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Ag^{I} and Cu^{I} binuclear macrocyclic complexes with 1-(3-pyridyl)ethanone oxime

Ingrid Socorro, Antonia Neels* and Helen Stoeckli-Evans

Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, CH-2007 Neuchâtel, Switzerland
Correspondence e-mail: antonia.neels@unine.ch

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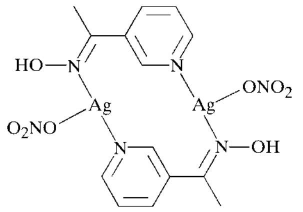
Bis[μ-1-(3-pyridyl)ethanone oxime-κ^2N:N']bis[nitratosilver(I)], [$Ag_2(NO_3)_2(C_7H_8N_2O)_2$], crystallizes as a centrosymmetric binuclear macrocylic complex containing silver(I) ions bridged by the organic 1-(3-pyridyl)ethanone oxime ligand. The ligand coordinates *via* the pyridine and the oxime N atoms. A similar metal–ligand arrangement was found in the copper(I) complex *catena*-poly[[bis[μ-1-(3-pyridyl)ethanone oxime-κ^2N:N']dicopper(I)]-di-μ-iodo], [$Cu_2I_2(C_7H_8N_2O)_2]_n$, but here the centrosymmetric macrocycles are connected by double anion bridges, resulting in the formation of a one-dimensional coordination polymer.

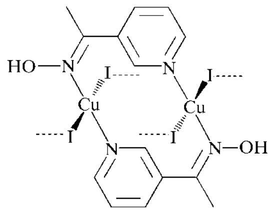
Comment

For the design of supramolecular architectures, it is necessary to use versatile molecular synthons as connectors, for example, for the assembly of metal-containing networks. Predictable assembly of some metal complexes has been obtained through the synthesis of coordination polymers. Porous solids with channels and cavities have been obtained with 3*d* metals and, for example, 4,4′-bipyridine or pyrazine (Moulton & Zaworotko, 2001). In crystal engineering, the use of hydrogen bonding as a steering force has also emerged as an important strategy (Aakeröy *et al.*, 2000). It has been shown that oxime–pyridine derivatives can be used in assembling coordination complexes into extended hydrogen-bonded networks (Aakeröy *et al.*, 1998, 1999). We present here two new coordination compounds formed with the ligand 1-pyridin-3-yl-ethanone oxime (commonly known as 3-acetyloximepyridine) using silver(I) nitrate and copper(I) iodide.

The silver(I) compound, (I), was revealed to be a centrosymmetric binuclear macrocylic complex containing silver(I) ions bridged by the organic oxime ligand (Fig. 1). Selected geometric parameters for (I) are listed in Table 1. Both the pyridine (py) and the oxime (ox) N atoms are involved in coordination. Each Ag atom is in a planar trigonal environment, having, in addition to the two ligand molecules in its coordination sphere, a nitrate anion coordinating in a monodentate fashion. The Ag1—N1$_{py}$ and Ag—N2$_{ox}$ distances are both 2.217 (2) Å, while the Ag1—O11$_{nitrate}$ distance [2.593 (2) Å] is relatively long. The Ag atom is displaced by 0.042 (1) Å from the plane defined by atoms N1^{i}, N2 and O11 [symmetry code: (i) $1 - x$, $-y$, $1 - z$]. The formation of the macrocyclic structure results in the C(CH_3)NOH group being twisted out of the plane of the pyridine ring by 46.7 (1)°. The intramolecular metal–metal distance in the macrocycle is 4.484 (1) Å.



