Table 2. *Selected bond distances (Å) and bond angles (°) of the title compound with e.s.d.'s in parentheses*

Co—S(1)	2·199 (1)	S(1)—C(11)	1·717 (4)
Co—S(2)	2·190 (1)	S(2)—C(21)	1·713 (5)
Co—S(3)	2·192 (1)	S(3)—C(31)	1·718 (4)
Co—O(1)	1·929 (3)	O(1)—N(1)	1·349 (5)
Co—O(2)	1·933 (3)	O(2)—N(2)	1·353 (5)
Co—O(3)	1·937 (3)	O(3)—N(3)	1·341 (4)
S(1)—Co—S(2)	92·04 (5)	S(3)—Co—O(2)	174·8 (1)
S(1)—Co—S(3)	90·66 (5)	S(3)—Co—O(3)	87·92 (9)
S(1)—Co—O(1)	88·20 (9)	O(1)—Co—O(2)	87·0 (1)
S(1)—Co—O(2)	94·3 (1)	O(1)—Co—O(3)	86·5 (1)
S(1)—Co—O(3)	174·4 (1)	O(2)—Co—O(3)	87·2 (1)
S(2)—Co—S(3)	90·74 (5)	Co—S(1)—C(11)	96·6 (1)
S(2)—Co—O(1)	174·8 (1)	Co—S(2)—C(21)	97·0 (1)
S(2)—Co—O(2)	87·88 (9)	Co—S(3)—C(31)	96·8 (1)
S(2)—Co—O(3)	93·4 (1)	Co—O(1)—N(1)	115·9 (2)
S(3)—Co—O(1)	94·42 (9)	Co—O(2)—N(2)	116·0 (2)
		Co—O(3)—N(3)	116·0 (2)

contains a listing of atomic positional parameters and their e.s.d.'s, and Table 2 selected interatomic distances and bond angles. Fig. 1 shows the *ORTEP* drawing (Johnson, 1976) of the molecule.*

Related literature. The title compound was synthesized as part of our investigation of transition-metal complexes with bidentate sulfur:oxygen ligands (Kang, Weng, Liu, Wu, Huang, Lu, Cai, Chen & Lu, 1990; Kang, Weng, Wu, Wang, Guo, Huang, Huang

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* Tables of anisotropic thermal parameters, structure factors and a complete list of bond distances and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54378 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

& Liu, 1988; Weng, Huang & Kang, 1989), whose precursor Co^{II} was found to be oxidized to Co^{III} compared to that reported (Robinson, 1964). Its structure is similar to that of $Co(mtb)_3$ (mtb = N-methylthiobenzohydroxamate; Freyberg, Abu-Dari & Raymond, 1979). The arrangement of the chelate ligands is such that all three sulfur atoms are *cis* to each other, giving a facial complex. Owing to the bite-distance limit (2·874 Å) of the ligands, the coordination about the cobalt atom is distorted from a regular octahedron with bite angles averaged to 88·0°.

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Structure Determination of a Copper–Histamine Croconate Complex [Cu(C5O5)(C5H9N3)(OH2)].H2O

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Abstract. Aquacroconatohistaminecopper(II) monohydrate, $C_{10}H_{11}CuN_3O_6.H_2O$, $M_r = 350.8$, monoclinic, $P2_1/n$, $a = 7.418$ (1), $b = 17.070$ (2), $c = 10.851$ (1) Å, $\beta = 108.48$ (1)°, $V = 1303.2$ (6) Å^3, $Z = 4$, $D_x = 1.788$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 1.72$ mm^{-1}, $F(000) = 716$, $T = 293$ K, full-matrix least-squares refinement based on 1751 reflections led to R and wR values of 0.031 and 0.032 respectively.

The metal is pentacoordinated. The coordination is ensured by one croconate molecule and one histamine molecule both acting as chelating ligands, and one water molecule.

