The Crystal and Molecular Structure of the Copper(II) Complex of 2-Nitroso-1-naphthol: $[\text{Cu}(\text{C}_{10}\text{H}_6\text{NO}_2)_2] \cdot \text{H}_2\text{O}$

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The crystal and molecular structure of the monohydrate of the copper(II) complex of 2-nitroso-1-naphthol ($\rightleftharpoons$ 1,2-naphthoquinone-2-oxime) has been determined by three-dimensional X-ray methods. The monoclinic cell dimensions are: $a = 6.395(4)$ Å, $b = 19.311(23)$ Å, $c = 14.274(24)$ Å, $\beta = 98.2(1)^\circ$. The space group is $P2_1/c$ and $Z = 4$. The structure was solved by conventional Patterson and Fourier methods and refined by least-squares procedures. The final R -value, based on 1473 reflections, is 0.073.

The complex has a distorted square pyramidal geometry with two oxime nitrogen atoms ($\text{Cu}-\text{N}$, 1.988(8) and 1.978(9) Å) and two naphtholic oxygen atoms ($\text{Cu}-\text{O}$, 1.976(8) and 1.971(7) Å) in an approximately square planar configuration, and the oxygen atom of the water molecule in apical position ($\text{Cu}-\text{O}$, 2.195(7) Å).

The dissimilarity in the behaviours of 1-nitroso-2-naphthol ($\rightleftharpoons$ 1,2-naphthoquinone-1-oxime) and 2-nitroso-1-naphthol ($\rightleftharpoons$ 1,2-naphthoquinone-2-oxime) toward metal ions has been reported by several authors. In solution, 1-nitroso-2-naphthol forms transition metal complexes of considerably higher stability than does 2-nitroso-1-naphthol.¹ This tendency is also valid for several derivatives of the isomers, and it cannot be explained by the different acid strengths of the ligands.² The visible, near ultraviolet, and infrared absorption spectra of metal complexes derived from the 1,2-isomers are also markedly different.³

It can be expected that the different properties of 1-nitroso-2-naphthol and 2-nitroso-1-naphthol complexes in solution are also reflected in the structures of the compounds in the solid state. In a previous paper, we

reported the crystal structure of the diacetone adduct of the copper(II) complex of 1-nitroso-2-naphthol.⁴ Our studies on solid copper(II) complexes of 1,2-nitrosonaphthols are now continuing with a 2-nitroso-1-naphthol type of ligand, and in this paper the crystal structure of bis(1,2-naphthoquinone-2-oximate)copper(II) monohydrate is described.

EXPERIMENTAL

Crystal preparation and analysis. The copper(II) complex of 2-nitroso-1-naphthol was prepared by a standard method.⁵ The precipitated reddish brown monohydrate was washed with water and ethanol and dried in air. The microcrystalline product was dissolved in warm acetone. On gradual cooling, crystals suitable for X-ray analysis formed within a few days. (Found: C 56.57; H 3.43; N 6.58; Cu 15.0. Calc. for $\text{C}_{20}\text{H}_{14}\text{O}_5\text{N}_2\text{Cu}$: C 56.40; H 3.31; N 6.58; Cu 14.92).

The copper(II) complexes of 1-nitroso-2-naphthol and 2-nitroso-1-naphthol are both precipitated from aqueous solution as their monohydrates. However, on recrystallization from acetone under similar conditions, the complexes behave differently. The crystalline compound obtained from the acetone solution of the 2-nitroso-1-naphthol complex is still monohydrate, whereas the copper(II) complex of 1-nitroso-2-naphthol yields a 1:2 acetone adduct.⁴

Crystal data. Weissenberg photographs showed that crystals of the present complex belong to the monoclinic system. The space group, from systematic absences, is $P2_1/c$.

Unit cell dimensions were obtained by least-squares procedures from a powder photograph taken by use of a Hägg-Guinier camera, $\text{CuK}\alpha$ radiation and calcium fluoride ($a = 5.4630$ Å) as internal standard. Based on four formula units in the cell, the calculated density of

1.621 g cm⁻³ is in agreement with that of 1.61 g cm⁻³ obtained by the flotation method. Crystal data for [Cu(C₁₀H₈NO₂)₂].H₂O are:

$$\begin{aligned} a &= 6.395(4) \text{ \AA} & V &= 1744.9 \text{ \AA}^3 \\ b &= 19.311(23) \text{ \AA} & FW &= 425.89 \\ c &= 14.274(24) \text{ \AA} & Z &= 4 \\ \beta &= 98.2(1)^\circ & \text{Space group} & P2_1/c \end{aligned}$$

Intensity data. The crystal selected for data collection had approximate dimensions 0.3 × 0.2 × 0.2 mm. Single-crystal intensity data from levels 0kl–5kl were collected by use of a Stoe-Gütinger diffractometer and Ni-filtered Cu radiation (CuK α , λ = 1.5418 Å). Of the 2634 recorded reflections, 1473 with $I > 3\sigma(I)$ were used for the structure analysis. The data were corrected for Lorentz and polarization effects. No correction for absorption was applied [$\mu(\text{CuK}\alpha) = 21.3 \text{ cm}^{-1}$].