(I)



(II)

The formation of a strong intermolecular hydrogen bond between the OH function of the oxime ligand and a neighbouring nitrate anion results in the formation of a hydrogen-bonded macrocycle and hence a one-dimensional polymer (Fig. 2 and Table 2). The Ag atoms are separated by only 4.444 (1) Å. The structure of (I) is very different to that of the known mononuclear silver(I) compounds bis(3-acetyloximepyridine)silver(I) hexafluorophosphate and bis(3-acetyloximepyridine)silver(I) perchlorate, both synthesized by Aakeröy *et al.* (1998). In those compounds, only the pyridine N atom coordinates to the Ag atom, and the Ag—N distances [2.13–2.16 Å] are shorter than those in (I). The coordinated ligand molecules are also more planar, with dihedral angles between the pyridine and C(CH_3)NOH groups in the range 10.2–18.7°, compared with a value of 46.7 (1)° in (I). In the free ligand (Aakeröy *et al.*, 2000), the corresponding dihedral angle is only 9.1°.

The copper(I) complex, (II), is similar to (I) but, in addition to the binuclear macrocyclic arrangement, the Cu atoms are bridged by iodide anions, thus linking these units into a one-dimensional polymer (Fig. 3). Selected geometric parameters

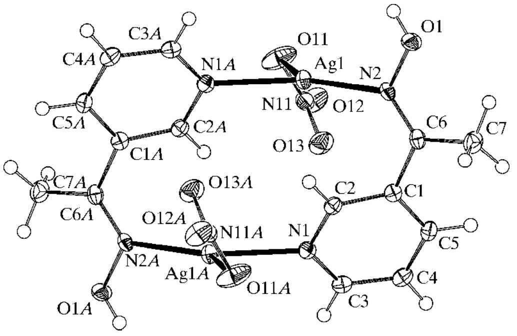


Figure 1
The molecular structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme. Atoms labelled with the additional letter *A* are in the symmetry postion ($1 - x$, $-y$, $1 - z$).

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for (II) are listed in Table 3. Two ligand molecules, one involving the pyridine N atom [Cu1—N1 = 2.047 (2) Å], the other involving the oxime N atom [Cu1—N2^{iii} = 2.055 (3) Å; symmetry code: (iii) 2 − *x*, 1 − *y*, 1 − *z*], are coordinated to the copper(I) ion. The tetrahedral coordination sphere of atom Cu1 is completed by two iodide anions [Cu1—I1,I1^{iv} = 2.6535 (5) and 2.7134 (7) Å; symmetry code: (iv) 1 − *x*, 1 − *y*, 1 − *z*]. In the chains, the intramolecular metal–metal distances are 5.149 (1) Å for the double ligand bridge and 2.8748 (8) Å for the double anion bridge. As in complex (I), the $C(CH_3)NOH$ group is twisted out of the plane of the pyridine ring by 49.8 (1)°. There exists within the polymer chains a hydrogen bond involving the oxime OH group and the bridging iodine atom I1^{v} [symmetry code: (v) 1 + *x*, *y*, *z*; see Table 4].

The crystal structures of (I) and (II) show a new coordination mode of the 1-(3-pyridyl)ethanone oxime ligand. The use of two N-donor atoms of the same ligand molecule results in the formation of metallomacrocycles. These are in turn connected by an N—OH···anion hydrogen bond [in (I)] or anion bridges [in (II)], thus forming zigzag one-dimensional polymeric arrangements.

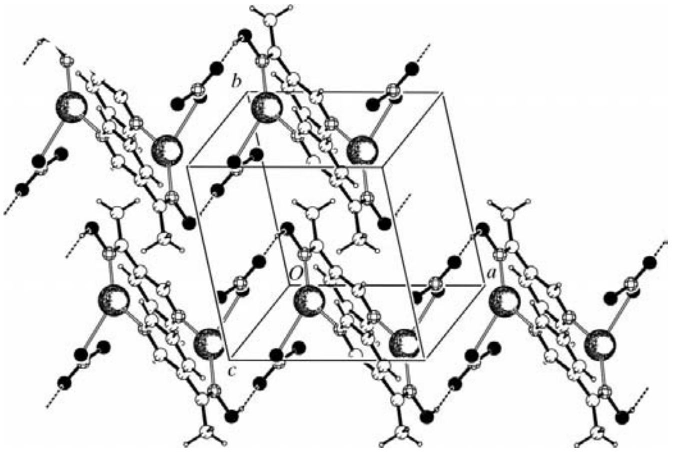

Figure 2
The molecular arrangement in the unit cell of (I), showing the O—H···O$_{nitrate}$ hydrogen bonds as dashed lines.

