

O4—Cu1—O5 ⁱ	167.9 (1)	O8 ⁱ —Cu1—O10	98.2 (1)
O4—Cu1—O7	89.4 (1)	Cu1—O4—C12	121.5 (2)
O4—Cu1—O8 ⁱ	88.5 (1)	Cu1 ⁱ —O5—C12	124.8 (2)
O4—Cu1—O10	94.9 (1)	Cu1—O7—C22	125.6 (2)
O5 ⁱ —Cu1—O7	90.1 (1)	Cu1 ⁱ —O8—C22	120.5 (2)
O5 ⁱ —Cu1—O8 ⁱ	89.5 (1)	Cu1—O10—C32	127.3 (2)
O5 ⁱ —Cu1—O10	97.1 (1)	O4—C12—O5	125.4 (2)
O7—Cu1—O8 ⁱ	167.9 (1)	O7—C22—O8	125.8 (2)
O7—Cu1—O10	93.9 (1)		

Symmetry code: (i) $1 - x, -y, -z$.

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$) for (I)

D—H...A	D—H	H...A	D...A	D—H...A
O10—H10...O11 ⁱ	0.959	1.696	2.645 (3)	170
O11—H11...O4	0.960	2.015	2.892 (2)	151

Symmetry code: (i) $1 - x, -y, -1 - z$.

Compound (II)

Crystal data

[Cu(C₁₀H₁₀ClO₃)₂(C₅H₅N)₂]

$M_r = 649.03$

Monoclinic

$P2_1/n$

$a = 6.728$ (2) \AA

$b = 16.958$ (1) \AA

$c = 13.388$ (2) \AA

$\beta = 101.38$ (2) $^\circ$

$V = 1497.5$ (5) \AA^3

$Z = 2$

$D_x = 1.439$ Mg m^{-3}

D_m not measured

Data collection

Rigaku AFC-5 diffractometer

θ - 2θ scans

Absorption correction:

by integration (Coppens, Leiserowitz & Rabinovich, 1965)

$T_{\min} = 0.546$, $T_{\max} = 0.678$

3815 measured reflections

3429 independent reflections

2674 reflections with

$|F_o| > 3\sigma(|F_o|)$

$R_{\text{int}} = 0.020$

$\theta_{\text{max}} = 27.5^\circ$

$h = 0 \rightarrow 8$

$k = 0 \rightarrow 22$

$l = -17 \rightarrow 17$

3 standard reflections

every 100 reflections

intensity decay: none

Refinement

Refinement on F^2

$R = 0.043$

$wR = 0.048$

$S = 1.34$

2674 reflections

187 parameters

H atoms riding

$w = 1/[\sigma^2(F) + 0.000225F^2]$

$(\Delta/\sigma)_{\text{max}} = 0.002$

$\Delta\rho_{\text{max}} = 0.33 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.66 \text{ e } \text{\AA}^{-3}$

Extinction correction: none

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 3. Selected geometric parameters (\AA , $^\circ$) for (II)

Cu1—O3	1.963 (2)	O3—C7	1.273 (3)
Cu1—O4	2.683 (1)	O4—C7	1.230 (3)
Cu1—N6	1.996 (2)	O5—C8	1.446 (3)
C12—C14	1.747 (3)	O5—C11	1.370 (3)
O3—Cu1—N6	91.3 (1)	Cu1—O3—C7	107.1 (2)
O4—Cu1—N6	83.2 (2)	O3—C7—O4	124.0 (2)
O3—Cu1—O4	54.2 (2)		

Hydroxyl H atoms of MeOH in (I) were located from difference syntheses. A riding model [O—H and C—H

distances of 0.96 \AA , and $U_{\text{iso}}(\text{H}) = 0.1 \text{\AA}^2$] was used for all H atoms in (I) and (II).

For both compounds, data collection: *AFC/MSD Diffractometer Control System* (Rigaku Corporation, 1993); cell refinement: *AFC/MSD Diffractometer Control System*; data reduction: local programs; program(s) used to solve structures: *CRYSTAN-GM* (Edwards *et al.*, 1996); program(s) used to refine structures: *CRYSTAN-GM*; molecular graphics: *CRYSTAN-GM*; software used to prepare material for publication: *CRYSTAN-GM*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1037). Services for accessing these data are described at the back of the journal.

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Diaquabis[N-(1-naphthyl)-N-nitrosohydroxylamino-O,O']cobalt(II)

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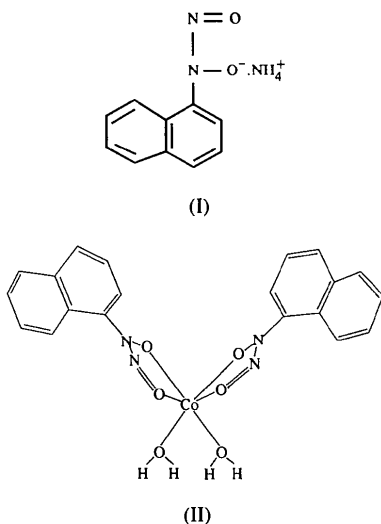
(Received 26 April 1996; accepted 15 October 1997)

Abstract

In the title compound, [Co(C₁₀H₇N₂O₂)₂(H₂O)₂], prepared from neocupferron and (NH₄)₂[Co(SO₄)₂(H₂O)₆], the Co^{II} ion has slightly distorted octahedral coordination defined by six O atoms from the two bidentate ligands and the two water molecules, in a *cis* arrangement [Co—O 2.073 (2)–2.124 (3) \AA]. The molecule has crystallographic C_2 symmetry. The plane of the nitrosohydroxylamino group is twisted out of the plane of the naphthyl ring.

