and 2–3° for the angles. Within these limits all of the distances and angles in the molecule are normal. The iodine atom is 0·14 Å out of the least-squares plane through the six ring atoms; the largest deviation of any of the eight light atoms from the plane is 0·03 Å.

The reason for studying this structure was to compare the packing with that of *p*-iodobenzonitrile. In *p*-iodobenzonitrile the molecules are aligned in linear chains held together by CN···I interactions between molecules (Schlemper & Britton, 1965). An interaction of this sort seemed a possibility for *o*-iodobenzonitrile. On the other hand, in 2,4,6-trichlorobenzonitrile and 2,4,6-tribromobenzonitrile (Carter & Britton, 1972) adjacent molecules are held together by pairs of non-linear CN···X interactions, the cyanide group and an *ortho* halogen atom on one molecule interacting, respectively, with the *ortho* halogen atom and the cyanide group on the next molecule. Although this geometry seems less reasonable than the previous one, given the location of the lone pair of electrons on the cyanide group, nevertheless it does occur, and it also seemed a possibility for an interaction in *o*-iodobenzonitrile.

However, the packing of the molecules, shown in Fig. 1, does not involve any CN···I interaction. Rather, there are short I···I contacts of 3·83 Å similar in arrangement to those in I_2, where the I···I distance is 3·56 Å (Kitaigorodskii, Khocjanova & Struckov, 1953), and in *p*-diiodobenzene, where it is 4·01 Å (Dun-Chaj & Struckov, 1959). In addition the cyanide

groups in adjacent molecules are approximately anti-parallel, which would favor dipole–dipole interactions, although the distance of 3·8 Å is not at all short. Indeed, in 4-cyanopyridine (Laing, Sparrow & Sommerville, 1971) where a similar arrangement occurs, except that the cyanide groups are exactly anti-parallel, the distance between groups is 3·6 Å. While the inter-molecular interactions are different in the *ortho* and *para* compounds, both compounds have the same molecular volume, 183 Å³; that is, the average efficiency of packing is the same in both compounds.

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μ3-Hydroxo(oxo)-tri-μ-(2-propylamino-2-methyl-3-butanone oximato)-triaquo-tricopper(II) Perchlorate.4H2O

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Abstract.

$[Cu_3(C_8H_{17}N_2O)_3(H_2O)_3OH_{1/2}](ClO_4)_{3/2}(H_2O)_4$, trigonal, $R\bar{3}$, $a = 14\cdot44$ (1), $c = 35\cdot05$ (4) Å; $\varrho_o = 1\cdot49$ (1), $\varrho_c = 1\cdot502$ (3) g cm^{-3} (six molecule ions per cell). In the trinuclear complex the copper atoms are arranged in an equilateral triangle (Cu–Cu = 3·246 Å) about a bridging oxygen on the threefold axis. Each copper atom is bonded to a square plane of ligand atoms including two nitrogen atoms (average Cu–N = 1·99 Å) and one oxygen atom of the bridging oxime groups and the central oxygen atom (average Cu–O = 1·95 Å). Above and below the square plane are a more weakly bonded perchlorate ion and a water molecule.

Experimental.

The copper complex (CuPrAO) was prepared as described in the literature (Young &

Murmann, 1963), and suitable crystals obtained by slow evaporation of an aqueous solution. The dark green hexagonal plates were mounted with a thin coating of epoxy resin to help prevent loss of water which occurred rapidly upon removal from the solvent.

Analysis: Calculated for $Cu_3C_{24}H_{65\cdot5}N_6O_{17}Cl_{1\cdot5}$ C = 30·04, H = 6·88, N = 8·76%. Found C = 30·83, H = 6·17, N = 9·03. This analysis reflects the partial dehydration which occurs spontaneously and may be compared with the dehydrated complex analysis (Young & Murmann, 1963). C = 33·53, H = 6·11, N = 9·97. Preliminary precession film studies using Cu $K\alpha$ radiation revealed trigonal symmetry with systematic absences on hkl for $-h+k+l = 3n$, indicative of rhombohedral space group $R3$ or $R\bar{3}$. The latter space group was indicated by the subsequent structure re-

finement as well as by the agreement between Friedel's pairs. The cell dimensions and crystal orientation were determined by careful centering of 22 reflections on a Picker four-circle diffractometer using Mo $K\alpha$ radiation.

