

The Crystal and Molecular Structures of Hexaaquacopper(II) Benzenesulphonate, Toluene-4-sulphonate and D-Camphor-10-sulphonate

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The structures of hexaaquacopper(II) benzenesulphonate (triclinic, $a = 22.51$, $b = 6.26$, $c = 6.96$ Å, $\alpha = 92.5$, $\beta = 93.0$, $\gamma = 89.5^\circ$, space group $P\bar{1}$, $Z = 2$, 2970 reflexions, $R_w = 0.041$), hexaaquacopper(II) toluene-4-sulphonate (monoclinic, $a = 5.85$, $b = 25.71$, $c = 7.35$ Å, $\beta = 105.4^\circ$, space group $P2_1/c$, $Z = 2$, 3645 reflexions, $R_w = 0.048$) and hexaaquacopper(II) D-camphor-10-sulphonate (monoclinic, $a = 17.17$, $b = 7.05$, $c = 11.64$ Å, $\beta = 94.1^\circ$, space group $P2_1$, $Z = 2$, 1920 reflexions, $R_w = 0.089$) have been determined from diffractometer intensity measurements. The overall packing arrangements in the three structures are broadly similar, but whilst the Cu^{II} ions in the arylsulphonates are in elongated, near tetragonally distorted, octahedral environments, that in the D-camphor-10-sulphonate is better described as a rhombically distorted octahedron. Details of these, and related structures, may be rationalized in terms of Jahn–Teller distortions and hydrogen bonding.

Introduction

The rarity of regular octahedral structures in Cu^{II} stereochemistry (Gažo *et al.*, 1976) has been rationalized in terms of the Jahn–Teller theorem, which requires any non-linear species with an electronically degenerate ground state, such as octahedral Cu^{II} , to distort so as to remove the degeneracy. Group-theoretical arguments establish that the possible distortions transform as the irreducible representations contained in the direct product of the irreducible representation of the degenerate orbital. In particular, for octahedral Cu^{II} , these correspond to the elongated and compressed tetragonal and rhombic distortions which are ubiquitous in Cu^{II} stereochemistry.

Theoretical arguments alone, however, afford no further information about the nature of the distortions; for example, they do not explain why the tetragonally distorted elongated octahedron is so much more common than the compressed tetragonal or rhombically distorted arrangements (Lohr & Lipscomb, 1963; Ballhausen & Johansen, 1965; Clack & Farri-mond, 1971; and references therein). Presumably, the exact nature and direction of distortion is dictated by the identity and environment of the ligands to which the Cu ion is coordinated. For example, the work of Prout and Rossotti (Prout, Armstrong, Carruthers, Forrest, Murray-Rust & Rossotti, 1968; Prout, Carruthers & Rossotti, 1971) on a range of hydrated Cu^{II} 2-substituted carboxylates (I), with $R' = \text{CH}_3$, $R = \text{H}$; $R' = \text{H}$, $R = \text{CH}_3$, C_2H_5 , C_6H_5 , has shown that, by

Table 1. Cu–O distances (Å) for a range of hydrated Cu^{II} 2-substituted carboxylates (I)

<i>R</i>	<i>R'</i>	Cu–OCO	Cu–OH ₂	Cu–OR
H ^a	CH ₃	1.89 (2)	2.56 (3)	2.01 (2)
CH ₃ ^a	H	1.93 (1)	2.16 (1)	2.13 (1)
C ₂ H ₅ ^b	H	1.97 (1)	1.99 (1)	2.38 (1)
C ₆ H ₅ ^a	H	1.94 (1)	1.97 (1)	2.50 (1)

References: (a) Prout, Armstrong, Carruthers, Forrest, Murray-Rust & Rossotti (1968); (b) Prout, Carruthers & Rossotti (1971).

varying the nature of *R*, it is possible to change from an elongated tetragonal structure, through a compressed structure, and back to an elongated structure but with the long bonds now to different ligands (Table 1). Though this may be due primarily to steric factors, the structures of bis(pyridine)bis(methoxyacetato)copper(II), aquabis(pyridine)bis(phenoxyacetato)copper(II) (Prout, Barrow & Rossotti, 1971) and tetrakis(imidazole)bis(methoxyacetato)copper(II) (Prout, Allison & Rossotti, 1971) imply that electronic factors are also important in determining the geometry of the Cu^{II} coordination sphere.

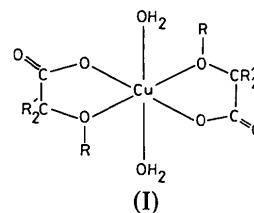


Table 2. The hydrogen-bonding environments of Cu(H₂O)₆²⁺ ions

Compound	Atom	Cu—O (Å)	Hydrogen bonds (Å)
Cu(C ₆ H ₅ SO ₃) ₂ ·6H ₂ O ^a	A	O(1) 1.958 2.708	2.746
		O(2) 1.979 2.730	2.731
		O(3) 2.259 2.834	2.835
	B	O(6) 1.961 2.715	2.734
		O(4) 1.986 2.748	2.734
		O(5) 2.264 2.796	2.841
Cu(CH ₃ ·C ₆ H ₄ ·SO ₃) ₂ ·6H ₂ O ^a	O(5) 1.953 2.714	2.767	
	O(6) 1.954 2.720	2.780	
	O(4) 2.423 2.747	2.789	
	O(1) 2.17 2.81	2.71	
Cu(C ₁₀ H ₁₅ OSO ₃) ₂ ·6H ₂ O ^a	O(2) 2.05 2.73	2.79	
	O(3) 1.97 2.78	2.71	
	O(4) 1.97 2.65	2.77	
	O(5) 2.02 2.75	2.81	
	O(6) 2.22 2.89	2.82	
	O(9) 1.966 2.683	2.732	
(NH ₄) ₂ Cu(SO ₄) ₂ ·6H ₂ O ^b	O(8) 2.073 2.707	2.743	
	O(7) 2.230 2.821	2.826	
	O(9) 1.944 2.657	2.668	
K ₂ Cu(SO ₄) ₂ ·6H ₂ O ^c	O(8) 2.279 2.711	2.764	
	O(7) 2.068 2.742	2.781	
	O(9) 1.937 2.654	2.677	
K ₂ Cu(SeO ₄) ₂ ·6H ₂ O ^d	O(8) 2.044 2.655	2.718	
	O(7) 2.297 2.868	2.821	
	O(9) 1.957 2.673	2.688	
Rb ₂ Cu(SO ₄) ₂ ·6H ₂ O ^e	O(8) 2.307 2.741	2.764	
	O(7) 2.031 2.717	2.754	
	O(9) 1.987 2.688	2.689	
Rb ₂ Cu(SO ₄) ₂ ·6H ₂ O ^f	O(8) 2.317 2.724	2.797	
	O(7) 2.002 2.736	2.747	
	O(9) 1.966 2.702	2.706	
Cs ₂ Cu(SO ₄) ₂ ·6H ₂ O ^g	O(8) 2.314 2.780	2.782	
	O(7) 2.004 2.722	2.714	
	O(9) 1.957 2.683	2.707	
Tl ₂ Cu(SO ₄) ₂ ·6H ₂ O ^h	O(8) 2.317 2.753	2.778	
	O(7) 2.017 2.730	2.758	
	O(1) 1.967 2.609‡	2.623‡	
K ₂ Cu(Zr ₂ F ₁₂)·6H ₂ O ⁱ	O(2) 2.024 2.689‡	2.711‡	
	O(3) 2.327 2.781‡	2.805‡	
	O(1) 1.937 2.548‡	2.829	
Cu ₂ (ZrF ₈)·12H ₂ O ^j	O(2) 1.942 2.576‡	2.594‡	
	O(3) 1.996 2.746	2.862‡	
	O(4) 2.027 2.648‡	2.655‡	
	O(6) 2.391 2.687‡	2.985	
	O(5) 2.424 2.666‡	2.787‡	
	O(1) 1.954 2.618‡	2.755‡	
Cu ₃ (Zr ₂ F ₁₄)·16H ₂ O ^k	O(2) 1.983 2.602‡	2.869‡	
	O(3) 2.355 2.568‡	2.658‡	
	O(1) 2.074 2.79‡	2.71‡	
CuSiF ₆ ·6H ₂ O ^l	B	O(3) 1.970 2.84	2.99‡
	O(2) 1.970 2.69‡	2.78‡	
	O(4) 2.367 2.78‡	2.97‡	
			2.84*