Comment

The *N*-nitroso compounds are known to be carcinogens (Nishimura *et al.*, 1985; Ishii *et al.*, 1994). In order to clarify the physiological effects of the nitroso compounds, it is important to know the structures of their complexes with biomaterials. The anion of *N*-(1-naphthyl)-*N*-nitrosohydroxylamine [the ammonium salt is known as neocupferron, (I)] is a well known chelating agent for metal ions. Accordingly, the crystal structures of complexes derived from neocupferron and metal ions are expected to be good models for the binding mode of the nitroso group to metal ions. Some physicochemical studies of dioxouranium(VI) complexes (Kundu & Bera, 1978, 1982), and sodium and uranium(IV) complexes of neocupferron (Yoshimura *et al.*, 1972*a,b*) by ultraviolet and infrared spectroscopy have been reported, but few investigations on the crystal structures of the chelate compounds have been reported. In a series of studies to clarify the binding modes of *N*-nitroso compounds with biologically important metal ions, the crystal structures of Ni^{II} and Al^{III} complexes of cupferron have been determined in our laboratory (Okabe & Tamaki, 1995*a,b*). In this paper, the crystal structure of the title compound, (II), is reported.



The Co^{II} ion has slightly distorted octahedral coordination, defined by six O atoms, four from the two chelating ligands and two from the water molecules, which are mutually *cis*. The Co^{II} ion lies on a crystallographic twofold axis. In each chelating ligand, the plane of the nitrosohydroxylaminato group is twisted out of the naphthyl ring plane [O(1)—N(1)—N(2)—O(2) 1.1 (4) and O(1)—N(1)—C(1)—C(2) 129.9 (3)°] and the two ligands are nearly perpendicular to each other [O(1)—Co(1)—O(1)(-x, y, 1/2 - z) 94.6 (1)°]. The complexes are linked together by intermolecular hydrogen bonds between the O atoms of the water ligands and the nitrosohydroxylaminato groups [O(3)—H(31)···O(2)(-x, -y,

1 - z) 2.863 (3) and O(3)—H(32)···O(1)(-x, -1 + y, 1/2 - z) 2.813 (4) Å]. No stacking interactions are observed between the naphthyl rings.

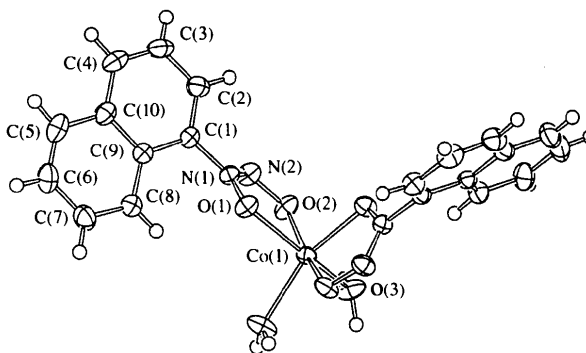


Fig. 1. ORTEP (Johnson, 1976) drawing of the title compound with the atomic numbering scheme. Ellipsoids for non-H atoms correspond to 50% probability.

Experimental

The red needle crystal used for analysis was obtained by the slow evaporation of an aqueous solution of a mixture containing neocupferron and (NH₄)₂[Co(SO₄)₂(H₂O)₆] in a 1:1 molar ratio at room temperature.

Crystal data

[Co(C₁₀H₇N₂O₂)₂(H₂O)₂]

M_r = 469.32

Monoclinic

C2/c

a = 31.647 (3) Å

b = 5.598 (5) Å

c = 11.327 (2) Å

β = 105.30 (2)°

V = 1936 (2) Å³

Z = 4

D_x = 1.610 Mg m⁻³

D_m not measured

Mo Kα radiation

λ = 0.71069 Å

Cell parameters from 20 reflections

θ = 15.6–22.2°

μ = 0.929 mm⁻¹

T = 296 K

Needle

0.30 × 0.10 × 0.02 mm

Red

Data collection

Rigaku AFC-5R diffractometer

ω-2θ scans

Absorption correction: none

2505 measured reflections

2460 independent reflections

1587 reflections with

I > σ(*I*)

R_{int} = 0.025

θ_{max} = 27.5°

h = 0 → 40

k = 0 → 7

l = -14 → 13

3 standard reflections

every 150 reflections

intensity decay: none

Refinement

Refinement on *F*

R = 0.040

wR = 0.041

S = 1.22

1763 reflections

177 parameters

All H atoms refined

w = 4*F_o*²/*σ*²(*F_o*²)

