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The Crystal and Molecular Structure of the Diacetone Adduct of the Copper(II) Complex of 1-Nitroso-2-naphthol: $[Cu(C_{10}H_6NO_2)_2].2(CH_3)_2CO$

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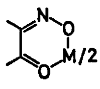
The crystal and molecular structure of the diacetone adduct of the copper(II) complex of 1-nitroso-2-naphthol ($\rightleftharpoons$1,2-naphthoquinone-1-oxime) has been determined from three-dimensional X-ray data. The crystals are dark brown, $P2_1/c$, with cell dimensions, $a = 8.001(5)$ Å, $b = 13.806(11)$ Å, $c = 11.012(18)$ Å, $\beta = 98.0(1)°$, and $Z = 2$. The structure was solved by the heavy atom method and refined by least-squares procedures. The final R-value, based on 1282 observed reflections, is 0.077.

The chelate rings in the complex are five-membered and the nearest positions around copper are occupied by two oxime nitrogen atoms (Cu–N, 1.988 Å) and two naphtholic oxygen atoms (Cu–O, 1.951 Å), forming an approximately square-planar configuration. The approximate octahedral arrangement around Cu is completed by two acetone oxygens at distances of 2.651 Å. The bond lengths in the complex suggest a resonance structure between bis(1-nitroso-2-naphtholato)copper(II) and bis(1,2-naphthoquinone-1-oximato)copper(II).

1-Nitroso-2-naphthol was apparently the first organic substance found to form precipitates with metal ions.[1] Until recently, this reagent, its 2-nitroso-1-naphthol isomer, and their water-soluble sulfonic acid derivatives have been used for the determination of several metal ions, especially the microdetermination of cobalt. Even though the complexes were discovered long time ago, their structure has been repeatedly debated.

It is well known that 1,2-nitrosonaphthols (and 1,2-nitrosophenols) can tautomerise to the corresponding quinonemonoximes. On the basis of infrared data it is mostly concluded that *o*-nitrosophenols, including 1-nitroso-2-naphthol, exist in their respective oxime forms in the solid state.[2] This is supported by the X-ray studies on β-5-propoxy-*o*-quinone-2-oxime and α-5-(2′-chloroethoxy)-*o*-quinone-2-oxime.[3,4] On the other hand, absorption spectra [4] and the effect of substituents on the protolysis of the compounds [5] suggest the existence of a nitrosophenol structure in solution.

The indefinite structure of the ligand is reflected in the various interpretations given for the structure of *o*-nitrosophenol complexes. Because of the complexity of the complexes, unambiguous conclusions can hardly be drawn from the known mass spectrometric, infrared or electronic spectral, or magnetic susceptibility data. Particularly the size of the chelate ring has remained in doubt. Several authors have interpreted the infrared spectra of the copper(II) complexes of 1-nitroso-2-naphthol as indicating the presence of six-membered chelate rings (*i.e.* coordination through naphtholic oxygen and oxime oxygen atoms, structure I).[6,7] However, a recent re-examination of the published IR data by Chakravorty, led to the conclusion that the five-membered ring structure II (*i.e.* coordination through naphtholic oxygen and oxime nitrogen atoms) could satisfy the IR data equally well.[8]



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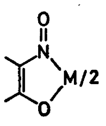

II

Table 1. Fractional atomic coordinates ($\times 10^4$) and thermal parameters[a] ($\times 10^3$). Estimated standard deviations are given in parentheses.

