

C(2)—C(5) [1.467 (7) Å] bonds. Atom C(6) shows the highest thermal anisotropy in the structure and perhaps a correction for this effect (not done here) may give a bond length closer to the other two.

The packing of the molecules viewed down the *a* and *c* axes is shown in Fig. 2. Intra- and intermolecular contacts show that there is no intramolecular H bonding between the hydroxyl groups of the dmgh<sub>2</sub> units but only a weak intermolecular H-bonding interaction of the type O—H...Cl [Cl...O(1) = 2.977 (4), Cl...O(2) = 3.053 (4), Cl...O(3) = 3.033 (5) Å] exists in the crystal lattice. Fig. 2 clearly depicts the interactions of chloride ions with the [Ru(dmgh<sub>2</sub>)<sub>3</sub>] cations *via* OH groups.

#### References

- ALCOCK, N. W., ATKINS, M. P., CURZON, E. H., GOLDING, B. T. & SELLARS, P. J. (1980). *J. Chem. Soc. Chem. Commun.* pp. 1238–1240.
- ALCOCK, N. W., ATKINS, M. P., GOLDING, B. T. & SELLARS, P. J. (1982). *J. Chem. Soc. Dalton Trans.* pp. 337–343.
- B. A. FRENZ & ASSOCIATES, INC. (1985). *SDP Structure Determination Package*. College Station, Texas, USA, and Enraf-Nonius, Delft, The Netherlands.
- BEKAROGLU, Ö., SARISABAN, S., KORAY, A. R., NUBER, B., WEIDENHAMMER, K., WEISS, J. & ZIEGLER, M. L. (1978). *Acta Cryst.* **B34**, 3591–3593.
- BURGER, K., RUFF, I. & RUFF, F. (1965). *J. Inorg. Nucl. Chem.* **27**, 179–190.
- CHAKRAVORTY, A. (1974). *Coord. Chem. Rev.* **13**(1), 1–46.
- DUNITZ, J. D. & SEILER, P. (1973). *Acta Cryst.* **B29**, 589–595.
- DWYER, F. P. & NYHOLM, R. S. (1946). *J. Proc. R. Soc. N. S. Wales*, **78**, 266–270.
- EVANS, I. P., SPENCER, A. & WILKINSON, G. (1973). *J. Chem. Soc. Dalton Trans.* pp. 204–209.
- GILLARD, R. D. & WILKINSON, G. (1963). *J. Chem. Soc.* pp. 6041–6044.
- HAMBLEY, T. W., KEYTE, P., LAY, P. A. & PADDON-ROW, M. N. (1991). *Acta Cryst.* **C47**, 941–943.
- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- KOMAN, M., MARIASSY, M. & ONDREJOVIC, G. (1991). *Acta Cryst.* **C47**, 1204–1206.
- KONNO, M., OKAMOTO, T. & SHIROTANI, I. (1989). *Acta Cryst.* **B45**, 142–147.
- MARIASSY, M. & ONDREJOVIC, G. (1990). *Acta Cryst.* **C46**, 561–562.
- NAKAHARA, A., FUJITA, J. & TSUCHIDA, T. (1956). *Bull. Chem. Soc. Jpn*, **29**, 296.
- NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- RILLEMA, D. P., JONES, D. S. & LEVY, H. A. (1979). *J. Chem. Soc. Chem. Commun.* pp. 849–851.
- SMOLENAERS, P. J., BEATTIE, J. K. & HUTCHINSON, N. D. (1981). *Inorg. Chem.* **20**, 2202–2206.
- STYNES, H. C. & IBERS, J. A. (1971). *Inorg. Chem.* **10**, 2304–2308.