References: (a) This work; (b) Brown & Chidambaram (1969); (c) Robinson & Kennard (1972); (d) Whitnall, Kennard, Nimmo & Moore (1975); (e) Van der Zee, Shields, Graham & Kennard (1972); (f) Smith, Moore & Kennard (1975); (g) Shields & Kennard (1972); (h) Shields, Van der Zee & Kennard (1972); (i) Fischer & Weiss (1973a); (j) Fischer, Elchinger & Weiss (1973); (k) Fischer & Weiss (1973b); (l) Ray, Zalkin & Templeton (1973).

* Indicates a hydrogen bond of type (b), i.e. Cu—O...H—O—.

† Data collected at liquid nitrogen temperature (77 K).

‡ Indicates an O...F hydrogen bond; all others are O...O hydrogen bonds.

There are some CuO₆ systems where the ligands are equivalent by crystal symmetry (Joesten, Hussain & Lenhart, 1970; Ray, Zalkin & Templeton, 1973) and in which the Cu—O distances are exactly the same. However, there are others where the ligands do not interact with the environment, and are non-equivalent by crystal symmetry, but are very closely equivalent chemically, and it seems that this situation leads to very nearly equal bond lengths; for example 2.067–2.110 Å for tris(tetraisopropylmethylenediphosphonate)copper(II) perchlorate (Miller, Lenhart & Joesten, 1973), 2.023–2.134 Å for tris(octamethylmethylenediphosphonic diamide)copper(II) perchlorate (Miller, Lenhart & Joesten, 1972).

In some compounds, the Cu ion is apparently surrounded by a regular octahedron of six identical ligands, all in equivalent environments. In this circumstance, of course, no one direction of distortion is any more favourable than the others, and the apparent violation of the Jahn–Teller theorem has been rationalized by postulating (i) an oscillation of each molecule amongst the three equivalent directions of distortion, so that on time average the molecule appears regular (the ‘dynamic Jahn–Teller effect’), or (ii) a random distribution of static distortions in the crystal so that on space average the molecule appears regular. Some evidence for this is provided by the structure of Cu(en)₃SO₄ (Cullen & Lingafelter, 1970), in which all the Cu—N lengths are equal (2.15 Å); although the thermal ellipsoids of all other atoms in the structure appear to be normal, those of the N atoms are unusually large, and lie with their major axes along the Cu–ligand bond direction. The dynamic–static Jahn–Teller theory has also been used to explain the regular octahedral environment in tris(octamethylpyrophosphoramidate)copper(II) perchlorate (Joesten, Hussain & Lenhart, 1970; Koch, Joesten & Venable, 1973).

The Cu(H₂O)₆²⁺ system lies between the two extremes, in that, although all the ligands are identical (unlike those in the carboxylate complexes discussed above), their environments are unlikely to be equivalent in most compounds because of the variety of hydrogen-bonding arrangements available. In the crystalline state, water molecules may be involved in two general types of hydrogen bonding, viz (a) O—H...X and (b) H—O...H—X where X is an electronegative element such as O or F. The dipole moment associated with the O atom of the water molecule should be increased by hydrogen bonding of type (a), and reduced by hydrogen bonding of type (b). If, therefore, the Cu—O interaction is primarily ion–dipole in nature, we may expect the hydrogen bonding, by changing the size of the dipole, to have an effect on the geometry of the Cu(H₂O)₆²⁺ species. Specifically, if an approximately inverse relation between the strength of a bond and its length is assumed, we may expect a positive correlation between short hydrogen bonds of type (a) and short

Cu—O bonds, and, conversely, between short hydrogen bonds of type (b) and long Cu—O bonds.

Relatively few $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ systems have been studied (Table 2). In this paper we report the structures of three more such complexes and consider also those whose structures are already known. Our choice was governed by a desire to find systems that are chemically very similar but crystallographically quite different. In particular, the necessarily non-centrosymmetric complex with D-camphor-10-sulphonic acid was examined since in the vast majority of studies the $\text{Cu}(\text{H}_2\text{O})_6^{2+}$ ion has been on a centre of symmetry.

Results and discussion

Projections of the crystal structures for each complex are shown in Figs. 1 to 3. Fractional coordinates are

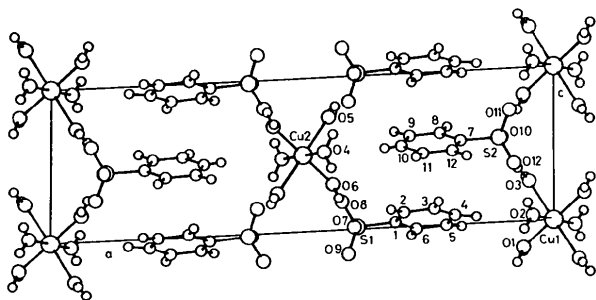


Fig. 1. The crystal structure of hexaaquacopper(II) benzenesulphonate projected down *b*.

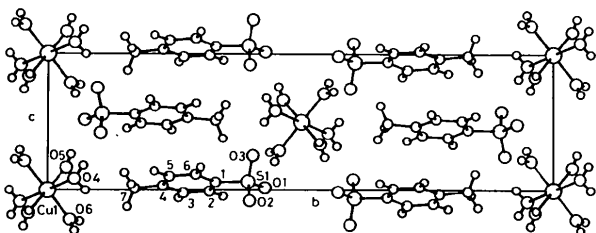


Fig. 2. The crystal structure of hexaaquacopper(II) toluene-4-sulphonate projected down *a*.

