Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

The co-crystal tetraaquabis(2-oxido-3,5-dinitrobenzoato)bis(2-oxido-3,5-dinitrobenzoic acid)tricopper–diaquabis(2-hydroxy-3,5-dinitrobenzoato)-(2-oxido-3,5-dinitrobenzoic acid)copper–water (0.54/0.92/4): a reformulation?

Jian-Rong Su* and Duan-Jun Xu

Department of Chemistry, Zhejiang University, People's Republic of China

Correspondence e-mail: sujr2401@hotmail.com

Received 8 June 2005
Accepted 1 July 2005
Online 9 July 2005

In the title compound, $[Cu_3(C_7H_3N_2O_7)_2(C_7H_2N_2O_7)_2(H_2O)_4]_{0.54}[Cu(C_7H_3N_2O_7)_2(H_2O)_2]_{0.92}\cdot 4H_2O$, the Cu^{II} ion located on an inversion centre has a fractional site occupancy of 0.54. When this Cu^{II} ion is present, a trinuclear complex also involving two adjacent Cu^{II} ions arises; when it is not, then the result is two discrete mononuclear complexes. A very similar structure was reported previously by Valigura, Melnık, Koman, Martiŝka, Korabik, Mroziński & Glowiak [*Inorg. Chem. Commun.* (2004), **7**, 548–552]. However, in their material, arising from a different synthesis, the Cu^{II} ion with $\overline{1}$ site symmetry is fully occupied, and thus only a trinuclear complex is formed. Here, the mononuclear Cu^{II} complex assumes a square-pyramidal coordination geometry, formed by two water molecules and two 3,5-dinitrosalicylate anions, one of which is monodentate and the other bidentate.

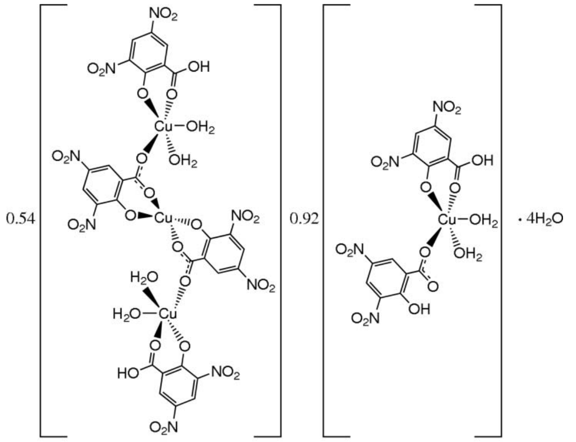
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.039
wR factor = 0.097
Data-to-parameter ratio = 10.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

The structures and properties of multinuclear complexes have attracted much scientific attention, due to their potentially useful electronic or magnetic properties (Holton *et al.*, 1983). As part of our investigations of multinuclear complexes (Su & Xu, 2005), the title compound, (I) (Figs. 1 and 2), has been prepared and its crystal structure is presented here. We interpret it as a co-crystal of two differerent types of Cu complex.



(I)

The Cu1 atom of $\overline{1}$ site symmetry in (I) has a fractional site occupancy of 0.54. When Cu1 is present, a centrosymmetric trinuclear Cu^{II} complex (Fig. 1) also involving two nearby Cu2 species arises. When Cu1 is absent, then a mononuclear complex containing Cu2 (Fig. 2) is the result. The ligand molecule containing atom C11 is bridging in the trinuclear complex and terminal (to Cu2) in the mononuclear complex.

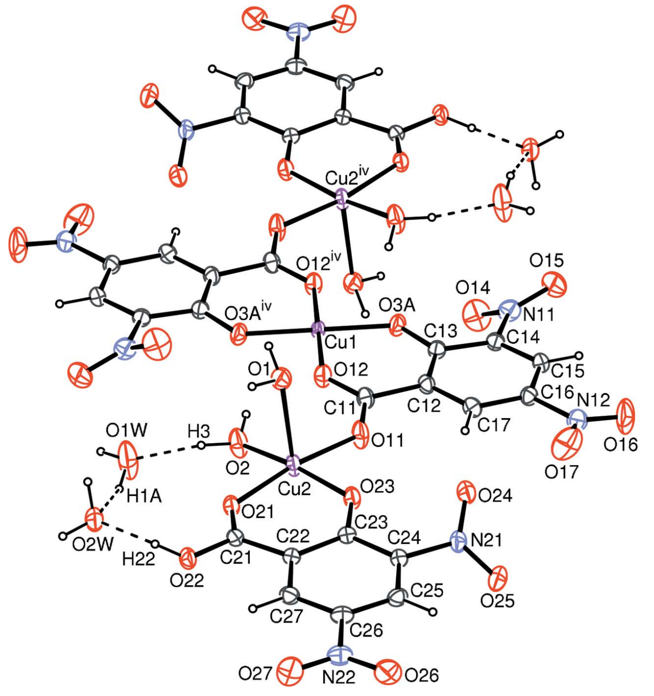


Figure 1

The centrosymmetric trinuclear Cu^{II} complex obtained when atom Cu1 is present [symmetry code: (iv) $-x$, $1 - y$, $1 - z$]. Dashed lines indicate hydrogen bonding. Displacement ellipsoids are drawn at the 30% probability level.

