Acta Cryst. (1996). C**52**, 51–56

Di-μ-sulfato-*O*:*O*′-bis[(2-aminopyrimidine-*N*^{1})triaquacobalt(II)] Dihydrate (1), *catena*-Poly[bis(2-aminopyrimidine-*N*^{1})diaquanickel(II)-μ-sulfato-*O*:*O*′ 2-Aminopyrimidine] (2), (2-Aminopyrimidine-*N*^{1})pentaaquanickel(II) Sulfate 2-Aminopyrimidine (3) and *catena*-Poly[bis(2-aminopyrimidine-*N*^{1})aquacopper(II)-μ-sulfato-*O*:*O*′ Dihydrate] (4)

PAAVO O. LUMME,[a] HILKKA KNUUTTILA[b] AND EVA LINDELL[c]

[a]*Division of Inorganic Chemistry, Department of Chemistry, University of Helsinki, Vuorik. 20, Box 6, SF-00014 Helsinki, Finland, and Department of Chemistry, University of Jyväskylä, Jyväskylä, Finland,* [b]*Department of Chemistry, University of Jyväskylä, Jyväskylä, Finland, and* [c]*Division of Inorganic Chemistry, Department of Chemistry, University of Helsinki, Vuorik. 20, Box 6, SF-00014 Helsinki, Finland*

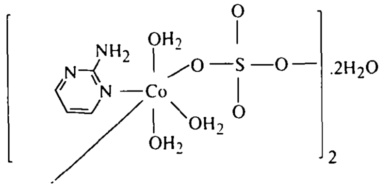
(*Received 23 May 1994; accepted 9 August 1995*)

Abstract

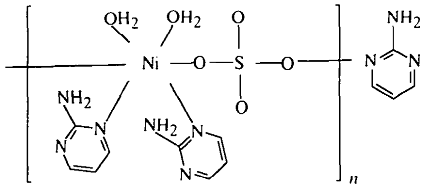
2-Aminopyrimidine complexes of aqueous Co$^{\rm II}$, Ni$^{\rm II}$ and Cu$^{\rm II}$ sulfate have been prepared and their structures determined by X-ray diffraction. Co$^{\rm II}$ forms a dimeric complex, $[Co(SO_4)(C_4H_5N_3)(H_2O)_3]_2.2H_2O$, (1), and Ni$^{\rm II}$ and Cu$^{\rm II}$ form polymeric complexes, $[Ni(SO_4)(C_4H_5N_3)_2(H_2O)_2].C_4H_5N_3$, (2), and $[Cu(SO_4)(C_4H_5N_3)_2(H_2O)].2H_2O$, (4). The sulfate ion acts as a bridging moiety between the metal atoms in these three complexes. The Ni$^{\rm II}$ ion also forms an ionic complex, $[Ni(C_4H_5N_3)(H_2O)_5]SO_4.C_4H_5N_3$, (3). The coordination of 2-aminopyrimidine to the metal is always through the ring N atom.

Comment

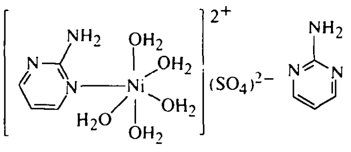
This investigation forms part of a study on the relationship between structures of transition metal complexes formed with biologically significant heterocyclic ligands and their physicochemical properties (Lumme & Mutikainen, 1980; Lumme, Mutikainen & Lindell, 1982, 1983). Preliminary reports on several 2-aminopyrimidine complexes (Lumme *et al.*, 1981) and on the crystal structure of di-μ-sulfato-*O*:*O*′-bis[2-aminopyrimidinetriaquacobalt(II)] dihydrate (Lumme, Knuuttila, Knuuttila & Valkonen, 1983) have been published. Recent reviews of coordination compounds and their structures can be found in Murphy (1993) for Cu, Davies (1993) for Co and Foulds (1990) for Ni. The structures of the title compounds are described in more detail in this paper.



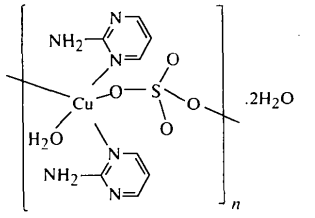
(1)



(2)



(3)



(4)

In compound (1), $[Co(SO_4)(C_4H_5N_3)(H_2O)_3]_2.2H_2O$, two $[Co(C_4H_5N_3)(H_2O)_3]^{2+}$ moieties are bridged through two sulfate anions to form a centrosymmetric dimer (Fig. 1). The coordination sphere around the Co atom is octahedral, with three water molecules [O1, O2 and O3] and one sulfate O atom [O5$^{\rm i}$; symmetry code: (i) $-x, -y, -z$] situated in the basal plane and the 2-aminopyrimidine ring (N1 coordinated) and one sulfate-O atom (O4) situated in the apical positions. The crystal packing shows partial stacking of the pyrimidine rings in the *a* direction. The three coordinated water molecules of the asymmetric unit probably form three internal (O3···O7, O3···O8 and O8···O3) and four external [O1···O7$^{\rm i}$, O1···O6$^{\rm ii}$, O2···O8$^{\rm iii}$ and O2···O4$^{\rm ii}$; symmetry codes: (ii) $1-x, -y, -z$; (iii) $1+x, y, z$] hydrogen bonds to sulfate O atoms and one external [O8···N2$^{\rm iv}$; symmetry code: (iv) $-x, 1-y, -z$] hydrogen bond to the cyclic N atom in the neighbouring pyrimidine ring. In total, three different types of hydrogen bond are present. The two uncoordinated water molecules exist as free lattice water.