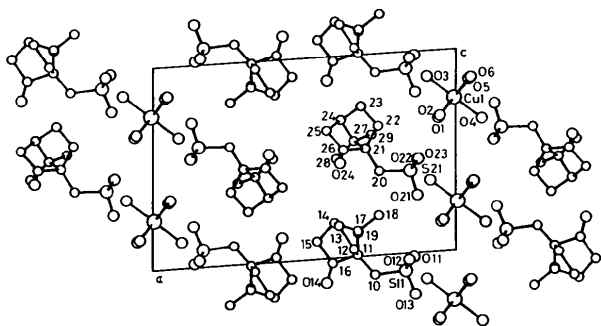


Fig. 3. The crystal structure of hexaaquacopper(II) D-camphor-10-sulphonate projected down *b*.

shown in Tables 3 to 5. Bond distances and angles, with estimated standard deviations calculated from the full variance-covariance matrix, are given in Tables 6, 7 and 8.

The dimensions of the five crystallographically independent sulphonate groups (two each in the benzene- and D-camphor-10-sulphonates, and one in the toluene-4-sulphonate) are very similar, with the S—O lengths varying only between 1.43 and 1.47 Å,

Table 3. *Hexaaquacopper(II) benzenesulphonate: fractional atomic coordinates and H isotropic thermal parameters ($\times 10^2$)*

	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso} (Å ²)
Cu(1)	0	0	0	
O(1)	0.0607 (2)	-0.1077 (7)	-0.1712 (6)	
O(2)	0.0418 (2)	0.2769 (6)	0.0351 (5)	
O(3)	0.0493 (2)	-0.1271 (7)	0.2627 (6)	
Cu(2)	0.5	0.5	0.5	
O(4)	0.4581 (2)	0.7801 (6)	0.5162 (5)	
O(5)	0.4494 (2)	0.3693 (7)	0.7413 (6)	
O(6)	0.4406 (2)	0.3948 (7)	0.3029 (5)	
S(1)	0.3914 (1)	0.8733 (2)	0.0152 (1)	
O(7)	0.3973 (1)	0.6418 (5)	0.0151 (4)	
O(8)	0.4220 (1)	0.9775 (5)	0.1842 (4)	
O(9)	0.4089 (1)	0.9604 (5)	-0.1638 (4)	
C(1)	0.3151 (2)	0.9328 (7)	0.0329 (5)	
C(2)	0.2979 (2)	1.1349 (8)	0.0945 (6)	
C(3)	0.2379 (2)	1.182 (1)	0.1086 (7)	
C(4)	0.1963 (2)	1.027 (1)	0.0610 (7)	
C(5)	0.2129 (2)	0.827 (1)	-0.0011 (8)	
C(6)	0.2731 (2)	0.7756 (8)	-0.0158 (6)	
S(2)	0.1085 (1)	0.3705 (2)	0.5568 (1)	
O(10)	0.1045 (1)	0.1387 (5)	0.5599 (4)	
O(11)	0.0879 (1)	0.4732 (5)	0.7338 (4)	
O(12)	0.0790 (1)	0.4575 (5)	0.3847 (4)	
C(7)	0.1852 (2)	0.4304 (7)	0.5497 (5)	
C(8)	0.2271 (2)	0.2810 (9)	0.6041 (6)	
C(9)	0.2869 (2)	0.332 (1)	0.5947 (8)	
C(10)	0.3031 (3)	0.528 (1)	0.5309 (8)	
C(11)	0.2606 (2)	0.674 (1)	0.4767 (7)	
C(12)	0.2014 (2)	0.6282 (9)	0.4857 (6)	
H(1)	0.073 (3)	-0.03 (1)	-0.27 (1)	2 (2)
H(2)	0.061 (3)	-0.19 (1)	-0.20 (1)	3 (2)
H(3)	0.059 (3)	0.36 (1)	-0.05 (1)	2 (2)
H(4)	0.052 (3)	0.32 (1)	0.12 (1)	4 (2)
H(5)	0.072 (3)	-0.04 (1)	0.35 (1)	3 (2)
H(6)	0.056 (3)	-0.22 (1)	0.29 (1)	4 (2)
H(7)	0.444 (3)	0.84 (1)	0.41 (1)	3 (2)
H(8)	0.441 (3)	0.82 (1)	0.63 (1)	3 (2)
H(9)	0.437 (3)	0.46 (1)	0.81 (1)	3 (2)
H(10)	0.443 (3)	0.25 (1)	0.77 (1)	6 (2)
H(11)	0.429 (3)	0.47 (1)	0.21 (1)	6 (2)
H(12)	0.442 (3)	0.28 (1)	0.29 (1)	2 (2)
H(13)	0.324 (3)	1.25 (1)	0.115 (9)	3 (2)
H(14)	0.229 (3)	1.34 (1)	0.154 (9)	6 (2)
H(15)	0.154 (3)	1.07 (1)	0.044 (9)	8 (2)
H(16)	0.183 (3)	0.71 (1)	-0.013 (9)	4 (2)
H(17)	0.283 (3)	0.63 (1)	-0.057 (9)	3 (2)
H(18)	0.212 (3)	0.14 (1)	0.642 (9)	4 (2)
H(19)	0.318 (3)	0.22 (1)	0.627 (9)	2 (2)
H(20)	0.337 (3)	0.56 (1)	0.521 (9)	7 (2)
H(21)	0.274 (3)	0.81 (1)	0.455 (9)	4 (2)
H(22)	0.173 (3)	0.72 (1)	0.447 (9)	2 (2)

Table 4. Hexaaquacopper(II) toluene-4-sulphonate: fractional atomic coordinates and H isotropic thermal parameters ($\times 10^2$)

	x	y	z	U_{iso} (Å ²)
Cu(1)	0	0	0	
O(4)	0.3567 (3)	0.0525 (1)	0.0837 (3)	
O(5)	-0.1588 (3)	0.0368 (1)	0.1644 (3)	
O(6)	-0.1565 (4)	0.0445 (1)	-0.2120 (3)	
S(1)	0.2679 (1)	0.3944 (1)	0.0615 (1)	
O(1)	0.0578 (3)	0.4280 (1)	0.0161 (3)	
O(2)	0.4022 (4)	0.3974 (1)	-0.0785 (3)	
O(3)	0.4170 (3)	0.4036 (1)	0.2526 (3)	
C(1)	0.1644 (4)	0.3298 (1)	0.0574 (3)	
C(2)	-0.0744 (4)	0.3180 (1)	-0.0090 (4)	
C(3)	-0.1440 (5)	0.2662 (1)	-0.0209 (4)	
C(4)	0.0195 (5)	0.2261 (1)	0.0316 (4)	
C(5)	0.2564 (6)	0.2389 (1)	0.1012 (5)	
C(6)	0.3292 (5)	0.2904 (1)	0.1153 (5)	
C(7)	-0.0593 (8)	0.1699 (1)	0.0121 (5)	
H(1)	0.356 (9)	0.074 (2)	-0.001 (8)	5 (2)
H(2)	0.372 (9)	0.070 (2)	0.180 (8)	6 (2)
H(3)	-0.103 (8)	0.046 (2)	0.261 (6)	1 (1)
H(4)	-0.309 (8)	0.035 (2)	0.151 (6)	3 (1)
H(5)	-0.112 (8)	0.054 (2)	-0.292 (7)	2 (1)
H(6)	-0.271 (8)	0.063 (2)	-0.225 (6)	2 (1)
H(7)	-0.192 (7)	0.345 (2)	-0.046 (5)	1 (1)
H(8)	-0.323 (8)	0.257 (2)	-0.058 (6)	2 (1)
H(9)	0.386 (8)	0.209 (2)	0.139 (6)	3 (1)
H(10)	0.493 (8)	0.300 (2)	0.167 (6)	3 (1)
H(11)	-0.25 (1)	0.164 (3)	0.04 (1)	10 (3)
H(12)	-0.06 (1)	0.156 (3)	-0.121 (9)	8 (2)
H(13)	0.02 (1)	0.150 (2)	0.128 (8)	6 (2)

and the S—C lengths between 1.76 and 1.77 Å. The O—S—O angles lie in the range 110.9 to 113.0°, and the O—S—C angles in the range 104.0 to 108.7°. The larger value of the former is almost certainly due to electrostatic repulsions between the O atoms.

