References

Bastiansen, O., Hedberg, L. & Hedberg, K. (1957). *J. Chem. Phys.* **27**, 1311.

Duchamp, D. J. (1964). *Amer. Cryst. Assoc. Meeting*, Paper B-14, p. 29. Bozeman, Montana.

International Tables for X-ray Crystallography (1962). Vol. III, p. 202. Birmingham: Kynoch Press.

Johnson, C. K. (1965). *ORTEP, a Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations.* Report ORNL-3794. Oak Ridge National Laboratory, Oak Ridge, Tennessee.

Karle, J. & Karle, I. L. (1966). *Acta Cryst.* **21**, 849.

Kaufman, H. S., Fankuchen, I. & Mark, H. (1948). *Nature, Lond.* **161**, 165.

Larson, A. C. (1967). *Acta Cryst.* **23**, 664.

Mathews, F. S. & Lipscomb, W. N. (1959). *J. Phys. Chem.* **63**, 845.

Schomaker, V. & Trueblood, K. N. (1968). *Acta Cryst.* B**24**, 63.

Shoemaker, D. P., Kindler, H., Sly, W. G. & Srivastava, R. C. (1965). *J. Amer. Chem. Soc.* **87**, 482.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175.

Wilson, A. J. C. (1942). *Nature, Lond.* **150**, 152.

Acta Cryst. (1972). B**28**, 1075

The Crystal and Molecular Structure of *N*-(1-methyl-3-oxo-butyliden)-*N'*-(1-methyl-2-isonitroso-3-oxobutyliden)ethylenediaminecopper(II), Cu(II) ($C_{12}H_{17}N_3O_3$)

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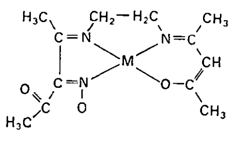
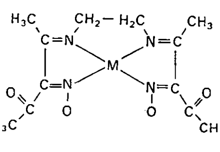
The crystal structure of *N*-(1-methyl-3-oxobutyliden)-*N'*-(1-methyl-2-isonitroso-3-oxobutyliden)ethylenediaminecopper(II), Cu(II) ($C_{12}H_{17}N_3O_3$), has been determined from 2538 independent reflexions, measured with Cu $K\alpha$ radiation by a single-crystal diffractometer and refined by the least-squares methods to $R=5\cdot1\%$. The triclinic ($P\bar{1}$) unit cell of dimensions $a=12\cdot11$ (1), $b=8\cdot15$ (1), $c=7\cdot92$ (1) Å, $\alpha=102\cdot1$ (1)°, $\beta=109\cdot6$ (1)°, $\gamma=105\cdot6$ (1)°, contains two complex molecules, where copper coordinates to two oxygen [Cu–O(1) = 1·887 (6) Å, Cu–O(2) = 1·926 (13) Å] and two nitrogen atoms [Cu–N(1) = 1·937 (14) Å, Cu–N(2) = 1·937 (7) Å] in a planar arrangement. The nitric oxide does not behave as a free ligand, but interacts with the organic molecule forming an oxime group which coordinates to metal through oxygen.

Introduction

The reaction of nitric oxide with bis(acetylacetone)-ethylenediimine metal-complexes was studied by Masuda, Tamaki & Shinra (1969), who found, from spectroscopic evidence, that the nitric oxide does not coordinate to metal as a free ligand in complexes containing Ni(II), Cu(II) and Pd(II). On the contrary, the NO group interacts with the organic ligand giving complex compounds for which they suggest the structural formulae:



(I)



(II)

(I) obtained by partial reaction, (II) by complete reaction of NO. The conclusion reached by these authors is quite right as far as the direct coordination of NO to the metal is concerned, but the role of the nitrous group, as given in their formulae, is not convincing. Therefore, to define this point, an X-ray analysis of (I) with M = Cu(II) was undertaken, also in connexion with a general programme, in progress in this laboratory, concerning structures of metal complexes of polydentate ligands containing nitrogen.

Experimental

Dark red-violet crystals of the compound were prepared by treatment of bis(acetylacetone)ethylenediimine-Cu(II) with nitric oxide as described by Masuda, Tamaki & Shinra (1969). The crystals are flattened prisms elongated along [001] showing pleochroic effects: observed perpendicularly to the flattening, they appear red or pinky-yellow depending on whether the electric vector vibrates perpendicular or parallel to the elongation.

