most acidic H of the oaoH_2, the oxime H, and the most basic atom of the complex molecule, the oxime O which formally carries a negative charge.

This compound is a model for an idea outlined by us (Endres, 1979) and by Brown & Wrobleski (1979). Possible H bridges are supposed to stabilize a structure in which stacks of additional molecules run parallel to stacks of metal complexes. If the additional molecules are chosen to allow an electronic interaction along the stacks, interesting physical properties similar to the organic metals could result.

$[Co(oaoH)_2].oaoH_2$ (Bekaroglu, Sarisaban, Koray & Ziegler, 1977) has a very similar structure with a close axial interaction of Co with NH_2 groups of adjacent complex molecules within a stack, 2·639 (5) Å. The free oaoH_2 molecules are present in the *s-trans* form as well and link the stacks to sheets *via* H bridges. A comparison of bond lengths is included in Fig. 3.

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The Structure of Diammine(orotato)copper(II)

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Abstract

Crystals of $[Cu(C_5H_2N_2O_4)(NH_3)_2]$ are monoclinic, space group $P2_1/n$, with $a = 7{\cdot}217\ (5)$, $b = 7{\cdot}617\ (5)$, $c = 15{\cdot}148\ (11)$ Å, $\beta = 100{\cdot}73\ (6)^\circ$, $Z = 4$. The structure was refined to $R = 0{\cdot}042$ for 1853 symmetry-independent reflections. The primary coordination sphere around the Cu atom is square planar with the bidentate orotato anion and two ammonia molecules occupying the four coordination sites. The coordination sphere is extended to (4 + 2)-coordination geometry *via* intermolecular interaction involving the O(2) atoms of two stacking complex molecules and the Cu—O($2^{\rm i}$) distance is 2·930 (4) Å. The conformation of the orotato anion differs only slightly from uncomplexed orotic acid, the C(6)—N(1)—C(2) angle being 4·8° smaller and the C(5)—C(6)—N(1) angle 3·7° larger. The crystal structure is dominated by columns of complexes along **a**. The stacking of the pyrimidine rings in these columns is fairly extensive. The stability of these columns is enhanced by the axial coordination of one exocyclic keto O atom to Cu. Interaction between the columns is primarily through hydrogen bonds.

Introduction

Orotic acid belongs to the class of pyrimidine derivatives, which are important components of nucleic acids and many enzymes with pronounced physiological action. Besides being biologically important the pyrimidines are interesting as ligands because the tautomerism between the ketonic and enolic forms makes multifaceted coordination possible.

There is general agreement that the preferred form for the pyrimidines at low and neutral pH is the ketonic (Tucci, Doody & Li, 1961). Coordination of metals at the hetero sites of the pyrimidine ring is thus less favourable than in other nucleic acid constituents, which have at least one ring N atom with an available lone pair. The situation is different in the enolic form, at higher pH, when the heterocyclic-ring N atoms are deprotonated and coordination is possible.

Three structures have been published for orotic acid compounds: the monohydrate of the Rb salt of 5-fluoroorotic acid (MacIntyre & Zirakzadeh, 1964), ammonium orotate monohydrate (Solbakk, 1971) and orotic acid monohydrate (Takusagawa & Shimada, 1973). Although some metal complexation works have

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been published (Tucci, Ke & Li, 1967; Sarpotdar & Burr, 1979) no information is available on the actual coordination sites with the transition metals.

The complexometric titration and spectrophotometric data suggest that the probable binding sites of orotic acid with transition metals are the carboxylate group and the adjacent ring N atoms. Because the latter at low pH are blocked by the protons the coordination is not as easy as at high pH when the ring N atoms are deprotonated. In an attempt to obtain crystallographic evidence of the coordination sites we have prepared the diammine(orotato)-copper(II) complex at the high pH of concentrated ammonia solution and undertaken its X-ray analysis.

Experimental

The complex was prepared by dissolving orotic acid in a solution of 50% ethanol and 50% 12 *M* aqueous NH_4OH and adding an equimolar amount of $CuCl_2.2H_2O$. The resulting dark-blue solution was evaporated at 313 K and after three days the complex precipitated as dark-purple plates. Weissenberg photographs established the space group $P2_1/n$ from systematic absences $h0l$ with $h + l$ odd and $0k0$ with k odd. The density was measured by flotation in a CCl_4/CH_3I mixture. Cell parameters (Table 1) were determined by least squares from the angular settings of 22 reflections measured on a Syntex $P2_1$ diffractometer.