The aromatic ring in the toluene-4-sulphonate is very regular with the C—C lengths varying between 1.384 and 1.389 Å, and the C—C—C angles between 118.3 and 121.7°. The rings in the benzenesulphonate are less regular, the C—C lengths being in the range 1.365 to 1.397 Å, and the C—C—C angles in the range 118.4 to 121.4°, but this is not unsatisfactory. The norbornane skeleton of the D-camphor-10-sulphonate anions have normal geometry (Fig. 4) (Phillips & Trotter, 1977; Rendle & Trotter, 1975; Bear & Trotter, 1975), and data for several least-squares planes are given in Table 9. The six-membered ring in each anion is a fairly symmetrical boat with two atoms [C(11) and C(14); C(21) and C(24), respectively] displaced 0.8 and 0.9 Å below the best plane through the other four atoms. The four-atom planes (2 and 3 for each anion in Table 9) are approximately planar, and the angles between these planes and the three-atom bridge plane (plane 4) are 126 and 125°, respectively, for both anions. Bond lengths and angles are close to normal, the bridgehead angles being 93.5 and 93.6° for anions

Table 5. Hexaaquacopper(II) D-camphor-10-sulphonate: fractional atomic coordinates

	x	y	z
Cu(1)	0.00567 (7)	0.7500	0.7575 (1)
O(1)	0.0590 (8)	0.527 (2)	0.662 (1)
O(2)	0.0536 (7)	0.971 (2)	0.6718 (9)
O(3)	0.0970 (5)	0.755 (3)	0.8701 (8)
O(4)	-0.0852 (5)	0.746 (3)	0.6446 (8)
O(5)	-0.0408 (7)	0.535 (2)	0.8451 (9)
O(6)	-0.0485 (8)	0.983 (3)	0.853 (1)
S(11)	0.1662 (1)	0.2467 (9)	-0.0846 (2)
O(11)	0.1382 (5)	0.094 (2)	-0.0189 (7)
O(12)	0.1545 (5)	0.431 (2)	-0.0324 (8)
O(13)	0.1347 (4)	0.243 (3)	-0.2030 (5)
O(14)	0.4270 (5)	0.171 (3)	-0.1184 (8)
C(10)	0.2677 (5)	0.216 (2)	-0.0940 (7)
C(11)	0.3243 (4)	0.261 (2)	0.0091 (7)
C(12)	0.3371 (7)	0.477 (2)	0.0388 (9)
C(13)	0.3868 (7)	0.465 (2)	0.159 (1)
C(14)	0.4017 (5)	0.253 (2)	0.1738 (8)
C(15)	0.4584 (6)	0.193 (3)	0.089 (1)
C(16)	0.4072 (6)	0.199 (2)	-0.0236 (9)
C(17)	0.3227 (5)	0.163 (2)	0.1266 (8)
C(18)	0.2547 (6)	0.228 (3)	0.1970 (8)
C(19)	0.323 (1)	-0.053 (2)	0.119 (1)
S(21)	0.1500 (1)	0.756 (1)	0.4077 (2)
O(21)	0.1269 (4)	0.761 (3)	0.2856 (5)
O(22)	0.1237 (7)	0.927 (2)	0.4649 (9)
O(23)	0.1266 (7)	0.586 (2)	0.462 (1)
O(24)	0.3832 (6)	1.000 (2)	0.467 (1)
C(20)	0.2532 (5)	0.765 (2)	0.4152 (7)
C(21)	0.2985 (4)	0.742 (2)	0.5316 (7)
C(22)	0.2574 (7)	0.818 (2)	0.6399 (9)
C(23)	0.3137 (7)	0.740 (3)	0.7426 (8)
C(24)	0.3808 (6)	0.651 (2)	0.6813 (8)
C(25)	0.4275 (7)	0.808 (2)	0.633 (1)
C(26)	0.3725 (7)	0.874 (2)	0.532 (1)
C(27)	0.3377 (5)	0.557 (2)	0.5729 (8)
C(28)	0.3963 (8)	0.478 (2)	0.490 (1)
C(29)	0.2795 (9)	0.401 (2)	0.599 (1)

I and II respectively. The angle between planes 5 and 6 for anion I is 120°, and that for anion II is 100°, showing that the second D-camphor-10-sulphonate molecule is twisted through 20° with respect to the first.

For the Cu(H₂O)₆²⁺ octahedra of the arylsulphonates there is a distinct elongated tetragonal distortion, the bond lengths breaking down fairly obviously into four short and two long (Tables 6 and 7). In the D-camphor-10-sulphonate the variation in the Cu—OH₂ lengths (Table 8) is not so pronounced, and there is an approximately even gradation of distances from 1.97 to 2.22 Å, so that the Cu environment is better described as a rhombically distorted octahedron.

From the point of view of their overall packing arrangements the three structures are broadly similar as might be expected. Each has rows of Cu(H₂O)₆²⁺ ions parallel to the short axis of the crystal (*a* in the toluene-4-sulphonate, and *b* in the benzene- and D-camphor-10-sulphonates). The toluene-4- and D-camphor-10-sulphonates have only one crystallographically in-

dependent Cu octahedron in the unit cell, but the benzenesulphonate has two, and these form alternate rows in the structure.

In the benzene- and toluene-4-sulphonates (Figs. 1 and 2), each of these rows is flanked on either side by two rows of aromatic sulphonate groups arranged so that the polar (*i.e.* $-\text{SO}_3$) ends are pointed towards the nearest Cu octahedra, which are held in a hydrogen-

bonding network. Each aromatic ring has its $-\text{SO}_3$ group pointing in the opposite direction to those of its nearest neighbours in the adjacent rows. In the toluene-4-sulphonate there are only two such nearest neighbours, one in each adjacent row, whereas in the benzenesulphonate there are four. The tilt of the plane of each aromatic ring in the toluene-4-sulphonate (relative to the *bc* plane of the crystal) is in the same

Table 6. *Hexaaquacopper(II) benzenesulphonate: bond distances (Å) and angles (°)*