A very similar structure was reported previously by Valigura *et al.* (2004*a*). However, in their study, the Cu1 site is fully occupied, and only a trinuclear complex is present. It should be noted that the syntheses are different: the present study began from a 1:1 molar ratio of Cu and 3,5-dinitrosalicylic acid in the presence of sodium carbonate, while Valigura *et al.* (2004*b*) began from a 1:2 Cu:ligand ratio without any added base. Analytical data from Valigura *et al.* (2004*b*) support the existence of the trinuclear complex (*i.e.* the Cu1 site fully occupied) and their structure does not show any anomalous atomic displacement parameters that might correlate with unmodelled partial site occupancies for some of the atoms.

The structure of the trinuclear complex in (I) is the same as that reported previously. In the mononuclear complex, the Cu2 atom is coordinated by two water molecules and two 3,5-dinitrosalicylate anions, one monodentate and one bidentate, resulting in a square-pyramidal coordination geometry. The hydroxy group of the phenolate monoanion is disordered and occupies two positions (Fig. 2). Both disordered hydroxy groups form O—H$\cdots$O hydrogen-bond interactions (Table 2). Because of the complex disorder in this co-crystal, some of the H-atom positions and partial site occupancies should be regarded as tentative.

Experimental

All reagents were of analytical grade and used as received. $CuCl_2{\cdot}2H_2O$ (0.17 g, 1 mmol), 3,5-dinitrosalicylic acid (0.25 g, 1 mmol) and Na_2CO_3 (0.05 g, 0.5 mmol) were dissolved in water (10 ml). The solution was refluxed for 5 h, then cooled to room temperature and filtered. Slow evaporation of the resulting filtrate yielded dark-green single crystals of (I) after 6 d.

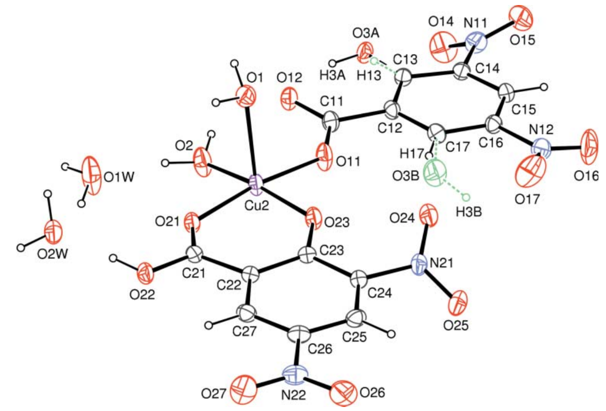


Figure 2

The mononulear Cu^{II} complex obtained when atom Cu1 is not present. Dashed lines show the minor disordered component. Displacement ellipsoids are drawn at the 30% probability level.

Crystal data

$[Cu_3(C_7H_3N_2O_7)_2(C_7H_2N_2O_7)_2\text{-}(H_2O)_4]_{0.54}[Cu(C_7H_3N_2O_7)_2\text{-}(H_2O)_2]_{0.92}{\cdot}4H_2O$
$M_r = 1212.89$
Monoclinic, $P2_1/c$
$a = 10.8491$ (3) Å
$b = 14.2301$ (3) Å
$c = 13.3928$ (3) Å
$\beta = 94.671$ (1)°
$V = 2060.76$ (9) Å^3
$Z = 2$
$D_x = 1.955$ Mg m^{-3}
$D_x = 1.935$ Mg m^{-3}, measured by flotation in $CH_2BrCH_2Br–CCl_4$
Mo $K\alpha$ radiation
Cell parameters from 11957 reflections
$\theta = 2.9–24.2°$
$\mu = 1.44$ mm^{-1}
$T = 295$ (2) K
Block, dark green
0.30 × 0.28 × 0.15 mm

Data collection

Rigaku R-AXIS RAPID diffractometer
ω scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.647$, $T_{max} = 0.802$
16047 measured reflections
3725 independent reflections
3466 reflections with $I > 2\sigma(I)$
$R_{int} = 0.025$
$\theta_{max} = 25.2°$
$h = -13 \rightarrow 13$
$k = -17 \rightarrow 16$
$l = -15 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.097$
$S = 1.20$
3725 reflections
349 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0308P)^2 + 3.2758P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.44$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