Structure determination. The structure was solved by the heavy atom method. The approximate position of the copper atom was determined from Harker vectors in a three-

dimensional Patterson synthesis. Subsequent Fourier syntheses gave the positions of other non-hydrogen atoms of the complex. The atomic scattering factors for Cu²⁺, O, N, and C were taken from International Tables for X-Ray Crystallography.⁶

The refinement of the structure was carried out by block-diagonal least-squares procedures. The weighting scheme was $w = 1/(a + |F_o|^2 + b|F_o|^3)$ with $a = 35.0$ and $b = 0.007$. Eight cycles of refinement with isotropic thermal parameters yielded a R -value of 0.087 ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$). The refinement was then continued with anisotropic thermal parameters. The final R -value was 0.073 for 1473 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.⁷

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 ₁₃	2U ₂₃
C(1)	664(16)	-217(7)	3127(7)	34(7)	41(6)	23(5)	5(9)	1(8)	18(8)
C(2)	-1324(16)	-299(5)	2492(7)	16(6)	46(6)	37(5)	-3(8)	-4(9)	7(8)
C(3)	-3054(17)	-709(6)	2724(8)	39(7)	43(6)	46(6)	3(10)	5(10)	35(11)
C(4)	-2815(19)	-1023(6)	3575(8)	53(8)	42(6)	39(6)	-13(11)	6(10)	34(11)
C(5)	-739(20)	-1286(6)	5136(8)	67(9)	34(6)	51(7)	5(11)	24(10)	58(12)
C(6)	1128(19)	-1214(6)	5771(8)	60(8)	44(7)	40(6)	41(11)	25(10)	14(11)
C(7)	2857(18)	-833(6)	5554(7)	54(8)	42(6)	29(5)	21(11)	17(10)	19(10)
C(8)	2694(19)	-518(6)	4683(7)	63(8)	41(6)	27(5)	7(12)	-12(10)	-21(10)
C(9)	801(16)	-561(5)	4019(6)	37(6)	27(5)	27(5)	19(9)	-1(8)	15(8)
C(10)	-905(17)	-965(5)	4256(7)	44(7)	35(6)	38(6)	5(10)	4(9)	20(10)
C(11)	1967(16)	1399(5)	175(7)	35(6)	36(6)	29(5)	11(9)	-9(8)	20(9)
C(12)	3921(18)	1477(5)	791(7)	48(7)	28(5)	42(6)	-24(9)	-4(9)	39(10)
C(13)	5586(19)	1900(6)	558(8)	48(8)	34(6)	58(7)	-23(11)	-3(11)	21(12)
C(14)	5318(20)	2250(6)	-286(9)	56(9)	45(7)	62(8)	-24(12)	-12(12)	46(13)
C(15)	3124(23)	2562(6)	-1781(9)	87(10)	30(6)	54(8)	-11(13)	15(11)	37(14)
C(16)	1241(27)	2510(6)	-2399(9)	130(13)	37(8)	47(9)	38(15)	34(13)	89(15)
C(17)	-387(22)	2099(6)	-2186(9)	82(10)	43(7)	46(7)	21(13)	36(11)	31(13)
C(18)	-161(19)	1727(5)	-1329(7)	63(8)	36(6)	34(6)	43(11)	12(9)	28(11)
C(19)	1692(18)	1767(5)	-702(7)	52(7)	28(5)	28(5)	9(10)	7(8)	27(9)
C(20)	3375(19)	2184(5)	-931(8)	55(8)	28(5)	45(6)	10(10)	3(10)	25(11)
N(1)	-1257(12)	34(5)	1668(5)	23(5)	51(5)	23(4)	5(8)	16(7)	1(7)
N(11)	3979(14)	1108(4)	1598(6)	51(6)	33(5)	29(5)	-9(8)	-4(8)	5(8)
O(1)	-2795(11)	1(4)	1006(5)	39(5)	60(5)	28(4)	-17(8)	12(7)	-4(7)
O(2)	2175(12)	150(4)	2899(5)	54(5)	48(4)	28(4)	-10(8)	15(7)	10(7)
O(3)	3019(11)	-341(3)	920(4)	42(5)	32(4)	27(3)	2(6)	1(6)	4(6)
O(11)	5574(11)	1148(4)	2227(5)	40(5)	58(5)	38(4)	-10(7)	-19(8)	-18(6)
O(12)	494(11)	1020(4)	423(5)	37(4)	39(4)	33(4)	-6(7)	22(6)	2(6)
Cu	1481(2)	503(1)	1593(1)	44(1)	48(1)	34(1)	-5(2)	8(2)	14(1)