The crystal used for data collection was 0·35 × 0·45 × 0·45 mm. The intensity measurements were carried out at room temperature on a Syntex $P2_1$ diffractometer with graphite-monochromated Mo $K\alpha$ radiation and the θ–2θ scan technique. The scan rate varied from 2·0 to 10·0° min^{-1}, depending on the number of counts measured in a fast preliminary scan through the peak. A set of 1853 unique reflections was obtained from the 2252 reflections measured up to the maximum value of $2\theta = 55°$. Three strong reflections monitored periodically exhibited no significant variation of intensity. The intensities were corrected for Lorentz and polarization effects and absorption correction was made from φ-scan data. A reflection was considered to be above background if $F_o > 3\sigma(F_o)$. The 150 reflections not satisfying this criterion were considered as unobserved.

Table 1. *Crystal data*

$C_5H_8CuN_4O_4$	$M_r = 251{\cdot}7$
Monoclinic, $P2_1/n$	$Z = 4$
$a = 7{\cdot}217\ (5)$ Å	$D_m = 2{\cdot}05$ Mg m^{-3}
$b = 7{\cdot}617\ (5)$	$D_c = 2{\cdot}04$
$c = 15{\cdot}148\ (11)$	$\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å
$\beta = 100{\cdot}73\ (6)°$	$\mu(\text{Mo } K\alpha) = 2{\cdot}77$ mm^{-1}
$V = 819{\cdot}3$ Å^3	

Structure determination

Coordinates for the Cu atom were obtained by direct methods. Fourier analysis allowed the positioning of the remaining non-hydrogen atoms. With anisotropic temperature factors for the non-hydrogen atoms, a difference map calculated after full-matrix refinement revealed the positions of all eight H atoms. Full-matrix least-squares refinement with all non-hydrogen atoms anisotropic and H atoms isotropic led to $R = \sum||F_o| - |F_c||/|F_o| = 0{\cdot}042$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0{\cdot}056$, where $w = 1/(90 + |F_o| + 0{\cdot}15|F_o|^2)$ for all data. Without the unobserved reflections the final $R = 0{\cdot}035$ and $R_w = 0{\cdot}045$. After the last cycle the average shift/error was 0·0022 and maximum shift/error 0·019. A final difference map was practically featureless.

Scattering factors were from Cromer & Mann (1968) and the anomalous-dispersion correction was applied (*International Tables for X-ray Crystallography*, 1974). Extinction was not regarded as being significant and no correction was made. All calculations were performed on a Univac 1108 computer with XRAY 76 (Stewart, 1976).*

Results and discussion

An *ORTEP* drawing (Johnson, 1965) and the numbering scheme of the molecule are shown in Fig. 1. Intramolecular bond lengths and angles are illustrated in Fig. 2, bond lengths and angles of the Cu coordination sphere in Fig. 3 and the packing of the molecules is shown in Figs. 4 and 5. The atomic

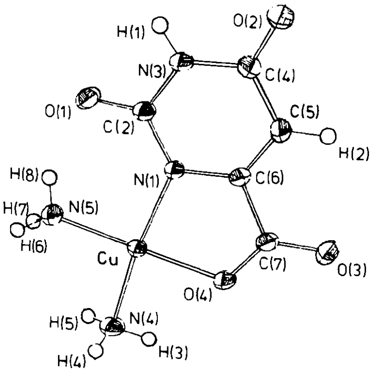

Fig. 1. *ORTEP* drawing and numbering scheme of the molecule. The 50% probability thermal ellipsoids are shown for non-hydrogen atoms.

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35383 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