(Δ/*σ*)_{max} < 0.001

Δρ_{max} = 0.30 e Å⁻³

Δρ_{min} = -0.25 e Å⁻³

Extinction correction: none

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (\AA , $^\circ$)

Co(1)—O(1)	2.095 (2)	C(2)—C(3)	1.405 (4)
Co(1)—O(2)	2.073 (2)	C(3)—C(4)	1.369 (5)
Co(1)—O(3)	2.124 (3)	C(4)—C(10)	1.410 (4)
O(1)—N(1)	1.327 (3)	C(5)—C(6)	1.352 (5)
O(2)—N(2)	1.300 (3)	C(5)—C(10)	1.419 (4)
N(1)—N(2)	1.285 (3)	C(6)—C(7)	1.398 (5)
N(1)—C(1)	1.440 (3)	C(7)—C(8)	1.368 (4)
C(1)—C(2)	1.358 (4)	C(8)—C(9)	1.417 (4)
C(1)—C(9)	1.427 (4)	C(9)—C(9)	1.422 (4)
O(1)—Co(1)—O(1')	94.6 (1)	N(1)—C(1)—C(9)	119.8 (2)
O(1)—Co(1)—O(2)	74.80 (7)	C(2)—C(1)—C(9)	122.3 (3)
O(1)—Co(1)—O(2')	96.80 (8)	C(1)—C(2)—C(3)	120.3 (3)
O(1)—Co(1)—O(3)	152.83 (8)	C(2)—C(3)—C(4)	119.7 (3)
O(1)—Co(1)—O(3')	95.5 (1)	C(3)—C(4)—C(10)	121.1 (3)
O(2)—Co(1)—O(2')	167.8 (1)	C(6)—C(5)—C(10)	121.2 (3)
O(2)—Co(1)—O(3)	79.00 (8)	C(5)—C(6)—C(7)	120.3 (3)
O(2)—Co(1)—O(3')	110.18 (9)	C(6)—C(7)—C(8)	121.0 (3)
O(3)—Co(1)—O(3')	86.8 (1)	C(7)—C(8)—C(9)	120.0 (3)
Co(1)—O(1)—N(1)	110.8 (1)	C(1)—C(9)—C(8)	124.3 (2)
Co(1)—O(2)—N(2)	117.7 (2)	C(1)—C(9)—C(10)	116.7 (2)
O(1)—N(1)—N(2)	123.3 (2)	C(8)—C(9)—C(10)	119.0 (2)
O(1)—N(1)—C(1)	119.7 (2)	C(4)—C(10)—C(5)	121.5 (3)
N(2)—N(1)—C(1)	116.9 (2)	C(4)—C(10)—C(9)	120.0 (3)
O(2)—N(2)—N(1)	113.5 (2)	C(5)—C(10)—C(9)	118.5 (3)
N(1)—C(1)—C(2)	117.9 (2)		

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

All H-atom positions were located in a difference Fourier map.

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985) and *DIRDIF* (Beurskens, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1101). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). **C54**, 197–199

Complexe de Cuivre(II) Di(nitriloacétatodiacétique) Dihydrate, $[\text{Cu}(\text{C}_6\text{H}_8\text{NO}_6)_2] \cdot 2\text{H}_2\text{O}$

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(Reçu le 27 mai 1997, accepté le 22 août 1997)

Abstract

The structure comprises $[\text{Cu}(\text{C}_6\text{H}_8\text{NO}_6)_2]$ complex units and H_2O molecules. Two molecules of the ligand chelate the metal in an octahedral fashion through four O and two N atoms: the four O atoms form the equatorial plane and the two N atoms occupy the apical positions. The complex molecules and the H_2O molecules are connected by $\text{O} \cdots \text{H} \cdots \text{O}$ hydrogen bonds.

Commentaire

Plusieurs études structurales et vibrationnelles portant sur des composés dérivant de l'acide nitrilotriacétique $\text{N}(\text{CH}_2\text{COOH})_3$ ont été reportées en bibliographie. On relève notamment dans une étude antérieure (Whitlow, 1973) les complexes de cuivre: $[\text{LiCuN}(\text{CH}_2\text{COO})_3] \cdot 3\text{H}_2\text{O}$ et $[\text{NaCuN}(\text{CH}_2\text{COO})_3] \cdot \text{H}_2\text{O}$. Cette étude a déjà fait allusion à l'existence du complexe $[\text{Cu}\{\text{H}_2\text{N}(\text{CH}_2\text{COO})_3\}_2] \cdot 2\text{H}_2\text{O}$ en se limitant à une détermination photographique des paramètres de la maille et du groupe d'espace. Ce travail est consacré à l'étude structurale par diffraction rayons-X sur un monocristal de $[\text{Cu}\{\text{H}_2\text{N}(\text{CH}_2\text{COO})_3\}_2] \cdot 2\text{H}_2\text{O}$, (I).

