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The structure of bis[dichloro-6-mercaptopuriniumcopper(I)] dihydrate: a refinement.*

By Anita L. Shoemaker, Phirtu Singh and Derek J. Hodgson, *Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina* 27514, *U.S.A.*

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The structure of bis[dichloro-6-mercaptopuriniumcopper(I)] dihydrate has been refined in the centrosymmetric space group $P\bar{1}$ instead of the previously reported $P1$. The structural results obtained are consistent with those found for other 6-mercaptopurine complexes and statistical tests demonstrate that $P\bar{1}$ is the correct space group.

We and others have recently been investigating the interactions of metal ions with purines and purine analogs (Purnell, Estes & Hodgson, 1976; Purnell, Shepherd & Hodgson, 1975; Heitner & Lippard, 1974; Sletten & Apeland, 1975; and references therein). We were, therefore, interested to see the report (Caira & Nassimbeni, 1975, hereinafter C & N) of the structure of a dimeric copper(I) complex of 6-mercaptopurine. Examination of the quantitative features of the above structure, however, suggested that there were large errors in the bond lengths and angles reported for the purine moieties since chemically equivalent distances and angles were in severe disagreement both with each other and with the values observed in the free ligand (Brown, 1969; Sletten & Apeland, 1975). Examination of the positional parameters reported by C & N suggested to us that the molecule may be centrosymmetric, while C & N chose to refine their structure in the noncentrosymmetric space group $P1$. Hence, we obtained a copy of their data (British Library Lending Division, Supplementary Publication No. SUP 30851) and have refined the structure in the centrosymmetric space group $P\bar{1}$.

Initial heavy atom parameters were obtained from C & N, using the values reported for their molecule *A* transformed so that the origin in $P\bar{1}$ was in the center of their reported Cu*A*–Cu*B* vector. Least-squares refinement was carried out on *F*; unit weights were applied to the data in order to facilitate the comparison of our results with those of C & N. Scattering factors for Cu were from Cromer & Waber (1965), those for S, Cl, N, O and C from *International Tables for X-ray Crystallography* (1962), and those for H from Stewart, Davidson & Simpson (1965). The effects of the anomalous dispersion of Cu, S, and Cl were included in calculations of F_c (Ibers & Hamilton, 1964), the values of $\Delta f'$ and $\Delta f''$ being taken from the tabulation of Cromer & Liberman (1970). The hydrogen atoms were located in a difference Fourier map, and were included in the final refinement. In the final cycle of least-squares refinement all heavy atoms were refined anisotropically and all hydrogen atoms were refined isotropically; the final values of the agreement indices $R_1(=\sum||F_o|-|F_c||/\sum|F_o|)$ and $R_2\{=[\sum(|F_o|-|F_c|)^2/\sum|F_o|^2]^{1/2}\}$ were 0·046 and 0·051, respectively.

In the final cycle of least-squares refinement, no atomic parameter exhibited a shift of more than 0·29σ, which is taken as evidence that the refinement had converged. A final difference Fourier map contained peaks as large as 1·0 e Å^{-3} in the vicinity of the copper atom. This residual density is presumably due to the neglect of absorption effects; since the indices of the faces and the orientation of the crystal used by C & N were not reported, we were unable to apply an absorption correction. Examination of the data suggested to us that no correction for secondary extinction was necessary, and none was applied.

Our final (centrosymmetric) refinement involved 1725 observations and 155 variables, and yielded a final *R* value of 0·046; the noncentrosymmetric refinement of C & N involved 1704 reflections and (presumably) 153 variables and yielded a final *R* value of 0·051. While statistical comparison should more properly be based on the values of R_2, since this is the function minimized in the least-squares process, we are unable to do this since C & N do not report a value for R_2. Since the two refinements used the same weighting scheme, however, statistical comparison on the basis of R_1 is valid. The observed improvement, using the same data, is significant at all meaningful confidence levels

Table 1. *Positional and thermal parameters for* $Cu(C_5H_5N_4S)_2Cl_2.H_2O$

Anisotropic thermal parameters × 10^4. The form of the anisotropic thermal ellipsoid is
$\exp[-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{33}kl)]$.