The unit-cell dimensions, determined from rotation and Weissenberg photographs and refined by an 'on-line' single-crystal automated Siemens diffractometer using Cu $K\alpha$ radiation ($\lambda = 1{\cdot}5418$ Å), are as follows:

$Cu(C_{12}H_{17}N_3O_3)$; F.W.314·9
$a = 12{\cdot}11$ (1), $b = 8{\cdot}15$ (1), $c = 7{\cdot}92$ (1) Å;
$\alpha = 102{\cdot}1$ (1)°, $\beta = 109{\cdot}6$ (1)°, $\gamma = 105{\cdot}6$ (1)°;
$V = 668{\cdot}7$ Å^3, $Z = 2$, $D_{obs} = 1{\cdot}56$ g.cm^{-3}, $D_{calc} = 1{\cdot}56$ g.cm^{-3}, $F(000) = 326$, $\mu = 24{\cdot}3$ cm^{-1} (Cu $K\alpha$).
Space group $P\bar{1}$ (from structural analysis).

Three-dimensional intensity data were collected on the same diffractometer using the $\omega/2\theta$ scan technique ($2\theta_{max} = 140°$) and Cu $K\alpha$ radiation. Intensities of 2538 reflexions were measured; of these 1633, having $I > 2\sigma(I)$, were used in the refinement.

The structure amplitudes were obtained after the usual Lorentz and polarization reduction and the absolute scale was established by successive comparison with the calculated values. No correction for absorption was applied, as the sample used to collect data was small enough to allow this (it was roughly a cylinder with a mean radius of 0·005 cm).

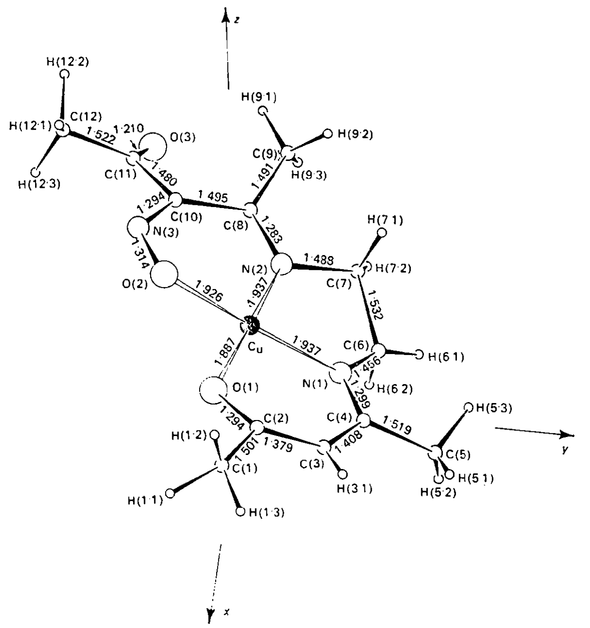


Fig.1. Cu(II) ($C_{12}H_{17}N_3O_3$): clinographic projection of the structure.

Determination and refinement of the structure

The structure was solved by the heavy-atom technique, starting from a three-dimensional Patterson distribution and only one Fourier synthesis was sufficient to localize all the non-hydrogen atoms. The refinement was carried out by block-diagonal least squares, minimizing the function $\sum w(\Delta F)^2$ [unit weights were assumed, being $\sum(\Delta F)^2/(m-n) = 0{\cdot}95$, where m is the number of observations and n the number of parameters (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961)]. This reduced R to 6·2%. All the hydrogen atoms were then directly located by a final $F_o - F_c$ synthesis and the complete least-squares refinement improved the conventional R index to 5·1%.

Table 1 shows the final atomic parameters and the corresponding e.s.d.'s. Copies of the observed and calculated structure factors are available from the authors on request.

The atomic scattering factors used throughout the calculations were those of Cromer & Mann (1968) for Cu, O, N and C and those of Stewart, Davidson & Simpson (1965) for H.

Table 1. *Final atomic fractional coordinates and temperature factors* ($8\pi^2$ Å^2)

Estimated standard deviations are given in parentheses. The anisotropic thermal parameters are given in the form:
$\exp[-0{\cdot}25(h^2B_{11}a^{*2} + \ldots + 2klB_{23}b^*c^*)]$.

Non-hydrogen atoms: Fractional coordinates are multiplied by 10^4.