Scintillation counter θ–2θ scans were used to measure the intensities of 3233 reflections out to a 2θ angle of 55°. From 0–25° three forms of each reflection were measured. All intensities were corrected for Lorentz–polarization, background, and absorption effects and averaged to yield 2432 independent reflections.

The structure was solved by conventional Patterson and Fourier techniques and refined by full-matrix least-squares calculations minimizing the function $\sum\omega(F_o^2 - F_c^2)^2$ to a conventional agreement index on F of 8·9% using the 1827 reflections with intensities greater than 3σ $(\sigma^2 = \sigma_{\text{counting}}^2 + 0.06F_c^2)$. The rather high agreement index is attributed to one or both of the
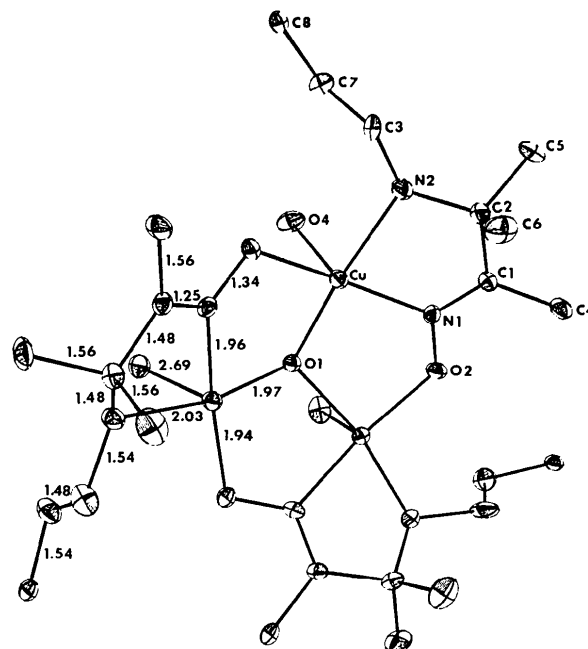
Table 1. *Positional parameters for* CuPrAO

Numbers in parentheses represent the standard deviations in this table and other portions of the paper.

	x	y	z
Cu	0·10147 (8)	0·14623 (8)	0·23286 (3)
Cl(1)	0·0	0·0	0·0
Cl(2)	0·0	0·0	0·3329 (1)
O(1)	0·0	0·0	0·2157 (3)
O(7)	0·0	0·0	0·1117 (6)
O(21)	0·0	0·0	0·2942 (4)
O(22)	0·095 (1)	0·009 (1)	0·3458 (5)
O(11)	0·0	0·0	0·0391 (6)
O(12)	0·061 (2)	0·105 (2)	0·0155 (9)
O(4)	0·1299 (6)	0·1877 (6)	0·1577 (2)
O(8)	0·2544 (8)	0·3195 (9)	−0·1702 (2)
O(2)	0·1942 (4)	0·0075 (4)	0·2354 (2)
C(4)	0·3737 (8)	0·1416 (9)	0·2737 (3)
N(1)	0·2088 (5)	0·1046 (6)	0·2438 (2)
N(2)	0·2302 (6)	0·2912 (6)	0·2437 (2)
C(1)	0·2908 (6)	0·1705 (7)	0·2613 (2)
C(2)	0·3009 (7)	0·2765 (7)	0·2709 (3)
C(3)	0·2078 (8)	0·3805 (7)	0·2534 (3)
C(5)	0·4168 (9)	0·3682 (8)	0·2646 (4)
C(6)	0·270 (1)	0·277 (1)	0·3121 (3)
C(7)	0·2287 (9)	−0·1960 (9)	0·2177 (4)
C(8)	0·346 (1)	−0·159 (2)	0·2256 (5)

Fig. 1. Bond distances in CuPrAO. Standard deviations are Cu–O (0·003–0·006 Å), Cu–N (0·007 Å), and N–O, N–C, C–C (0·01–0·02 Å).

