metal-organic compounds

catena-Poly[[trans-bis(ethane-1,2-diamine-κ²N,N′)copper(II)]-μ-dithionato-κ²O:O′] and trans-diaquabis-(propane-1,3-diamine-κ²N,N′)-copper(II) dithionate

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In title anhydrous *catena*-poly[[*trans*-bis(ethane-1,2-diamine-κ^2N,N')copper(II)]-μ-dithionato-$\kappa^2O:O'$], [Cu(S$_2$O$_6$)(C$_2$H$_8$N$_2$)$_2$]$_n$ or [{H$_2$N(CH$_2$)$_2$NH$_2$}$_2$Cu(O·O$_2$SSO$_2$·O)]$_\infty$, successive Cu atoms are bridged by a single doubly charged dithionate group, forming a one-dimensional polymer with inversion centres at the metal atoms and the mid-point of the S—S bond [Cu—O = 2.5744 (15) Å]. In title (hydrated) *trans*-diaquabis-(propane-1,3-diamine-κ^2N,N')copper(II) dithionate, [Cu-(C$_3$H$_{10}$N$_2$)$_2$(H$_2$O)$_2$](S$_2$O$_6$) or [{H$_2$N(CH$_2$)$_3$NH$_2$}$_2$Cu(OH$_2$)$_2$]-(S$_2$O$_6$), both ions have imposed 2/*m* symmetry. The 'axial' anion components are displaced by a pair of water ligands [Cu—O = 2.439 (3) Å], the shorter Cu—O distance being compensated by the lengthened Cu—N distance [2.0443 (18), *cf.* 2.0100 (13) and 2.0122 (16) Å].
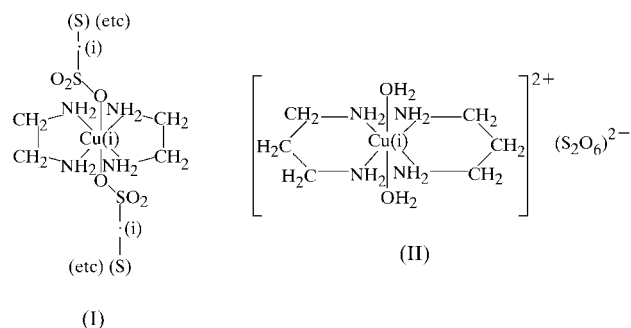
Comment

Copper(II) in the presence of the dithionate counter-ion crystallizes from an aqueous solution of ethane-1,2-diamine to yield an anhydrous complex *catena*-poly[[*trans*-bis(ethane-1,2-diamine-κ^2N,N')copper(II)]-μ-dithionato-$\kappa^2O:O'$], (I); the propane-1,3-diamine counterpart is a dihydrate, *viz.* *trans*-diaquabis(propane-1,3-diamine-κ^2N,N')copper(II) dithionate, (II). In both cases, the Cu atom lies on a crystallographic inversion centre [the actual symmetry in (II) is 2/*m*] in a typical (Melník *et al.*, 1998) *trans* six-coordinate Cu(II)(N$_2$)$_2$O$_2$ environment.
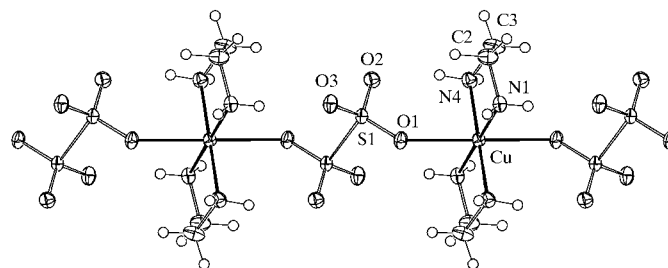
In (I), the *trans* O-atom donors form successive ends of the doubly charged dithionate anion ($^-$O·O$_2$SSO$_2$·O$^-$), linking successive translation-related Cu atoms into a single-stranded polymer parallel to *c*, with inversion centres also lying at the centres of the S—S bonds (Fig. 1). The Cu—N distances are
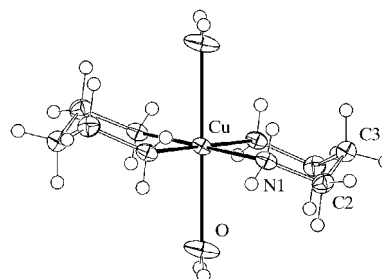
2.0100 (13) and 2.0122 (16) Å, the Cu—O distance is 2.5744 (15) Å, and the Cu—O—S angle is 125.84 (7)°, the coordinated O—S distance being comparable to the uncoordinated distance (Table 1). Both ligand conformations are necessarily the same and of the $\delta\lambda$ form, with quasi-twofold symmetry about the line through the C—C bonds, the angles in the chelate rings (outwardly from the Cu atom) being 12.7 (4), 15.7 (2), −38.1 (2), −40.5 (2) and 52.2 (3)°. Hydrogen bonds from the amine groups to the anions are detailed in Table 2.