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Cu	494 (1)	368 (1)	2357 (1)	4·25 (3)	3·55 (3)	3·94 (3)	1·59 (2)	2·07 (2)	1·74 (2)
O(1)	1907 (3)	− 185 (5)	2333 (5)	3·52 (16)	3·67 (16)	5·39 (20)	1·63 (13)	2·67 (15)	2·79 (15)
O(2)	−92 (3)	−1860 (4)	2831 (5)	3·40 (16)	3·28 (15)	4·65 (18)	1·61 (13)	2·36 (14)	2·06 (14)
O(3)	−4208 (4)	−2788 (6)	1786 (7)	3·27 (18)	5·85 (24)	8·80 (30)	1·79 (17)	2·35 (19)	2·84 (22)
N(1)	1086 (4)	2691 (5)	2037 (6)	3·52 (19)	2·86 (17)	3·22 (19)	1·02 (15)	1·68 (16)	1·49 (15)
N(2)	− 919 (4)	963 (5)	2527 (6)	3·14 (18)	2·58 (16)	3·20 (19)	1·23 (14)	1·73 (15)	1·25 (14)
N(3)	−1202 (4)	−2648 (6)	2801 (6)	2·80 (18)	3·63 (19)	3·74 (20)	1·33 (15)	1·64 (16)	1·73 (16)
C(1)	3906 (6)	149 (9)	2308 (11)	4·30 (30)	6·65 (37)	10·21 (50)	3·21 (28)	4·52 (33)	5·56 (37)
C(2)	2893 (5)	888 (8)	2285 (8)	3·30 (23)	4·74 (27)	3·96 (26)	1·70 (21)	2·03 (21)	1·96 (22)
C(3)	3056 (5)	2590 (7)	2152 (8)	3·06 (23)	4·03 (25)	5·10 (29)	1·23 (20)	2·09 (22)	2·00 (22)
C(4)	2171 (5)	3435 (7)	2012 (7)	3·91 (24)	2·69 (20)	3·53 (24)	0·67 (18)	1·80 (20)	0·97 (18)
C(5)	2535 (6)	5281 (7)	1776 (9)	5·70 (33)	2·96 (24)	6·63 (36)	1·17 (23)	3·49 (29)	2·29 (24)
C(6)	137 (5)	3512 (7)	1734 (8)	4·35 (26)	2·92 (22)	5·17 (29)	1·77 (20)	2·66 (23)	2·04 (21)
C(7)	− 654 (5)	2917 (7)	2809 (9)	4·98 (28)	2·71 (21)	5·78 (32)	2·13 (21)	3·06 (26)	1·76 (21)
C(8)	−1821 (4)	51 (6)	2854 (7)	2·88 (20)	3·36 (21)	2·65 (21)	1·60 (18)	1·20 (17)	1·34 (17)
C(9)	−2614 (5)	887 (8)	3538 (9)	4·63 (28)	4·86 (28)	5·60 (31)	3·06 (24)	3·18 (25)	2·84 (25)
C(10)	−2012 (4)	−1871 (6)	2720 (7)	3·12 (21)	3·21 (21)	3·13 (22)	1·05 (18)	1·72 (18)	1·54 (18)
C(11)	−3261 (5)	−3112 (8)	2405 (8)	3·25 (23)	4·48 (26)	4·21 (27)	1·56 (21)	1·91 (21)	1·46 (22)
C(12)	−3358 (6)	−4882 (8)	2802 (10)	4·66 (29)	4·37 (28)	6·65 (37)	1·19 (24)	3·26 (28)	3·00 (27)

Table 1 (*cont.*)

Hydrogen atoms: Fractional coordinates are multiplied by 10^3.

	x/a	y/b	z/c	B
H(1.1)	343 (5)	−126 (8)	111 (8)	6·5 (1·5)
H(1.2)	430 (5)	8 (8)	341 (8)	6·1 (1·5)
H(1.3)	441 (6)	69 (8)	174 (8)	7·1 (1·6)
H(3.1)	383 (5)	317 (7)	231 (7)	4·2 (1·2)
H(5.1)	333 (5)	577 (8)	210 (8)	6·0 (1·4)
H(5.2)	187 (5)	523 (7)	53 (7)	5·4 (1·3)
H(5.3)	259 (5)	617 (7)	299 (7)	5·2 (1·3)
H(6.1)	49 (6)	457 (8)	206 (9)	7·0 (1·6)
H(6.2)	− 51 (5)	313 (7)	26 (8)	5·4 (1·4)
H(7.1)	− 19 (5)	366 (7)	427 (7)	4·6 (1·2)
H(7.2)	−150 (5)	302 (7)	212 (7)	4·6 (1·2)
H(9.1)	−302 (5)	24 (7)	410 (7)	4·7 (1·3)
H(9.2)	−219 (5)	203 (7)	453 (7)	5·3 (1·3)
H(9.3)	−319 (6)	104 (8)	276 (9)	7·2 (1·6)
H(12.1)	−259 (5)	−485 (7)	361 (8)	5·4 (1·3)
H(12.2)	−374 (5)	−484 (8)	380 (8)	6·7 (1·5)
H(12.3)	−363 (6)	−565 (9)	143 (9)	8·1 (1·7)