Table 2. *Final thermal parameters for* CuPrAO

Anisotropic temperature factors are of the form:

$$\exp\left[-2\pi^2(h^2 U_{11}a^{*2} + k^2 U_{22}b^{*2} + l^2 U_{33}c^{*2} + 2kka^*b^* U_{12} + 2hla^*c^* U_{13} + 2klb^*c^* U_{23})\right] \text{ and } U_{\text{iso}} = B/8\pi^2.$$

	$U(1,1)$ or U_{iso}	$U(2,2)$	$U(3,3)$	$U(1,2)$	$U(1,3)$	$U(2,3)$
Cu	0·0428 (6)	0·0437 (6)	0·0716 (6)	0·0204 (4)	−0·0076 (6)	−0·0088 (5)
Cl(1)	0·072 (2)	0·072 (2)	0·073 (4)	0·036 (1)	0·0	0·0
Cl(2)	0·097 (3)	0·097 (3)	0·051 (3)	0·048 (1)	0·0	0·0
O(1)	0·043 (4)	0·043 (4)	0·060 (6)	0·021 (2)	0·0	0·0
O(7)	0·15 (1)	0·15 (1)	0·15 (1)	0·075 (6)	0·0	0·0
O(21)	0·13 (1)	0·13 (1)	0·072 (7)	0·064 (5)	0·0 ·	0·0
O(12)	0·16 (2)	0·12 (2)	0·21 (3)	0·053 (9)	−0·083 (9)	−0·070 (9)
O(22)	0·25 (2)	0·20 (2)	0·25 (2)	0·10 (1)	−0·15 (1)	0·02 (1)
O(4)	0·110 (6)	0·087 (4)	0·080 (5)	0·055 (4)	0·036 (4)	0·029 (4)
O(8)	0·124 (7)	0·180 (9)	0·090 (6)	0·095 (8)	−0·010 (5)	−0·024 (6)
O(2)	0·050 (4)	0·036 (3)	0·081 (4)	0·018 (2)	0·000 (3)	0·000 (3)
C(4)	0·071 (7)	0·079 (6)	0·129 (9)	0·034 (5)	−0·053 (8)	0·000 (8)
N(1)	0·040 (3)	0·057 (4)	0·059 (4)	0·026 (3)	0·000 (4)	0·011 (4)
N(2)	0·053 (4)	0·050 (4)	0·087 (6)	0·021 (4)	−0·011 (4)	−0·013 (4)
C(1)	0·042 (5)	0·054 (5)	0·060 (5)	0·017 (4)	−0·004 (4)	0·000 (4)
C(2)	0·054 (5)	0·058 (6)	0·058 (5)	0·018 (4)	−0·012 (4)	0·000 (4)
C(3)	0·066 (6)	0·049 (5)	0·107 (6)	0·023 (4)	−0·018 (4)	−0·030 (5)
C(5)	0·066 (6)	0·061 (7)	0·13 (1)	0·007 (5)	−0·010 (5)	0·004 (5)
C(6)	0·17 (1)	0·092 (9)	0·062 (7)	0·056 (9)	−0·004 (9)	0·008 (9)
C(7)	0·074 (9)	0·098 (8)	0·108 (9)	0·052 (7)	0·021 (7)	0·020 (7)
C(8)	0·094 (9)	0·18 (1)	0·15 (1)	0·097 (9)	0·010 (9)	0·031 (9)
O(11)	0·201 (9)					

following factors: (1) disorder of the perchlorate groups and (2) decomposition of the crystal during data collection (30% loss of intensity for two monitored reflections measured after each 50 data points).

The coordinates of the atoms are presented in Table 1. The more important intramolecular distances and the atom labeling system for the complex are found in Fig. 1. A stereoscopic view of the complex can be seen in Fig. 2. The thermal parameters are presented in Table 2, and the more important bond angles in Table 3.*

Discussion. The primary interest in the structure of this complex arose from its low magnetic moment (~ 1 B.M.) (Young & Murmann, 1963) which suggested a di- or polynuclear complex with interaction of the un-

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* The table of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30322 (10 pp., 1 microfiche). Copies may be obtained through the Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

paired electrons on the copper atoms lowering the magnetic moment. A reasonable dimeric structure was proposed by the authors but not confirmed. Since previous amine–oxime metal complex structures (e.g., Schlemper, 1968) have been shown to exhibit a short intermolecular O$\cdots$O hydrogen bond through loss of one proton from one of two coordinated oxime groups, the possibility of that hydrogen bond was also of interest.