Compound (II) (Fig. 2), by contrast, is a dihydrate in which a pair of aqua ligands now coordinate in the *trans* monodentate sites, supplanting the anionic moieties so that the complex is now ionic rather than polymeric; both the anion and the cation are centrosymmetric. In (II), the Cu—N distances increases to 2.0443 (18) Å (Table 3), compensating the shorter Cu—O distance [2.439 (3) Å] associated with the stronger O-atom donor; this distance is appreciably shorter

Figure 1
A projection of a section of the polymer of (I). Displacement ellipsoids are shown at the 50% probability level and H atoms are shown as circles of arbitrary radii (0.1 Å) (also for Fig. 2).

Figure 2
A projection of the cation of (II).

than those recorded for other examples of this cation that are also centrosymmetric [2.637 (6) (Emsley *et al.*, 1988), 2.587 (8) and 2.555 (7) (Sundberg & Klinga, 1994), and 2.618 (2) Å (Sundberg & Uggla, 1997)]. The water H atoms form hydrogen bonds with O atoms in the anion [H···O = 2.08 (4) Å; Table 4]. The O-atom environment is planar, but, in the present circumstances, the elongated displacement envelope of the O atom may be a foil for unresolved disorder or off-axis displacement. The chelate rings are of the low-energy C_3-chair form (Niketic *et al.*, 1976); the torsion angles (outward from the Cu atom) are −22.5 (2), 47.7 (3) and −72.8 (3)°.

Experimental

The title complexes (which appear to be new) were prepared from aqueous solutions of copper(II) chloride with two equivalents of the appropriate diamine (ethane-1,2-diamine or propane-1,2-diamine dihydrate), by the addition of lithium dithionate solutions. Crystals were deposited after slow evaporation under ambient conditions. For (I), analysis found: C 14.3, H 5.2, N 16.1%; $C_4H_{16}CuN_4O_6S_2$ requires: C 13.97, H 4.69, N 16.29%. For (II), analysis found: C 18.2, H 6.1, N 13.5%; $C_6H_{24}CuN_4O_8S_2$ requires: C 17.67, H 5.93, N 13.7%.

Compound (I)

Crystal data

$[Cu(S_2O_6)(C_2H_8N_2)_2]$	$D_x = 1.812$ Mg m^{-3}
$M_r = 343.87$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 3259
$a = 8.4727$ (10) Å	reflections
$b = 10.2699$ (10) Å	$\theta = 2.5$–28.2°
$c = 8.0696$ (10) Å	$\mu = 2.09$ mm^{-1}
$\beta = 116.170$ (2)°	$T = 150$ (2) K
$V = 630.19$ (12) Å^3	Prism, purple
$Z = 2$	0.10 × 0.05 × 0.04 mm

Data collection

Bruker SMART CCD	1608 independent reflections
diffractometer	1441 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.023$
Absorption correction: multi-scan	$\theta_{max} = 29.2°$
(*SADABS*; Sheldrick, 1996)	$h = -11 \rightarrow 10$
$T_{min} = 0.809$, $T_{max} = 0.928$	$k = -14 \rightarrow 14$
6260 measured reflections	$l = -10 \rightarrow 10$

