

- JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- LEE, T.-J., CHANG, Y., CHUNG, C.-S. & WANG, Y.-M. (1990). *Acta Cryst.* **C46**, 2360–2363.
- LISS, I. B. & SCHLEMPER, E. O. (1975). *Inorg. Chem.* **14**, 3035–3039.
- NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- PAL, J., MURMANN, R. K., SCHLEMPER, E. O., FAIR, C. K. & HUSSAIN, M. S. (1986). *Inorg. Chim. Acta*, **115**, 153–161.
- VASSIAN, E. G. & MURMANN, R. K. (1967). *Inorg. Chem.* **6**, 2043–2047.

Acta Cryst. (1991). **C47**, 714–716

Transition-Metal Complexes with Hydrazides and Hydrazones. II.* The Structure of Aqua(4-methyl-1-naphth-1-yl-2,3-diaza-1,3,5-heptatriene-1,6-diolato)copper(II)

BY REFIK FAZLIĆ

Faculty of Electrical Engineering, University of Tuzla, Yugoslavia

VLADIMIR DIVJAKOVIĆ† AND VUKADIN M. LEOVAC

Faculty of Sciences, University of Novi Sad, I. Djuričića 4, Yu-21000 Novi Sad, Yugoslavia

AND STEPAN YU. CHUNDAK

Faculty of Chemistry, University of Uzhgorod, USSR

(Received 17 March 1990; accepted 12 September 1990)

Abstract. [Cu(C₁₆H₁₄N₂O₂)(H₂O)], $M_r = 347.9$, monoclinic, $P2_1/c$, $a = 26.871$ (5), $b = 8.113$ (2), $c = 14.575$ (3) Å, $\beta = 101.95$ (2)°, $V = 3108.6$ (1) Å³, $Z = 8$, $D_x = 1.49$, $D_m = 1.50$ g cm⁻³, $\mu = 14.0$ cm⁻¹, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $F(000) = 1432$, final $R = 0.057$ for 3711 observed [$F_o > 3\sigma(F_o)$] reflections. There are two complex molecules in the asymmetric unit. The Cu atom assumes a nearly square-planar coordination with two O and one N atom from the dianion of the tridentate (ONO) chelate 4-methyl-1-naphth-1-yl-2,3-diaza-1,3,5-heptatriene-1,6-diolato ligand, and a water molecule. Copper is in a pseudo-octahedral environment involving the C atoms of the naphthalene residues from neighbouring molecules.

Introduction. Various properties of hydrazones and of their complexing affinities toward different transition metals have been reported (Kitaev, 1977; Katyal & Dutt, 1975). We have recently reported the synthesis and physicochemical characteristics of the complexes of some 3d elements with 1-naphthoyl-hydrazones (Chundak, Gerbeleu & Butsko, 1984; Leovac, Bjelica, Jovanović & Chundak, 1986; Obadović, Petrović, Leovac & Chundak, 1990). We report here the crystal structure of a newly synthesized complex of copper(II) with 4-methyl-1-naphth-1-yl-2,3-diaza-3-heptene-1,6-dione [Cu(L)(H₂O)], where L is the dianion of the mentioned ligand.

* Part I: Obadović, Petrović, Leovac & Chundak (1990).

† To whom correspondence should be addressed.

Experimental. Single crystals were obtained by slow evaporation (at room temperature) of the methanolic solution prepared by dissolving stoichiometric amounts of the ligand and copper(II) acetate and heating. Density was determined by flotation. The space group was determined by inspection of Weissenberg and oscillation photographs. Dark-brown prismatic crystal of size 0.40 × 0.30 × 0.30 mm was used for intensity measurements on an Enraf-Nonius CAD-4 diffractometer using the ω -2 θ scan technique; lattice parameters from setting angles of 20 reflections with $\theta_{\text{max}} = 25^\circ$; 8990 independent reflections measured to $(\sin\theta)/\lambda = 0.70$ Å⁻¹, $2\theta_{\text{max}} = 60^\circ$. Maximum values of h , k , l were 37, 11, ± 20 , respectively; no absorption correction was applied; three standard reflections (10,2,3, 13,1,4, 235), no significant variation during data collection. The structure was solved by direct methods using *SHELXS86* (Sheldrick, 1985). All non-H atoms were found on an *E* map based on 220 reflections with $E > 1.2$. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The structure was refined by block-diagonalized least squares (*SHELX76*; Sheldrick, 1976), F magnitudes, 414 parameters. All non-H atoms were refined with anisotropic thermal parameters. Water H atoms were located in a difference synthesis and were refined isotropically. All other H atoms were placed in geometrically calculated positions, and a unique temperature factor