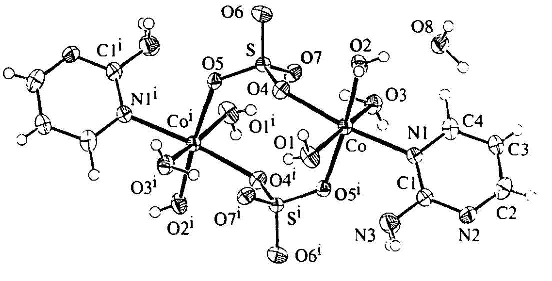


Fig. 1. Molecular structure of compound (1). Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes: as in Table 2.

In compound (2), $[NiSO_4(C_4H_5N_3)_2(H_2O)_2].C_4H_5N_3$, the octahedral coordination sphere around the Ni^{II} atom may be considered to be formed from two water (O5 and O6) and two 2-aminopyrimidine molecules (chemically equivalent N1 and N4) in the basal plane with the O atoms [O1 and O2^i; symmetry code: (i) $x-1, y-1, z$] of separate sulfate ions situated in the apical positions (Fig. 2). The sulfate anions bridge the Ni^{II} moieties to form —Ni—O—S—O—Ni— chains in the *a* direction. The third (uncoordinated) 2-aminopyrimidine molecule forms separate columns between the chains in the *a* direction. Five types of hydrogen bond probably exist, four internal [from amino N atoms to a sulfate O atom (N3···O1 and N6···O1), from a ring C atom to a sulfate O atom (C8···O2) and from a water O atom to a ring N atom (O5···N8)] and seven external {from amino N atoms to ring N atoms [N3···N7^i, N6···N5^{ii}, N9···N2^{iv}; symmetry codes: (ii) $-x, 1-y, 1-z$; (iv) $1+x, 1+y, z$], from an amino N atom to a sulfate O atom [N9···O4^v; symmetry code: (v) $1+x, y, z$] and from water O atoms to sulfate O atoms [O5···O3^{iii}, O6···O3^{iii} and O6···O4^{iii}; symmetry code: (iii) $-x, 1-y, -z$]}.

The 2-aminopyrimidine molecules are planar within experimental error and the amino N atoms lie approximately in the corresponding molecular planes. The angle between the rings containing N1 and N4 is 79.4 (5)° and the angles these rings make with the ring containing N7 are 24.8 (5) and 104.2 (5)°, respectively.

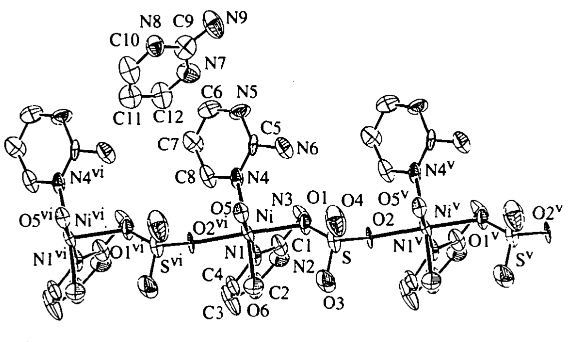


Fig. 2. Molecular structure of compound (2). Displacement ellipsoids are drawn at the 50% probability level. H atoms have been removed for clarity. Symmetry codes: (vi) $x-1, y, z$; and as in Table 4.

In compound (3), $[Ni(C_4H_5N_3)(H_2O)_5]SO_4.C_4H_5N_3$, the absolute configuration (for the crystal used) is that shown (see *Experimental*). The substitution of one 2-aminopyrimidine molecule by three water molecules changes the structure completely [*i.e.* compound (2) to compound (3)] and results in a change to non-centrosymmetric orthorhombic ($P2_12_12_1$) symmetry. The coordination sphere around the Ni^{II} atom is still octahedral (Fig. 3). Four water molecules (O1, O3, O4 and O5) may be considered to be situated in the basal plane and the fifth water molecule (O2) and a 2-aminopyrimidine molecule (N1 coordinated) to occupy the apical positions. The second 2-aminopyrimidine molecule and the sulfate ion lie between the metal moieties. Stacking between the pyrimidine rings to some extent seems obvious.

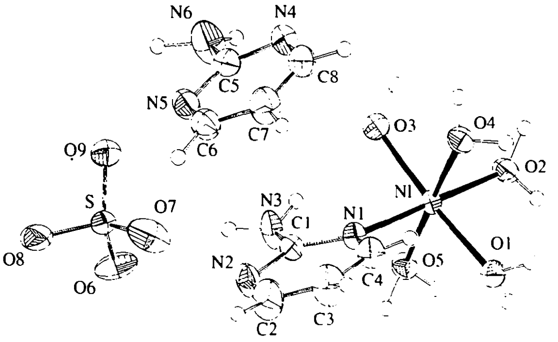


Fig. 3. Molecular structure of compound (3). Displacement ellipsoids are drawn at the 50% probability level.