All calculations were performed on the CDC 6600 computer of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale (Bologna), using programs of Immirzi (1967).

Description of the structure and discussion

As already observed from infrared spectrum evidence by Masuda, Tamaki & Shinra (1969), the NO molecule does not act as a free ligand, and the complex is not a nitrosyl one, but a reaction occurs between NO and bis(acetylacetone)ethylenediimine-Cu(II) in the γ-position of an acetylacetone group, giving an oxime derivative. An important difference is however observed with respect to the structure postulated from the infrared spectra by Masuda *et al.* In fact, the coordination does not involve the nitrogen atom, but the oxygen atom of the oxime group, as can be seen from the projections of Figs. 1 and 2.

Coordination around the metal is planar and involves two nitrogen atoms N(1) and N(2) from the ethylenediimine moiety and two oxygen atoms O(1) and O(2) from the CO and NO groups of the ligand. The four ligand atoms define a plane,† from which copper is displaced by 0·05 Å. The *N*-(1-methyl-3-oxobutyliden)-*N'*-(1-methyl-2-isonitroso-3-oxobutyliden)-ethylenediamine molecule acts as a tetradentate ligand and this results in the formation of one five-membered and two six-membered coordination rings. Of these only the O(1)C(2)C(3)C(4)N(1) residue, resulting from the acetylacetone moiety of the ligand, is planar.‡ The other two rings are distorted: the five-membered ring as a consequence of the ethylenediimine conformation (the internal rotation angle around C(6)–C(7) bond is 42·0°); the second six-membered ring as a consequence of the double bond localization between C(8)–N(2) = 1·283 (8) Å and between C(10)–N(3) = 1·294 (9) Å. This is in agreement with the single-bond character of the C(8)–C(10) = 1·495 (15) Å bond [expected value for C(sp^2)=N(sp^2) is 1·266 Å (Donohue, Lavine & Rollett, 1956) and for C(sp^2)–C(sp^2) is 1·487 Å (Allmann & Elner, 1968)]. The internal rotation angle around C(8)–C(10) is 23·8°.

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† The least-squares plane is: $0{\cdot}1013X' + 0{\cdot}1123Y' + 0{\cdot}9884Z' = 1{\cdot}6446$. The orthogonal X', Y', Z' coordinates, expressed in Å, are obtained from the x, y, z triclinic ones using the matrix:

$$\begin{pmatrix} \sin\gamma & 0 & -\sin\alpha\cos\beta^* \\ \cos\gamma & 1 & \cos\alpha \\ 0 & 0 & \sin\alpha\sin\beta^* \end{pmatrix}.$$

‡ The least-squares plane is: $-0{\cdot}0088X' + 0{\cdot}0764Y' + 0{\cdot}9970Z' = 1{\cdot}5363$.