	x	*y*	*z*	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	1·15299 (7)	0·1533 (1)	1·0909 (1)	48 (1)	163 (2)	135 (2)	43 (1)	−19 (1)	−68 (1)
Cl(1)	1·1752 (2)	0·3028 (2)	1·4058 (2)	53 (1)	128 (3)	90 (3)	42 (2)	−31 (2)	−72 (2)
Cl(2)	1·3713 (1)	0·1298 (2)	1·0879 (2)	38 (1)	109 (2)	88 (3)	13 (1)	5 (2)	−19 (2)
S	0·9661 (1)	0·1777 (2)	0·8274 (2)	31 (1)	85 (2)	78 (3)	21 (1)	−5 (2)	−36 (2)
N(1)	0·8893 (5)	0·3452 (6)	1·1158 (7)	36 (5)	81 (8)	70 (9)	17 (5)	−21 (6)	−37 (7)
N(3)	0·6789 (4)	0·4451 (5)	1·0986 (6)	41 (5)	71 (7)	77 (9)	15 (5)	1 (5)	−26 (7)
N(7)	0·6396 (4)	0·2421 (6)	0·6129 (6)	43 (5)	75 (8)	50 (9)	12 (5)	−12 (5)	−19 (7)
N(9)	0·5141 (5)	0·3747 (6)	0·7593 (6)	32 (5)	97 (8)	79 (10)	24 (5)	−3 (6)	−7 (7)
C(2)	0·8055 (5)	0·4233 (7)	1·1963 (8)	36 (6)	76 (9)	68 (12)	10 (6)	−14 (6)	−37 (8)
C(4)	0·6408 (5)	0·3760 (6)	0·9021 (7)	29 (5)	43 (8)	65 (11)	5 (5)	0 (6)	−7 (7)
C(5)	0·7200 (5)	0·2942 (6)	0·8111 (7)	31 (5)	36 (8)	51 (10)	2 (5)	−12 (6)	−11 (7)
C(6)	0·8564 (5)	0·2747 (6)	0·9195 (7)	31 (5)	33 (8)	57 (11)	−2 (5)	−4 (6)	−16 (7)
C(8)	0·5186 (6)	0·2909 (7)	0·5885 (8)	34 (6)	83 (9)	62 (12)	14 (6)	−21 (7)	−2 (8)
O	0·7217 (8)	0·0494 (8)	0·3580 (10)	125 (8)	150 (11)	94 (12)	65 (8)	−9 (8)	−47 (9)

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* *Editorial note*: – The main points of this paper have already been made [Pope, Laing, Caira & Nassimbeni, *Acta Cryst.* (1976), B32, 612–613]. It is however, thought worth while to publish it, as an illustration of the reproducibility of crystallographic data refined by different procedures. The biggest difference in bond length seems to be for N(7)–C(8), where it amounts to 2·4 times the combined standard deviations.

Table 1 (*cont.*)

	x	*y*	*z*	*B* (Å^2)
H(N9)	0·444 (6)	0·398 (7)	0·791 (8)	0·8 (10)
H(N7)	0·672 (6)	0·190 (8)	0·525 (9)	1·7 (12)
H(C2)	0·838 (6)	0·453 (8)	1·341 (9)	2·0 (12)
H(N1)	0·959 (7)	0·323 (8)	1·196 (10)	1·9 (13)
H(C8)	0·452 (8)	0·280 (9)	0·482 (11)	3·3 (16)
H(O1)	0·768 (11)	0·003 (14)	0·386 (16)	5·1 (31)
H(O2)	0·698 (13)	0·021 (16)	0·286 (17)	7·3 (40)

(Hamilton, 1965) and strongly supports the conclusion that the correct space group is $P\bar{1}$. This conclusion is further supported by the derived bond lengths and angles (*vide infra*).

The positional and thermal parameters, along with their associated standard deviations as estimated from the inverse matrix, are presented in Table 1. The standard deviations are smaller than those reported by C & N by a factor of about 5.