Cu(1)—O(1)	1.958 (3)	Cu(2)—O(4)	1.986 (3)
Cu(1)—O(2)	1.979 (3)	Cu(2)—O(5)	2.264 (3)
Cu(1)—O(3)	2.259 (4)	Cu(2)—O(6)	1.961 (3)
S(1)—O(7)	1.454 (3)	S(2)—O(10)	1.456 (3)
S(1)—O(8)	1.463 (3)	S(2)—O(11)	1.460 (3)
S(1)—O(9)	1.457 (3)	S(2)—O(12)	1.461 (3)
S(1)—C(1)	1.764 (4)	S(2)—C(7)	1.774 (4)
C(1)—C(2)	1.377 (6)	C(7)—C(8)	1.374 (6)
C(2)—C(3)	1.388 (6)	C(8)—C(9)	1.390 (7)
C(3)—C(4)	1.372 (8)	C(9)—C(10)	1.380 (8)
C(4)—C(5)	1.365 (8)	C(10)—C(11)	1.370 (8)
C(5)—C(6)	1.397 (7)	C(11)—C(12)	1.370 (7)
C(6)—C(1)	1.389 (6)	C(12)—C(7)	1.392 (6)
O(1)—Cu(1)—O(2)	90.3 (2)	O(4)—Cu(2)—O(5)	92.7 (2)
O(1)—Cu(1)—O(3)	92.5 (2)	O(4)—Cu(2)—O(6)	90.2 (2)
O(2)—Cu(1)—O(3)	91.4 (2)	O(5)—Cu(2)—O(6)	92.5 (2)
O(7)—S(1)—O(8)	112.0 (2)	O(10)—S(2)—O(11)	111.4 (2)
O(7)—S(1)—O(9)	112.5 (2)	O(10)—S(2)—O(12)	112.9 (2)
O(8)—S(1)—O(9)	112.1 (2)	O(11)—S(2)—O(12)	112.2 (2)
C(1)—S(1)—O(7)	106.8 (2)	C(7)—S(2)—O(10)	106.4 (2)
C(1)—S(1)—O(8)	106.3 (2)	C(7)—S(2)—O(11)	106.7 (2)
C(1)—S(1)—O(9)	106.6 (2)	C(7)—S(2)—O(12)	106.7 (2)
C(2)—C(1)—S(1)	119.5 (3)	C(8)—C(7)—S(2)	119.8 (3)
C(6)—C(1)—S(1)	119.6 (3)	C(12)—C(7)—S(2)	118.8 (3)
C(6)—C(1)—C(2)	120.8 (4)	C(12)—C(7)—C(8)	121.4 (4)
C(1)—C(2)—C(3)	119.6 (4)	C(7)—C(8)—C(9)	118.4 (5)
C(2)—C(3)—C(4)	119.8 (5)	C(8)—C(9)—C(10)	120.3 (5)
C(3)—C(4)—C(5)	121.0 (5)	C(9)—C(10)—C(11)	120.4 (5)
C(4)—C(5)—C(6)	120.1 (5)	C(10)—C(11)—C(12)	120.5 (5)
C(5)—C(6)—C(1)	118.6 (5)	C(11)—C(12)—C(7)	119.1 (5)

Table 7. *Hexaaquacopper(II) toluene-4-sulphonate: bond distances (Å) and angles (°)*

Cu(1)—O(4)	2.423 (2)	C(1)—C(2)	1.386 (4)
Cu(1)—O(5)	1.953 (2)	C(2)—C(3)	1.389 (4)
Cu(1)—O(6)	1.954 (2)	C(3)—C(4)	1.389 (4)
S(1)—O(1)	1.466 (2)	C(4)—C(5)	1.384 (4)
S(1)—O(2)	1.453 (2)	C(5)—C(6)	1.386 (4)
S(1)—O(3)	1.463 (2)	C(6)—C(1)	1.385 (3)
S(1)—C(1)	1.765 (2)	C(4)—C(7)	1.512 (4)
O(4)—Cu(1)—O(5)	95.3 (1)	C(2)—C(1)—S(1)	121.4 (3)
O(4)—Cu(1)—O(6)	93.8 (1)	C(6)—C(1)—S(1)	118.4 (3)
O(5)—Cu(1)—O(6)	90.6 (1)	C(6)—C(1)—C(2)	120.2 (3)
O(1)—S(1)—O(2)	112.7 (1)	C(1)—C(2)—C(3)	118.9 (3)
O(1)—S(1)—O(3)	111.9 (1)	C(2)—C(3)—C(4)	121.7 (3)
O(2)—S(1)—O(3)	112.0 (1)	C(3)—C(4)—C(5)	118.3 (3)
C(1)—S(1)—O(1)	106.7 (1)	C(4)—C(5)—C(6)	120.8 (3)
C(1)—S(1)—O(2)	106.6 (1)	C(5)—C(6)—C(1)	120.0 (3)
C(1)—S(1)—O(3)	106.4 (1)	C(3)—C(4)—C(7)	120.9 (3)
		C(5)—C(4)—C(7)	120.8 (3)

Table 8. *Hexaaquacopper(II) D-camphor-10-sulphonate: bond distances (Å) and angles (°)*