A strong hydrogen-bond net stabilizes the crystal structure of (3). Five different types of hydrogen bond are postulated: from water O atoms to three different sulfate O atoms [O1···O9^{iv}, O1···O8^v; O2···O6^v, O2···O9^{vi}; O4···O6^{iv}, O4···O8^{vi}; O3···O7^{vi} and O5···O7^v; symmetry codes: (iv) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$; (v) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$; (vi) $\frac{3}{2}-x, 1-y, \frac{1}{2}+z$], from water O atoms to ring N atoms [O3···N5^{iv} and O5···N4^{vii}; symmetry code: (vii) $x, 1+y, z$], from an amino N atom to a water O atom [N3···O3^i and N6···O2^{iii}; symmetry codes: (i) $x, y-1, z$; (iii) $1-x, y-\frac{1}{2}, \frac{3}{2}-z$], from an amino N atom to a sulfate O atom [N3···O7^{ii}; symmetry code: (ii) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$] and from an amino N atom to a ring N atom (N6···N2^{iii}). Altogether there are fourteen external hydrogen bonds.

The ring containing the N1 atom is slightly chair like in the coordination direction and the amino N atom N3 is displaced 0.350 (8) Å from the pyrimidine plane. The uncoordinated pyrimidine ring is planar within experimental error, with the amino N atom (N6) displaced only −0.039 (9) Å from the plane. The angle between the two 2-aminopyrimidine planes is 22.4 (1)°.

In compound (4), $[CuSO_4(C_4H_5N_3)_2(H_2O)].2H_2O$, the Cu^{II} atom is pentacoordinated by two 2-aminopyrimidine molecules [N1 and N1^i; symmetry code:

(i) x, $\frac{1}{2}-y$, z], one water molecule (O4) and two sulfate O atoms [O1 and O3^{ii}; symmetry code: (ii) $x-1, y, z$] (Fig. 4). The coordination sphere around the central Cu^{II} atom is a distorted square pyramid where the two O atoms (O1 and O4) and two N atoms (N1 and N1^{i}) form the basal plane and the O atom O3^{ii} occupies the apical position. The two coordinated sulfate anions form bridges between the neighbouring Cu^{II} atoms resulting in chains in the a direction. The amino group forms hydrogen bonds with sulfate O atoms (N3···O2^{ii} and N3···O3^{ii}) and a ring N atom [N3···N2^{iii}; symmetry code: (iii) $-x, 1-y, -z$]. The uncoordinated water molecule forms external hydrogen bonds with the neighbouring sulfate O atoms [O5···O2^{iv} and O5···O2^{v}; symmetry codes: (iv) $x-1, y, 1+z$; (v) $x, y, 1+z$] and an internal hydrogen bond with the coordinated water (O4···O5). Altogether there are four types of hydrogen bond, one internal and five external.

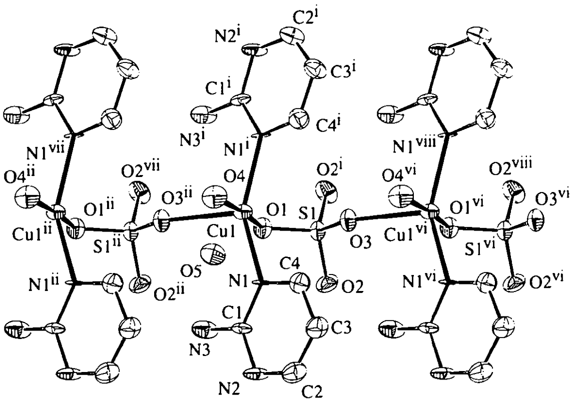


Fig. 4. Molecular structure of compound (4). Displacement ellipsoids are drawn at the 50% probability level. H atoms have been removed for clarity. Symmetry codes: (vi) $x+1, y, z$; (vii) $x-1, \frac{1}{2}-y, z$; (viii) $1+x, \frac{1}{2}-y, z$; and as in Table 8.

The 2-aminopyrimidine ring is planar within experimental error. The Cu1, S1, O1, O3 and O4 atoms are also planar. The coordination about Cu^{II} is remarkably similar to that found around Cu in *catena*-poly[triaquacopper(II)-μ-1,3,5-benzenetricarboxylato(2−)] (Pech & Pickardt, 1988).

The bond distances and angles around the central metal atoms are quite normal with M—O and M—N distances ranging 1.94–2.17 and 2.05–2.20 Å, respectively. The coordination polyhedra in compounds (1)–(3) are distorted octahedra, whereas in compound (4) it is a distorted square pyramid.

The bond distances and angles of 2-aminopyrimidine in all four complexes are similar to those found in other complexes (O'Reilly, Smith & Kennard, 1984; Kennard, Stewart, O'Reilly, Smith & White, 1985; Etter, Adsmond & Britton, 1990; Zanchini & Willett, 1990) and for the free ligand (Scheinbeim & Schempp, 1976; Furberg, Grøgaard & Smedsrud, 1979).

In all four compounds the hydrogen-bond net stabilizes the overall crystal structure. The tendency to form polymeric sulfato-bridged structures seems to increase among the present compounds in the order Co < Ni < Cu.

Experimental

The syntheses, composition analyses, density measurements (flotation) and preliminary X-ray studies of the compounds have been described (Lumme *et al.*, 1981; Lumme & Knuuttila, 1995). The crystals of (2) and (3) were placed in Lindemann glass capillaries.