Refinement

Refinement on F	All H-atom parameters refined
$R = 0.023$	$w = 1/[\sigma^2(F) + 0.0004F^2]$
$wR = 0.031$	$(\Delta/\sigma)_{max} = 0.014$
$S = 1.1$	$\Delta\rho_{max} = 0.57$ e Å^{-3}
1441 reflections	$\Delta\rho_{min} = -0.41$ e Å^{-3}
111 parameters	

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

Cu—N1	2.0100 (13)	Cu—O1	2.5744 (15)
Cu—N4	2.0122 (16)		
N1—Cu—N4	85.02 (6)	Cu—N1—C2	108.81 (11)
N1—Cu—O1	87.64 (6)	Cu—N4—C3	108.05 (12)
N4—Cu—O1	93.78 (6)		

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4B···O2	0.92 (2)	2.09 (3)	2.980 (2)	162 (2)
N1—H1A···O3^i	0.85 (3)	2.15 (3)	2.993 (2)	174 (2)
N1—H1B···O3^{ii}	0.90 (2)	2.13 (2)	3.025 (2)	173 (2)
N4—H4A···O2^{iii}	0.88 (2)	2.20 (2)	2.997 (2)	152 (2)

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

Compound (II)

Crystal data

$[Cu(C_3H_{10}N_2)_2(H_2O)_2](S_2O_6)$	Mo $K\alpha$ radiation
$M_r = 407.96$	Cell parameters from 3669
Orthorhombic, $Pnnm$	reflections
$a = 15.500$ (2) Å	$\theta = 2.4$–28.2°
$b = 7.098$ (1) Å	$\mu = 1.68$ mm^{-1}
$c = 7.224$ (1) Å	$T = 150$ (2) K
$V = 794.78$ (19) Å^3	Plate, blue
$Z = 2$	0.40 × 0.40 × 0.09 mm
$D_x = 1.705$ Mg m^{-3}	

Data collection

Bruker SMART CCD	1104 independent reflections
diffractometer	1002 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.040$
Absorption correction: multi-scan	$\theta_{max} = 29.0°$
(*SADABS*; Sheldrick, 1996)	$h = -20 \rightarrow 20$
$T_{min} = 0.605$, $T_{max} = 0.894$	$k = -9 \rightarrow 9$
7799 measured reflections	$l = -9 \rightarrow 9$

Refinement

Refinement on F	All H-atom parameters refined
$R = 0.035$	$w = 1/[\sigma^2(F) + 0.0003F^2]$
$wR = 0.041$	$(\Delta/\sigma)_{max} = 0.017$
$S = 1.21$	$\Delta\rho_{max} = 1.14$ e Å^{-3}
1002 reflections	$\Delta\rho_{min} = -0.88$ e Å^{-3}
82 parameters	

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

Cu—O	2.439 (3)	Cu—N1	2.0443 (18)
O—Cu—N1	86.75 (8)	Cu—N1—C2	122.03 (14)
N1—Cu—N1^{iv}	93.50 (7)		

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

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

D—H···A	D—H	H···A	D···A	D—H···A
O—H···O1^v	0.79 (4)	2.08 (4)	2.854 (2)	167 (3)
N1—H1B···O2^v	0.86 (3)	2.25 (3)	3.108 (2)	176 (3)
N1—H1A···O1^{vi}	0.85 (3)	2.31 (3)	3.080 (3)	151 (2)
N1—H1B···O2^{vii}	0.86 (3)	2.25 (3)	3.108 (3)	176 (3)

Symmetry codes: (v) $-x, 2 - y, z$; (vi) $-x, 1 - y, z$; (vii) $-x, 2 - y, -z$.

H atoms were located from difference Fourier maps and placed at idealized positions (C—H = 0.95 Å), and then their positional parameters and U_{iso} values were refined.

metal-organic compounds

For both title compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *Xtal*3.5 *User's Manual* (Hall *et al.*, 1995); program(s) used to solve structure: *Xtal*3.5 *User's Manual*; program(s) used to refine structure: *CRYLSQ* in *Xtal*3.5 *User's Manual*; molecular graphics: *Xtal*3.5 *User's Manual*; software used to prepare material for publication: *BONDLA* and *CIFIO* in *Xtal*3.5 *User's Manual*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1422). Services for accessing these data are described at the back of the journal.

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