Atom	X/a	Y/b	Z/c	U_{11}	U_{22}	U_{33}	$2U_{12}$	$2U_{23}$	$2U_{13}$
C(1)	818(9)	−438(4)	2509(6)	35(4)	27(3)	30(3)	0(6)	5(5)	17(5)
C(2)	−335(8)	−1153(4)	1942(5)	39(4)	31(3)	27(3)	2(5)	5(5)	18(5)
C(3)	−865(9)	−1936(4)	2656(6)	53(5)	28(3)	36(4)	0(6)	7(5)	31(6)
C(4)	−234(9)	−1996(5)	3863(6)	52(5)	41(4)	41(4)	22(7)	30(6)	41(7)
C(5)	1466(10)	−1375(6)	5751(6)	47(5)	72(5)	37(4)	29(8)	15(8)	23(7)
C(6)	2563(10)	−697(6)	6348(6)	55(5)	74(5)	33(4)	28(8)	12(7)	4(7)
C(7)	3125(11)	77(6)	5693(6)	54(6)	74(5)	34(4)	34(9)	16(8)	−7(7)
C(8)	2588(10)	189(5)	4425(6)	54(5)	50(4)	34(4)	6(7)	−10(6)	−1(6)
C(9)	1454(9)	−498(5)	3811(6)	37(4)	41(4)	26(3)	12(6)	0(5)	12(5)
C(10)	930(9)	−1285(5)	4476(5)	46(5)	44(4)	23(3)	12(6)	6(6)	13(5)
C(11)	−3889(11)	1461(6)	11(8)	60(6)	55(5)	65(5)	2(8)	24(9)	39(8)
C(12)	−4770(14)	1128(11)	−1197(9)	76(8)	158(12)	59(6)	70(15)	−19(14)	−33(10)
C(13)	−4714(14)	2230(8)	680(11)	90(8)	72(6)	103(8)	44(11)	−12(13)	82(13)
N(1)	1164(7)	232(3)	1690(5)	39(4)	21(2)	31(3)	−2(4)	3(4)	19(5)
O(1)	2179(7)	914(3)	1987(4)	63(4)	36(3)	45(3)	−30(5)	5(4)	2(5)
O(2)	−924(6)	−1105(3)	788(4)	57(3)	32(2)	26(2)	−21(4)	1(4)	5(4)
O(3)	−2532(7)	1116(4)	466(5)	64(4)	73(4)	58(3)	30(6)	5(6)	7(6)
Cu	0000	0000	0000	69(1)	40(1)	33(1)	−18(1)	5(1)	12(1)

[a] The anisotropic thermal parameters are of the form $\exp[-2\pi^2(h^2a^{*2}U_{11}+k^2b^{*2}U_{22}+l^2c^{*2}U_{33}+2hka^*b^*U_{12}+2klb^*c^*U_{23}+2hla^*c^*U_{13}]$.

X-Ray studies on the metal complexes of the nitrosonaphthol type are scarce. McPartlin[9] reports that the 1:1 pyridine adduct of bis(4-methyl-1-quinone-2-oximato)copper(II) complex has a square planar structure with five-membered chelate rings and ligands of predominantly quinonoid form. The crystal structure of tris(4-chloro-1-quinone-2-oximato)nickelate(II) anion, reported by Carreck *et al.*,[10] is essentially similar. A third complex of this ligand class is ferroverdin (an iron-containing pigment isolated from an unidentified species of *Streptomyces*).[11] In this complex, too, the chelate rings are five-membered, but the bond distances suggest considerable contribution from the nitrosophenol structure.

The present study of a copper(II) complex of 1-nitroso-2-naphthol has been carried out in order to obtain further information about the structure of such compounds.

EXPERIMENTAL

Crystal preparation and analysis. 1-Nitroso-2 naphthol (Merck AG, "zur Synthese", 2 mol) was dissolved in 1:1 acetic acid, after which copper nitrate solution (1 mol) was added. The precipitated bis complex was washed with water and dried in air. The crude product was first recrystallized from chloroform. Well-developed lustrous crystals were obtained, but on standing in air they soon lost their luster and disintegrated. When recrystallized from acetone, crystals containing two molecules of acetone were formed within a few days. They proved to be sufficiently stable for X-ray studies. Anal. (air-dried material): Calc. for $C_{26}H_{24}O_6N_2Cu$: C 59.59; H 4.62; O 18.32; N 5.35. Found: C 59.57; H 4.39; O 18.54; N 5.54. Thermogravimetric analysis showed that acetone was smoothly lost between 80 °C and 120 °C (weight loss 22 %, calc. 22.2 %). After the acetone had escaped, the crystals were stable to about 275 °C, at which temperature they decomposed explosively. The IR spectra of the complex (KBr pellet and Nujol mull) indicated a strong $\nu(C=O)$ stretching vibration of acetone at 1700 cm^{-1} which disappeared when the material was dried at 120 °C.

The formation of the 1:2 acetone adduct of the complex was unexpected in view of the earlier observations: it is precipitated from aqueous solution as monohydrate, forms an anhydrous 1:1 adduct with pyridine, but fails to form adducts with several other strong donors, such as methyl cyanide, triethylamine, and dimethyl sulfoxide.[12]

Crystal data. Rotation photographs and Weissenberg photographs, taken with Cu*Kα* radiation (1.5418 Å), show that the crystals are monoclinic. The space group, from systematic absences, is $P2_1/c$.