Compound (1)

Crystal data

$[Co(SO_4)(C_4H_5N_3)(H_2O)_3]_2.2H_2O$
$M_r = 644.31$
Monoclinic
$P2_1/c$
$a = 6.814\,(2)$ Å
$b = 12.083\,(6)$ Å
$c = 13.762\,(7)$ Å
$\beta = 96.15\,(3)°$
$V = 1126.6\,(9)$ Å^3
$Z = 2$
$D_x = 1.906$ Mg m^{-3}
$D_m = 1.922$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 21 reflections
$\theta = 4.47–19.98°$
$\mu = 1.73$ mm^{-1}
$T = 296\,(2)$ K
Prism
$0.20 \times 0.12 \times 0.12$ mm
Red

Data collection

Nicolet $P3F$ four-circle diffractometer
ω–2θ scans
Absorption correction: ψ scan
$T_{min} = 0.70$, $T_{max} = 1.00$
2908 measured reflections
2576 independent reflections
1545 observed reflections [$F > 6\sigma(F)$]

$R_{int} = 0.025$
$\theta_{max} = 27.5°$
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 17$
$l = -21 \rightarrow 21$
2 standard reflections monitored every 48 reflections intensity decay: not significant

Refinement

Refinement on F
$R = 0.061$
$wR = 0.055$
$S = 2.44$
1545 reflections
154 parameters
$w = 1/\sigma(F)$
$(\Delta/\sigma)_{max} = 0.11$

$\Delta\rho_{max} = 1.61$ e Å^{-3}
$\Delta\rho_{min} = -1.40$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (1)

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Co	0.2458 (2)	0.16570 (8)	0.03148 (7)	0.0202 (3)
O1	0.3201 (7)	0.1509 (5)	−0.1136 (3)	0.032 (2)
O2	0.5378 (7)	0.1414 (4)	0.0883 (4)	0.031 (2)

O3	0.1251 (8)	0.1736 (4)	0.1635 (3)	0.028 (2)
O4	0.2367 (8)	−0.0136 (4)	0.0364 (4)	0.025 (2)
N1	0.2746 (9)	0.3467 (5)	0.0434 (4)	0.024 (2)
C1	0.234 (1)	0.4232 (6)	−0.0275 (6)	0.024 (2)
N3	0.188 (1)	0.3860 (6)	−0.1193 (5)	0.038 (2)
N2	0.238 (1)	0.5331 (5)	−0.0134 (4)	0.028 (2)
C2	0.287 (1)	0.5697 (7)	0.0779 (7)	0.039 (3)
C3	0.337 (1)	0.4981 (7)	0.1532 (6)	0.035 (3)
C4	0.332 (1)	0.3859 (7)	0.1337 (6)	0.033 (3)
S	0.1539 (3)	−0.0955 (1)	0.1019 (1)	0.0188 (5)
O5	0.0413 (7)	−0.1794 (4)	0.0401 (3)	0.024 (2)
O6	0.3151 (7)	−0.1513 (4)	0.1615 (3)	0.028 (2)
O7	0.0250 (7)	−0.0401 (4)	0.1673 (3)	0.025 (2)
O8	−0.2068 (8)	0.3005 (4)	0.1536 (4)	0.030 (2)

Table 2. *Selected geometric parameters (Å, °) for* (1)

Co—O3	2.075 (5)	Co—O1	2.119 (5)
Co—O2	2.080 (5)	Co—O4	2.169 (5)
Co—O5^{i}	2.100 (5)	Co—N1	2.201 (6)
O3—Co—O2	97.5 (2)	O2—Co—O1	91.5 (2)
O3—Co—O1	170.3 (2)	O5^{i}—Co—O1	82.5 (2)
O3—Co—O4	90.2 (2)	O5^{i}—Co—N1	91.6 (2)
O3—Co—N1	86.0 (2)	O1—Co—O4	87.4 (2)
O2—Co—O5^{i}	173.3 (2)	O4—Co—N1	173.4 (2)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O7^{i}	0.743 (5)	2.063 (5)	2.738 (7)	151.1 (4)
O1—H2···O6^{ii}	0.893 (5)	1.896 (5)	2.639 (7)	139.4 (4)
O2—H3···O8^{iii}	0.743 (5)	2.049 (5)	2.683 (7)	143.4 (4)
O2—H4···O4^{ii}	1.006 (5)	2.291 (5)	2.873 (8)	115.6 (3)
O3—H5···O7	0.951 (5)	1.725 (5)	2.673 (7)	174.6 (4)
O3—H6···O8	0.741 (5)	1.985 (5)	2.723 (7)	174.2 (4)
O8—H12···O3	0.863 (5)	2.122 (5)	2.723 (7)	126.4 (4)
O8—H13···N2^{iv}	1.043 (5)	1.863 (6)	2.779 (8)	144.4 (3)

Symmetry codes: (i) $-x, -y, -z$; (ii) $1 - x, -y, -z$; (iii) $1 + x, y, z$; (iv) $-x, 1 - y, -z$.

Compound (2)

Crystal data

$[\mathrm{Ni(SO_4)(C_4H_5N_3)_2(H_2O)_2}].\mathrm{C_4H_5N_3}$
$M_r = 476.10$
Triclinic
$P\overline{1}$
$a = 6.426$ (3) Å
$b = 11.027$ (6) Å
$c = 13.68$ (1) Å
$\alpha = 93.11$ (6)°
$\beta = 90.64$ (6)°
$\gamma = 95.06$ (4)°
$V = 964$ (1) Å^3
$Z = 2$
$D_x = 1.646$ Mg m^{-3}
$D_m = 1.700$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 24 reflections
$\theta = 4.89$–18.72°
$\mu = 1.16$ mm^{-1}
$T = 295$ (1) K
Prism
0.2 × 0.2 × 0.2 mm
Green