Table 1. Atomic positional parameters ($\times 10^4$) and equivalent isotropic temperature factors ($\times 10^2$) for the non-H atoms with e.s.d.'s in parentheses

Molecule <i>A</i>	$U_{eq} = (U_1U_2U_3)^{1/3}$			$U_{eq}(\text{\AA}^2)$
	<i>x</i>	<i>y</i>	<i>z</i>	
Cu	3438 (1)	211 (1)	3201 (1)	4.5 (1)
O(1)	2782 (1)	-845 (4)	2931 (3)	4.3 (3)
O(2)	4106 (1)	1104 (5)	3447 (3)	5.1 (3)
O(w)	3139 (2)	2455 (7)	3250 (4)	7.9 (4)
N(1)	3274 (2)	-3198 (6)	3141 (3)	4.7 (3)
N(2)	3671 (2)	-2011 (6)	3238 (3)	4.6 (3)
C(1)	2355 (2)	-3423 (7)	2964 (4)	4.2 (4)
C(2)	2323 (3)	-4517 (8)	3683 (4)	5.0 (5)
C(3)	1862 (3)	-5309 (8)	3703 (5)	6.2 (5)
C(4)	1425 (3)	-5021 (8)	3047 (4)	6.5 (5)
C(5)	1440 (2)	-3917 (7)	2293 (4)	5.0 (5)
C(6)	994 (3)	-3602 (9)	1581 (5)	6.6 (6)
C(7)	1013 (3)	-2564 (10)	896 (5)	6.9 (6)
C(8)	1464 (2)	-1775 (8)	805 (4)	5.6 (5)
C(9)	1911 (2)	-2035 (7)	1452 (4)	4.5 (4)
C(10)	1909 (2)	-3109 (7)	2225 (4)	4.1 (4)
C(11)	2838 (2)	-2420 (7)	2996 (4)	4.1 (4)
C(12)	4251 (2)	-4393 (8)	3326 (5)	7.4 (6)
C(13)	4138 (2)	-2556 (9)	3338 (4)	5.5 (5)
C(14)	4555 (2)	-1405 (9)	3452 (5)	5.6 (5)
C(15)	4518 (2)	247 (9)	3508 (4)	5.1 (5)
C(16)	4995 (2)	1291 (8)	3652 (4)	6.7 (5)

Molecule <i>B</i>	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}(\text{\AA}^2)$
Cu	1537 (1)	1701 (1)	1951 (1)	4.4 (1)
O(1)	2199 (1)	2316 (5)	1749 (2)	4.2 (3)
O(2)	859 (1)	1212 (5)	2077 (2)	5.1 (3)
O(w)	1793 (3)	538 (9)	3170 (5)	8.6 (5)
N(1)	1728 (2)	3328 (6)	366 (3)	4.0 (3)
N(2)	1323 (1)	2694 (6)	746 (3)	4.1 (3)
C(1)	2639 (2)	3690 (8)	698 (4)	3.7 (4)
C(2)	2641 (2)	5253 (8)	396 (4)	4.3 (4)
C(3)	3106 (2)	5977 (8)	222 (4)	4.9 (5)
C(4)	3538 (2)	5078 (8)	325 (4)	5.4 (5)
C(5)	3542 (2)	3396 (8)	608 (4)	4.3 (4)
C(6)	3985 (2)	2354 (10)	671 (5)	5.6 (5)
C(7)	3982 (3)	772 (9)	927 (5)	6.4 (6)
C(8)	3546 (2)	63 (8)	1115 (4)	5.4 (5)
C(9)	3100 (2)	957 (8)	1046 (4)	4.2 (4)
C(10)	3083 (2)	2659 (8)	795 (4)	3.4 (4)
C(11)	2159 (2)	3055 (7)	954 (3)	4.0 (4)
C(12)	753 (2)	3832 (8)	-674 (4)	6.4 (5)
C(13)	859 (2)	2900 (9)	267 (4)	5.0 (5)
C(14)	438 (2)	2282 (9)	627 (4)	5.5 (5)
C(15)	455 (2)	1496 (9)	1454 (4)	6.1 (5)
C(16)	-31 (2)	892 (10)	1705 (4)	7.8 (6)

was refined. Convergence at $R = 0.057$, $wR = 0.040$ ($w = 1.0177/\sigma^2$) for 3711 observed reflections with $F_o > 3\sigma(F_o)$; max. shift/e.s.d. = 0.60; max. peak on final difference map was 0.75 e \AA^{-3} .

