2(4)
H3	0.357(2)	0.363(1)	0.153(2)	4.4(3)
H4	0.937(2)	0.762(1)	0.377(2)	4.4(3)
H5	0.896(2)	0.440(1)	0.129(2)	7.6(4)
H6	0.898(2)	0.955(1)	0.295(2)	8.1(5)
[Ni(6-picO)₂(H₂O)₂]				
H1	0.262(8)	0.648(3)	0.329(7)	4(1)
H2	0.324(7)	0.801(3)	0.256(6)	2(1)
H3	0.358(8)	0.366(3)	0.163(7)	5(1)
H4	0.931(10)	0.762(4)	0.373(8)	7(2)
H5	0.880(10)	0.968(4)	0.305(8)	7(2)
H6	0.876(8)	0.455(3)	0.120(7)	3(1)
[Cu(<i>N</i>-picO)₂(H₂O)₂]				
H1	0.501(1)	0.729(1)	0.293(1)	2.5(1)
H2	0.486(1)	0.266(1)	0.413(1)	4.4(2)
H3	0.174(1)	0.233(1)	0.312(1)	5.8(2)
H4	0.888(1)	0.215(1)	0.489(1)	3.5(1)
H5	0.599(1)	0.274(1)	0.135(1)	4.6(2)
H6	0.740(1)	0.333(1)	0.142(1)	5.7(2)

also a diagonal hydrogen bond in the *ab* plane, (Figs. 2 and 3). The observed bond distances between the hydrogen and carbon or oxygen atoms vary from 0.5 to 1.1 Å, with the shortest values in the coordinated water molecule (Table 3).

According to earlier X-ray structure determinations of pyridine *N*-oxide metal complexes, the angle N–O–M varies between 116.7 and 134° when the central metal ion is Fe(II),¹⁴ Co(II),^{14–16} Ni(II)^{17,18} or Cu(II).^{14,19–22} In the present complexes the same angle varies from 116.1(1) to 120.9(1)°. As in the published pyridine *N*-oxide complexes it is found that the angle N–O–M is smallest for the copper complex. If it is assumed that

the *N*-oxide oxygen uses its sp^2 orbitals for bonding with the nitrogen and the metal atom, and the N–O bond is pure double bond, then the theoretical M–O–N angle is 120° .

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