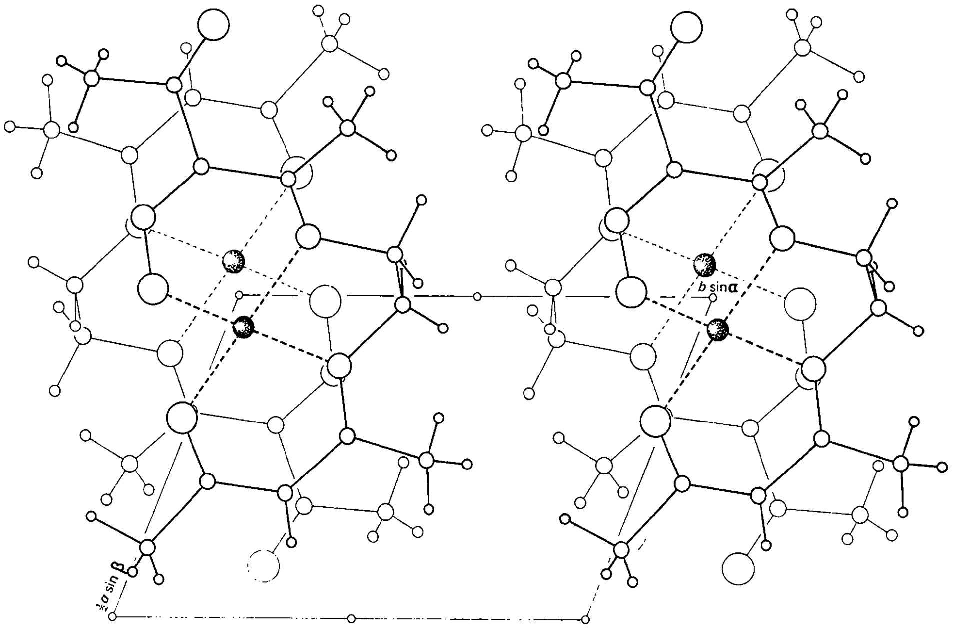

Fig. 2. Cu(II) ($C_{12}H_{17}N_3O_3$): projection of the structure on (001).

Table 2. *Distances and angles*

i	$\bar{x}$	$\bar{y}$	$\bar{z}$	iv	$x-1$	y	z
ii	$\bar{x}$	$\bar{y}$	$1-z$	v	x	$y-1$	z
iii	$\bar{x}-1$	$\bar{y}-1$	$\bar{z}$	vi	$\bar{x}$	$1-y$	$1-z$

(*a*) In the coordination plane

Cu–O(1)	1·887 (6) Å	O(1)–Cu–O(2)	87·6 (2)°
Cu–O(2)	1·926 (13)	O(2)–Cu–N(2)	91·5 (2)
Cu–N(1)	1·937 (14)	N(1)–Cu–N(2)	86·5 (2)
Cu–N(2)	1·937 (7)	O(1)–Cu–N(1)	94·2 (2)

(*b*) In the complex molecule

O(1)—C(2)	1·294 (8) Å	C(1)—C(2)	1·501 (12) Å
O(2)—N(3)	1·314 (7)	C(2)—C(3)	1·379 (15)
O(3)—C(11)	1·210 (9)	C(3)—C(4)	1·408 (11)
N(1)—C(4)	1·299 (8)	C(4)—C(5)	1·519 (14)
N(1)—C(6)	1·456 (10)	C(6)—C(7)	1·532 (9)
N(2)—C(7)	1·488 (14)	C(8)—C(9)	1·491 (9)
N(2)—C(8)	1·283 (8)	C(8)—C(10)	1·495 (15)
N(3)—C(10)	1·294 (9)	C(10)–C(11)	1·480 (9)
C(11)–C(12)	1·522 (16)		
Cu—O(1)—C(2)	125·6 (4)°	C(4)—N(1)—C(6)	122·5 (3)°
Cu—O(2)—N(3)	127·4 (3)	N(1)—C(6)—C(7)	108·3 (5)
Cu—N(1)—C(4)	125·6 (4)	C(6)—C(7)—N(2)	108·4 (5)
Cu—N(1)—C(6)	111·8 (4)	C(7)—N(2)—C(8)	119·6 (5)
Cu—N(2)—C(8)	128·2 (4)	N(2)—C(8)—C(9)	122·2 (5)
Cu—N(2)—C(7)	110·0 (4)	C(10)–C(8)—C(9)	118·4 (5)
O(1)—C(2)—C(1)	115·7 (6)	N(2)—C(8)—C(10)	119·1 (5)
C(3)—C(2)—C(1)	118·8 (6)	C(8)—C(10)–C(11)	119·3 (5)
O(1)—C(2)—C(3)	125·5 (6)	N(3)—C(10)–C(11)	113·2 (5)
C(2)—C(3)—C(4)	125·7 (6)	C(8)—C(10)–N(3)	127·5 (5)
C(3)—C(4)—C(5)	116·2 (6)	C(10)–N(3)—O(2)	123·2 (5)
N(1)—C(4)—C(5)	120·7 (6)	C(10)–C(11)–O(3)	122·1 (6)
C(3)—C(4)—N(1)	123·1 (6)	C(10)–C(11)–C(12)	118·7 (6)
O(3)—C(11)–C(12)	119·2 (6)		

