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

Zr1—Cl5	2.3856 (14)	Zr1—Cl2	2.4263 (14)
Zr1—Cl6	2.396 (2)	Zr1—Cl4	2.5949 (13)
Zr1—Cl3	2.4181 (15)	Zr1—Cl4^{i}	2.6184 (14)
Cl5—Zr1—Cl6	101.63 (5)	Cl4—Zr1—Cl4^{i}	77.72 (4)
Cl3—Zr1—Cl2	174.08 (5)		

Symmetry code: (i) $2 - x, -y, -z$.

The data collection strategy nominally covered a hemisphere of reciprocal space by the combination of four scans (φ = 0 and 90° for χ = 0 and 90°) for 0.2° increments in ω, following previously described procedures (Drake *et al.*, 1993). However, higher angle data were very weak and zero or negative intensities were excluded from the refinement, resulting in only 87% completeness.

Data collection: *MADNES* (Pflugrath & Messerschmidt, 1989). Cell refinement: *MADNES*. Data reduction: *ABSMAD* (Karaulov, 1992). Program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*b*). Molecular graphics: *CAMERON* (Watkin *et al.*, 1995).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1324). Services for accessing these data are described at the back of the journal.

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[μ-*N*,*N'*-Bis(2-pyridylethyl)oxamide]bis[acetatocopper(II)]

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Abstract

The structure of the title compound, $[Cu_2(CH_3COO)_2(C_{16}H_{16}N_4O_2)]$, was determined by single-crystal X-ray diffraction and revealed binuclear complex molecules which lie about inversion centers. The Cu^{II} atom has square-pyramidal coordination, with an additional non-bonded Cu···O contact of 2.818 (4) Å, which helps the maintenance of the crystal packing.

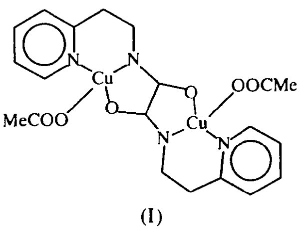
Comment

The chelating properties of *N*,*N'*-disubstituted oxamide ligands revealed four different coordination modes in a number of compounds (Journaux *et al.*, 1985; Zhang *et al.*, 1989, 1996; Lloret *et al.*, 1992; Chen *et al.*, 1994; Sanz *et al.*, 1996; Casellato *et al.*, 1997; Ojima & Nonoyama, 1988).

The diversity of structural possibilities motivated us to study the products of the reaction of *N*,*N'*-bis(2-pyridylethyl)oxamide, H$_2$aepo, with Co^{II}, Cu^{II} and Zn^{II}.

H$_2$aepo crystallizes in a *trans* configuration, and is planar with a center of symmetry in the middle of the ethyl C1—C1^{i} bond [symmetry code: (i) $-x, -y, -z$; Casellato *et al.*, 1997].

During the complexation reaction with Cu(CH$_3$COO)$_2$·4H$_2$O, H$_2$aepo loses its two H atoms. In the product, (I), a binuclear complex, the aepo^{2-} ligand retains the *trans* conformation, with the center of symmetry in the middle of C1—C1^{i} bond, and acts as a bis-tridentate chelate ligand bridging two Cu^{II} ions, which are equivalent by the center of symmetry (Fig. 1).



(I)

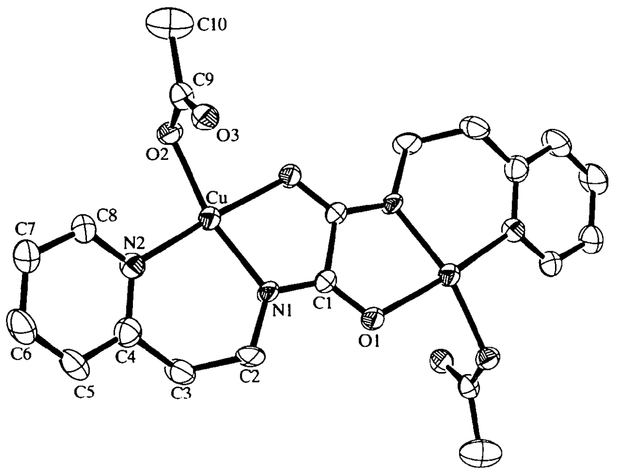


Fig. 1. View of complex (I) with displacement ellipsoids plotted at the 50% probability level.