Cu1—O12	1.975 (2)	Cu2—O11	1.946 (2)
Cu1—O3*A*	1.845 (3)	Cu2—O21	1.951 (2)
Cu2—O1	2.372 (3)	Cu2—O23	1.906 (2)
Cu2—O2	1.920 (2)		
O12—Cu1—O3*A*	89.81 (11)	O2—Cu2—O11	93.91 (10)
O12—Cu1—O3*A*^{i}	90.19 (11)	O2—Cu2—O21	90.73 (10)
O1—Cu2—O2	95.72 (11)	O2—Cu2—O23	169.99 (12)
O1—Cu2—O11	94.12 (10)	O11—Cu2—O21	172.32 (10)
O1—Cu2—O21	91.51 (9)	O11—Cu2—O23	83.65 (10)
O1—Cu2—O23	94.14 (10)	O21—Cu2—O23	90.74 (9)

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

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O17$^{\mathrm{ii}}$	0.90	2.26	2.943 (4)	133
O1—H1···O24$^{\mathrm{ii}}$	0.90	2.51	3.239 (3)	139
O1—H2···O27$^{\mathrm{iii}}$	0.91	2.03	2.916 (3)	164
O2—H3···O1*W*	0.88	1.71	2.579 (4)	169
O2—H4···O12	0.86	2.08	2.742 (3)	133
O1*W*—H1*A*···O2*W*	0.81	2.27	2.954 (4)	143
O1*W*—H1*B*···O16$^{\mathrm{iv}}$	0.88	2.19	2.889 (4)	136
O1*W*—H1*B*···O15$^{\mathrm{i}}$	0.88	2.51	3.226 (4)	139
O2*W*—H2*A*···O1$^{\mathrm{ii}}$	0.82	1.99	2.775 (3)	159
O2*W*—H2*B*···O23$^{\mathrm{ii}}$	0.89	2.16	2.949 (3)	148
O2*W*—H2*B*···O24$^{\mathrm{ii}}$	0.89	2.20	2.903 (3)	136
O22—H22···O2*W*	0.89	1.64	2.532 (3)	178
O3*A*—H3*A*···O12	0.92	1.83	2.698 (4)	157
O3*B*—H3*B*···O1*W*$^{\mathrm{v}}$	0.91	2.64	3.423 (16)	145

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

Modelling atom Cu1 with full occupancy resulted in a very large displacement parameter, suggesting partial site occupancy. The fractional site occupancy of Cu1 was refined and rapidly converged to 0.536 (2), and was fixed at 0.54 in the final cycles of refinement. The hydroxy O atom of the carboxylate anion occurred in two positions and the occupancies converged to 0.826 (3) and 0.174 (3) for atoms O3*A* and O3*B*, respectively. They were fixed at 0.8 and 0.2 in the final cycles of refinement. Thus, the occupancies of atoms H17 and H13 were also fixed at 0.8 and 0.2, respectively. The occupancies of atoms H3*A* and H3*B* were fixed at 0.26 and 0.2, respectively. In this way, the charge of (I) becomes zero. H atoms on the aromatic rings were placed in calculated positions, with C—H = 0.93 Å, and were refined as riding, with $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{carrier})$. Other H atoms (including H3*A* and H3*B*) were located in a difference map and refined as riding in their as-found relative positions, with a fixed isotropic displacement parameter of 0.08 Å^2.

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2002); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

The project was supported by the National Natural Science Foundation of China (grant No. 20443003).

References

Altomare, A., Cascarano, G., Giacovazzo, C. & Guagliardi, A. (1993). *J. Appl. Cryst.* **26**, 343–350.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.

Holton, J., Lappert, M. F., Pearce, R. & Yarrow, P. I. W. (1983). *Chem. Rev.* **83**, 135–155.

Rigaku (1998). *PROCESS-AUTO*. Version 1.06. Rigaku Corporation, Tokyo, Japan.

Rigaku/MSC (2002). *CrystalStructure*. Version 3.00. Rigaku/MSC, 9009 New Trails Drive, The Woodlands, TX 77381-5209, USA.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Su, J.-R. & Xu, D.-J. (2005). *Acta Cryst.* C**61**, m256–m258.

Valigura, D., Melnık, M., Koman, M., Martiŝka, L., Korabik, M., Mroziński, J. & Glowiak, T. (2004*a*). *Inorg. Chem. Commun.* **7**, 548–552.

Valigura, D., Melnık, M., Koman, M., Martiŝka, L., Korabik, M., Mroziński, J. & Glowiak, T. (2004*b*). *Polyhedron*, **23**, 2447–2456.