We thank the Natural Sciences and Engineering Research Council, Canada, for providing the diffractometer through an equipment grant to the University of Calgary.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: FG1074). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 2279–2282

Tetrakis(μ-acetato-*O*:*O*′)bis(1,5,9-triazacyclododecane-2,4-dione-N^9)dicopper(II)(*Cu*—*Cu*)

Adam J. Clarke, Adrian J. Carmichael,
William Errington and Peter Moore

Department of Chemistry, University of Warwick, Coventry CV4 7AL, England

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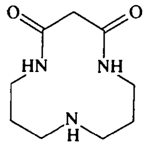
Abstract

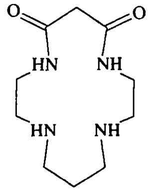
The title compound, $[Cu_2(C_2H_3O_2)_4(C_9H_{17}N_3O_2)_2]$, is centrosymmetric and consists of a tetrakis(acetato)-bridged dinuclear copper(II) core with two unidentate N-donor axial ligands, each coordinated *via* the secondary amine N atom rather than through one of the two amide N atoms. The Cu—Cu distance of 2.702 (3) Å is longer than previously reported for copper(II) acetate dimers of this type. Intermolecular hydrogen bonding occurs between the amide O and N atoms.

Comment

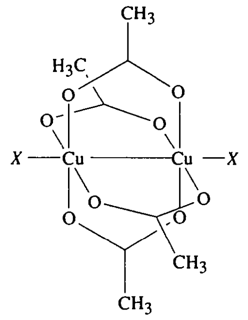
Diamine tetraaza macrocycles such as dioxocyclam, (II), have been shown (Kimura, Koike, Machida, Nagai & Kodama, 1984; Machida, Kimura & Kodama, 1983) to coordinate divalent metal cations (*e.g.* Cu^{2+}, Ni^{2+} and Co^{2+}) within the macrocyclic cavity, with simultaneous loss of the two amide protons and the formation of uncharged square-planar complexes. An objective of this work was to investigate whether the ligand 1,5,9-triazacyclododecane-2,4-dione, (I), would react in an analogous manner. The macrocycle (I) has been used previously as a precursor in the synthesis of several pendent-arm macrocyclic ligands (Helps, Parker, Jankowski, Chapman & Nicholson, 1989; Rawle, Clarke, Moore & Alcock, 1992) but its complexation characteristics have never been investigated.



(I)



(II)



(III)

The reaction of (I) with copper(II) acetate monohydrate produced the title compound (IV), the molecular structure of which is shown in Fig. 1. Clearly, the macrocycle only acts as a monodentate ligand in this complex, and has simply replaced the axial water molecules in the original acetate structure. The coordination is *via* the secondary amine N atom and the amide protons are not dissociated [*i.e.* the reaction is not analogous to those of the ligand (II)].

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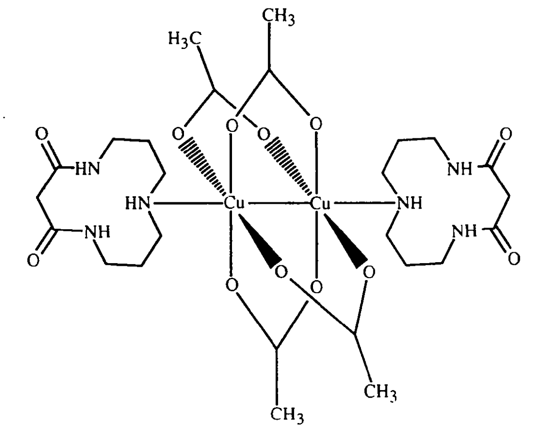

(IV)