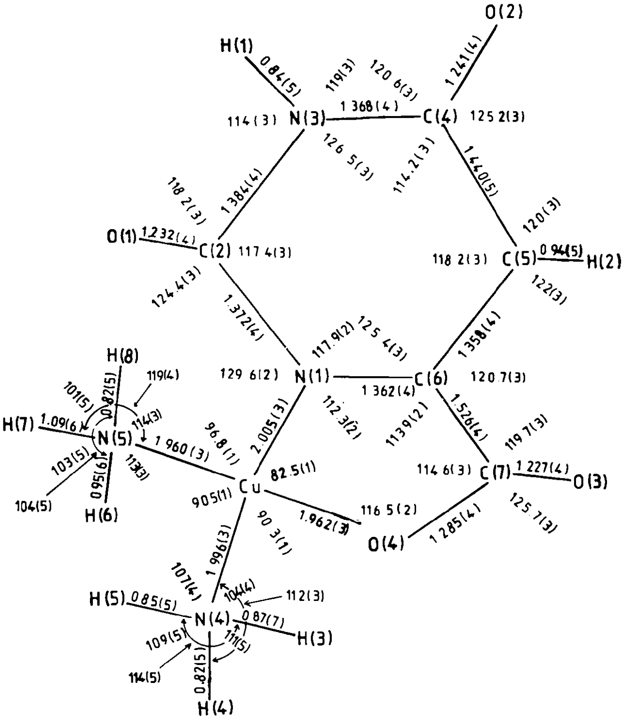

Fig. 2. Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses.

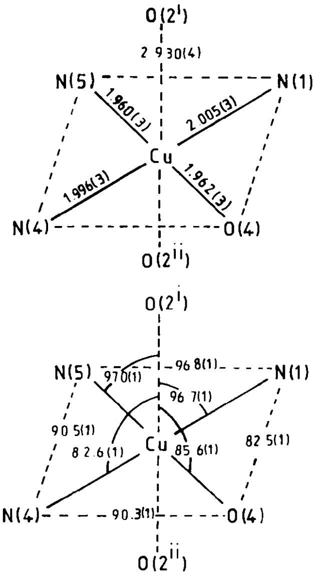

Fig. 3. Bond lengths (Å) and angles (°) of the Cu coordination sphere. E.s.d.'s are in parentheses.

coordinates and $U_{eq.}$ values (Hamilton, 1959) are listed in Table 2, the least-squares plane of the pyrimidine ring and distances of various atoms from it in Table 3 and hydrogen-bond distances and angles in Table 4.

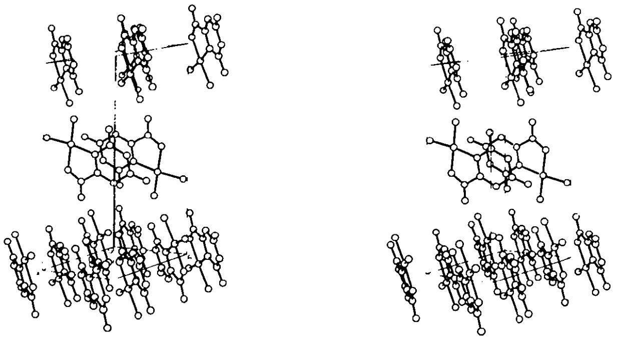

Fig. 4. Arrangement of the molecules in the unit cell.

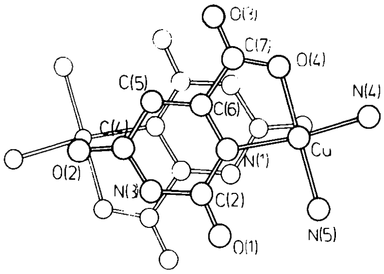

Fig. 5. Molecular overlap of the complex molecules in the columnar stacking. The view direction is normal to the least-squares plane of the pyrimidine ring.

Table 2. *Fractional atomic coordinates* ($\times 10^4$ *for non-hydrogen atoms;* $\times 10^3$ *for* H) *and equivalent values of the anisotropic temperature factor coefficients* ($\times 10^4$)

	x	y	z	$U_{eq.}$ (Å^2)
Cu	1009 (1)	7006 (1)	4008 (1)	200
N(1)	2198 (4)	4817 (3)	4592 (2)	199
C(2)	2660 (4)	3286 (4)	4208 (2)	227
O(1)	2186 (4)	2923 (3)	3406 (2)	351
N(3)	3729 (4)	2075 (4)	4764 (2)	248
C(4)	4377 (5)	2244 (4)	5667 (2)	247
O(2)	5472 (4)	1141 (4)	6080 (2)	411
C(5)	3713 (5)	3792 (4)	6057 (2)	247
C(6)	2713 (4)	4989 (4)	5498 (2)	187
C(7)	2125 (4)	6731 (4)	5860 (2)	206
O(3)	2394 (4)	6985 (3)	6673 (2)	290
O(4)	1381 (4)	7829 (3)	5253 (2)	275
N(4)	−134 (5)	9312 (4)	3582 (2)	316
N(5)	540 (5)	6115 (4)	2774 (2)	297
H(1)	403 (6)	119 (6)	449 (3)	
H(2)	400 (6)	396 (7)	668 (3)	
H(3)	−54 (8)	972 (8)	404 (4)	
H(4)	64 (7)	998 (7)	343 (3)	
H(5)	−100 (7)	910 (7)	314 (4)	
H(6)	138 (7)	659 (7)	242 (3)	
H(7)	−84 (9)	632 (9)	236 (4)	
H(8)	67 (6)	504 (7)	273 (3)	