Data collection

Nicolet *P*3*F* four-circle diffractometer
ω–2θ scans
Absorption correction: none
4143 measured reflections
3745 independent reflections
1648 observed reflections [$F > 6\sigma(F)$]
$R_{\mathrm{int}} = 0.051$

$\theta_{\max} = 27.5°$
$h = 0 \rightarrow 9$
$k = -15 \rightarrow 15$
$l = -18 \rightarrow 18$
2 standard reflections monitored every 50 reflections
intensity decay: not significant

Refinement

Refinement on *F*
$R = 0.092$
$wR = 0.069$
$S = 3.02$
1648 reflections
262 parameters
$w = 1/\sigma(F)$
$(\Delta/\sigma)_{\max} = 0.645$

$\Delta\rho_{\max} = 2.78$ e Å^{-3}
$\Delta\rho_{\min} = -2.59$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for* (2)

$$U_{\mathrm{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
Ni	0.1578 (3)	0.3318 (2)	0.1543 (1)	0.0318 (7)
S	−0.3313 (5)	0.3885 (3)	0.1123 (3)	0.042 (1)
O1	−0.166 (1)	0.3389 (7)	0.1715 (6)	0.038 (3)
O2	0.473 (1)	0.3176 (7)	0.1347 (7)	0.037 (3)
O3	−0.287 (2)	0.363 (1)	0.0065 (8)	0.074 (5)
O4	−0.341 (2)	0.5157 (9)	0.134 (1)	0.088 (6)
O5	0.194 (1)	0.5221 (6)	0.1634 (6)	0.035 (3)
O6	0.120 (1)	0.3382 (7)	0.0056 (6)	0.041 (3)
N1	0.116 (2)	0.1379 (9)	0.1405 (9)	0.039 (4)
C1	−0.015 (2)	0.059 (1)	0.186 (1)	0.046 (6)
N2	−0.014 (2)	−0.0623 (9)	0.1808 (8)	0.044 (4)
C2	0.120 (2)	−0.111 (1)	0.119 (1)	0.055 (6)
C3	0.250 (2)	−0.040 (1)	0.062 (1)	0.077 (8)
C4	0.239 (2)	0.083 (1)	0.072 (1)	0.045 (5)
N3	−0.145 (2)	0.1083 (9)	0.2530 (9)	0.051 (5)
N4	0.223 (1)	0.3276 (9)	0.3072 (8)	0.035 (4)
C5	0.134 (2)	0.393 (1)	0.382 (1)	0.034 (5)
N5	0.211 (2)	0.408 (1)	0.4721 (9)	0.050 (5)
C6	0.380 (2)	0.353 (1)	0.495 (1)	0.054 (6)
C7	0.471 (2)	0.280 (1)	0.423 (1)	0.059 (7)
C8	0.384 (2)	0.269 (1)	0.330 (1)	0.050 (6)
N6	−0.041 (2)	0.446 (1)	0.3589 (9)	0.056 (8)
N7	0.495 (2)	0.913 (1)	0.336 (1)	0.059 (5)
C9	0.475 (3)	0.797 (1)	0.295 (1)	0.059 (7)
N8	0.304 (2)	0.716 (1)	0.308 (1)	0.050 (5)
C10	0.161 (3)	0.753 (1)	0.363 (1)	0.067 (7)
C11	0.167 (3)	0.867 (1)	0.408 (1)	0.064 (7)
C12	0.343 (3)	0.942 (1)	0.389 (1)	0.066 (7)
N9	0.634 (2)	0.759 (1)	0.243 (1)	0.071 (6)

Table 4. *Selected geometric parameters (Å, °) for* (2)

Ni—O6	2.051 (9)	Ni—O1	2.102 (8)
Ni—O2	2.063 (8)	Ni—N1	2.13 (1)
Ni—O5	2.088 (7)	Ni—N4	2.13 (1)
O6—Ni—O1	90.0 (3)	O5—Ni—N1	178.2 (4)
O6—Ni—N1	89.9 (4)	O5—Ni—N4	90.8 (4)
O6—Ni—N4	175.5 (4)	O1—Ni—N1	90.3 (4)
O2—Ni—O1	177.6 (3)	N1—Ni—N4	91.0 (4)
O2—Ni—N1	87.5 (3)		

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N3—H4···O1	0.99 (1)	1.999 (9)	2.84 (1)	141.9 (8)
N3—H5···N7^{i}	1.00 (1)	2.30 (1)	3.28 (2)	168.6 (8)
C8—H8···O2	1.01 (1)	2.336 (9)	2.81 (2)	107.8 (9)
N6—H9···O1	0.98 (1)	1.935 (8)	2.84 (1)	151.2 (7)
N6—H10···N5^{ii}	1.03 (1)	1.99 (1)	3.02 (2)	174.5 (7)
O5—H11···O3^{iii}	1.05 (1)	1.98 (1)	2.75 (1)	128.0 (5)
O5—H12···N8	0.993 (7)	2.23 (1)	2.87 (1)	120.7 (6)
O6—H14···O3^{iii}	1.020 (8)	2.40 (1)	3.39 (1)	162.1 (5)
N9—H18···N2^{iv}	1.01 (1)	2.04 (1)	3.02 (2)	164.6 (9)
N9—H19···O4^{v}	1.00 (1)	2.04 (1)	3.02 (2)	165.6 (9)
O6—H13···O4^{iii}	1.005 (9)	2.36 (1)	2.87 (1)	110.4 (5)

Symmetry codes: (i) $x-1, y-1, z$; (ii) $-x, 1-y, 1-z$; (iii) $-x, 1-y, -z$; (iv) $1+x, 1+y, z$; (v) $1+x, y, z$.