This type of paddlewheel dimer, (III), with a variety of axial unidentate ligands (*X*) is well known, and such compounds have been studied extensively (Melnik, 1982) because of interest in their magnetic properties and in the nature of the metal–metal interaction. A survey (14 March 1995) of the structures listed in the EPSRC's Chemical Database at Daresbury (Allen *et al.*, 1991) gives a mean Cu—Cu distance of 2.618 (6) Å for 14 structures with O-donor axial ligands and 2.640 (5) Å for 17 structures with N-donor organic ligands in the axial positions. The majority of the N-donor ligands in this survey are pyridine (Barclay & Kennard, 1961; Hanic, Stempelova & Hanicova, 1964; Uekusa *et al.*, 1989; Antsyshkina, Sadikov, Porai-Koshits & Kogan, 1993) and substituted pyridines (Pavelcik & Hanic, 1978; Minacheva, Khodashova, Porai-Koshits & Tsivadze, 1981; Tsintsadze, Kiguradze, Shnulin & Mamedov, 1984; Melnik, Smolander & Sharrock, 1985; Newkome, Theriot, Gupta, Balz & Fronczek, 1986; Antsyshkina *et al.*, 1987) but also include hexamethylenetetraamine (Pickardt, 1981), benzimidazole (Bukowska-Strzyzewska, Skoweranda & Tosik, 1982), 2,4-diamino-5-(3′,4′,5′-trimethoxybenzyl)pyrimidine (Naldini *et al.*, 1984) and 2-cyanoguanidine (Begley, Hubberstey, Spittle & Walton, 1993). Thus, the Cu—Cu distance of 2.702 (3) Å in (IV) is longer than any previously reported for this type of compound. Large variations are not expected since the most important factor in controlling the Cu—Cu distance is likely to be the restricted bite associated with the bridging carboxylate groups. The Cu—N distance of 2.266 (4) Å in this complex also exceeds any previously reported for these paddlewheel complexes [mean value 2.176 (7) Å; maximum 2.240, minimum 2.125 Å].

An interesting aspect of the structure of (IV) is the intermolecular hydrogen bonding between macrocycles. The two amide O atoms in the macrocycle point 'up' and 'down', thus enabling them to form polymeric structures *via* hydrogen bonding to the NH protons in adjacent rings. The $O1\cdots N3^{i}$ and $O2\cdots N2^{ii}$ hydrogen-bonded distances are 2.875 (4) and 2.803 (4) Å, respectively [symmetry codes: (i) $1 - x, -y, -z$; (ii) $1 - x, 1 - y, -z$]; the corresponding O···H—N bond angles are 157.6 (1) and 143.0 (1) °, but are unlikely to be accurate since the H atoms were simply inserted at calculated positions.

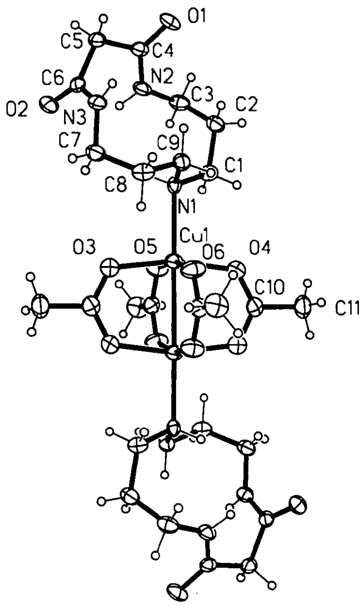

Fig. 1. View of the molecule showing the atomic numbering for the asymmetric unit. Displacement ellipsoids are drawn at the 50% probability level.

Experimental

The title compound was prepared by the reaction of 1,5,9-triazacyclododecane-2,4-dione (0.16 g, 0.80 mmol) with copper(II) acetate monohydrate (0.099 g, 0.40 mmol) in methanol (10 cm³). The reaction mixture was heated at 323 K for 18 h under dinitrogen. Upon cooling a green precipitate (0.11 g, 0.14 mmol, yield 73%) formed. Crystals were grown by slow diffusion of diethyl ether into a solution of the compound in nitromethane. The crystal was held at 200 K with the Oxford Cryosystems Cryostream Cooler (Cosier & Glazer, 1986).

Crystal data

$[Cu_2(C_2H_3O_2)_4(C_9H_{17}N_3O_2)_2]$
$M_r = 761.8$
Triclinic
$P\bar{1}$
$a = 8.568 (9)$ Å
$b = 9.333 (4)$ Å
$c = 11.972 (13)$ Å
$\alpha = 75.52 (8)°$
$\beta = 69.61 (7)°$
$\gamma = 80.45 (7)°$
$V = 865.6 (14)$ Å³
$Z = 1$
$D_x = 1.461$ Mg m^{-3}

Mo *K*α radiation
$\lambda = 0.71073$ Å
Cell parameters from 18 reflections
$\theta = 9–10°$
$\mu = 1.293$ mm^{-1}
$T = 200 (2)$ K
Rectangular block
0.51 × 0.19 × 0.14 mm
Blue

Data collection

Siemens *P*3*R*3 diffractometer
ω–2θ scans
Absorption correction:
  Gaussian (Alcock, 1970)
  $T_{\min} = 0.81$, $T_{\max} = 0.85$
2953 measured reflections
2733 independent reflections
2333 observed reflections
  $[I > 2\sigma(I)]$