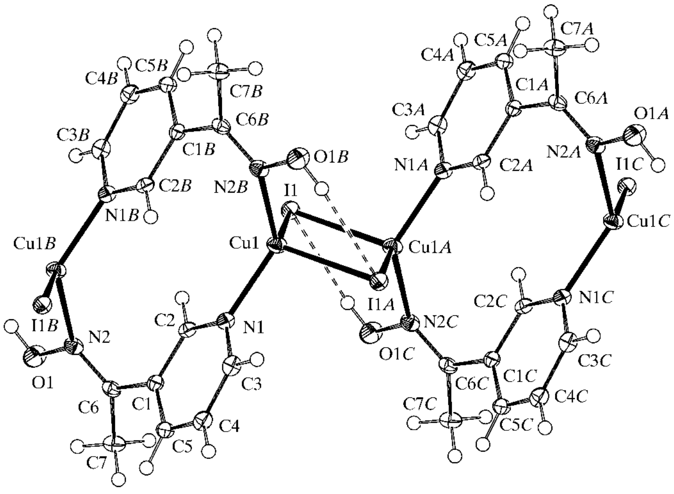

Figure 3
The molecular structure of (II), showing 50% probability displacement ellipsoids of a section of the infinite chain, O—H···I hydrogen bonds and the atom-numbering scheme. Atoms labelled with the additional letters *A*, *B* and *C* are in the symmetry positions (1 − *x*, 1 − *y*, 1 − *z*), (2 − *x*, 1 − *y*, 1 − *z*) and (−1 + *x*, *y*, *z*), respectively.

Experimental

Compound (I) was synthesized by adding a solution of 1-(3-pyridyl)ethanone oxime (10 mg, 0.073 mmol) in ethanol (10 ml) to an aqueous solution of silver(I) nitrate (12.5 mg, 0.073 mmol, 10 ml). Colourless transparent crystals were obtained by slow evaporation of the solvent at room temperature. Compound (II) was synthesized by adding 1-(3-pyridyl)ethanone oxime (25 mg, 0.184 mmol) to a solution of copper(I) iodide (35 mg, 0.184 mmol) in acetonitrile (20 ml). After some days, brown crystals were obtained by slow evaporation of the solvent at room temperature.

Compound (I)

Crystal data

$[Ag_2(NO_3)_2(C_7H_8N_2O)_2]$
$M_r = 612.07$
Triclinic, $P\overline{1}$
$a = 8.076$ (1) Å
$b = 8.084$ (1) Å
$c = 8.808$ (1) Å
$\alpha = 105.34$ (2)°
$\beta = 114.53$ (2)°
$\gamma = 102.51$ (2)°
$V = 468.28$ (18) Å^3

$Z = 1$
$D_x = 2.170$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5158 reflections
$\theta = 2.9$–25.9°
$\mu = 2.15$ mm^{-1}
$T = 153$ (2) K
Block, colourless
0.35 × 0.30 × 0.20 mm

Data collection

Stoe IPDS diffractometer
φ scans
Absorption correction: multi-scan (*MULABS* in *PLATON*; Spek, 2003)
$T_{min} = 0.478$, $T_{max} = 0.701$
3502 measured reflections

1622 independent reflections
1579 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 25.9°$
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.053$
$S = 1.09$
1622 reflections
138 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0322P)^2 + 0.2699P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.56$ e Å^{-3}
$\Delta\rho_{min} = -0.75$ e Å^{-3}