Compound (3)

Crystal data

$[Ni(C_4H_5N_3)(H_2O)_5]SO_4.$-$C_4H_5N_3$
M_r = 435.05
Orthorhombic
$P2_12_12_1$
a = 7.280 (2) Å
b = 10.391 (3) Å
c = 22.329 (7) Å
V = 1689.1 (9) Å^3
Z = 4
D_x = 1.717 Mg m^{-3}
D_m = 1.730 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 16 reflections
θ = 5.35–15.70°
μ = 1.33 mm^{-1}
T = 295 (1) K
Needle
0.2 × 0.2 × 0.2 mm
Green

Data collection

Nicolet $P3F$ four-circle diffractometer
ω–2θ scans
Absorption correction: ψ scan
$T_{\min}$ = 0.82, $T_{\max}$ = 1.00
2275 measured reflections
2249 independent reflections
1948 observed reflections [$F > 6\sigma(F)$]

$R_{\rm int}$ = 0.0305
$\theta_{\max}$ = 27.51°
$h = 0 \rightarrow 9$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 28$
2 standard reflections monitored every 48 reflections intensity decay: not significant

Refinement

Refinement on F
R = 0.034
wR = 0.036
S = 2.48
1948 reflections
226 parameters
$w = 1/\sigma(F)$
$(\Delta/\sigma)_{\max}$ = 1.154

$\Delta\rho_{\max}$ = 0.77 e Å^{-3}
$\Delta\rho_{\min}$ = −1.18 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

Table 5. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2) for* (3)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Ni	0.73680 (8)	0.94826 (4)	0.89449 (2)	0.0216 (1)
O1	0.5416 (4)	0.9616 (5)	0.9622 (1)	0.032 (1)
O2	0.7395 (5)	0.7472 (2)	0.9016 (1)	0.0321 (8)
O3	0.9347 (4)	0.9227 (4)	0.8286 (1)	0.030 (1)
O4	0.9359 (4)	0.9695 (4)	0.9584 (1)	0.029 (1)
O5	0.5306 (4)	0.9250 (4)	0.8322 (1)	0.031 (1)
N1	0.7269 (6)	1.1504 (3)	0.8834 (1)	0.027 (1)
N2	0.6769 (6)	1.3433 (3)	0.8273 (2)	0.042 (1)
N3	0.7337 (8)	1.1535 (3)	0.7799 (1)	0.043 (1)
C1	0.7151 (6)	1.2161 (4)	0.8315 (2)	0.030 (1)
C2	0.6546 (9)	1.4050 (5)	0.8782 (3)	0.056 (2)
C3	0.6791 (9)	1.3485 (4)	0.9337 (2)	0.052 (2)
C4	0.7144 (7)	1.2191 (4)	0.9337 (2)	0.035 (1)
S	0.2543 (2)	0.29052 (8)	0.40903 (4)	0.0260 (2)
O6	0.0947 (4)	0.3558 (5)	0.4347 (2)	0.048 (1)
O7	0.2325 (7)	0.2742 (4)	0.3451 (1)	0.065 (1)
O8	0.2651 (6)	0.1616 (3)	0.4363 (2)	0.064 (1)
O9	0.4232 (4)	0.3629 (4)	0.4231 (2)	0.035 (1)
N4	0.2779 (6)	0.1272 (3)	0.8311 (2)	0.041 (1)
N5	0.1663 (6)	0.3075 (4)	0.7751 (2)	0.037 (1)
N6	0.254 (1)	0.1198 (4)	0.7283 (2)	0.060 (2)
C5	0.2319 (7)	0.1868 (4)	0.7794 (2)	0.036 (1)
C6	0.1433 (7)	0.3713 (5)	0.8258 (2)	0.041 (2)
C7	0.1804 (8)	0.3175 (5)	0.8811 (2)	0.048 (2)
C8	0.2516 (9)	0.1941 (4)	0.8807 (2)	0.044 (1)

Table 6. *Selected geometric parameters (Å, °) for* (3)

Ni—O4	2.045 (3)	Ni—O1	2.080 (3)
Ni—O5	2.061 (3)	Ni—O2	2.096 (3)
Ni—O3	2.077 (3)	Ni—N1	2.116 (3)
O4—Ni—O5	178.2 (1)	O5—Ni—O3	90.7 (1)
O4—Ni—O3	90.9 (1)	O3—Ni—O1	176.3 (2)
O4—Ni—O1	88.3 (1)	O3—Ni—O2	85.4 (1)
O4—Ni—O2	92.8 (1)	O3—Ni—N1	93.9 (1)
O4—Ni—N1	89.9 (2)	O2—Ni—N1	177.2 (1)