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## Structure of *catena*-Poly[{tetrakis- $\mu$ -(acetato-*O*:*O*)-dicopper(II)}- $\mu$ -{1,8-bis-(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane-*N*<sup>2</sup>,*N*<sup>2'</sup>}]

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**Abstract.** Asymmetric unit  $\text{Cu}(\text{bddo})_{0.5}(\text{acetate})_2 = 0.5[\text{Cu}_2(\text{C}_{16}\text{H}_{26}\text{N}_4\text{S}_2)(\text{C}_2\text{H}_3\text{OO})_4]$ ,  $M_r = 350.90$ , triclinic,  $P\bar{1}$ ,  $a = 8.501$  (1),  $b = 8.590$  (1),  $c = 10.854$  (2) Å,  $\alpha = 84.54$  (2),  $\beta = 82.10$  (2),  $\gamma = 84.73$  (2)°,  $V = 779$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.49$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71073$  Å,  $\mu = 15.4$  cm<sup>-1</sup>,  $F(000) = 364$ ,  $T = 298$  K,  $R = 0.041$  and  $wR = 0.047$  for 1648 unique reflections [ $I > 2\sigma(I)$ ]. The structure of this new compound consists of dinuclear  $\text{Cu}_2(\text{CH}_3\text{COO})_4$

units linked to a chain by the ligand 1,8-bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiaoctane (bddo) along the body diagonal of the unit cell. The Cu atoms are coordinated by four O atoms from the acetates and one N atom from the ligand bddo in a square pyramidal geometry with the pyrazole N atom in the apical position. In the copper acetate dimer the basal planes of two square pyramids are facing each other. The Cu—O(acetate) distances in the dinuclear copper acetate unit can be regarded as normal, as well as the Cu—N(bddo) distances. The Cu—Cu

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distance is 2.682 (2) Å. The thioether S atoms of the bddo ligand are not involved in coordination to the Cu<sup>II</sup> atoms.

**Introduction.** In the course of our programme (Haanstra, Driessen, Reedijk, Turpeinen & Hämäläinen, 1989; Haanstra, van der Donk, Driessen, Reedijk & Wood, 1990) towards the design and development of model compounds for the blue-copper active site (Karin & Zubieta, 1984; Bouwman, Driessen & Reedijk, 1990) several N<sub>2</sub>S<sub>2</sub> ligands were synthesized. In order to investigate the coordination behaviour towards copper, several coordination compounds of the ligand 1,8-bis(3,5-dimethyl-1-pyrazolyl)-3,6-dithiooctane (bddo) were prepared (Haanstra *et al.*, 1989, 1990). The crystalline coordination compound of bddo with copper(II) acetate, with formula Cu<sub>2</sub>(CH<sub>3</sub>COO)<sub>4</sub>(bddo), appeared to be bichromatic: green coloured from one side and when turned through 90°, blue coloured. The absence of a normal copper(II) EPR signal indicated the possible presence of a copper acetate dimer (Hathaway, 1984). The single-crystal structure determination of Cu<sub>2</sub>(CH<sub>3</sub>COO)<sub>4</sub>(bddo) was undertaken to investigate the presence of the dinuclear units and the role of the ligand bddo in the coordination towards the copper acetate dimers.

**Experimental.** The synthesis of the ligand bddo has been described elsewhere (Haanstra *et al.*, 1989). Synthesis of Cu<sub>2</sub>(CH<sub>3</sub>COO)<sub>4</sub>(bddo) was performed by mixing hot ethanolic solutions of 2 mmol copper(II) acetate and 2 mmol of bddo. On cooling to room temperature a crystalline solid was obtained with the composition Cu<sub>2</sub>(CH<sub>3</sub>COO)<sub>4</sub>(bddo). A crystal suitable for X-ray structure determination was isolated from this batch.