The trinuclear structure (Fig. 1) found for this complex should not have been surprising in view of the similar structure observed for μ_3-hydroxo-tri-μ-(pyridine-2-carbaldehyde oximato)-μ_3-sulphato-tricopper-(II).16·3 water (CuPCAO) (Beckett & Hoskins, 1972), which has similar magnetic properties. Like that complex, the present structure has a μ_3 oxygen [O(1)] which in this case is apparently 50% oxo and 50% hydroxo through the crystal in order to provide charge balance. The presence of a half hydrogen on this oxygen was not confirmed by this study however. Unlike the CuPCAO complex, this complex has a water molecule bonded weakly to each copper(II) atom nearly perpendicular

Table 3. *Selected bond angles and distances in CuPrAO*

N(1)–Cu—N(2)	79·8 (3)	N(2)—C(2)—C(1)	106·1 (7)°
N(2)–Cu—O(2)	98·0 (3)	C(1)—C(2)—C(6)	109·7 (8)
O(2)–Cu—O(1)	93·3 (3)	C(8)—C(7)—C(3)	110·6 (9)
O(1)–Cu—N(1)	90·5 (3)	C(7)—C(3)—N(2)	105·2 (9)
O(4)–Cu—N(1)	101·8 (3)	C(2)—N(2)—Cu	108·2 (5)
O(4)–Cu—N(2)	89·7 (3)	C(3)—N(2)—Cu	116·5 (5)
O(4)–Cu—O(1)	83·7 (3)	C(3)—N(2)—C(2)	115·5 (7)
O(4)–Cu—O(2)	91·1 (3)	Cu——O(1)—Cu	110·9 (4)
C(1)–N(1)–O(2)	119·9 (9)	N(1)—O(2)—Cu	112·0 (5)
Cu—N(1)–C(1)	117·2 (6)	O(11)–Cl(1) –O(12)	112·0 (1)
Cu—N(1)–O(2)	122·8 (5)	O(21)–Cl(2) –O(22)	108·6 (7)
C(2)–C(1)–C(4)	121·9 (8)		
C(2)–C(1)–N(1)	117·3 (8)	Cu——Cu	3·246 (3) Å
N(1)–C(1)–C(4)	120·7 (8)	Cl(1) –O(11)	1·37 (2)
N(2)–C(2)–C(5)	108·2 (8)	Cl(1) –O(12)	1·36 (2)
C(5)–C(2)–C(6)	109·3 (9)	Cl(2) –O(21)	1·43 (2)
C(5)–C(2)–C(1)	110·6 (8)	Cl(2) –O(22)	1·38 (2)
N(2)–C(2)–C(6)	112·8 (9)		

Table 4. *Comparison of bond distances in CuPrAO and CuPCAO*

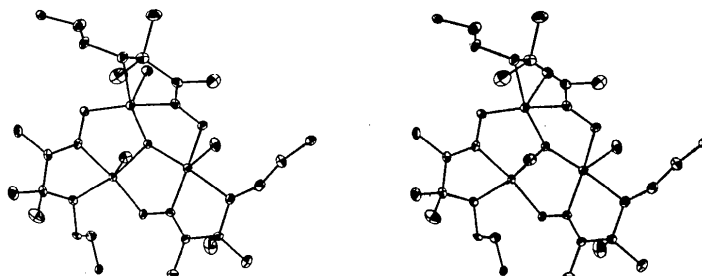|	Cu–Cu	Cu–N(oxime)	Cu–N(amine)	Cu–O(oxime)	Cu–O(μ_3)
CuPrAO	3·246 (3)	1·96 (1)	2·03 (1)	1·94 (1)	1·97 (1)
CuPCAO	3·220 (3)	1·98 (1)	1·97 (1)	1·98 (1)	1·99 (1)

Fig. 2. Stereoscopic view of the trimeric complex. (Atom labeling as in Fig. 1.)

to the more strongly bonded square plane. A tabulation (Table 4) of comparable distances in the two complexes shows a marked similarity.