D—H···A	D—H	H···A	D···A	D—H···A
N3—H4···O3$^{\rm i}$	0.937 (4)	2.208 (4)	3.011 (5)	143.2 (2)
N3—H5···O7$^{\rm ii}$	0.918 (3)	2.016 (3)	2.890 (4)	158.4 (3)
N6—H9···N2$^{\rm iii}$	0.919 (4)	2.386 (4)	3.170 (5)	143.1 (4)
N6—H10···O2$^{\rm iii}$	1.076 (4)	2.118 (3)	3.189 (5)	173.5 (2)
O1—H11···O9$^{\rm iv}$	0.937 (3)	1.848 (4)	2.769 (5)	166.8 (4)
O1—H12···O8$^{\rm v}$	0.881 (4)	1.758 (4)	2.638 (5)	177.7 (3)
O2—H13···O9$^{\rm vi}$	0.951 (3)	1.836 (3)	2.752 (5)	160.9 (2)
O2—H14···O6$^{\rm v}$	0.849 (3)	1.931 (4)	2.759 (5)	164.5 (2)
O3—H15···O7$^{\rm vi}$	0.953 (3)	2.243 (5)	3.193 (6)	175.3 (2)
O3—H16···N5$^{\rm iv}$	0.832 (3)	1.891 (4)	2.707 (5)	166.7 (3)
O4—H17···O8$^{\rm vi}$	0.854 (3)	1.810 (4)	2.614 (5)	156.4 (3)
O4—H18···O6$^{\rm iv}$	0.979 (3)	1.705 (4)	2.673 (6)	169.8 (3)
O5—H19···O7$^{\rm v}$	0.950 (4)	1.889 (4)	2.835 (6)	174.4 (3)
O5—H20···N4$^{\rm vii}$	1.065 (4)	1.746 (4)	2.793 (6)	166.6 (2)

Symmetry codes: (i) $x, y-1, z$; (ii) $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$; (iii) $1-x, y-\frac{1}{2}, \frac{3}{2}-z$; (iv) $1-x, \frac{1}{2}+y, \frac{3}{2}-z$; (v) $\frac{1}{2}-x, 1-y, \frac{1}{2}+z$; (vi) $\frac{3}{2}-x, 1-y, \frac{1}{2}+z$; (vii) $x, 1+y, z$.

Compound (4)

Crystal data

$[Cu(SO_4)(C_4H_5N_3)_2(H_2O)].$-$2H_2O$
M_r = 403.86
Monoclinic
$P2_1/m$
a = 4.927 (2) Å
b = 19.119 (9) Å
c = 7.930 (4) Å
β = 94.77 (3)°
V = 744.4 (6) Å^3
Z = 2
D_x = 1.808 Mg m^{-3}
D_m = 1.842 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 16 reflections
θ = 4.26–18.72°
μ = 1.65 mm^{-1}
T = 295 (1) K
Prism
0.4 × 0.1 × 0.1 mm
Dark green

Data collection

Nicolet $P3F$ four-circle diffractometer
ω–2θ scans
Absorption correction: none
1355 measured reflections
1238 independent reflections
860 observed reflections [$F > 6\sigma(F)$]
$R_{\rm int}$ = 0.036

$\theta_{\max}$ = 27.5°
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 12$
$l = -28 \rightarrow 28$
2 standard reflections monitored every 48 reflections intensity decay: not significant

Refinement

Refinement on F
R = 0.039
wR = 0.035
S = 2.06
860 reflections
112 parameters
$w = 1/\sigma(F)$
$(\Delta/\sigma)_{\max}$ = 0.009

$\Delta\rho_{\max}$ = 0.655 e Å^{-3}
$\Delta\rho_{\min}$ = −0.807 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Tables 2.2B and 2.3.1)

Table 7. *Fractional atomic coordinates and equivalent isotropic displacement parameters* ($Å^2$) *for* (4)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cu1	0.2306 (2)	1/4	0.1580 (1)	0.025 (4)
S1	0.6009 (3)	1/4	−0.1249 (2)	0.0212 (7)
O1	0.3103 (8)	1/4	−0.0786 (5)	0.026 (2)
O2	0.6394 (6)	0.3139 (2)	−0.2235 (4)	0.033 (2)
O3	0.7840 (8)	1/4	0.0323 (5)	0.027 (2)
N1	0.3341 (7)	0.3527 (2)	0.1965 (4)	0.018 (2)
C3	0.643 (1)	0.4304 (4)	0.3492 (6)	0.033 (2)
N3	0.0071 (9)	0.3998 (2)	0.0034 (5)	0.035 (2)
C2	0.511 (1)	0.4852 (4)	0.2634 (6)	0.037 (2)
C4	0.5497 (9)	0.3644 (4)	0.3116 (6)	0.031 (2)
C1	0.2182 (9)	0.4093 (4)	0.1194 (5)	0.021 (2)
N2	0.2976 (8)	0.4761 (3)	0.1514 (5)	0.031 (2)
O4	0.1031 (9)	1/4	0.3825 (5)	0.032 (2)
O5	0.1168 (6)	0.3520 (2)	0.6096 (3)	0.034 (1)

Table 8. *Selected geometric parameters* (Å, °) *for* (4)

Cu1—O4	1.937 (4)	Cu1—N1'	2.045 (5)
Cu1—O1	1.948 (4)	Cu1—N1	2.045 (5)
O4—Cu1—O1	172.7 (2)	O1—Cu1—N1	94.4 (1)
O4—Cu1—N1^{i}	87.6 (1)	N1^{i}—Cu1—N1	147.5 (1)
O4—Cu1—N1	87.6 (1)		

D—H···A	D—H	H···A	D···A	D—H···A
N3—H4···O2^{ii}	0.881 (5)	2.312 (3)	2.946 (5)	135.4 (3)
N3—H4···O3^{ii}	0.881 (5)	2.468 (2)	3.083 (5)	133.5 (3)
N3—H5···N2^{iii}	0.835 (5)	2.193 (5)	3.015 (7)	167.8 (3)
O5—H8···O2^{iv}	0.879 (3)	2.078 (3)	2.887 (5)	152.6 (2)
O5—H9···O2^{v}	1.024 (3)	1.880 (3)	2.889 (4)	167.6 (2)
O4—H6···O5	0.894 (4)	2.166 (4)	2.652 (5)	113.5 (1)

Symmetry codes: (i) $x, \frac{1}{2} - y, z$; (ii) $x - 1, y, z$; (iii) $-x, 1 - y, -z$; (iv) $x - 1, y, 1 + z$; (v) $x, y, 1 + z$.