$R_{\rm int} = 0.0237$
$\theta_{\max} = 25.06°$
$h = -10 \rightarrow 0$
$k = -11 \rightarrow 10$
$l = -14 \rightarrow 13$
3 standard reflections
  monitored every 200
    reflections
  intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0358$
$wR(F^2) = 0.0863$
$S = 1.068$
2721 reflections
210 parameters
H-atom parameters not
  refined
$w = 1/[\sigma^2(F_o^2) + (0.034P)^2$
  $+ 1.68P]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.48$ e Å^{-3}
$\Delta\rho_{\min} = -0.87$ e Å^{-3}
Extinction correction: none
Atomic scattering factors
  from *International Tables*
  for Crystallography (1992,
  Vol. C, Tables 4.2.6.8 and
  6.1.1.4)

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

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

	x	y	z	$U_{\rm eq}$
Cu1	0.06554 (6)	0.43495 (4)	0.40273 (3)	0.0247 (2)
O1	0.4171 (4)	0.1025 (3)	−0.1209 (2)	0.0334 (6)
O2	0.6770 (4)	0.4209 (3)	−0.0313 (2)	0.0363 (7)
O3	0.2748 (4)	0.5252 (3)	0.3814 (2)	0.0347 (6)
O4	−0.1664 (4)	0.3704 (3)	0.4547 (2)	0.0407 (7)
O5	−0.0099 (4)	0.6245 (3)	0.3073 (2)	0.0337 (6)
O6	0.1139 (4)	0.2688 (3)	0.5299 (2)	0.0379 (7)
N1	0.1808 (4)	0.3156 (3)	0.2458 (2)	0.0209 (6)
N2	0.3540 (4)	0.3187 (3)	−0.0540 (2)	0.0268 (7)
N3	0.6239 (4)	0.2022 (3)	0.1052 (3)	0.0269 (7)
C1	0.0396 (5)	0.3030 (4)	0.2032 (3)	0.0283 (8)
C2	0.0746 (5)	0.2364 (4)	0.0899 (3)	0.0293 (8)
C3	0.1735 (5)	0.3278 (4)	−0.0332 (3)	0.0300 (8)
C4	0.4626 (5)	0.2063 (3)	−0.0939 (3)	0.0239 (8)
C5	0.6467 (5)	0.2107 (4)	−0.1038 (3)	0.0273 (8)
C6	0.6547 (4)	0.2863 (4)	−0.0068 (3)	0.0252 (8)
C7	0.5674 (5)	0.2635 (4)	0.2163 (3)	0.0298 (8)
C8	0.4247 (5)	0.1785 (4)	0.3155 (3)	0.0295 (8)
C9	0.2720 (5)	0.1693 (4)	0.2771 (3)	0.0257 (8)
C10	−0.2820 (5)	0.3958 (4)	0.5486 (3)	0.0284 (8)
C11	−0.4456 (6)	0.3253 (5)	0.5810 (4)	0.0417 (10)
C12	0.0792 (5)	0.2673 (4)	0.6415 (3)	0.0267 (8)
C13	0.1267 (6)	0.1237 (4)	0.7200 (4)	0.0400 (10)

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

Cu1—O6	1.985 (3)	O5—C12$^{\rm i}$	1.267 (4)
Cu1—O5	1.994 (3)	O6—C12	1.260 (4)
Cu1—O4	2.012 (4)	N1—C9	1.486 (4)
Cu1—O3	2.016 (4)	N1—C1	1.498 (5)
Cu1—N1	2.266 (4)	N2—C4	1.346 (4)
Cu1—Cu1$^{\rm i}$	2.702 (3)	N2—C3	1.470 (5)
O1—C4	1.251 (4)	N3—C6	1.334 (5)
O2—C6	1.248 (4)	N3—C7	1.473 (4)
O3—C10$^{\rm i}$	1.268 (4)	C10—C11	1.533 (6)
O4—C10	1.258 (5)	C12—C13	1.517 (5)
O6—Cu1—O5	166.81 (10)	O4—Cu1—O3	166.99 (10)
O6—Cu1—O4	88.67 (15)	N1—Cu1—Cu1$^{\rm i}$	176.99 (7)
O5—Cu1—O4	88.74 (15)	O4—C10—O3$^{\rm i}$	125.7 (4)
O6—Cu1—O3	90.30 (14)	O6—C12—O5$^{\rm i}$	125.6 (3)
O5—Cu1—O3	89.32 (14)		

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

H atoms were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms; each H atom was given an isotropic displacement parameter equal to 1.2 (1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of the C or N atom to which it is attached. Refinement was on F^2 for all reflections except for 12 with very negative F^2 or flagged by the user for potential systematic errors.