Experimental. Green parallelepiped crystals obtained by equimolar reaction between histamine ($C_5H_9N_3$), $CuCl_2.2H_2O$ and croconic acid ($C_5H_2O_5$) in water. Compound recrystallized in water. Analysis: calculated C 34·19, H 3·74, N 11·98; found C 34·24, H 3·71, N 11·84. Data collection crystal of dimensions 0·35 × 0·10 × 0·05 mm. Space group from absences $h0l$ with $h + l$ odd and $0k0$ with k odd. Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$, cell dimensions from setting angles of 25 reflections having $8·2 < \theta < 12°$, 2740 reflections measured, using $\omega/2\theta$ scan from 2θ from 3 to 56°, $0 \le h \le 9$, $0 \le k \le 21$, $-13 \le l \le 13$, scan range $(0·80 + 0·35\tan\theta)°$. Intensities of three reflections (080, 40$\overline{4}$, 20$\overline{4}$) measured every 2 h showed ±0·3% random variation, no decay corrections. Corrections for Lp and absorption by ψ scans (North, Phillips & Mathews, 1968), min. relative transmission 0·89. 2540 unique data; $R_{int} = 0·021$ for averaging redundant $0kl$ and $0k\overline{l}$ data. Heavy-atom method followed by Fourier and least-squares techniques using 1751 reflections having $F_o^2 > 3\sigma(F_o^2)$ based on counting statistics. Full-matrix least-squares refinement (on F) minimizing $\sum w(||F_o| - |F_c||)^2$, with anisotropic thermal parameters for all non-H atoms. All H atoms located by ΔF, water molecule H atoms refined, other H atoms in constrained geometry (C—H = N—H = 0·97 Å). Isotropic U_H allowed to vary (one for water molecule H atoms, one for other H atoms).

$R = 0·034$, $wR = 0·032$, 204 variables, unit weights. Mean and max. parameter shifts $0·001\sigma$ and $0·029\sigma$ respectively. Max. and min. height in final ΔF map 0·31 and $-0·26$ e Å^{-3}. Scattering factors including real and imaginary parts of anomalous dispersion from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99–101, 149) and from Stewart, Davidson & Simpson (1965) for H atoms. MicroVAX 3400 DEC computer. *SDP-Plus* (Frenz, 1985), *SHELX*76 (Sheldrick, 1976), *SHELXS*86 (Sheldrick, 1986), *ORFFE* (Busing, Martin & Levy, 1964) and *NRC* (Ahmed, Hall, Pippy & Huber, 1966) programs.

Related literature. The final positional and equivalent isotropic thermal parameters are listed in Table 1,* bond lengths and angles in Table 2. The thermal

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* Lists of structure factors, anisotropic thermal parameters and least-squares-planes equations have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54398 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and isotropic or equivalent isotropic temperature factors* ($\text{Å}^2 \times 10^2$) *with e.s.d.'s in parentheses*

$$U_{eq} = \tfrac{1}{3}\text{trace } \mathbf{U}.$$

	x	y	z	U_{eq}/U_{iso}
Cu	0·25733 (7)	0·43182 (2)	0·61634 (4)	2·67 (7)
Ow(1)	0·5653 (4)	0·4372 (2)	0·7373 (3)	4·8 (6)
Ow(2)	−0·0773 (4)	0·1711 (2)	0·4757 (3)	3·8 (5)
O(1)	0·2724 (4)	0·3164 (1)	0·5807 (2)	3·5 (5)
O(2)	0·2891 (4)	0·4460 (1)	0·4396 (2)	3·3 (4)
O(3)	0·3293 (4)	0·3991 (2)	0·1830 (3)	3·9 (5)
O(4)	0·3339 (5)	0·2268 (2)	0·1826 (3)	4·8 (5)
O(5)	0·2813 (5)	0·1715 (1)	0·4234 (3)	4·2 (5)
N(1)	0·2249 (4)	0·5445 (2)	0·6311 (3)	2·7 (5)
N(2)	0·1947 (5)	0·6699 (2)	0·5910 (3)	3·5 (6)
N(3)	0·1499 (5)	0·4031 (2)	0·7568 (3)	3·0 (5)
C(1)	0·2918 (5)	0·3101 (2)	0·4698 (3)	2·6 (6)
C(2)	0·3012 (5)	0·3782 (2)	0·3960 (4)	2·5 (6)
C(3)	0·3187 (5)	0·3558 (2)	0·2711 (4)	2·7 (6)
C(4)	0·3203 (5)	0·2683 (2)	0·2703 (4)	2·8 (6)
C(5)	0·2988 (5)	0·2406 (2)	0·3950 (4)	2·7 (6)
C(6)	0·2207 (6)	0·5997 (2)	0·5448 (4)	3·1 (6)
C(7)	0·1809 (6)	0·6590 (2)	0·7132 (4)	3·6 (7)
C(8)	0·1997 (5)	0·5810 (2)	0·7380 (4)	2·9 (6)
C(9)	0·1974 (6)	0·5353 (2)	0·8551 (4)	3·9 (7)
C(10)	0·0681 (6)	0·4641 (2)	0·8202 (4)	3·8 (7)
H1(Ow1)	0·622 (6)	0·400 (2)	0·803 (3)	7·6 (9)
H2(Ow1)	0·621 (6)	0·487 (1)	0·763 (4)	7·6 (9)
H1(Ow2)	−0·100 (6)	0·148 (3)	0·549 (3)	7·6 (9)
H2(Ow2)	0·055 (1)	0·170 (3)	0·487 (4)	7·6 (9)

ellipsoid plot of the molecule (*ORTEP*; Johnson, 1965) is shown in Fig. 1 with the atomic numbering. The hydrogen-bonding scheme is shown in Fig. 2. The packing of the molecules in the unit cell is enhanced by hydrogen bonds between the water molecules (the coordinated one and the crystallization one) and the croconate anion, and between the histamine non-metal bonded N atom and the crystallization water molecule or the croconate anion.