Structure solutions were performed by Patterson and Fourier syntheses using *SHELXS*86 (Sheldrick, 1985), refinements by full-matrix least squares using *SHELX*76 (Sheldrick, 1976) and *Xtal*3.2 (Hall, Flack & Stewart, 1992); anomalous-dispersion was recognized. In compounds (1) and (2), the $\Delta\rho_{max} > 1.0$ Å^{-3} were located close to the metal atoms. All H atoms were located from the difference Fourier maps after the refinements of all heavy atoms. The H-atom parameters were refined with fixed coordinates and displacement parameters (U_{iso} = 0.05 Å^2) because of the untenability of their positions and the lability of the compounds. The high R value for compound (2) compared with those of the other structures is due to the instability of the compound, which is also apparent from the high reduction of the used reflections. In the case of compound (3) the refinement of the inverted structure gave R = 0.034 and wR = 0.037. Figs. 1 to 4 were prepared using *PLATON* (Spek, 1990). Computers used were VAX 8650 and Convex C 3840.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, along with packing diagrams, have been deposited with the IUCr (Reference: HR1034). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Davies, M. B. (1993). *Coord. Chem. Rev.* **124**, 107–181.

Etter, M. C., Adsmond, D. A. & Britton, D. (1990). *Acta Cryst.* C**46**, 933–934.

Foulds, C. A. (1990). *Coord. Chem. Rev.* **98**, 1–122.

Furberg, S., Grøgaard, J. & Smedsrud, B. (1979). *Acta Chem. Scand. Ser. B*, **33**, 715–724.

Hall, S. R., Flack, H. D. & Stewart, J. M. (1992). Editors. *Xtal*3.2 *Reference Manual.* Universities of Western Australia, Australia, Geneva, Switzerland, and Maryland, USA.

Kennard, C. H. L., Stewart, S. W., O'Reilly, E. J., Smith, G. & White, A. H. (1985). *Polyhedron*, **4**, 697–705.

Lumme, P. O., Kekarainen, P., Knuuttila, H., Kurkirinne, T., Latvala, M., Rönkönharju, L. & Salonen, S. (1981). *Finn. Chem. Lett.* pp. 25–28.

Lumme, P. O. & Knuuttila, H. (1995). *Polyhedron*, **14**, 1553–1563.

Lumme, P. O., Knuuttila, H., Knuuttila, P. & Valkonen, J. (1983). Eighth Eur. Crystallogr. Meet., Liège, Belgium. Abstracts, p. 176.

Lumme, P. O. & Mutikainen, I. (1980). *Acta Cryst.* B**36**, 2251–2254.

Lumme, P. O., Mutikainen, I. & Lindell, E. (1982). Seventh Eur. Crystallogr. Meet., Jerusalem, Israel. Abstracts, p. 148.

Lumme, P. O., Mutikainen, I. & Lindell, E. (1983). *Inorg. Chim. Acta*, **71**, 217–226.

Murphy, B. P. (1993). *Coord. Chem. Rev.* **124**, 63–105.

O'Reilly, E. J., Smith, G. & Kennard, C. H. L. (1984). *Inorg. Chim. Acta*, **90**, 63–71.

Pech, R. & Pickardt, J. (1988). *Acta Cryst.* C**44**, 992–994.

Scheinbeim, J. & Schempp, E. (1976). *Acta Cryst.* B**32**, 607–609.

Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination.* University of Cambridge, England.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.

Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.

Zanchini, C. & Willett, R. D. (1990). *Inorg. Chem.* **29**, 3027–3030.

Acta Cryst. (1996). C**52**, 56–59

A Polymeric Cu^I Complex of Bis(1-pyrazolylmethyl)(2-pyridylmethyl)amine (BPPA), $[Cu_2(\mu\text{-BPPA})(\mu\text{-I})_2]_n$

Shiann-Cherng Sheu, Gene-Hsiang Lee, Tong-Ing Ho, Yuan-Chuan Lin and Shie-Ming Peng

Department of Chemistry, National Taiwan University, Taipei, Taiwan

(*Received 30 March 1995; accepted 12 July 1995*)

Abstract

The title complex, *catena*-poly[copper-di-μ-iodo-copper-μ-{bis(1-pyrazolylmethyl)(2-pyridylmethyl)amine}-$N,N':N^2,N^{2'}$], $[Cu_2I_2(C_{14}H_{16}N_6)]$, is reported. The BPPA ligand, bis(1-pyrazolylmethyl)(2-pyridylmethyl)-amine, acts as a bis-bidentate ligand reacting with copper(I) iodide in acetonitrile to form the title complex. In the repeat unit of the title complex, one Cu^I atom is ligated by two pyrazole groups from one ligand and the other Cu^I atom is ligated by one pyridine group and an amine from another ligand. The Cu^+ ions are separated by a distance of 2.587 (1) Å.

Acta Crystallographica Section C
ISSN 0108-2701 ©1996