Unit cell dimensions were found from powder photographs taken with a Hägg-Guinier camera,

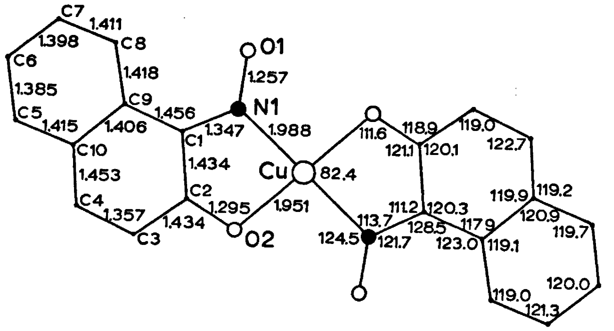

Fig. 1. Schematic representation of the complex showing bond lengths and angles. The e.s.d.'s in bond lengths are: Cu – O, 0.004 Å; Cu – N, 0.005 Å; N – O, 0.007 Å; C – O, 0.008 Å; C – N, 0.008 Å; C – C, 0.009 – 0.012 Å. The e.s.d.'s in angles are in the range 0.2 – 0.7°.

using Cu*K*α radiation with calcium fluoride ($a = 5.4630$ Å) as internal standard. There are two formula units in the cell; the calculated density is 1.44 g cm^{-3}, and the density found by flotation is 1.4 g cm^{-3}. The crystal data (calculated by least-squares procedures) are:

$a = 8.001(5)$ Å
$b = 13.806(11)$ Å
$c = 11.012(18)$ Å
$\beta = 98.0(1)°$
$V = 1204.6$ Å^3
FW = 524.03
$Z = 2$
Space group $P2_1/c$

Intensity data. A crystal with approximate dimensions 0.2 × 0.2 × 0.3 mm was used for the intensity measurements. Ni-filtered Cu radiation (Cu*K*α, $\lambda = 1.5418$ Å) and a Stoe-Güttinger diffractometer equipped with a scintillation counter and pulse height analyser were used to measure the intensities of 1807 reflections from the levels 0*kl* – 6*kl*. The background-peak-background technique was used. Only 1282 reflections had intensities greater than twice the standard deviations calculated from counting statistics. The data were corrected for Lorentz and polarization effects. No correction for absorption was applied (μ(Cu*K*α) = 16.9 cm^{-1}).

Structure determination. The structure was solved by the heavy atom method. The copper atom was placed at the origin and the approximate positions of the naphthalene carbons were found from a three-dimensional Patterson map. Three-dimensional Fourier syntheses were used to locate the other nonhydrogen atoms. The atomic scattering factors for Cu^{2+}, O, N, and C were taken from International Tables for X-Ray Crystallography.[13]

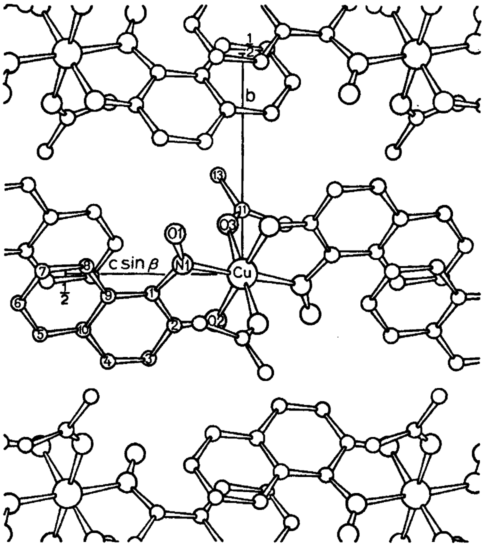

Fig. 2. Projection of the structure along the *a* axis.

Table 2. The bond lengths (Å) and angles (°) of the acetone molecule with their standard deviations.

C(11) – C(12)	1.488(15)	C(11) – O(3) – Cu	143.4(6)
C(11) – C(13)	1.497(14)	C(12) – C(11) – C(13)	118.2(9)
C(11) – O(3)	1.227(10)	C(12) – C(11) – O(3)	121.8(8)
Cu – O(3)	2.651(6)	C(13 – C(11) – O(3)	120.0(8)
		N(1) – Cu – O(3)	89.8(2)
		O(2) – Cu – O(3)	91.2(2)

Table 3. The least-squares plane defined by the naphthalene carbon ring. Deviations (Å) of different atoms from the plane are given. X', Y', and Z' are orthogonal axes related to X, Y, and Z by $X'=X+Z\cos\beta$, $Y'=Y$, and $Z'=Z\sin\beta$.

Plane C(1) – C(10): $-0.8121X'+0.5454Y'+0.2074Z'-0.0202=0$

Atom	Distance	Atom	Distance	Atom	Distance	Atom	Distance
C(1)	−0.002	C(5)	0.008	C(9)	−0.004	N(1)	−0.013
C(2)	0.010	C(6)	0.016	C(10)	−0.023	O(1)	−0.051
C(3)	0.015	C(7)	0.003	Cu	0.020	O(2)	0.024
C(4)	−0.016	C(8)	−0.008				

The refinement of the structure was carried out by block-diagonal least-squares procedures in which the function $\sum w(|F_o|-|F_c|)^2$ was minimized. After 7 cycles of refinement with isotropic thermal parameters, the R-index $\sum||F_o|-|F_c||/\sum|F_o|$ was 0.12. The refinement was then continued with anisotropic thermal parameters, and the final R-value is 0.077 for 1282 reflections.