A green rod-like crystal (0.15 × 0.2 × 0.3 mm) was mounted in a glass capillary. Diffraction data were collected on a CAD-4 diffractometer with graphite-monochromated Mo K $\alpha$  radiation. The unit-cell parameters were refined from 25 reflections with 10 <  $\theta$  < 12°. In total 2392 reflections were collected for 2.0 < 2 $\theta$  < 43.0° and 0 <  $h$  < 9, -9 <  $k$  < 9 and -11 <  $l$  < 12 in the  $\omega$ -2 $\theta$  scan mode. In the refinement, 1648 unique reflections with  $I > 2\sigma(I)$  were used. Five standard reflections, *viz.* 005, 11 $\bar{4}$ , 3 $\bar{2}0$ , 402 and 232, were monitored. Over the time period of the experiment no significant variation (0%) in intensity was observed. Corrections for Lorentz and polarization effects were applied. The  $\psi$  scans indicated that absorption correction was not necessary. Linear absorption coefficient,  $\mu = 15.4 \text{ cm}^{-1}$ . Atomic scattering factors and anomalous-dispersion corrections were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The structure was solved in the space group  $P\bar{1}$ . The fractional coordinates of

Table 1. Fractional coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>) of the non-H atoms of Cu(CH<sub>3</sub>COO)<sub>4</sub>(bddo)<sub>0.5</sub> with *e.s.d.*'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
Cu	0.0469 (1)	0.0311 (1)	0.8777 (1)	0.0414 (4)
S	0.4446 (3)	-0.4296 (2)	0.6945 (2)	0.069 (1)
O(11)	-0.0522 (6)	-0.1658 (5)	0.8667 (4)	0.054 (3)
O(21)	0.1277 (6)	0.2186 (5)	0.9306 (4)	0.055 (3)
O(31)	0.2461 (5)	-0.0903 (5)	0.9141 (4)	0.056 (3)
O(41)	-0.1659 (5)	0.1447 (5)	0.8830 (4)	0.051 (3)
N(11)	0.1878 (6)	-0.0239 (5)	0.5904 (4)	0.041 (3)
N(12)	0.1192 (6)	0.0795 (6)	0.6733 (4)	0.042 (3)
C(11)	-0.1131 (7)	-0.2494 (7)	0.9602 (6)	0.043 (4)
C(12)	-0.1754 (9)	-0.4008 (7)	0.9312 (7)	0.062 (5)
C(13)	0.1028 (7)	0.2155 (7)	0.6052 (5)	0.043 (4)
C(14)	0.1604 (8)	0.1993 (7)	0.4805 (5)	0.048 (4)
C(15)	0.2144 (8)	0.0432 (8)	0.4752 (5)	0.047 (4)
C(16)	0.0288 (9)	0.3609 (7)	0.6629 (6)	0.061 (4)
C(17)	0.2883 (9)	-0.0436 (8)	0.3646 (6)	0.061 (5)
C(18)	0.2233 (8)	-0.1913 (7)	0.6318 (6)	0.045 (4)
C(19)	0.3968 (8)	-0.2238 (7)	0.6503 (6)	0.048 (4)
C(21)	0.2673 (8)	-0.1488 (7)	1.0208 (6)	0.044 (4)
C(22)	0.4282 (8)	-0.2301 (8)	1.0380 (7)	0.071 (5)
C(32)	0.4359 (11)	-0.5185 (8)	0.5488 (8)	0.090 (6)

$$U_{eq} = (1/3) \text{ trace } U.$$

Table 2. Bond lengths (Å) and bond angles (°) of Cu<sub>2</sub>(CH<sub>3</sub>COO)<sub>4</sub>(bddo) with *e.s.d.*'s in parentheses