(*c*) Involving hydrogen

C(1)—H(1.1)	1·17 (6) Å	C(7)—H(7.1)	1·05 (5) Å
C(1)—H(1.2)	0·86 (6)	C(7)—H(7.2)	1·02 (6)
C(1)—H(1.3)	0·95 (7)	C(9)—H(9.1)	0·91 (6)
C(3)—H(3.1)	0·88 (6)	C(9)—H(9.2)	0·95 (6)
C(5)—H(5.1)	0·85 (6)	C(9)—H(9.3)	0·82 (7)
C(5)—H(5.2)	1·03 (5)	C(12)—H(12.1)	0·92 (6)
C(5)—H(5.3)	1·04 (5)	C(12)—H(12.2)	1·04 (6)
C(6)—H(6.1)	0·79 (7)	C(12)—H(12.3)	1·02 (7)
C(6)—H(6.2)	1·08 (6)		
C(2)—C(1)–H(1.1)	108 (3)°	H(6.1)—C(6)—H(6.2)	105 (6)°
C(2)—C(1)–H(1.2)	112 (4)	N(2)—C(7)—H(7.1)	110 (3)
C(2)—C(1)–H(1.3)	113 (4)	N(2)—C(7) H(7.2)	107 (3)
H(1.1)–C(1)–H(1.2)	112 (6)	C(6)—C(7)—H(7.1)	112 (3)
H(1.1)–C(1)–H(1.3)	94 (5)	C(6)—C(7)—H(7.2)	105 (3)
H(1.2)–C(1)–H(1.3)	117 (6)	H(7.1)—C(7)—H(7.2)	115 (5)
C(2)—C(3)–H(3.1)	112 (4)	C(8)—C(9)—H(9.1)	113 (4)
C(4)—C(3)–H(3.1)	122 (4)	C(8)—C(9)—H(9.2)	117 (4)
C(4)—C(5)–H(5.1)	113 (4)	C(8)—C(9)—H(9.3)	119 (5)
C(4)—C(5)–H(5.2)	109 (3)	H(9.1)—C(9)—H(9.2)	100 (5)
C(4)—C(5)–H(5.3)	105 (3)	H(9.1)—C(9)—H(9.3)	102 (6)
H(5.1)–C(5)–H(5.2)	122 (5)	H(9.2)—C(9)—H(9.3)	103 (6)
H(5.1)–C(5)–H(5.3)	92 (5)	C(11)—C(12)–H(12.1)	112 (4)
H(5.2)–C(5)–H(5.3)	114 (5)	C(11)—C(12)–H(12.2)	104 (4)
N(1)—C(6)–H(6.1)	108 (5)	C(11)—C(12)–H(12.3)	96 (4)
N(1)—C(6)–H(6.2)	114 (3)	H(12.1)–C(12)–H(12.2)	95 (5)
C(7)—C(6)–H(6.1)	114 (5)	H(12.1)–C(12)–H(12.3)	112 (6)
C(7)—C(6)–H(6.2)	108 (3)	H(12.2)–C(12)–H(12.3)	137 (6)

(*d*) van der Waals contacts

Cu—N(1^{i})	3·362 (7) Å	C(9)–C(1^{iv})	3·834 (13) Å
O(1)—N(2^{i})	3·482 (8)	C(1)–C(5^{v})	3·735 (29)
N(1)—O(2^{i})	3·481 (8)	C(9)–O(1^{ii})	3·304 (10)
N(2)—O(2^{ii})	3·304 (7)	C(9)–O(2^{ii})	3·310 (8)
N(3)—N(2^{ii})	3·430 (8)	C(7)–C(7^{vi})	3·813 (15)
C(12)–O(3^{iii})	3·522 (10)	Cu—Cu^{i}	3·377 (5)

The Cu–O and Cu–N distances quoted in Table 2 and in Fig. 1 agree well with those found in other complexes, the C–N being on the shorter side of the range usually observed for this bond (Biagini Cingi, Guastini, Musatti & Nardelli, 1970; Ghilardi & Lingafelter, 1970; Matthew & Kunchur, 1970; Gurr, 1968).