Data collection: Siemens *P*3*R*3 system. Cell refinement: Siemens *P*3*R*3 system. Data reduction: *SHELXTL-Plus* (Sheldrick, 1991). Program(s) used to solve structure: *SHELXTL-Plus*. Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993).

We wish to acknowledge the use of the EPSRC Chemical Database Service at Daresbury, the mass spectrometry service at Swansea, and the EPSRC for provision of X-ray facilities.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1015). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 2282–2285

Bis(acetato-*O*)bis(urea-*O*)zinc(II), $[Zn(H_2NCONH_2)_2(CH_3COO)_2]$

Ogei Yar and Leslie Lessinger

Department of Chemistry, Barnard College, New York, NY 10027-6598, USA

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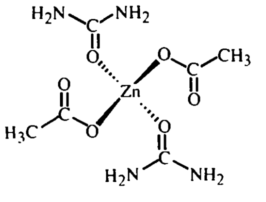
Abstract

The title molecular complex, $[Zn(C_2H_3O_2)_2(CH_4N_2O)_2]$, crystallized from an aqueous solution of urea and zinc acetate in a 2:1 ratio. Zn^{II} is coordinated by four O atoms in a systematically distorted tetrahedral arrangement, while the complex as a whole has an approximate twofold rotation axis. Each urea ligates *via* its carbonyl O atom, while each acetate is monodentate. Each non-ligating carbonyl O atom of the acetate ligands accepts an intramolecular hydrogen bond from urea. Intermolecular hydrogen bonds give rise to a layer structure, with the layers stacked by van der Waals attractions only.

Comment

Homogeneous precipitation of substances insoluble in basic solution, accomplished by the decomposition of urea to NH_3 and CO_2, is a well known technique used for the preparation of various insoluble basic salts of transition metals, including some salts containing Zn^{II} and acetate. One such experiment, however, starting with a 2:1 ratio of urea to zinc acetate, in almost saturated aqueous solution, yielded crystals which were soluble in water. IR and NMR spectral evidence indicated the probable presence of urea as well as acetate ligands. The density of the crystal and its unit-cell parameters gave a likely formula of $[Zn(H_2NCONH_2)_2(CH_3COO)_2]$, (I), which was confirmed by the present X-ray structure determination.



(I)

The title molecular complex, (I) (Fig. 1), has Zn^{II} coordinated by four O atoms in a systematically distorted tetrahedral arrangement, while the complex as a whole has an approximate twofold rotation axis. The degree of distortion from a regular tetrahedron is severe, with O—Zn—O angles ranging from 89.5 to 126.8° (see Table 2).

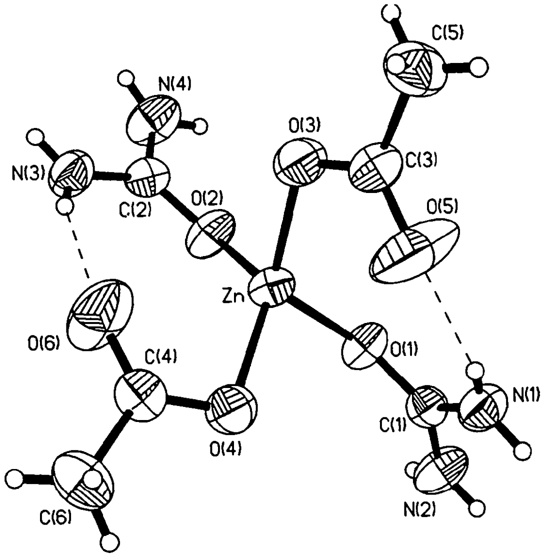


Fig. 1. The title molecular complex, viewed down its approximate twofold axis, showing 50% probability displacement ellipsoids.

In (I), urea binds as a monodentate ligand through its carbonyl O atom, as is also seen in hexakis(urea)zinc(II) nitrate (van de Giesen & Stam, 1972). The title complex is a neutral tetrahedral molecular complex and the urea O—Zn distances [1.997 (2) and 1.994 (2) Å] are significantly shorter than the three independent O—Zn distances in the octahedral $[Zn(urea)_6]^{2+}$ cation [2.147 (2), 2.073 (3) and 2.091 (3) Å]. However, the urea–Zn–urea O—Zn—O angle of 89.5 (1)° in (I) is intermediate in the range 84.6–96.5° for the seven independent O—Zn—O angles in the hexakis(urea)zinc ion. Moreover, in both complexes, urea binds with a characteristic C═O···Zn angle, *i.e.* in (I), 128.0 (2) and 130.4 (2)°, and in the hexakis(urea)zinc(II) ion,