The Cu^{II} atom has square-pyramidal geometry. There is an additional Cu···O3 interaction of 2.818 (4) Å, which is too long for a coordination bond, but this interaction helps the maintenance of the crystal packing, building an infinite two-dimensional network (Bell & Theocharis, 1987). Selected bond distances and angles are given in Table 1.

The polymerization of complexes connected by acetate molecules was also observed in the structure of $[Cu_2\{N,N'\text{-bis(3-aminopropyl)oxamide}\}(CH_3CO_2)_2]\cdot 2H_2O$, where one acetate O atom occupies one vertex of the coordination polyhedron and bonds simultaneously with two equivalent Cu^{II} atoms at distances of 1.957 (4) and 2.456 (4) Å (Sanz *et al.*, 1996).

The strong absorption at 3220 cm^{-1} observed in the IR spectra for N—H in H_2aepo is absent in the IR spectra of the complexes. The absorptions attributed to C=O stretching frequencies [1677 (as C=O) and 1364 cm^{-1} (as C=O) in H_2aepo] have shifted to a lower wavenumber, indicating coordination from oxygen to the metal (the values are 1608 and 1326, 1628 and 1332, and 1603 and 1324 cm^{-1}, respectively, for the Co^{II}, Cu^{II} and Zn^{II} complexes). Alterations of the pyridine-ring stretching vibrations indicate coordination of nitrogen to the metal.

The IR spectra allow us to conclude that coordination compounds of H_2aepo with Co^{II} and Zn^{II} have the same structure as the complex with Cu^{II}.

Experimental

Dimethyloxalate, 2-(2-aminoethyl)pyridine and metal(II) acetates were obtained from commercial sources and were used as received. The compound *N*,*N'*-bis(2-pyridylethyl)oxamide, H_2aepo, was prepared as described previously (Zhang *et al.*, 1996). Colorless crystals of H_2aepo were obtained by slow evaporation of an ethanolic solution [yield 90% (1.5 g), m.p. 453–455 K]. Analysis found: C 63.8, H 5.9, N 18.4%; calculated for $C_{16}H_{18}N_4O_2$: C 64.4, H 6.1, N 18.8, O 10.75%. The coordination compounds were prepared by addition of H_2aepo (0.5 mmol) dissolved in hot EtOH (15 ml) to $M(CH_3COO)_2\cdot nH_2O$ (n = 1, 4 and 2, for M = Co^{II}, Cu^{II} and Zn^{II}, respectively; 1 mmol) dissolved in the same solvent, under constant stirring. The Co^{II} and Zn^{II} compounds precipitated immediately as lilac and white powders in high yields (*ca* 80–90%). They were removed by filtration, washed with EtOH, then Et_2O, and dried *in vacuo*. Elemental analyses performed in a Perkin–Elmer analyzer (model 240) indicated for $[Co_2(aepo)(CH_3COO)_2]$, found: C 44.3, H 4.2, N 10.2%; calculated: C 45.1, H 4.2, N 10.5%; and for $[Zn_2(aepo)(CH_3COO)_2]$, found: C 43.7, H 4.0, N 10.1%; calculated: C 44.1, H 4.1, N 10.3%. Blue prismatic crystals of $[Cu_2(aepo)(CH_3COO)_2]$ suitable for X-ray diffraction were obtained by slow evaporation of an ethanolic solution. The crystals were filtered off, washed with ethanol and air dried (yield: 80%). Found: C 43.1, H 4.0, N 9.7%; calculated for $C_{20}H_{22}Cu_2N_4O_6$: C 44.36, H 4.09, N 10.35%. IR spectra were recorded on a Nicolet 5ZDX-FT instrument in the 4000–400 cm^{-1} range using KBr pellets. The IR spectra (KBr pellets) for the free ligand and the complex showed absorptions (C=O) at 1667 and 1628 cm^{-1}, respectively, indicating Cu—O bonds in the complex. These results are indicative of the bis-tridentate behavior of the oxamide (Sanz *et al.*, 1996).