Cu(1)—O(1)	2.17 (2)	Cu(1)—O(4)	1.97 (3)
Cu(1)—O(2)	2.05 (2)	Cu(1)—O(5)	2.02 (3)
Cu(1)—O(3)	1.97 (3)	Cu(1)—O(6)	2.22 (2)
S(11)—O(11)	1.43 (1)	S(21)—O(21)	1.45 (1)
S(11)—O(12)	1.46 (1)	S(21)—O(22)	1.46 (1)
S(11)—O(13)	1.44 (1)	S(21)—O(23)	1.43 (1)
S(11)—C(10)	1.77 (1)	S(21)—C(20)	1.77 (1)
C(10)—C(11)	1.52 (1)	C(20)—C(21)	1.52 (1)
C(11)—C(12)	1.57 (1)	C(21)—C(22)	1.58 (1)
C(12)—C(13)	1.58 (1)	C(22)—C(23)	1.58 (1)
C(13)—C(14)	1.53 (2)	C(23)—C(24)	1.53 (2)
C(14)—C(15)	1.50 (1)	C(24)—C(25)	1.50 (2)
C(15)—C(16)	1.53 (1)	C(25)—C(26)	1.53 (1)
C(16)—C(11)	1.56 (1)	C(26)—C(21)	1.57 (1)
C(14)—C(17)	1.56 (1)	C(24)—C(27)	1.56 (1)
C(11)—C(17)	1.54 (1)	C(21)—C(27)	1.53 (1)
C(17)—C(18)	1.54 (1)	C(27)—C(28)	1.54 (1)
C(17)—C(19)	1.52 (2)	C(27)—C(29)	1.53 (2)
C(16)—O(14)	1.20 (1)	C(26)—O(24)	1.19 (1)
O(1)—Cu(1)—O(2)	95.8 (9)	O(2)—Cu(1)—O(6)	83.0 (5)
O(1)—Cu(1)—O(3)	90.6 (9)	O(3)—Cu(1)—O(4)	179.6 (9)
O(1)—Cu(1)—O(4)	89 (1)	O(3)—Cu(1)—O(5)	90 (1)
O(1)—Cu(1)—O(5)	85.0 (8)	O(3)—Cu(1)—O(6)	89.7 (9)
O(1)—Cu(1)—O(6)	178.8 (9)	O(4)—Cu(1)—O(5)	90.2 (9)
O(2)—Cu(1)—O(3)	88.9 (8)	O(4)—Cu(1)—O(6)	90.2 (8)
O(2)—Cu(1)—O(4)	91 (1)	O(5)—Cu(1)—O(6)	96 (1)
O(2)—Cu(1)—O(5)	179 (2)		
O(11)—S(11)—O(12)	113.0 (5)	O(21)—S(21)—O(22)	110.9 (8)
O(11)—S(11)—O(13)	112.4 (8)	O(21)—S(21)—O(23)	112.8 (8)
O(12)—S(11)—O(13)	111.2 (8)	O(22)—S(21)—O(23)	112.6 (4)
C(10)—S(11)—O(11)	108.1 (6)	C(20)—S(21)—O(21)	104.6 (4)
C(10)—S(11)—O(12)	107.6 (6)	C(20)—S(21)—O(22)	106.8 (6)
C(10)—S(11)—O(13)	104.0 (4)	C(20)—S(21)—O(23)	108.7 (6)
S(11)—C(10)—C(11)	120.0 (5)	S(21)—C(20)—C(21)	119.1 (5)
C(10)—C(11)—C(12)	116.7 (7)	C(20)—C(21)—C(22)	116.4 (7)
C(10)—C(11)—C(16)	106.9 (7)	C(20)—C(21)—C(26)	107.4 (7)
C(10)—C(11)—C(17)	123.9 (8)	C(20)—C(21)—C(27)	123.8 (8)
C(11)—C(12)—C(13)	101.7 (8)	C(21)—C(22)—C(23)	101.7 (8)
C(12)—C(13)—C(14)	103.2 (8)	C(22)—C(23)—C(24)	103.2 (7)
C(13)—C(14)—C(15)	108 (1)	C(23)—C(24)—C(25)	108 (1)
C(13)—C(14)—C(17)	102.8 (6)	C(23)—C(24)—C(27)	102.9 (6)
C(15)—C(14)—C(17)	104.1 (7)	C(25)—C(24)—C(27)	104.1 (7)
C(14)—C(15)—C(16)	101.3 (8)	C(24)—C(25)—C(26)	101.3 (8)
C(15)—C(16)—C(11)	106.2 (8)	C(25)—C(26)—C(21)	106.1 (8)
C(15)—C(16)—O(14)	127.2 (9)	C(25)—C(26)—O(24)	127.0 (9)
C(11)—C(16)—O(14)	126.6 (9)	C(21)—C(26)—O(24)	126.9 (9)
C(11)—C(17)—C(18)	113.7 (7)	C(21)—C(27)—C(28)	113.7 (7)
C(11)—C(17)—C(19)	113.3 (7)	C(21)—C(27)—C(29)	113.4 (7)
C(14)—C(17)—C(18)	111.4 (7)	C(24)—C(27)—C(28)	111.3 (7)
C(14)—C(17)—C(19)	115.1 (7)	C(24)—C(27)—C(29)	115.1 (7)
C(18)—C(17)—C(19)	109 (1)	C(28)—C(27)—C(29)	109 (1)
C(11)—C(17)—C(14)	93.5 (8)	C(21)—C(27)—C(24)	93.6 (8)

direction as those of its nearest neighbours; in the benzenesulphonate, the tilt (relative to the *ab* plane) is in the opposite direction to those of the rings in the adjacent rows.

The sheets of hydrated Cu^{II} ions in the D-camphor-10-sulphonate (Fig. 3) have sheets of anions on either side, these having the sulphonate groups facing the Cu^{II} ion. Because of this arrangement, the D-camphor-10-sulphonate groups between the two sheets of Cu^{II} ions are arranged back to back, *i.e.* with the organic residues facing each other.

There is a complex network of hydrogen bonds in each of the three structures. For the benzene- and D-camphor-10-sulphonates, the hydrogen-bonding occurs between the Cu^{II} hydration sphere H atoms and the SO₃⁻ groups on the sulphonate anions. Each water sphere O atom is involved in two hydrogen-bonded contacts with SO₃⁻ group O atoms, the distances involved being in the range 2.71 to 2.89 Å (Table 2). Although each hydration sphere O atom in the toluene-4-sulphonate is involved in two hydrogen bonds, one of these, one from O(4) (Table 2), is different in that it is an interaction between the water O atoms of one Cu^{II} hydration sphere and the water H atoms of the next. Table 2 lists data for the hydrogen-bonding networks in these, and other, Cu(H₂O)₆²⁺ complexes.

The most obvious point to emerge from the data in Table 2 is that the Cu(H₂O)₆²⁺ ion can be found in a wide variety of stereochemistries, ranging from the regular octahedron in CuSiF₆·6H₂O (presumably a time or space average of the possible Jahn–Teller distortions) to the extremely tetragonally distorted octahedron in Cu(CH₃·C₆H₄SO₃)·6H₂O and the rhombically distorted octahedron in Cu₂(ZrF₈)·12H₂O. CuSiF₆·6H₂O shows that, even in the same crystal, it is possible for two Cu(H₂O)₆²⁺ ions to have different geometries.

In the distorted ions, there is a noticeable variation in the length of the long bonds, which range from 2.22 to 2.423 Å. This is particularly well illustrated by the aryl-

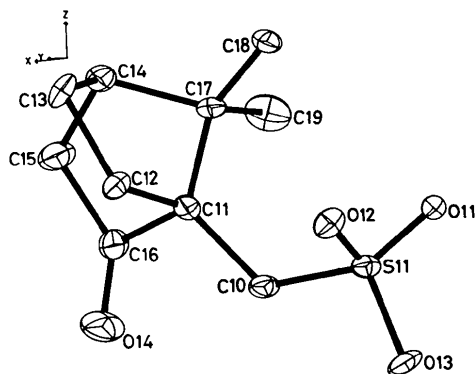


Fig. 4. View of one of the D-camphor-10-sulphonate anions showing the thermal ellipsoids.

sulphonates, where the addition of a methyl group causes the long bond to increase by 0.16 Å: clearly, even an apparently trivial change in the counter-ion may drastically alter the geometry of the Cu(H₂O)₆²⁺ ion. There is a similar variation in the lengths of the short bonds, though this is by no means as pronounced.

As might be expected, both on steric and electronic grounds, there is a marked interdependence of the lengths of the Cu–O bonds within an ion, so that the shorter the long bonds are, the longer are the short ones. Consequently, the length of a Cu–OH₂ bond will depend not only on the environment of the water molecule involved in the bond, but also on the environment of the other water molecules.

The suggested correlation between the Cu–O lengths and the lengths of the hydrogen bonds in which the

Table 9. Equations of least-squares planes for the D-camphor-10-sulphonate anions and, in square brackets, distances (Å) of atoms from the planes

The equations are referred to the crystal axes and *x, y, z* are fractional coordinates.