Discussion. The two independent molecules (*A* and *B*) are very similar in bond lengths and angles; one of them is shown in Fig. 1. Table 1 lists the fractional atomic coordinates, Table 2 shows the bond lengths and angles.* The geometry of the molecules was calculated using the CSU program (Vicković, 1988).

The dihedral angle between the mean planes through the naphthalene residue and the copper

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53569 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (\AA) and angles ($^\circ$) for molecules *A* and *B* with e.s.d.'s in parentheses

	<i>A</i>	<i>B</i>
Cu—O(1)	1.925 (4)	1.928 (4)
Cu—O(2)	1.901 (4)	1.909 (4)
Cu—N(2)	1.906 (5)	1.909 (4)
Cu—O(w)	1.998 (6)	2.004 (7)
N(1)—N(2)	1.421 (7)	1.416 (6)
N(1)—C(11)	1.311 (7)	1.310 (6)
N(2)—C(13)	1.311 (8)	1.307 (6)
O(1)—C(11)	1.287 (7)	1.289 (6)
C(1)—C(11)	1.524 (8)	1.507 (8)
C(1)—C(2)	1.390 (9)	1.343 (9)
C(2)—C(3)	1.400 (10)	1.450 (9)
C(3)—C(4)	1.372 (9)	1.352 (9)
C(4)—C(5)	1.425 (9)	1.425 (9)
C(5)—C(6)	1.438 (9)	1.448 (9)
C(5)—C(10)	1.441 (9)	1.448 (9)
C(6)—C(7)	1.316 (11)	1.337 (11)
C(7)—C(8)	1.400 (10)	1.382 (10)
C(8)—C(9)	1.380 (8)	1.387 (9)
C(9)—C(10)	1.425 (8)	1.427 (9)
C(10)—C(1)	1.458 (7)	1.438 (8)
O(2)—C(15)	1.294 (8)	1.284 (7)
C(12)—C(13)	1.521 (10)	1.540 (8)
C(13)—C(14)	1.440 (9)	1.433 (9)
C(14)—C(15)	1.347 (10)	1.355 (9)
C(15)—C(16)	1.513 (9)	1.511 (9)

O(w)—Cu—O(1)	93.2 (2)	95.7 (3)
O(w)—Cu—O(2)	91.0 (2)	88.6 (3)
O(1)—Cu—N(2)	82.3 (2)	82.0 (2)
O(2)—Cu—N(2)	93.6 (2)	93.8 (3)
O(w)—Cu—N(2)	173.5 (2)	175.6 (2)
O(1)—Cu—O(2)	175.8 (2)	175.6 (2)
C(11)—O(1)—Cu	109.9 (3)	110.5 (3)
C(15)—O(2)—Cu	124.7 (4)	125.3 (4)
C(11)—N(1)—N(2)	108.5 (5)	109.2 (4)
N(1)—N(2)—Cu	113.8 (3)	113.9 (3)
C(13)—N(2)—Cu	128.6 (4)	128.1 (4)
C(13)—N(2)—N(1)	117.6 (5)	118.0 (5)
C(11)—C(1)—C(2)	120.2 (5)	117.8 (5)
C(11)—C(1)—C(10)	119.6 (5)	120.7 (5)
C(10)—C(1)—C(2)	120.0 (5)	121.5 (6)
C(1)—C(2)—C(3)	120.1 (5)	120.1 (6)
C(2)—C(3)—C(4)	122.7 (6)	120.8 (6)
C(3)—C(4)—C(5)	119.1 (6)	120.3 (6)
C(4)—C(5)—C(6)	121.0 (6)	122.3 (6)
C(4)—C(5)—C(10)	120.3 (5)	119.7 (6)
C(6)—C(5)—C(10)	118.7 (6)	117.9 (6)
C(5)—C(6)—C(7)	120.2 (6)	121.7 (6)
C(6)—C(7)—C(8)	122.4 (6)	120.6 (7)
C(7)—C(8)—C(9)	120.8 (6)	121.5 (6)
C(8)—C(9)—C(10)	119.2 (6)	120.5 (6)
C(9)—C(10)—C(1)	123.7 (5)	124.8 (5)
C(9)—C(10)—C(5)	118.6 (5)	117.7 (5)
C(1)—C(10)—C(5)	117.7 (5)	117.5 (6)
C(1)—C(11)—O(1)	116.3 (5)	117.8 (4)
C(1)—C(11)—N(1)	118.4 (5)	117.8 (5)
N(1)—C(11)—O(1)	125.1 (5)	124.4 (5)
N(2)—C(13)—C(12)	121.1 (6)	121.2 (5)
N(2)—C(13)—C(14)	119.8 (6)	119.8 (5)
C(12)—C(13)—C(14)	119.1 (6)	118.9 (5)
C(13)—C(14)—C(15)	126.0 (6)	127.3 (5)
O(2)—C(15)—C(14)	127.0 (6)	125.6 (6)
O(2)—C(15)—C(16)	113.3 (6)	114.7 (5)
C(14)—C(15)—C(16)	119.7 (6)	119.7 (5)

