

A heterotrimetallic Cu–Co–Zn complex with the 2,2'-iminodiethanol ligand

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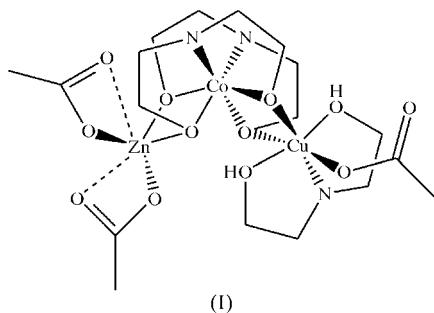
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The crystal structure of the title compound, triacetato-1 κ O;-3 κ^4 O,-O'-(2,2'-iminodiethanol)-1 κ^3 O,N,O'-bis(μ -2,2'-iminodiethanolato)-1 κ^2 O:2 κ^6 O,N,O':3 κ^2 O'-cobalt(III)copper(II)-zinc(II), [CoCuZn(C₄H₉NO₂)₂(C₂H₃O₂)₃(C₄H₁₁NO₂)], shows a molecule with a triangular three-metal core. The metal sites were refined with full occupancies, but the possibility that the Zn and Cu positions are actually mixed Cu/Zn sites cannot be excluded. The intermetallic Cu···Co and Co···Zn distances are 2.924 (3) and 2.906 (3) Å, respectively. The neutral molecules are held together by N–H···O hydrogen bonds involving amine groups from the 2,2'-iminodiethanol ligands and acetate groups to build two-dimensional layers.

Comment

The coordination chemistry of heterometallic complexes of transition metals is currently an active and rapidly expanding research area. Special effort has been focused on the



preparation and characterization of heterotrimetallic complexes, for example, Cu/Co/Ni (Nesterov *et al.*, 2004), Cu/Fe/Gd (Gheorghie *et al.*, 2003) or Co/Fe/Ni (Berlinguette & Dunbar, 2005). Such interest is a result of the many potential applications of these complexes as, for instance, molecular

magnets (Liu *et al.*, 2004; Verani *et al.*, 2000) or catalysts (Becker *et al.*, 2001). We have recently reported the first Cu/Co/Zn heterotrimetallic complexes, containing a trinuclear CuCoZnO₄ core, which could be viewed as a distorted cube in which one corner site is vacant (Nesterov *et al.*, 2005). We report here the preparation and crystal structure of the new heterotrimetallic complex [CuCoZn(L)₂(H₂L)(OAc)₃] (L is 2,2'-iminodiethanol), (I), of a different type; the trinuclear CuCoZnO₁₁N₃ core now represents a triangle with a Cu···Co···Zn angle of 107.6 (1)° (Fig. 1). The metal atoms are bridged through the O atoms from the deprotonated 2,2'-iminodiethanol ligand (H₂L). A similar molecular geometry was observed in the Cu/Co/Cd compound having the same ligand (Nesterov *et al.*, 2004) but different anions.

Selected bond distances are given in Table 1. The Cu atom is in an O₅N tetragonally distorted octahedral environment with

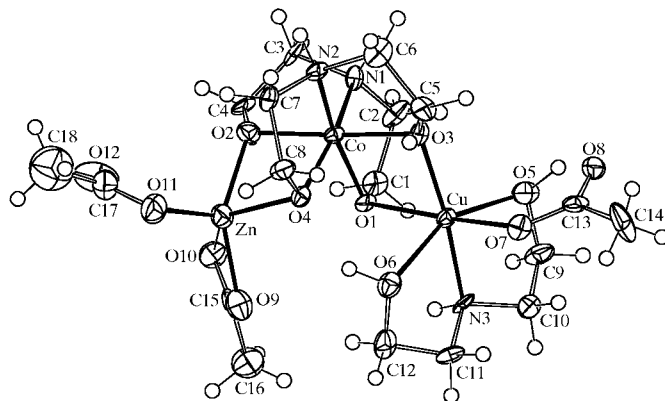


Figure 1

The structure of (I), showing the atomic numbering scheme. Non-H atoms are shown as 50% probability displacement ellipsoids.