The first oxocarbon, croconic acid, was obtained by Gmelin (1825). Recognition that the oxocarbons $C_nO_n^{2-}$ were members of a class of hitherto unknown aromatic substances (West, Niu, Powell & Evans, 1960) led to a greatly renewed interest in this area. A series of divalent transition-metal salts of general formula $(C_5O_5)M(OH_2)_3$ (where M = Co, Cu, Ni, Fe, Mn) has been prepared (West & Niu, 1963) which are isostructural. More recently (Deguenon, Bernardinelli, Tuchagues & Castan, 1990) we have structurally identified manganese complexes involving croconic acid and bipyridyl or imidazole; they are monomeric but afford an extended network of intermolecular hydrogen bonds.

In this paper we report on the crystal structure of a copper complex involving croconic acid and histamine as ligands.

In this complex the coordination number of copper is five, whereas in copper croconate itself the coordination is six (Glick, Downs & Dahl, 1964). Moreover copper croconate consists of infinite chains resulting from the bonding of the metal to

Table 2. *Interatomic bond lengths (Å) and angles (°) with e.s.d.'s in parentheses*

Cu—O(1)	2·017 (2)	Cu—N(1)	1·951 (3)
Cu—O(2)	2·020 (3)	Cu—N(3)	1·992 (4)
Cu—Ow(1)	2·247 (3)		
C(1)—C(2)	1·426 (5)	C(1)—O(1)	1·261 (5)
C(2)—C(3)	1·453 (6)	C(2)—O(2)	1·264 (4)
C(3)—C(4)	1·493 (5)	C(3)—O(3)	1·232 (5)
C(4)—C(5)	1·489 (6)	C(4)—O(4)	1·216 (5)
C(5)—C(1)	1·447 (5)	C(5)—O(5)	1·238 (4)
N(1)—C(6)	1·322 (5)	N(1)—C(8)	1·381 (5)
C(6)—N(2)	1·336 (5)	C(8)—C(9)	1·496 (6)
N(2)—C(7)	1·374 (6)	C(9)—C(10)	1·519 (6)
C(7)—C(8)	1·357 (5)	C(10)—N(3)	1·480 (6)

O(1)—Cu—O(2)	84·5 (1)	O(2)—Cu—N(3)	162·1 (1)
O(1)—Cu—N(1)	173·7 (1)	O(2)—Cu—Ow(1)	98·4 (1)
O(1)—Cu—N(3)	88·1 (1)	N(1)—Cu—N(3)	95·2 (1)
O(1)—Cu—Ow(1)	92·5 (1)	N(1)—Cu—Ow(1)	92·4 (1)
O(2)—Cu—N(1)	90·8 (1)	N(3)—Cu—Ow(1)	98·2 (1)
Cu—O(1)—C(1)	107·3 (2)	Cu—O(2)—C(2)	106·8 (2)
O(1)—C(1)—C(2)	120·4 (3)	O(3)—C(3)—C(4)	126·4 (4)
O(1)—C(1)—C(5)	129·9 (3)	C(2)—C(3)—C(4)	105·8 (3)
C(2)—C(1)—C(5)	109·6 (3)	O(4)—C(4)—C(3)	126·2 (4)
O(2)—C(2)—C(1)	121·0 (4)	O(4)—C(4)—C(5)	125·9 (3)
O(2)—C(2)—C(3)	128·9 (3)	C(3)—C(4)—C(5)	107·9 (3)
C(1)—C(2)—C(3)	110·1 (3)	O(5)—C(5)—C(4)	125·4 (4)
O(3)—C(3)—C(2)	127·8 (3)	O(5)—C(5)—C(1)	128·0 (4)
C(4)—C(5)—C(1)	106·5 (3)		
Cu—N(1)—C(6)	128·4 (3)	C(7)—C(8)—N(1)	108·0 (4)
Cu—N(1)—C(8)	124·5 (2)	C(7)—C(8)—C(9)	130·8 (4)
C(6)—N(1)—C(8)	107·1 (3)	N(1)—C(8)—C(9)	121·3 (3)
N(1)—C(6)—N(2)	110·3 (4)	C(8)—C(9)—C(10)	112·5 (3)
C(6)—N(2)—C(7)	107·7 (3)	C(9)—C(10)—N(3)	111·0 (4)
N(2)—C(7)—C(8)	106·9 (4)	C(10)—N(3)—Cu	120·4 (3)