Anion I

Plane 1: C(12), C(13), C(15), C(16)

$$12.054x + 4.286y - 4.896z = 5.898$$

[C(12) 0.018, C(13) -0.018, C(15) 0.019, C(16) -0.019, C(11) -0.915, C(14) -0.823]

Plane 2: C(11), C(12), C(13), C(14)

$$14.749x + 0.291y - 6.645z = 4.821$$

[C(11) -0.023, C(12) 0.032, C(13) -0.033, C(14) 0.023]

Plane 3: C(11), C(16), C(15), C(14)

$$-4.438x - 6.752y + 1.709z = -3.189$$

[C(11) 0.003, C(16) -0.005, C(15) 0.005, C(14) -0.003]

Plane 4: C(11), C(17), C(14)

$$-8.915x + 5.506y + 4.471z = -1.413$$

Plane 5: S(11), C(10), C(11)

$$-1.672x - 6.638y + 3.835z = -2.240$$

Plane 6: C(10), C(11), C(17)

$$-11.184x + 4.932y + 3.963z = -2.303$$

Anion II

Plane 1: C(22), C(23), C(25), C(26)

$$0.585x + 6.539y + 4.302z = 8.236$$

[C(22) 0.017, C(23) -0.017, C(25) 0.018, C(26) -0.018, C(21) -0.921, C(24) -0.826]

Plane 2: C(21), C(22), C(23), C(24)

$$8.454x + 6.137y - 0.600z = 6.782$$

[C(21) -0.022, C(22) 0.032, C(23) -0.033, C(24) 0.023]

Plane 3: C(21), C(26), C(25), C(24)

$$8.068x - 4.603y - 7.295z = -4.890$$

[C(21) 0.004, C(26) -0.005, C(25) 0.005, C(24) -0.004]

Plane 4: C(21), C(27), C(24)

$$-14.101x - 1.448y + 6.869z = -1.633$$

Plane 5: S(21), C(20), C(21)

$$-0.733x + 6.975y + 1.671z = 5.847$$

Plane 6: C(20), C(21), C(27)

$$-14.963x - 1.949y + 5.435z = -3.024$$

water molecules are involved is well illustrated by the simple cases in which all the hydrogen bonds are of type (a), e.g. $\text{Cu}(\text{C}_6\text{H}_5\text{SO}_3)_2 \cdot 6\text{H}_2\text{O}$. Hydrogen bonds of type (b) seem to have a particularly important influence: thus, (i) the shortest $\text{Cu}-\text{OH}_2$ contact to a water molecule involved in such a bond is 2.027 Å, and the next shortest is 2.355 Å, and (ii) the major influence on the $\text{Cu}-\text{O}(3)$ contact in $\text{Cu}_3(\text{Zr}_2\text{F}_{14}) \cdot 16\text{H}_2\text{O}$ appears to be the very short type-(b) bond formed by O(3) rather than the short type-(a) bonds. The type-(b) bond in which O(4) of the toluene-4-sulphonate is involved presumably accounts for the difference in the length of the long $\text{Cu}-\text{OH}_2$ bonds in the aryl-sulphonates.

It is not possible to say that a water molecule forming hydrogen bonds of a given length will always form a $\text{Cu}-\text{OH}_2$ bond of a given length. This is not surprising, however, since in view of the interdependence of Cu -ligand lengths in a coordination polyhedron, it is clearly invalid to consider the environment of a ligand in isolation: it must be considered in relation to the environments of the other ligands in the coordination polyhedron.

Experimental

Preparation

(a) Hexaaquacopper(II) benzenesulphonate. A slightly acidified dilute aqueous solution of CuSO_4 (1 mol) was added slowly to a near boiling dilute aqueous solution of barium benzenesulphonate (1 mol). After filtering off the BaSO_4 and evaporation, pale-blue crystals of hexaaquacopper(II) benzenesulphonate were deposited {found C, 29.6; H, 4.63%. $\text{Cu}(\text{H}_2\text{O})_6[\text{C}_6\text{H}_5\text{SO}_3]_2$ requires C, 29.7; H, 4.56%}.

(b) Hexaaquacopper(II) toluene-4-sulphonate was prepared by the addition of excess CuCO_3 to a boiling dilute solution of the acid, filtering off the excess CuCO_3 , adjusting the pH to ~4, concentrating and crystallizing out the salt {found C, 32.8; H, 4.96%. $\text{Cu}(\text{H}_2\text{O})_6[\text{CH}_3 \cdot \text{C}_6\text{H}_4\text{SO}_3]_2$ requires C, 32.7; H, 5.10%}.

(c) Hexaaquacopper(II) D-camphor-10-sulphonate was prepared by the same method as the toluene-4-sulphonate and recrystallized from an ethanol/water mixture {found C, 37.9; H, 6.39%. $\text{Cu}(\text{H}_2\text{O})_6[\text{C}_{10}\text{H}_{15}\text{OSO}_3]_2$ requires C, 37.9; H, 6.68%}.

Crystal data

(a) Hexaaquacopper(II) benzenesulphonate, $\text{C}_{12}\text{H}_{22}\text{CuO}_{12}\text{S}_2$, $M_r = 486.0$. Triclinic, $a = 22.51(2)$, $b = 6.26(1)$, $c = 6.96(1)$, $\alpha = 92.5(2)$, $\beta = 93.0(2)$, $\gamma = 89.5(2)^\circ$, $U = 978.6 \text{ \AA}^3$, $D_m = 1.63$ (by flotation), $Z = 2$, $D_c = 1.65 \text{ g cm}^{-3}$. Space group $P\bar{1}$ (from the structure analysis, no systematic extinctions). Four-

circle diffractometer data, $\text{Mo } K\alpha$ radiation, $\lambda = 0.7107 \text{ \AA}$, $\mu = 13.8 \text{ cm}^{-1}$, 2970 independent reflexions.

Weibull (1887, 1889) concluded from optical goniometer measurements that the crystals were monoclinic, $a:b:c = 3.653:1:1.114$ and $\beta = 93^\circ$. Preliminary X-ray photography (Weissenberg and precession) appeared to confirm Weibull's conclusions and suggested space group $P2_1$. However, the single-crystal ESR spectrum was not consistent with monoclinic symmetry. Further systematic precession photography showed the crystals to be triclinic.

A crystal was set up on a Hilger & Watts four-circle diffractometer. The cell dimensions and orientation matrix were determined and refined by least squares from the θ values of 14 reflexions. 2970 independent reflexions with $I > 3\sigma$ were measured by an ordinate analysis procedure (Watson, Shotton, Cox & Muirhead, 1970). These data were corrected for Lorentz, polarization and absorption effects, the latter by the empirical procedure of North, Phillips & Mathews (1968).

The Patterson synthesis was consistent with two independent Cu cations at symmetry centres at 0,0,0 and $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. The S atoms and then from the subsequent Cu and S phased F_o synthesis all non-hydrogen atoms except C(9) were located. This last atom was found from the difference synthesis calculated after least-squares refinement with isotropic temperature factors and unit weights. Further cycles with anisotropic temperature factors reduced R to 0.054 when the H atoms were located from difference syntheses. The model with all atoms including H was refined by full-matrix least squares with isotropic temperature factors for H and anisotropic temperature factors for all other atoms. The weighting scheme was $w = (50 + |F_o| + 0.1|F_o|^2)^{-1}$. The refinement converged to $R_w = 0.041$.

