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The Crystal Structure of Tetra-μ[2,4-dichloro-5-methylphenylthio)acetato-*O,O′*]-bis[aquacopper-(II)]·acetone (1/2)

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The crystal structure of the second chemical polymorph {[$Cu_2(DCMPTA)_4(H_2O)_2$]·2(acetone)} (2), formed by dissolution of copper(II) (2,4-dichloro-5-methylphenylthio)acetate in acetone has been determined by X-ray diffraction. The complex is a tetracarboxylate bridged dimer similar to polymorph (1) {[$Cu_2(DCMPTA)_4(acetone)_2$]} but with the axially coordinated acetone molecules of (1) replaced by water while the acetones are molecules of solvation. The dimer cage is centrosymmetric but the overall structure is disordered in space group $P\bar{1}$ as a result of subtle differences between related (phenylthio)acetate ligands.

The previous article [1] on metal–(phenylthio)-acetic acid interactions reported the crystal data and chemical analyses for the title compound (2). It is one of two chemical polymorphs formed as the major product by the dissolution in acetone of the copper-(II) complex of (2,4-dichloro-5-methylphenylthio)-acetic acid (DCMPTAH). The crystal structure of the first polymorph (**1**) revealed a tetra-carboxylate bridged dimer of the type [$Cu_2(DCMPTA)_4(acetone)_2$] with axially coordinated acetone molecules while it was suggested that the title compound, [$Cu_2(DCMPTA)_4(acetone)_2(H_2O)_2$] differed from (1) merely in the nature of attachment of acetone/water in the dimer structure. This determination confirms the presence of a partially disordered centrosymmetric dimeric system, in contrast to the ordered and stable complex system found for (**1**).

Experimental

The preparation of the title compound (2) was described in ref. [1].

Crystal Data

$C_{42}H_{44}Cl_8Cu_2O_{12}S_4$, $Mr = 1279.8$, $a = 8.140(3)$, $b = 9.501(5)$, $c = 18.58(1)$ Å, $\alpha = 90.73(5)$, $\beta = 99.56(5)$, $\gamma = 108.72(4)°$, $V = 1338.6(13)$ Å^3, $D_f = 1.60$, $D_c = 1.587$ g cm^{-3}, $Z = 1$ (dimer), Mo-Kα radiation, $\lambda = 0.71069$ Å, μ(Mo-Kα) = 14.3 cm^{-1}, $F(000) = 650$, space group $P\bar{1}$.

Data Collection, Structure Solution and Refinement

Intensity data were collected from a crystal (0.22 × 0.20 × 0.04 mm) on a Nicolet R3m diffractometer using graphite monochromatized Mo-Kα radiation. 1222 reflections with $I > 2.0\sigma(I)$ were considered observed out of 2357 in a unique set collected up to $2\theta_{max} = 45°$. The structure could not be solved by the conventional direct methods of SHELX-76 [2], used either in the automatic mode or by the hand selection of starting phases. The position of the copper atom, provided by these methods and verified in a three-dimensional Patterson Synthesis would not allow the phasing of the structure by difference-Fourier methods. However, use of the tangent refinement method aided by partial phasing via the copper atom coordinates, revealed molecular fragments, and finally after several refinement/weighted difference-Fourier cycles, all atoms of a partially disordered dimer structure. The disorder in ligand (**A**) extends out from the α-carbon of the acetate group while in ligand (**B**), the disorder begins at the sulphur atom. Because the centrosymmetric (inversion) relationship was correct for the other atoms, these were refined with site occupancy factors = 1.0 while the atoms of the four ligand systems were given a value of 0.5, with the phenyl rings treated as rigid bodies. The latter constraints were released in the final cycle of weighted refinement. Blocked-matrix least squares refinement with anisotropic thermal parameters for only the copper and the oxygens of the coordination sphere gave a final $R[=\Sigma\|F_o - F_c\|/|F_o|] = 0.105$ and $R_w\ [=\Sigma w(\|F_o - F_c\|^2/\Sigma w|F_o|^2)^{1/2}] = 0.103$. A value of $w = 1.92/(\sigma^2F_o + 2.4 \times 10^{-3}\ F_o^2)$ was used. The problems associated with the refinement of coincident or near-coincident atoms in the disordered ligand systems in (2) were not resolved, with a resultant poor convergence and inconsistent interatomic distances and angles. However, those within the ordered part of the molecule are quite reliable. No attempt was made to refine the structure in space group $P1$. Hydrogens were not included in the refinement. The acetones, found to be present as molecules of solva-