A view of the dimeric unit is shown in Fig. 1. While the gross structural features are, of course, similar to those reported by C & N, the purine ring geometry derived from our refinement differs markedly from that obtained previously. The bond lengths found for the coordinated purine ligand here are compared with those of C & N, and also with those reported for the free ligand and for other transition metal complexes of 6-mercaptopurine (Heitner & Lippard, 1974; Sletten & Apeland, 1975) in Table 2. It is apparent from an examination of Table 2 that the values which we have determined are consistent with those found in the related systems. The bond lengths associated with the copper atom are shown in Fig. 1, and are similar to Cu–Cl and Cu–S distances reported by other workers (Hunt & Amma, 1973).

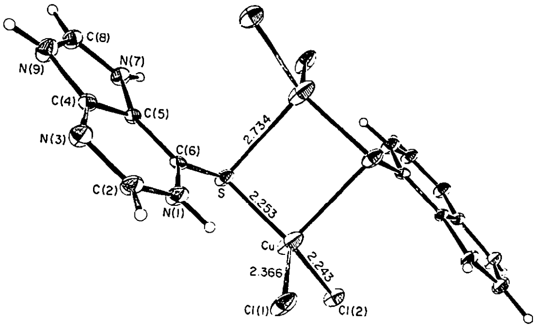

Fig. 1. View of the dimeric unit, showing the bond lengths involving copper. Hydrogen atoms are shown as open circles of arbitrary size. Thermal ellipsoids are drawn at the 50% probability level.

The hydrogen bonding in the complex is as reported by C & N, with the exception that we observe an additional probable O–H···Cl(1) hydrogen bond with O···Cl(1) = 3·315 Å, and an O–H···Cl(1) angle of 143°. This interaction meets the criterion (Hamilton & Ibers, 1968) that both the O–H and the H···Cl separations are less than the appropriate sums of the van der Waals radii (Pauling, 1960; Bondi, 1964) and hence is probably a weak hydrogen bond.

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Table 2. *Bond lengths* (Å) *in the* 6-*mercaptopurine* (6-MP) *ligand*

Bond	This work	C & N (*a*)		Pd(9-Bz-6-MP)$_2$ (*b*)		Cu(9-Me-6-MP)Cl (*c*)	6-MP-H$_2$O (*d*)
N(1)–C(2)	1·343 (7)	1·31 (4)	1·37 (4)	1·35 (2)	1·37 (2)	1·368	1·354
C(2)–N(3)	1·308 (7)	1·39 (3)	1·24 (3)	1·36 (2)	1·36 (2)	1·306	1·308
N(3)–C(4)	1·364 (7)	1·33 (3)	1·40 (3)	1·34 (1)	1·34 (1)	1·351	1·363
C(4)–C(5)	1·364 (7)	1·32 (4)	1·41 (3)	1·39 (1)	1·37 (1)	1·372	1·396
C(5)–C(6)	1·406 (7)	1·39 (3)	1·44 (3)	1·37 (1)	1·37 (1)	1·378	1·401
C(6)–N(1)	1·370 (7)	1·44 (3)	1·33 (3)	1·35 (1)	1·34 (1)	1·357	1·378
C(6)–S	1·686 (6)	1·72 (2)	1·65 (3)	1·72 (1)	1·72 (1)	1·692	1·678
C(5)–N(7)	1·386 (7)	1·43 (3)	1·36 (2)	1·37 (1)	1·36 (1)	1·364	1·372
N(7)–C(8)	1·307 (7)	1·29 (3)	1·36 (3)	1·34 (1)	1·34 (1)	1·316	1·349
C(8)–N(9)	1·343 (7)	1·39 (3)	1·27 (4)	1·37 (1)	1·35 (1)	1·361	1·330
N(9)–C(4)	1·376 (7)	1·36 (3)	1·39 (3)	1·38 (1)	1·37 (1)	1·360	1·366

(*a*) Caira & Nassimbeni (1975), (*b*) Heitner & Lippard (1974), (*c*) Sletten & Apeland (1975), (*d*) values given are the averages of two: Brown (1969); Sletten, Sletten & Jensen (1969).