(b) Hexaaquacopper(II) toluene-4-sulphonate, $\text{C}_{14}\text{H}_{26}\text{CuO}_{12}\text{S}_2$, $M_r = 514.0$. Monoclinic, $a = 5.85(1)$, $b = 25.71(2)$, $c = 7.35(1) \text{ \AA}$, $\beta = 105.4(2)^\circ$, $U = 1065.7 \text{ \AA}^3$, $D_m = 1.58$ (by flotation), $Z = 2$, $D_c = 1.60 \text{ g cm}^{-3}$. Space group $P2_1/c$ (second setting, systematic extinctions $0k0$, $k = 2n + 1$, and $h0l$, $l = 2n + 1$). Four-circle diffractometer data, $\text{Mo } K\alpha$ radiation, $\lambda = 0.7107 \text{ \AA}$, $\mu = 12.7 \text{ cm}^{-1}$, 3645 independent reflexions with $I > 3\sigma$.

The space group and preliminary cell dimensions were obtained from Weissenberg and precession photographs. The refined cell dimensions and X-ray intensities were measured with a four-circle diffractometer following the same procedure as for the benzenesulphonate.

The Patterson synthesis showed the Cu atoms at centres of symmetry arbitrarily chosen as 0,0,0 and $0, \frac{1}{2}, \frac{1}{2}$, and suggested S atom positions. The F_o synthesis phased on Cu and S revealed all non-hydrogen atoms. The model was refined by full-matrix least squares, first with unit weights and isotropic temperature factors,

then with anisotropic temperature factors and the weighting scheme $w = (100 + |F_o| + 0.1|F_o|^2)^{-1}$. R was then 0.055 and the H atoms could be located from a difference synthesis. The refinement of the model including H atoms with isotropic temperature factors converged to $R_w = 0.048$.

(c) Hexa-aquacopper(II) D-camphor-10-sulphonate, C₂₀H₄₂CuO₁₄S₂, $M_r = 634.2$. Monoclinic, $a = 17.17$ (3), $b = 7.05$ (2), $c = 11.64$ (2) Å, $\beta = 94.1$ (2)°, $U = 1405$ Å³, $D_m = 1.47$ (by flotation), $D_c = 1.50$ g cm⁻³ for $Z = 2$; space group $P2_1$ (second setting, systematic extinctions $0k0, k = 2n + 1$). Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å, $\mu = 9.8$ cm⁻¹, Hilger & Watts linear diffractometer data, 1920 independent reflexions.

The cell dimensions and systematic absences were determined from Weissenberg and precession photographs. A crystal (0.3 × 0.4 × 0.2 mm) was mounted about **b** on a Hilger & Watts linear diffractometer modified to scan both peak and background. The cell dimensions were refined and the intensities of 1920 independent reflexions with $I > 3\sigma$ were measured (layers $h0l-h8l$). The intensities were corrected for Lorentz and polarization effects but not absorption.

Systematic extinctions suggest space groups $P2_1$ or $P2_1/m$ but the latter may be rejected because the crystal contains only the D-enantiomorph of the anion. However, the Patterson function was consistent with Cu and two S atoms occupying the mirror planes at $\frac{1}{4}$ and $\frac{3}{4}$ with symmetry $P2_1/m$. The heavy-atom F_o synthesis indicated positions for the CuO₆ octahedron and the two SO₃C tetrahedra again without loss of mirror symmetry. The F_o synthesis phased with these 17 atoms had a very large number of peaks in the region of the C atoms of the anions. A group of eight atoms, four from each anion, was found that led to F_o syntheses giving 33 and then all 37 non-hydrogen atoms to give a trial structure built up from the hexa-aquacopper(II) cation and two crystallographically independent D-camphor-10-sulphonate anions with the same conformation. In the crystal the greater part of the scattering matter has symmetry $P2_1/m$. Therefore, to guard against ill-conditioned normal matrices which lead to spurious parameter shifts, the following constraints were introduced by Waser's (1963) technique (Rollett, 1969). In the two independent anions (i) pairs of bonds were equalized in length with a standard deviation of 0.01 Å, (ii) equivalent bond angles were considered to differ by 0° with standard deviations of (a) 0.2° for the internal angles of the camphor skeleton, (b) 0.5° for the external angles of the camphor skeleton and (c) 0.8° for the angles at S, and (iii) the vibrational amplitudes of two bonded atoms were considered to differ in the direction of the bond by 0 Å² with a standard deviation of 0.006 Å². With these constraints the refinement converged to $R_w = 0.089$ with anisotropic temperature factors. Each reflexion was assigned a weight according to $w = 1/\sum_{r=1}^n A_r T_r^*(X)$ where n is

the number of coefficients, A_r , for a Chebyshev series, T_r^* is the polynomial function, and X is $F_o/F_{o(\max)}$. Two coefficients, A_r , were used with values 8.8 and 6.8 respectively (Rollett, 1965). The cation was given anisotropic thermal parameters after three cycles and the refinement was fully anisotropic after the fifth cycle. H atoms could not be located although at various stages of the refinement there was some evidence of their presence in difference maps.

Calculations for the two arylsulphonates used a system devised by Sheldrick (1972) and those for the D-camphor-10-sulphonate the Oxford CRYSTALS package (Carruthers, 1975). All were performed on the Oxford University ICL 1906A computer. Complex neutral atom scattering factors for the D-camphor-10-sulphonate were taken from *International Tables for X-ray Crystallography* (1962), and Sheldrick's program used those of Cromer & Waber (1965).*

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* The observed and calculated structure amplitudes and the anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33288 (67 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

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The Nature of the S–S Bonds in Different Compounds. V. The Crystal Structure of ZnS₂O₄·Pyridine

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X-ray diffraction data, collected with a CAD-4 diffractometer, were used to determine the structure of the zinc dithionite–pyridine complex. Crystals of the compound are orthorhombic, space group *Pnma*, $Z = 4$, with $a = 8.493$ (2), $b = 11.095$ (3) and $c = 9.161$ (2) Å. The structure was found from a Patterson map. Least-squares refinement with 998 independent observed reflexions led to an R_w of 0.030. The conformation of the dithionite ion in ZnS₂O₄·pyridine is very similar to that observed in Na₂S₂O₄, i.e. eclipsed with a very long S–S bond (2.386 Å). However, slight differences in the valence angles can be explained qualitatively from packing differences in the two compounds. A qualitative explanation of the dithionite conformation has been obtained by comparison of the S₂O₄²⁻ ion with the isoelectronic species P₂F₄ and Cl₂O₄ (hypothetical molecule) and with N₂O₄.

Introduction

The present paper is part of a series in which the variations in bond lengths and valence angles in groups or ions of the type $-(SO_x)-(SO_y)-$ with $x, y = 1-3$ are studied (part IV: Kiers, Piepenbroek & Vos, 1978). The

structure of the dithionite ion $^{-}O_2S-SO_2^{-}$ especially attracted our attention. Dunitz (1956) had found an eclipsed conformation and a very long S–S bond of 2.39 Å for this ion in Na₂S₂O₄ from two-dimensional X-ray data. In solutions of dithionites SO₂⁻ radical ions are present, as has been shown by Raman (Simon &