Cu—O(11)	1.978 (4)	Cu—O(21)	1.971 (4)
Cu—O(31)	1.972 (4)	Cu—O(41)	1.971 (4)
Cu—N(12)	2.230 (5)	Cu—Cu'	2.682 (2)
O(11)—C(11)	1.264 (7)	O(31)—C(21)	1.248 (7)
O(21)'—C(11)	1.226 (7)	O(41)'—C(21)	1.261 (7)
C(12)—C(11)	1.525 (9)	C(22)—C(21)	1.505 (9)
N(11)—N(12)	1.361 (6)	N(11)—C(15)	1.324 (8)
N(12)—C(13)	1.329 (8)	C(13)—C(14)	1.389 (8)
C(14)—C(15)	1.382 (9)	C(13)—C(16)	1.500 (9)
C(15)—C(17)	1.507 (9)	N(11)—C(18)	1.481 (8)
C(18)—C(19)	1.513 (9)	C(19)—S	1.812 (7)
S—C(32)	1.835 (8)	C(32)—C(32)''	1.447 (14)
O(11)—Cu—O(31)	90.3 (2)	O(11)—Cu—O(41)	88.9 (2)
O(21)—Cu—O(31)	89.0 (2)	O(21)—Cu—O(41)	88.8 (2)
O(11)—Cu—O(21)	166.6 (2)	O(31)—Cu—O(41)	166.9 (2)
N(12)—Cu—O(11)	96.3 (2)	N(12)—Cu—O(21)	97.1 (2)
N(12)—Cu—O(31)	96.7 (2)	N(12)—Cu—O(41)	96.5 (2)
O(11)—C(11)—O(21)'	126.2 (4)	O(31)—C(21)—O(41)'	125.7 (4)
O(21)'—C(11)—C(12)	118.3 (4)	O(31)—C(21)—C(22)	117.8 (4)
O(11)—C(11)—C(12)	115.5 (5)	O(41)'—C(21)—C(22)	116.5 (5)
N(12)—N(11)—C(15)	112.3 (4)	N(12)—N(11)—C(18)	120.7 (4)
C(15)—N(11)—C(18)	126.9 (5)	N(11)—N(12)—C(13)	104.8 (4)
N(12)—C(13)—C(16)	121.3 (5)	C(14)—C(13)—C(16)	127.8 (5)
N(12)—C(13)—C(14)	110.9 (4)	C(13)—C(14)—C(15)	105.4 (5)
C(14)—C(15)—C(17)	129.6 (5)	N(11)—C(15)—C(17)	123.8 (4)
C(14)—C(15)—N(11)	106.7 (4)	N(11)—C(18)—C(19)	110.7 (4)
C(18)—C(19)—S	111.4 (4)	C(19)—S—C(32)	101.9 (3)
S—C(32)—C(32)''	113.8 (5)		

Symmetry code: (') -*x*, -*y*, 2 - *z*; (") 1 - *x*, -1 + *y*, 1 - *z*.

the Cu and S atoms were determined using the Patterson function. The remaining atoms, including the H atoms, were located by difference Fourier maps. Refinement was with the XTAL2.4 program (Hall & Stewart, 1988); *F* values were used in the refinement; least-squares refinement of H atom and non-H positional parameters and of non-H anisotropic thermal parameters was performed. Function minimized:  $\sum(w|F_o| - |F_c|)^2$  with  $w = 1/\sigma^2(F)$ . The refinement was considered complete when maximum  $\Delta/\sigma < 0.1$ , with  $R = 0.041$ ,  $wR = 0.047$  and g.o.f. = 1.55. Maximum and minimum electron densities in

the final difference Fourier map were 0.5 and  $-0.3 \text{ e } \text{Å}^{-3}$ , respectively. The fractional coordinates of the non-H atoms with isotropic thermal parameters are given in Table 1 and interatomic distances and angles in Table 2.\*

**Discussion.** In Fig. 1 an impression of the chain of  $\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{bddo})$  is shown. Fig. 2 shows the adopted atomic labelling scheme. The  $\text{Cu}^{\text{II}}$  atoms are linked together by four bidentate bridging acetate anions. Each Cu ion is coordinated by four O atoms

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55023 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI0117]

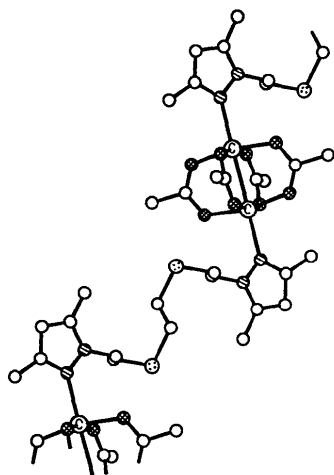


Fig. 1. *PLUTO* (Motherwell & Clegg, 1978) drawing showing the polymeric nature of  $\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{bddo})$ . H atoms are omitted for clarity.