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TABLE I. Atomic Coordinates (×10^4), Isotropic and Equivalent Isotropic Thermal Parameters (Å^2; ×10^3). O(2)Ac′ is the Disordered Site of O(2)Ac while Ligands C′ and D′ are the Disordered Equivalent of Ligands B and A Respectively ($U_{eq} = (U_{11} \cdot U_{22} \cdot U_{33})^{1/3}$).

Atom	*x/a*	*z/b*	*z/c*	$U_{iso/eq}$^{a}	Atom	*x/a*	*x/b*	*z/c*	$U_{iso/eq}$^{a}
Cu	689(4)	1348(3)	4784(2)	36(2)^{a}	C(3)Ac	4457(62)	5304(56)	6728(32)	232(19)
Ow	2226(20)	3443(17)	4473(12)	72(14)^{a}	O(2)Ac	4076(42)	5927(35)	5481(20)	57(9)^{b}
C(1)Ac	1713(38)	5579(32)	6013(18)	88(9)	O(2)Ac′	4780(57)	6944(50)	6020(26)	111(14)^{b}
C(2)Ac	3617(43)	6036(36)	6080(19)	67(10)					
		ligand A					ligand D′		
C(1)	1581(64)	−2202(72)	2824(28)	52(17)^{b}		1680(78)	−3046(86)	2854(37)	53(19)^{b}
C(2)	721(59)	−3032(52)	2195(29)	17(9)^{b}		809(67)	−4307(60)	2297(32)	59(15)^{b}
Cl(2)	644(24)	−4828(21)	2182(11)	101(6)^{b}		1072(72)	−5890(20)	2551(10)	79(15)^{b}
C(3)	−321(100)	−2402(91)	1541(46)	17(31)^{b}		−66(75)	−4057(72)	1666(36)	81(18)^{b}
C(4)	−62(47)	−1004(44)	1572(22)	24(10)^{b}		98(47)	−2818(44)	1603(22)	24(10)^{b}
Cl(4)	−1004(21)	−375(18)	838(10)	89(5)^{b}		−1235(21)	−2444(18)	685(10)	89(5)^{b}
C(5)	987(105)	116(96)	2233(48)	65(21)^{b}		623(60)	−1356(56)	2052(29)	44(13)^{b}
C(51)	1005(65)	1499(62)	2149(30)	72(16)^{b}		575(65)	109(62)	1857(30)	72(16)^{b}
C(6)	1773(45)	−549(44)	2786(20)	49(13)^{b}		1744(127)	−1436(121)	2707(60)	50(10)^{b}
S(7)	2666(21)	−2758(19)	3514(10)	52(5)^{b}		2821(21)	−3244(19)	3737(10)	52(5)
C(8)	3668(28)	−1381(24)	4234(13)	49(6)					
C(9)	2227(31)	−908(30)	4557(14)	46(7)					
O(10)	1218(21)	−1848(17)	4851(10)	65(12)^{a}					
O(11)	2354(17)	395(16)	4473(9)	45(10)a					
		ligand B					ligand C′		
C(1)	−5152(71)	−9789(62)	−1677(34)	57(17)^{b}		−4811(66)	−1430(59)	1650(32)	61(16)^{b}
C(2)	−4339(145)	−10607(121)	−1242(68)	112(50)^{b}		−5575(63)	−779(52)	1098(29)	45(14)^{b}
Cl(2)	−5094(31)	−12572(26)	−1473(13)	54(18)^{b}		−5184(63)	1048(52)	1230(29)	45(13)^{b}
C(3)	−3480(59)	−10153(50)	−588(27)	34(13)^{b}		−6599(64)	−1831(55)	439(29)	50(14)^{b}
C(4)	−3144(41)	−8738(35)	−413(19)	22(9)^{b}		−6770(57)	−3165(52)	435(26)	62(12)^{b}
Cl(4)	−1593(21)	−7881(18)	437(10)	85(5)^{b}		−8173(23)	−3994(20)	−424(11)	95(6)^{b}
C(5)	−3723(82)	−7727(70)	−862(39)	74(20)^{b}		−6289(80)	−4010(62)	913(36)	23(18)^{b}
C(51)	−3234(109)	−6012(99)	−547(52)	153(31)^{b}		−6447(64)	−5567(56)	848(29)	80(15)^{b}
C(6)	−4901(58)	−8304(50)	−1495(27)	40(13)^{b}		−5182(60)	−2981(52)	1594(28)	52(13)^{b}
S(7)	−6669(18)	−10704(17)	−2526(18)	55(4)^{b}		−3614(60)	−401(17)	2514(8)	47(4)^{b}
C(8)	−2993(64)	−920(63)	2935(29)	54(15)^{b}		−2875(60)	−1753(60)	2986(27)	53(14)^{b}
C(9)	−1827(35)	−657(34)	3772(15)	49(7)					
O(10)	−905(21)	600(19)	3828(18)	51(12)^{a}					
O(11)	2011(20)	1710(20)	5801(11)	68(13)^{a}					