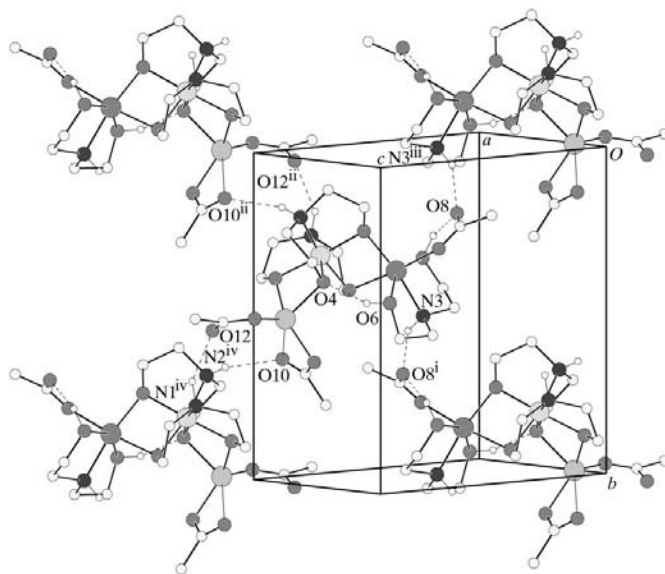


Figure 2

The hydrogen-bonding scheme of (I). The H atoms of the CH₂ groups have been omitted for clarity. [Symmetry codes: (i) $-x + 1, y + \frac{1}{2}, -z + 1$; (ii) $-x + 2, y - \frac{1}{2}, -z + 2$; (iii) $-x + 1, y - \frac{1}{2}, -z + 1$; (iv) $-x + 2, y + \frac{1}{2}, -z + 2$.]

axial lengths equal to 2.595 (15) and 2.345 (14) Å (atoms O5 and O6, respectively). One of the equatorial positions is occupied by the O atom of an acetate anion. The Co atom has an almost regular octahedral arrangement, with Co—O(N) distances ranging from 1.884 (10) to 1.943 (15) Å and *trans*-angles ranging from 167.5 (5) to 177.4 (5)°. Such geometry is typical of a six-coordinated low-spin cobalt(III) ion (Wells, 1986). The Zn atom displays a distorted tetrahedral environment with an O₄ chromophore. The two acetate groups coordinating to Zn exhibit monodentate coordination. However, considering the Zn—O10 and Zn—O12 distances [2.491 (16) and 2.780 (17) Å, respectively], the presence of weak bonding between the metal atom and uncoordinated acetate O atoms can be presumed.

The molecules form a two-dimensional network involving H atoms from the 2,2'-iminodiethanol ligands (Fig. 2). Atom O8 participates in both inter- (O5—H5O···O8) and intramolecular (N3—H3···O8ⁱⁱ) hydrogen-bond contacts (see Table 2). Two other intermolecular hydrogen bonds involve amine and acetate groups.

Experimental

For the preparation of the title compound, copper powder (0.16 g, 2.5 mmol), Co(OAc)₂·4H₂O (0.62 g, 2.5 mmol), Zn(OAc)₂·2H₂O (0.55 g, 2.5 mmol), dimethyl sulfoxide (20 ml) and 2,2'-iminodiethanol (2 ml) were heated to 323–333 K and stirred magnetically until total dissolution of the copper was observed (1 h). Dark-green crystals suitable for X-ray analysis were obtained from the dark-green solution after successive addition of an isopropanol–diethyl ether (1:3) mixture. The crystals were filtered off, washed with dry isopropanol and finally dried *in vacuo* at room temperature [yield 0.9 g, 53% (per copper)]. Analysis found: C 31.7, H 5.5, Co 8.6, Cu 9.0, N 6.2, Zn 9.9%; calculated: C 31.96, H 5.66, Co 8.71, Cu 9.39, N 6.21, Zn 9.67%. IR (KBr, cm⁻¹): 1600 [$\nu_{\text{as}}(\text{COO})$], 1580 [$\nu_{\text{as}}(\text{COO})$], 1455 [$\nu_{\text{s}}(\text{COO})$].

Crystal data

| | |
|---|---|
| [CoCuZn(C ₄ H ₉ NO ₂) ₂ ·(C ₂ H ₃ O ₂) ₃ (C ₄ H ₁₁ NO ₂)] | $V = 1295.8 (7) \text{ \AA}^3$ |
| $M_r = 676.45$ | $Z = 2$ |
| Monoclinic, $P2_1$ | $D_x = 1.734 \text{ Mg m}^{-3}$ |
| $a = 8.353 (3) \text{ \AA}$ | Mo $K\alpha$ radiation |
| $b = 12.357 (4) \text{ \AA}$ | $\mu = 2.43 \text{ mm}^{-1}$ |
| $c = 12.934 (4) \text{ \AA}$ | $T = 150 (2) \text{ K}$ |
| $\beta = 103.916 (5)^\circ$ | Fragment, dark green |
| | $0.14 \times 0.09 \times 0.06 \text{ mm}$ |

Data collection

| | |
|---|--|
| Bruker SMART CCD diffractometer | 11690 measured reflections |
| ω scans | 5068 independent reflections |
| Absorption correction: multi-scan (SADABS; Sheldrick, 1996) | 3927 reflections with $I > 2\sigma(I)$ |
| $T_{\text{min}} = 0.62$, $T_{\text{max}} = 0.86$ | $R_{\text{int}} = 0.062$ |
| | $\theta_{\text{max}} = 26.3^\circ$ |