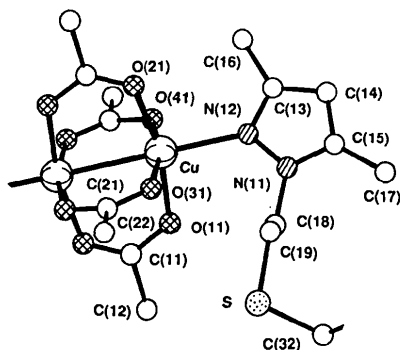


Fig. 2. *PLUTO* (Motherwell & Clegg, 1978) drawing of the asymmetric unit  $\text{Cu}(\text{CH}_3\text{COO})_2(\text{bddo})_{0.5}$ , with the atomic labelling scheme. H atoms are omitted for clarity.

from the acetates and one N atom from the ligand bddo in a square pyramidal geometry. In the copper acetate dimer the basal planes of the two square pyramids face one another. The acetate O—Cu bond lengths are in the range 1.971 (4)–1.978 (4) Å (see Table 2). The Cu—Cu distance is 2.682 (2) Å. The N pyrazole donor of the ligand bddo coordinates at 2.230 (5) Å, which is common for the axial position in square pyramidal  $\text{Cu}^{\text{II}}$  coordination compounds (Melnik, 1982). The structure of  $\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{bddo})$  (Fig. 2) resembles the classical  $\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{H}_2\text{O})_2$  structure. The copper acetate dimers are linked together by the ligand bddo, forming a chain-like structure. Inspection of the crystal packing of the chains did not reveal any contacts, other than normal van der Waals interactions.

The colour of the crystals depends on their orientation. This is owing to polarization of the electronic transitions. The diffuse reflectance ligand-field spectrum of microcrystalline  $\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{bddo})$  shows one (broad) absorption band at  $12.0 \times 10^3 \text{ cm}^{-1}$ , which is in good agreement with spectroscopic data reported for this class of compounds (Dubicki, 1972). The EPR spectrum of powdered  $\text{Cu}_2(\text{CH}_3\text{COO})_4(\text{bddo})$  at room temperature is also in good agreement with EPR spectra observed for copper acetate dimers (Melnik, 1982).

Copper acetate dimers are usually easily synthesized and they are known with a great variety of axial ligands. In the review written by Melnik (1982) a linear relationship is suggested between the Cu—Cu distance and the copper to axial ligand distance. The relationship suggests that with increasing donor strength of the axial ligand the copper to axial ligand distance decreases and the Cu—Cu distance increases. The distances in the present copper acetate dimer unit fit very well with this correlation.

## References

- BOUWMAN, E., DRIESSEN, W. L. & REEDIJK, J. (1990). *Coord. Chem. Rev.* **104**, 143–172.
- DUBICKI, L. (1972). *Aust. J. Chem.* **25**, 1141–1149.
- HAANSTRA, W. G., DRIESSEN, W. L., REEDIJK, J., TURPEINEN, U. & HÄMÄLÄINEN, R. (1989). *J. Chem. Soc. Dalton Trans.* pp. 2309–2314.
- HAANSTRA, W. G., VAN DER DONK, W. A. J. W., DRIESSEN, W. L., REEDIJK, J. & WOOD, J. S. (1990). *J. Chem. Soc. Dalton Trans.* pp. 3123–3128.
- HALL, S. R. & STEWART, J. M. (1988). Editors. *XTAL2.4 User's Manual*. Univ. of Western Australia, Australia, and Maryland, USA.
- HATHAWAY, B. J. (1984). *Struct. Bonding (Berlin)*, **57**, 55–118.
- KARLIN, K. D. & ZUBIETA, J. (1984). Editors. *Biological and Inorganic Copper Chemistry*, Vols. I and II. New York: Adenine Press.
- MELNIK, M. (1982). *Coord. Chem. Rev.* **42**, 259–293.
- MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO*. Program for plotting molecular and crystal structures. Univ. of Cambridge, England.