^{a}Atoms refined anisotropically. ^{b}Atoms refined with site occupancy factors = 0.5

TABLE II. Bond Distances (Å) and Angles (degrees) about the Coordination Sphere for $[Cu_2(DCMPTA)_4(H_2O)_2] \cdot 2(acetone)$. Primed Atoms are Generated by an Inversion Operation.

a. distances					
Cu–O(10)A	1.98(2)	Cu–O(11)A′	2.01(2)	Cu–Ow	2.13(2)
Cu–O(10)B	1.99(1)	Cu–O(11)B′	1.98(2)	Cu–Cu′	2.639(5)
b. angles					
Ow–Cu–O(10)A	102.2(7)	O(10)A–Cu–O(11)A′	167.6(6)	C(9)A–O(10)A–Cu	118.5(6)
Ow–Cu–O(10)B	98.3(7)	O(10)A–Cu–O(11)B′	88.1(8)	C(9)B–O(10)B–Cu	117.0(7)
Ow–Cu–O(11)A′	90.2(7)	O(10)B–Cu–O(11)A′	88.7(7)	C(9)A′–O(11)A′–Cu	123.3(6)
Ow–Cu–O(11)B′	93.0(7)	O(10)B–Cu–O(11)B′	168.7(7)	C(9)B′–O(11)B′–Cu	120.6(6)
O(10)A–Cu–O(10)B	89.7(7)	O(10)A′–Cu–O(11)B′	91.1(7)		

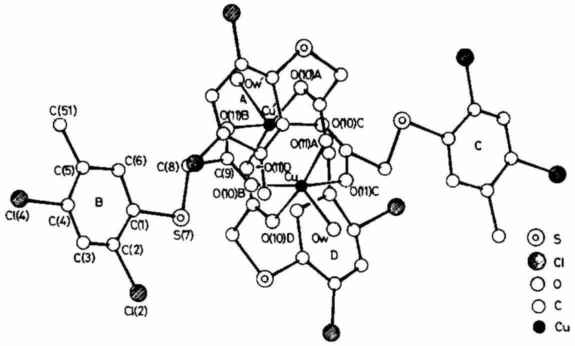

Fig. 1. Atom naming scheme for $[Cu_2(DCMPTA)_4(H_2O)_2]\cdot 2(acetone)$ (2).