Ow(1)—H1(Ow1)	0·95 (3)	Ow(1)—H2(Ow1)	0·95 (2)
Cu—Ow(1)—H1(Ow1)	123 (3)	Cu—Ow(1)—H2(Ow1)	119 (2)
H1(Ow1)—Ow(1)—H2(Ow1)	110 (3)		

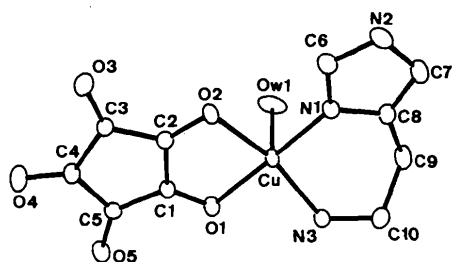|			
Ow(2)—H1(Ow2)	0·95 (4)	Ow(2)—H2(Ow)	0·95 (1)
H1(Ow2)—Ow(2)—H2(Ow2)	109 (4)		

Fig. 1. *ORTEP* plot showing 40% probability thermal ellipsoids.

two adjacent O atoms of one croconate and to a single O atom of a second croconate molecule, such that each croconate is three-coordinated. In the histamine–croconate complex, the croconate ligand is only two-coordinated; the Cu atom is situated at a center of a plane defined by the N(1) and N(3) N atoms of histamine and O(1) and O(2) O atoms of the chelated croconate dianion. The Cu—O (croconate) distances in this complex are 2·020 (3) and 2·017 (2) Å, though the croconate ligand is asymmetrically coordinated in the copper–croconate complex with short (1·975 Å) and long (2·320 Å) metal–
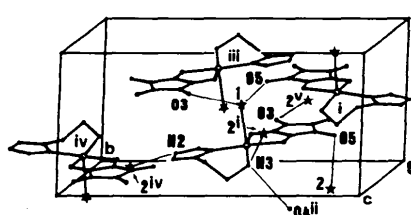

Fig. 2. An *ORTEP* view of the hydrogen-bonding scheme (fine lines) in the unit cell. Water molecules are drawn as stars [Ow(1)···O(5^i) = 2·834 (4), H1(Ow1)···O(5^i) = 1·90 (3) Å, Ow(1)—H1(Ow1)···O(5^i) = 168 (4)°, Ow(1)···O(3^{iii}) = 2·957 (4), H2(Ow1)···O(3^{iii}) = 2·03 (2) Å, Ow(1)—H2(Ow1)···O(3^{iii}) = 165 (4)°, Ow(2^v)···O(3) = 2·822 (4), H1(Ow2^v)···O(3) = 1·88 (4) Å, Ow(2^v)—H1(Ow2^v)···O(3) = 174 (3)°, Ow(2)···O(5) = 2·891 (5), H2(Ow2)···O(5) = 2·01 (3) Å, Ow(2)—H2(Ow2)···O(5) = 154 (4)°, N(2)···Ow(2^{iv}) = 2·872 (4), H(N2)···Ow(2^{iv}) = 2·02 Å, N(2)—H(N2)···Ow(2^{iv}) = 146°, N(3)···Ow(2^i) = 2·880 (4), H1(N3)···Ow(2^i) = 1·92 Å, N(3)—H1(N3)···Ow(2^i) = 170°, N(3)···O(4^{ii}) = 3·141 (4), H2(N3)···O(4^{ii}) = 2·19 Å, N(3)— H2(N3)···O(4^{ii}) = 167°]. Symmetry operators: (i) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (ii) $-\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $1 - x, 1 - y, 1 - z$; (iv) $-x, 1 - y, 1 - z$; (v) $\frac{1}{2} + x, \frac{1}{2} - y, -\frac{1}{2} + z$.

oxygen bonds. The croconate ligand is planar, in the limits of error, but the 1·426 (5) Å [C(1)—C(2)] bond is shorter than the others in the ring [1·493 (5) to 1·447 (5) Å] and suggests a partial localization of the π electrons. Histamine is coordinated to copper by its two N atoms; bond lengths and bond angles in the histamine moiety are not markedly different from those described in other histamine–copper complexes (Bonnet & Jeannin, 1970).

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