The Cu *coordination sphere*

The Cu atom is involved in square-planar coordination and is situated in the centre of the plane defined by the deprotonated ring N(1), carboxylate

Table 3. *The least-squares plane for the pyrimidine ring*

The equation is expressed in direct space as $6{\cdot}3645X + 3{\cdot}4228Y - 4{\cdot}6172Z = 0{\cdot}89724$. Asterisks denote atoms defining the plane. Displacements from the plane are in Å and e.s.d.'s are in parentheses.

N(1)*	0·031 (3)	C(5)*	−0·033 (3)	C(7)	0·054 (3)
C(2)*	−0·022 (3)	C(6)*	−0·002 (4)	O(3)	−0·063 (3)
N(3)*	−0·014 (4)	O(1)	−0·078 (4)	O(4)	0·234 (3)
C(4)*	0·040 (4)	O(2)	0·169 (4)		

Table 4. *Bond lengths* (Å) *and angles* (°) *involving hydrogen bonds*

D	H	*A*	*D*—H	*D*···*A*	H···*A*	*D*—H···*A*
N(5)	H(8)	O(1)[a]	0·82 (5)	2·796 (4)	2·11	141
N(3)	H(1)	O(2)[b]	0·84 (5)	2·871 (4)	2·04	173
N(4)	H(3)	O(4)[c]	0·87 (7)	3·044 (5)	2·29	147
N(5)	H(7)	O(3)[d]	1·09 (6)	2·937 (4)	1·97	146
N(5)	H(6)	O(1)[e]	0·95 (6)	2·981 (5)	2·04	170

Symmetry position of atom *A*: (*a*) x,y,z; (*b*) $1-x, -y, 1-z$; (*c*) $-x, 2-y, 1-z$; (*d*) $\frac{1}{2}+x, \frac{3}{2}-y, \frac{1}{2}+z$; (*e*) $\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

O(4) and two ammonia molecules. The Cu—ligand lengths agree well with those found in other Cu^{II} complexes (Hathaway, 1973). The bond angles indicate a distorted geometry, N(1)—Cu—O(4) having rather a small value of 82·5 (1)° because of the steric hindrance arising from coordination directly to ring N and adjacent carboxylate O atoms.

Square-planar Cu^{II} has a decided tendency to extend its coordination sphere to five, the so-called (4 + 1)-coordination geometry, and to six, the (4 + 2)- and (4 + 1 + 1)-coordination geometries (Hathaway, 1973). In the present compound the coordination sphere is extended to (4 + 2) geometry by two exocyclic keto O atoms O(2^{i}) and O(2^{ii}) of two stacking complex molecules approximately parallel with the original molecule. The Cu—O(2^{i}) distance is long, 2·930 (3) Å, compared with the bond distances of water or small anions occupying axial positions in Cu^{II} complexes (Hodgson, 1977). The exocyclic O atoms are situated almost in the ideal axial positions, the largest deviation being only 7·4°. In view of this and the van der Waals radius of double-bonded O (Bondi, 1964), O(2^{i}) and O(2^{ii}) can be considered as semi-coordinated to the Cu atom, but the interaction between the Cu atom and the axial O atoms is extremely weak.

The ammonia ligands

The distances from the Cu atom to the ammonia ligands agree well with those observed in Cu^{II}–ammine complexes (Hathaway, 1973; Hodgson, 1977). The N—H lengths and angles in the ammonia molecules are also typical of those observed in Cu^{II}–ammine complexes.

The orotate-ligand structure

Comparison of the structural parameters of the orotate anion with those of ammonium orotate monohydrate (Solbakk, 1971) and orotic acid monohydrate (Takusagawa & Shimada, 1973) shows that the bond lengths appear to be rather similar, while the bond angles display some marked differences. The C(2)—N(1)—C(6) angle is 117·9 (2)° and thus 4·7 and 4·8° smaller and the N(1)—C(6)—C(5) angle is 125·4 (3)° and thus 4·3 and 3·7° larger than in ammonium orotate and orotic acid, respectively.