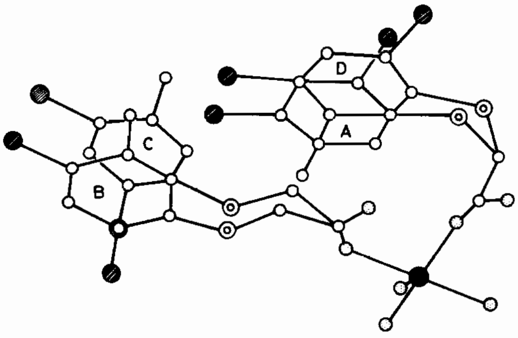

Fig. 2. The relationship between the disordered DCMPTA ligands in (2), transformed across the inversion centre.

tion, were also essentially related by the inversion centre except for the oxygen which appears to be disordered over the two sites. Furthermore, one of the methyl groups is vibrationally active. The data were corrected for absorption while three extinction-affected reflections were removed from the refinement.

Atomic coordinates are listed in Table I while bond distances and angles about the copper atom are given in Table II. Thermal parameters, observed and calculated structure factors and intraligand bond distances and angles are available on request from the authors.

Discussion

Although the structure determination of the title compound, $[Cu_2(DCMPTA)_4(H_2O)_2]\cdot 2(acetone)$, (2) lacks the precision of (1) [1] because of the disorder inherent in the thioether side-chains, the basic structural features of the two complexes are comparable (Fig. 1). The tetracarboxylate bridged dimer has similar dimensions: Cu–O (equatorial), 1.99(2) Å mean; Cu–Cu, 2.639(5) Å, [*cf.* 1.961(4) Å and 2.646(1) Å for (1)]. The major difference is in the axial positions of the dimer where water molecules replace the acetones of (1), with a significant contraction in the Cu–O bond length, from 2.206(3) Å (1) to 2.13(2) (2). However, both distances are within the range found for axial Cu–O distances among the examples of dimeric copper(II) complexes of this series [3] {2.09 Å in $[Cu_2(CH_3CO_2)_4(urea)_2]\cdot H_2O$ and $[Cu_2(o\text{-}C_6H_4OH\cdot CO_2)_4(diox)_2]\cdot H_2O$ to 2.28 Å in $[Cu_2(C_2H_5CO_2)_4]$: 2.16 Å mean for 24 examples}. The role of the acetones in (2) is as molecules of solvation with the carbonyl oxygen linked by hydrogen bonds to the axial water [O····O, 2.83 Å (*intra*-dimer) and 2.86 Å (*inter*-dimer)].

Another interesting difference between the two dimer systems is the disorder which exists between the four phenylthio ligand groups in (2), effectively destroying in part the centrosymmetric relationship in the molecule, required by the space group inversion. This is maintained for the dimer core and extends to the carboxylate carbon [C(9)] in ligand A and to the α-carbon in ligand B. The relationship between the disordered sets across the inversion centre is shown in Fig. 2, and may be visualized as a slip of one ring system subtly across the other while maintaining coplanarity. Thus ligands A and B give rise to the disordered pairs D and C and the perfect inversion centre is removed. However, there is coincidence of some atoms of the two ring planes, *e.g.* C(1)A and C(6)D; Cl(2)A and C(2)D; C(5)A and C(3)D; C(3)A and C(51)D; C(6)B and C(1)C.

Disorder is also known for some of the (phenylthio)acetate complexes, but in these examples, it has been the result of rotation of the ring system about the S(7)–C(1) bond. The reason for the relatively high incidence of disorder in the phenylthio analogues [4, 5] compared to the complexes of phenoxy acids may be attributed to the greater flexibility in the group, allowed by the poorer stabilization of the S····O (carboxyl) *vs.* O(ether)···O(carboxyl) interaction. This results in a more regular distance in the phenoxy acids and their complexes, hence a more rigid molecular conformation is assumed. In contrast there is no regularity in this distance among the phenylthio complexes nor with the parent acid, (phenylthio)acetic acid. In the case of (1), the insertion of acetone, with its extended chain, rather than water, into the axial position of the dimer, may be instrumental in stabilizing the DCMPTA ligands in the structure.

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