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

Table 2. Equations of mean planes and, in square brackets, deviations (Å) of atoms from these planes. 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 I: N(1), N(11), O(2), O(12)
$-0.4605X' + 0.7680Y' + 0.4451Z' = 1.6513$
[N(1) -0.027 , N(11) -0.026 , O(2) 0.024 , O(12) 0.022 ,
Cu -0.191 , O(1) -0.102 , O(11) 0.017]
Plane II: C(1)–C(10)
$-0.4295X' + 0.8126Y' + 0.3940Z' = 1.4836$
[C(1) 0.007 , C(2) 0.015 , C(3) -0.004 , C(4) -0.014 ,
C(5) 0.008 , C(6) 0.017 , C(7) -0.001 , C(8) -0.022 ,
C(9) 0.004 , C(10) -0.010 , Cu -0.076 , O(1) -0.068 , O(2) 0.020 , N(1) -0.012]
Plane III: C(11)–C(20)
$-0.4401X' + 0.7778Y' + 0.4488Z' = 1.6772$
[C(11) -0.004 , C(12) 0.009 , C(13) 0.008 , C(14) -0.002 ,
C(15) 0.003 , C(16) 0.008 , C(17) 0.004 , C(18) 0.008 ,
C(19) -0.007 , C(20) -0.020 , Cu -0.186 , O(11) 0.088 , O(12) 0.023 , N(11) 0.023]

Table 3. Mean bond lengths (Å) of the coordination planes of *o*-nitrosophenol and 1,2-nitrosonaphthol complexes.

Compound	C–O	C–N	N–O	M–O	M–N	Ref.
Ferroverdin ^a	1.30	1.42	1.25	1.95	1.84	9
Bis(4-methyl-1-quinone-2-oximato)Cu, py	1.27	1.35	1.25	1.97	2.00	8
Tris(4-chloro-1-quinone-2-oximato)Ni, K ⁺ , (CH ₃) ₂ CO	1.25	1.33	1.27	2.06	2.01	10
Bis(1,2-naphthoquinone-1-oximato)Cu, 2(CH ₃) ₂ CO	1.30	1.35	1.26	1.95	1.99	4
Bis(1,2-naphthoquinone-2-oximato)Cu, H ₂ O	1.28	1.35	1.26	1.97	1.98	This work
Diaqua(1,2-naphthoquinone-2-oximato-4-sulfonate)Cu, 3H ₂ O	1.26	1.35	1.25	1.95	1.96	11
α -5-(2'-Chloroethoxy)- <i>o</i> -quinone-2-oxime	1.25	1.31	1.37			12

^a $\text{K}[\text{Fe}(\text{qo})_3]$, where $\text{qoH} = 4$ -vinylphenyl ester of 4-hydroxy-3-nitrosobenzoic acid.

RESULTS AND DISCUSSION

The bond lengths and bond angles of the complex with their standard deviations can be seen in Fig. 1. It shows a nearly square planar configuration around Cu^{2+} with two oxime nitrogen atoms and two naphtholic oxygen atoms at the mean distances of 1.98 and 1.97 Å, respectively. The chelate rings are thus five-membered, which is in agreement with the structures recently found for several other similar compounds (*cf.* Table 3). The naphthalene planes are in *trans*-position intersecting at an angle of about 4°, so that the

structure of the complex is noticeably planar (Table 2).

The 4+1 coordination around Cu^{2+} is completed by the water oxygen atom at a distance of 2.195(7) Å, which indicates a relatively strong interaction between the atoms. A quite similar 4+1 coordination was observed in the 1:1 pyridine adduct of bis(4-methyl-1-quinone-2-oximato)copper(II) complex.⁸

A projection of the structure of the present complex along the *b*-axis is illustrated in Fig. 2, where the shortest intermolecular distances are also shown. It can be seen that the shortest distances (2.74 and 2.81 Å) are formed between

here has mainly been influenced by the well-established patterns of the short and long C—C bonds in the nitrosophenol complexes.^{8,10} These are characteristic for the *o*-quinone molecule. The resemblance of the chelating groupings in the nitrosophenol and nitrosonaphthol complexes and additionally the significantly short C(3)—C(4) bond (1.34(1) to 1.37(2) Å) found in the nitrosonaphthol compounds studied support the equal naming of all the complexes.

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