The ethylene bridge C(6)–C(7) is *trans* with respect to the coordination plane [C(6) and C(7) are out of the coordination plane by $-0\cdot19$ and $+0\cdot38$ Å respectively]. This situation, which is usual for bridged compounds of this sort, is not observed in the adduct formed by *N,N'*-ethylenebis(acetylacetoneiminato)-copper(II) with methylammonium perchlorate, in which Baker, Hall & Waters (1970) found a *cis*-ethylene bridge. The C(6)–C(7) distance (1·532 (9) Å) corresponds well to the theoretical value for $C(sp^3)$–$C(sp^3)$ single bonds.

The acetylacetone moiety of the molecule, in agreement with the π-delocalization indicated by the bond lengths, is planar excepting the C(1) and C(5) methyl groups which are out of the plane, both by 0·07 Å. This plane is not coincident with the coordination plane, but forms with it a dihedral angle of 6·7°. The mean plane through O(2)N(3)C(10)C(8)N(2) forms a dihedral angle of 6·0° with the coordination plane. The C(10)C(11)C(12)O(3) group is planar (the least-squares plane is: $0\cdot2597X'-0\cdot2324Y'-0\cdot9372Z'=-2\cdot3273$) with a double bond localized between C(11)–O(3) = 1·210 (9) Å and the plane is rotated around C(10)–C(11) by 18·5°, in agreement with the single-bond character of this bond. All the methyl groups are involved in bonds of $C(sp^3)$–$C(sp^2)$ type and the distances (quoted in Table 2) are consistent with this situation (expected value for $C(sp^3)$–$C(sp^2)$ = 1·501 Å; Lide, 1962).

Two complex molecules are related by a centre of symmetry in such a way that the distance between adjacent copper atoms along [010] is 3·377 (5) Å. The angle formed by the $Cu–Cu^{i}$ direction and the coordination plane is 81·8°, so that the whole structure can be considered as formed by discrete molecules which seem to be joined together in dimers through a very feeble metal–metal interaction.

All the other contacts are consistent with the van der Waals radii requirements as shown in Table 2.

References

Allmann, R. A. & Elner, H. E. (1968). *Chem. Ber.* **101**, 2522.

Baker, E. N., Hall, D. & Waters, T. N. (1970). *J. Chem. Soc.* (*A*), p. 396.

Biagini Cingi, M., Guastini, C., Musatti, A. & Nardelli, M. (1970). *Acta Cryst.* **B26**, 1836.

Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* **A24**, 321.

Cruickshank, D. W. J., Pilling, D. E., Bujosa, A., Lovell, F. M. & Truter, M. R. (1961). In *Computing Methods and the Phase Problem in X-Ray Crystal Analysis*. Edited by R. Pepinsky, J. M. Robertson & J. C. Speakman, p. 47.

Donohue, J., Lavine, L. R. & Rollett, J. S. (1956). *Acta Cryst.* **9**, 655.

Ghilardi, C. A. & Lingafelter, E. C. (1970). *Acta Cryst.* **B26**, 1807.

Gurr, G. E. (1968). *Acta Cryst.* **B24**, 1511.

Immirzi, A. (1967). *Ric. Sci.* **37**, 743.

Lide, D. R. (1962). *Tetrahedron*, **17**, 125.

Masuda, I., Tamaki, M. & Shinra, K. (1969). *Bull. Chem. Soc. Japan*, **42**, 157.

Matthew, M. & Kunchur, N. R. (1970). *Acta Cryst.* **B26**, 2054.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175.

Acta Cryst. (1972). **B28**, 1079

Etude Cristallographique du Tétrachlorobaltate(II) d'Histamine Diprotonée

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The tetrachlorocobaltate(II) of diprotonated histamine crystallizes in space group $Pna2_1$ of the orthorhombic system. 804 *hkl* reflexions were measured on a single crystal at room temperature. Refinement by full-matrix least-squares methods led to an *R* value of 0·045. The crystal is formed from very distorted tetrahedral $(CoCl_4)^{2-}$ ions: the largest difference of the Co–Cl bond lengths is 0·062 Å and the largest difference of the Cl–Co–Cl angles, 9·6°; it also contains almost planar $(Hist.\ H_2)^{2+}$ cations in which two protons are attached to the histamine molecule through the nitrogen atoms of the cetimine group of the imidazole ring and the primary amine group of the side chain.

Introduction

Ce travail se place dans le cadre général de l'étude cristallochimique des composés de coordination de l'histamine avec certains métaux de transition, notamment ceux de la fin de la première série de transition (Bonnet, Jeannin, Jeannin & Rzotkiewicz, 1969; Bonnet & Jeannin, 1970*a*, *b*, *c*, 1971).