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

Ag1—N2	2.217 (2)	N2—O1	1.403 (2)
Ag1—N1^{i}	2.217 (2)	C1—C6	1.487 (3)
Ag1—O11	2.593 (2)	C6—C7	1.481 (4)
N2—C6	1.288 (3)		
N2—Ag1—N1^{i}	144.35 (7)	C6—N2—Ag1	129.26 (16)
N2—Ag1—O11	133.60 (8)	O1—N2—Ag1	117.57 (13)
N1^{i}—Ag1—O11	81.93 (8)	N11—O11—Ag1	99.22 (15)
C6—N2—O1	113.1 (2)		
O1—N2—C6—C1	179.26 (18)	C2—C1—C6—N2	−46.5 (3)

Symmetry code: (i) 1 − *x*, −*y*, 1 − *z*.

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Table 2
Hydrogen-bonding geometry (Å, °) for (I).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1O$\cdots$O12^{ii}	0.84	1.94	2.767 (3)	168

Symmetry code: (ii) $-x, -y, 1-z$.

Compound (II)

Crystal data

[$Cu_2I_2(C_7H_8N_2O)_2$]
$M_r = 326.60$
Triclinic, $P\overline{1}$
$a = 7.512$ (1) Å
$b = 8.015$ (1) Å
$c = 8.886$ (1) Å
$\alpha = 111.88$ (2)°
$\beta = 101.38$ (2)°
$\gamma = 106.57$ (2)°
$V = 447.28$ (17) Å^3
$Z = 2$
$D_x = 2.425$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8000 reflections
$\theta = 2.2$–25.1°
$\mu = 5.84$ mm^{-1}
$T = 153$ (2) K
Plate, pale yellow
0.40 × 0.40 × 0.25 mm

Data collection

Stoe IPDS diffractometer
φ scans
Absorption correction: empirical, refined from ΔF (*DELABS* in *PLATON*; Spek, 2003)
$T_{min} = 0.225$, $T_{max} = 0.689$
3418 measured reflections
1588 independent reflections
1522 reflections with $I > 2\sigma(I)$
$R_{int} = 0.028$
$\theta_{max} = 25.8°$
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -10 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.020$
$wR(F^2) = 0.050$
$S = 1.07$
1588 reflections
110 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0291P)^2 + 0.3665P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.67$ e Å^{-3}
$\Delta\rho_{min} = -0.65$ e Å^{-3}

Table 3
Selected interatomic distances (Å) for (II).

I1—Cu1	2.6535 (5)	Cu1—N2^{iii}	2.055 (3)
Cu1—N1	2.047 (2)	Cu1—I1^{iv}	2.7134 (7)

Symmetry codes: (iii) $2-x, 1-y, 1-z$; (iv) $1-x, 1-y, 1-z$.

Table 4
Hydrogen-bonding geometry (Å, °) for (II).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1O$\cdots$I1^{v}	0.85	2.59	3.402 (3)	161

Symmetry code: (v) $1+x, y, z$.

H atoms attached to C atoms were all located from difference Fourier maps but were included in calculated positions and treated as riding atoms, with C—H distances of 0.95–0.98 Å and U_{iso}(H) values equal to $1.2U_{eq}$(C aromatic) and $1.5U_{eq}$(C methyl). In (I), the hydroxy H atom was included in a calculated position (AFIX 147), with an O—H distance of 0.84 Å and U_{iso}(H) equal to $1.5U_{eq}$(O1). In (II), the hydroxy H atom was initially located from a difference Fourier map, but in the final cycles of refinement its position was fixed [O—H = 0.85 Å and $U_{iso}(H) = 1.5U_{eq}(O1)$]. Using an image-plate distance of 70 mm to obtain maximum resolution for the triclinic system, only 90 [for (I)] and 92% [for (II)] of the full data sets ($\theta = 25.85°$) could be measured.

For both compounds, data collection: *EXPOSE* (Stoe & Cie, 2000); cell refinement: *CELL* (Stoe & Cie, 2000); data reduction: *INTEGRATE* (Stoe Cie, 2000); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1683). Services for accessing these data are described at the back of the journal.

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