Crystal data

$[Cu_2(C_2H_3O_2)_2(C_{16}H_{16}N_4O_2)]$
$M_r = 541.34$
Monoclinic
$P2_1/c$
$a = 9.438\ (2)$ Å
$b = 12.6375\ (18)$ Å
$c = 9.7641\ (13)$ Å
$\beta = 110.953\ (14)^\circ$
$V = 1087.6\ (3)$ Å^3
$Z = 2$
$D_x = 1.654$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 10$–18°
$\mu = 2.062$ mm^{-1}
$T = 293\ (2)$ K
Prism
0.15 × 0.13 × 0.10 mm
Blue

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.765$, $T_{max} = 0.814$
3334 measured reflections
3165 independent reflections

1945 reflections with $I > 2\sigma(I)$
$R_{int} = 0.062$
$\theta_{max} = 29.94^\circ$
$h = -13 \rightarrow 0$
$k = 0 \rightarrow 17$
$l = -12 \rightarrow 13$
3 standard reflections frequency: 120 min intensity decay: 0.29%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.184$
$S = 1.23$
3165 reflections
145 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0869P)^2 + 0.1585P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.02$ e Å^{-3}
$\Delta\rho_{min} = -0.85$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Cu—N1	1.957 (4)	C1—O1	1.266 (5)
Cu—O2	1.957 (3)	C1—N1	1.290 (6)
Cu—O1^{i}	2.028 (3)	C1—C1^{i}	1.528 (9)
Cu—N2	2.062 (4)	O2—C9	1.279 (5)
Cu—O3^{ii}	2.302 (4)	O3—C9	1.236 (5)
Cu···O3	2.818 (4)		
N1—Cu—O1^{i}	82.47 (15)	N2—Cu—O3	88.24 (13)
O2—Cu—O1^{i}	86.61 (13)	O3^{ii}—Cu—O3	144.72 (12)
N1—Cu—N2	92.44 (15)	O1—C1—N1	129.1 (4)
O2—Cu—N2	96.86 (15)	O1—C1—C1^{i}	117.2 (5)
N1—Cu—O3^{ii}	97.28 (16)	C1—N1—C2	119.5 (4)
O2—Cu—O3^{ii}	93.75 (13)	C1—N1—Cu	115.0 (3)
O1^{i}—Cu—O3^{ii}	98.27 (14)	C2—N1—Cu	125.6 (3)
N2—Cu—O3^{ii}	90.73 (14)	C4—N2—C8	118.0 (4)
N1—Cu—O3	118.01 (15)	C4—N2—Cu	123.1 (3)
O2—Cu—O3	51.48 (12)	C8—N2—Cu	118.8 (3)
O1^{i}—Cu—O3	86.72 (13)		

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

The maximum and minimum electron-density peaks are at 0.83 and 0.81 Å, respectively, from the Cu^{II} atom.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP* (Frenz, 1978). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*III (Burnett & Johnson, 1996). Software used to prepare material for publication: *SHELXL*97.

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Dichlorobis(pyrimidine-*N*)cobalt(II) and its bromo derivative

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Abstract

The title compounds, [$CoCl_2(C_4H_4N_2)_2$] and [$CoBr_2$-($C_4H_4N_2)_2$], show weak ferromagnetism below 5 K. The relationship between the magnetic properties and the structure is discussed. The crystals of the Cl and Br derivatives are isomorphous. The Co atom is coordinated with two halogen atoms and four N atoms of pyrimidine molecules at axial and equatorial positions, respectively, to form the octahedral geometry. The nearest neighbouring Co atoms are bridged by the pyrimidine molecules to form a three-dimensional network. As the pyrimidine molecules are considered to conduct antiferromagnetic interactions, the weak ferromagnetism may result from the chiral structure of the crystals.

Comment

Pyrimidine-bridged transition metal complexes have been studied as molecular magnets (Mitsubori, Ishida, Nogami & Iwamura, 1994; Mitsubori, Ishida, Nogami, Iwamura *et al.*, 1994; Ishida *et al.*, 1995; Oshio & Ichida, 1995; Francesconi *et al.*, 1979; Lloret *et al.*, 1998). Some Cu^{II}–pyrimidine complexes were analysed by X-rays to clarify the origin of the magnetic properties. In most of the complexes, the Cu atoms are linked together through the pyrimidine molecules to form one-dimensional chains and the magnetic properties are related to the coordination positions of the pyrimidine molecules to the Cu atoms (Ishida & Nogami, 1997; Ishida *et al.*, 1997). Recently, it was found that