Refinement

| | |
|---------------------------------|--|
| Refinement on F | $w = 1/[\sigma^2(F) + 0.001F^2]$ |
| $R[F^2 > 2\sigma(F^2)] = 0.065$ | $(\Delta/\sigma)_{\text{max}} = 0.001$ |
| $wR(F^2) = 0.092$ | $\Delta\rho_{\text{max}} = 1.07 \text{ e \AA}^{-3}$ |
| $S = 1.33$ | $\Delta\rho_{\text{min}} = -0.74 \text{ e \AA}^{-3}$ |
| 3927 reflections | Absolute structure: Flack (1983), |
| 316 parameters | 2328 Friedel pairs |
| H-atom parameters not refined | Flack parameter: 0.05 (5) |

Table 1
Selected bond lengths (Å).

| | | | |
|--------|------------|-------|------------|
| Zn—O2 | 1.954 (12) | Cu—O6 | 2.345 (14) |
| Zn—O4 | 2.099 (11) | Cu—O7 | 2.000 (11) |
| Zn—O9 | 1.964 (14) | Cu—N3 | 2.041 (16) |
| Zn—O10 | 2.491 (16) | Co—O1 | 1.905 (11) |
| Zn—O11 | 1.990 (14) | Co—O2 | 1.910 (11) |
| Zn—O12 | 2.780 (17) | Co—O3 | 1.884 (10) |
| Cu—O1 | 2.034 (10) | Co—O4 | 1.917 (12) |
| Cu—O3 | 1.950 (12) | Co—N1 | 1.915 (14) |
| Cu—O5 | 2.595 (15) | Co—N2 | 1.943 (15) |

Table 2
Hydrogen-bond geometry (Å, °).

| $D-H\cdots A$ | $D-H$ | $H\cdots A$ | $D\cdots A$ | $D-H\cdots A$ |
|---------------------------|-------|-------------|-------------|---------------|
| O6—H6O···O4 | 0.93 | 1.86 | 2.631 (16) | 139 |
| O5—H5O···O8 | 0.93 | 1.95 | 2.625 (18) | 128 |
| N1—H1···O12 ⁱⁱ | 0.94 | 2.07 | 2.92 (2) | 150 |
| N2—H2···O10 ⁱⁱ | 0.93 | 2.19 | 3.02 (2) | 148 |
| N3—H3···O8 ⁱ | 0.94 | 2.11 | 2.95 (2) | 148 |

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

In general, the non-H atoms were refined anisotropically. The assignment of Cu and Co atoms was largely achieved on refinement and coordination geometry. The third metal atom was assigned as Zn from the analytical data. It has a distorted tetrahedral environment with two longer bonds to the other two O atoms (O10 and O12) of the acetate groups. This geometry is unusual not only for zinc but also for copper. Although elemental analysis suggested the absence of metal scrambling within the molecule, taking into account the refinement, the possibility that both the Zn and the Cu positions are mixed Cu/Zn sites cannot be excluded. Two 2,2'-iminodiethanol ligands have both O atoms bridging and hence the —OH groups were assigned as deprotonated. From the interatomic distances in the O6···O4 and O5···O8 atom pairs [2.631 (16) and 2.625 (18) Å, respectively], two strong intramolecular hydrogen bonds (O6—H6O···O4 and O5—H5O···O8) can be identified; the H atoms were located on atoms O5 and O6. Other H atoms were initially placed at idealized positions [$C-H = 0.95 \text{ \AA}$, $U_{\text{iso}}(\text{H}) = 1.25U_{\text{eq}}(\text{C})$ for CH₂ and $1.5U_{\text{eq}}(\text{C})$ for CH₃] and not refined. The C—O bonds of the acetate ligands are indicative of carboxylate but not carboxylic acid groups [C—O bonds range from 1.21 (3) to 1.30 (3) Å]. Acetate atom C18 was refined with isotropic displacement parameters. Attempts to refine this atom as disordered did not improve the model. All bond distances and angles within the 2,2'-iminodiethanol and acetate ligands are as expected.

Data collection: SMART (Siemens, 1995); cell refinement: SAINT (Siemens, 1995); data reduction: SAINT; program(s) used to solve structure: Xtal3.5 (Hall *et al.*, 1995); program(s) used to refine structure: CRYLSQ in Xtal3.5; molecular graphics: Xtal3.5; software used to prepare material for publication: BONDLA and CIFIO in Xtal3.5.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BG1028). Services for accessing these data are described at the back of the journal.

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