The bridging (μ_3) oxygen atom is 0·7 Å out of the plane of the equilateral triangle of copper(II) atoms so that the Cu–O–Cu angles [110·9 (4)°] are near tetrahedral. Bond distances and angles within the amine-oxime ligands (Fig. 1 and Table 3) are similar to those previously observed (Schlemper, 1968). The difference in Cu–N(oxime) and Cu–N(amine) distances of 0·07 Å is comparable to that difference in Ni–N distances of 0·05 Å. The square planar coordination about each copper is not perfect, with the maximum deviation of 0·25 (1) Å from the least-squares coordination plane exhibited by N(1) (see Fig. 2).

There is considerable intermolecular hydrogen bonding between the disordered perchlorate oxygen [O(11)], the noncoordinated waters [O(7) and O(8)], the coordinated water [O(4)], the oxime oxygen [O(2)], and the amine nitrogen [N(2)] as shown in Table 5. The shortest bond (2·54 Å) is between the disordered perchlorate oxygen [O(11)] and the noncoordinated water

on the threefold axis [O(7)]. There is also an apparent intra-ionic hydrogen bond between the amine nitrogen [N(2)] and the oxime oxygen [O(2)].

Table 5. *Probable hydrogen-bond distances*

O(7)···O(11)	2·54 (3) Å	O(8)···O(8)	2·77 (2) Å
O(1)···O(21)	2·75 (2)	O(4)···O(7)	2·90 (1)
O(4)···O(8)	2·75 (1)	O(2)···N(2)	2·99 (1)
O(2)···O(8)	2·77 (1)	O(4)···O(8)	3·39 (1)
		N(2)···O(8)	3·37 (1)

The magnetic properties (Young & Murmann, 1963) have been confirmed by Gary Long (private communication) and are easily interpreted on the basis of this structure and electron pairing through magnetic exchange leaving a single unpaired electron per trimer.

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2,3,6,7-Tetrahydro-4*H*-thiazolo[3,2-*a*]*s*-triazin-2-on-4-thione, C5H5S2N3O
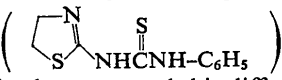
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Abstract. C5H5S2N3O, orthorhombic, *Pbca*, $a = 8\cdot234$ (8), $b = 14\cdot579$ (15), $c = 12\cdot459$ (13) Å, $Z = 8$, $D_x = 1\cdot66$ g cm^{-3}. The molecule is planar to within $\pm 0\cdot016$ Å. The structure shows hydrogen bonding and short S···(triazine ring) intermolecular approaches.

Experimental. The exo- and endocyclic nitrogen atoms

of 2-amino-2-thiazoline ([structure]) exhibit different nucleophilic character and this difference has been the subject of many studies. The reaction of this molecule with carbethoxy isothiocyanate (C2H5O–C–NCS) could lead to either or both of two possible products (A or B).
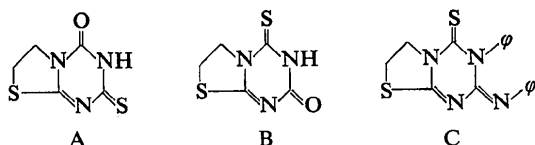
[structures A, B, C]

However, only a single isomer was produced in the reaction and this X-ray study established that the reaction product has the structure B. A detailed study of the chemistry of these compounds will be published (Klayman, Woods & Flippen, 1974). Crystals were
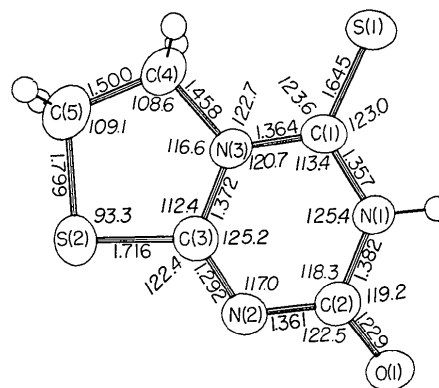

Fig. 1. Bond distances and angles. Based solely on least-squares parameters, standard deviations are on the order of 0·005 Å for bond lengths and 0·3° for angles.