The least-squares plane through the six non-hydrogen atoms of the pyrimidine ring (Table 3) reveals that the ring is not quite as planar as in the compared compounds, the largest deviation being 0·040 (4) Å for C(4). Deviations of this magnitude are not uncommon for pyrimidine rings (Voet & Rich, 1970). The exocyclic non-hydrogen atoms O(1), O(2), C(7), O(3) and O(4) are all significantly out of the ring plane. The carboxylate group is both twisted and bent in relation to the pyrimidine ring. The angle between the ring and the carboxylate group is 8·2°, but because O(4) is coordinated to the Cu atom, the angle differs by 16·7 and 10·4° from those observed in ammonium orotate and orotic acid, respectively.

Molecular arrangement and hydrogen-bond system

The crystal packing is illustrated in the stereoview of Fig. 4 and the stacking of the molecules seen along the normal to the pyrimidine ring in Fig. 5. One of the principal features is the columnar packing along **a**. These columns are stabilized by the axial semi-coordination of O(2) atoms to Cu. The overlap of the molecular π systems is similar to that found in molecular systems with extensive π networks (Voet & Rich, 1970) and the distance of 3·38 Å between the stacking pyrimidine rings is also normal. The stability of the columns is further enhanced by the formation of an extensive intermolecular hydrogen-bond system between the ammonia molecules and the ring and carboxylate O atoms. This network also connects the columnar stacks together and stabilizes the whole crystal structure. An intramolecular hydrogen bond is formed between N(5) and O(1). The details of the hydrogen bonds are shown in Table 4.

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The Structure of Triaquabis(uracilato)cadmium(II)

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Abstract

$C_8H_{12}CdN_4O_7$, $[Cd(C_4H_3N_2O_2)_2(H_2O)_3]$, is orthorhombic, space group *Fdd*2, with $a = 24\cdot833$ (8), $b = 9\cdot517$ (2), $c = 10\cdot420$ (3) Å, $Z = 8$. Final $R = 0\cdot018$ for 634 unique reflections. The coordination sphere about Cd is a trigonal bipyramid with the N(3) atoms of two symmetry-related uracilato monoanions and one water molecule occupying the equatorial sites at distances of 2·211 (4) and 2·269 (8) Å, respectively. The axial sites are occupied by two symmetry-related water molecules at 2·439 (4) Å. The coordination alters the uracil ring geometry by closing the angle at the coordination site, N(3), and widening the adjacent angles. The ring is also more non-planar than in uncoordinated uracil. The uracil rings form columns approximately along the [011] and [01$\bar{1}$] directions. The rings in the columns are not parallel, but form angles of 8·72° with each other. The stacking pattern is characterized by minimal base overlap and the keto O atoms at C(2) point in the same direction. The Cd atoms and water molecules lie between the columns and the structure is held together by a hydrogen-bond network in which two water molecules and the N atom not involved in coordination act as donors and the exocyclic keto O atoms as acceptors.

Introduction

Few structural studies have been reported of metal complexes of uracil and thymine (Hodgson, 1977), owing to the weak coordination of the bases at low and neutral pH. At high pH, where they assume their enolic forms, there are several good coordination sites: the exocyclic O(2) and O(4) and the ring N(1) and N(3), both of which are deprotonated at pH > 9·5 (Nakanishi, Suzuki & Yamazaki, 1961).

One difficulty arising at high pH is the precipitation of the metals as hydroxides. This can be overcome by use of suitable complexation agents to keep the metals in solution. In the preparation of the Cu–thyminato complex, Kistenmacher, Sorrell & Marzilli (1975) used diethylenetriamine to form a soluble Cu complex and added thymine to this solution. We have used ammonia to form soluble metal complexes and to deprotonate the uracil base in the preparation of diamminediaquabis(uracilato)nickel(II) (Lumme & Mutikainen, 1980). Though ammonia is only useful with those metals that form soluble ammine complexes, it has the benefit of being a small molecule and causing only slight steric hindrance in the metal–uracil complexation.

In uracil and thymine both N(1) and N(3) are deprotonated at high pH and it is difficult to deduce the preferred coordination site. In fact, metal, reaction time and packing factors probably have a more pronounced influence on the site of coordination than the negligible difference in the nucleophilicities at the deprotonated ring N atoms (Snyder, Shulman & Neumann, 1970). In both Cu—thyminato and Ni—uracilato complexes, the coordination site is the deprotonated N(1). In our attempt to study the effect of the metal, we chose to use Cd because Cd^{2+} is not a transition-metal ion and the coordination is purely electrostatic. Cd, with its strong

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