The final atomic coordinates and thermal parameters together with their estimated standard deviations are given in Table 1. A list of the observed and calculated structure factors is obtainable on request from the authors. All calculations were carried out on an Elliott 803 B computer using programmes of Daly, Stephens, and Wheatley.[14]

RESULTS AND DISCUSSION

The bond lengths and bond angles of the complex are presented in Fig. 1, and the dimensions of the acetone molecule are given in Table 2. A projection of the structure along the a axis is shown in Fig. 2. It can be seen, that the Cu^{2+} ion is bonded to the ligand anions through the oxime nitrogen and naphtholic oxygen atoms, thus confirming the correctness of the five-membered chelate ring alternative. The ligands are in *trans*-position giving rise to a nearly planar structure (Table 3). Within the limits of experimental error, the naphthalene planes do not deviate from the coordination plane of Cu^{2+} ion, and even the oxime oxygens can be included in this plane.

Table 4. The least-squares plane defined by the acetone molecule. The equation and the deviations of the atoms are given as in Table 3.

Plane C(11) – C(13), O(3):
$-0.5471X'-0.7016Y'+0.4566Z'-0.2976=0$

Atom	Distance	Atom	Distance
C(11)	−0.004	C(13)	0.001
C(12)	0.001	O(3)	0.001

Table 5. Intermolecular distances (Å; below 3.5 Å). Roman numerals refer to the following equivalent positions: I $\bar{x},\frac{1}{2}+y,\frac{1}{2}-z$; II $x,-\frac{1}{2}-y,-\frac{1}{2}+z$; III $1-x,\bar{y},1-z$.

O(1) – C(3)$^{\mathrm{I}}$	3.191
O(1) – C(4)$^{\mathrm{I}}$	3.349
O(3) – C(4)$^{\mathrm{I}}$	3.433
O(2) – C(4)$^{\mathrm{II}}$	3.464
C(8) – C(7)$^{\mathrm{III}}$	3.470

Judging from the bond lengths in the complex there is contributions from the nitrosonaphthol as well as the quinone oxime structure. The observed C(1) – N distance (1.35 Å) is somewhat greater than the corresponding bond length in several typical oximates (*e.g.* in *vic*-dioximates the average value is 1.30 Å) but shorter than could be expected for nitrosonaphthalene compounds, 1.44 Å (*cf.* 1.42 Å in ferroverdin).[8,11,15] The N – O distance in oximates (1.34 Å, av.) is greater than the one found here (1.26 Å).[8] Furthermore, the C(2) – O bond (1.30 Å) cannot be described as a single nor as a double bond; *e.g.* the equivalent bond in salicylaldoxime [16] and salicylaldehyde [17] complexes varies from 1.31 Å to 1.36 Å and, on the other hand, the C – O double bond in naphthoquinones (1.22 Å) [18] can alter on complex formation. Moreover, as C(3) – C(4) is the only carbon-carbon bond with pronounced double bond character, the distribution of longer or shorter bonds in the naphthalene nucleus does not unambiguously indicate the quinonoid form. This being the case, the complex cannot be categorically labelled as bis(1-nitroso-2-naphtholato)copper(II) nor bis(1,2-naphthoquinone-1-oximato)copper(II).

It is of interest to note that the N–O and C(2)–O distances in the present complex are approximately equal to the corresponding distances in ferroverdin, in the 1:1 pyridine adduct of bis(4-methyl-1-quinone-2-oximato)copper(II), as well as in the tris(4-chloro-1-quinone-2-oximato)nickelate(II) anion (naming of the complexes is from the original authors).[9,10,11] As a whole, the main difference between the nitrosophenolate groupings in all these complexes is the lengthened C–N bond of ferroverdin.

The acetone oxygen atoms complete the distorted octahedral arrangement around the Cu^{2+} ion. The distance between copper and acetone oxygen (2.651 Å) indicates a relatively weak interaction which seems to have practically no influence on the planarity of the acetone molecule (*cf.* Table 4) or its bond lengths and bond angles.

There are only weak interactions between separate complex units, *cf.* Table 5, and the structure is therefore monomeric. This differs from the complexes $Cu(qo)_2$ and $Ni(qo)_2$ (qoH = 1-nitroso-2-naphthol or *o*-nitrosophenol derivative) for which polymeric or dimeric structure has been proposed.[19]

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