coordination moiety are 55.2 (1) (*A*) and 49.5 (1) $^\circ$ (*B*), and the torsion angle C(2)—C(1)—C(11)—O(1) is -124.6 (7) (*A*) and -130.3 (6) $^\circ$ (*B*).

The coordination geometry of the Cu atom is almost square planar. Deviations from the mean Cu, O(1), N(2), O(2), O(w) plane do not exceed 0.08 (5) \AA .

The Cu atom tends to form a pseudo-octahedral environment involving C atoms of the naphthalene residues from neighbouring molecules; one of the apical positions consists of two C atoms. In molecule

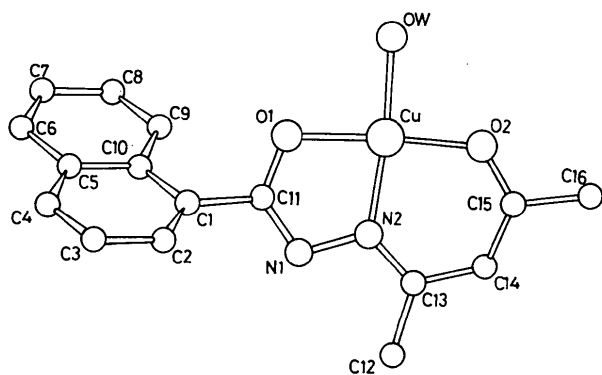


Fig. 1. Perspective view of the complex molecule with the atom-labelling scheme.

A: Cu(*A*)...C(8*B*) = 3.116 (6) Å and Cu(*A*)...C(9*B*) = 3.142 (6) Å on one side, and Cu(*A*)...C(4*B*ⁱ) = 3.061 (7) Å [(i) *x*, 0.5 - *y*, 0.5 + *z*] on the other side of the coordination plane. These copper-carbon interactions cause an arrangement of complex molecules parallel to *z*. Molecule *B* has somewhat longer Cu(*B*)...C distances: Cu(*B*)...C(8*A*) = 3.263 (6) Å and Cu(*B*)...C(9*A*) = 3.321 (7) Å on one side, and Cu(*B*)...C(4*A*ⁱⁱ) = 3.149 (8) Å [(ii) *x*, 1 + *y*, *z*], on the other side of the coordination plane. These interactions give rise to chains running parallel to *y*.

Similar intermolecular copper-carbon contacts were observed in bis(3-methylpentane-2,4-dionato)-copper(II) (distance 3.216 Å) (Robertson & Truter, 1967), and similar intramolecular contacts in di-μ-[1-[2-(dimethylamino)phenyl]-2-(4-methylphenyl)-

1-propenyl-*N,C*}-tetracopper(I) (distances 3.28–3.56 Å; Smeets & Spek, 1987).

Other intermolecular contacts involve hydrogen bonding: O(*wA*)—H(*w1*)...O(1*B*) = 2.981 (7) Å [H(*w1*)...O(1*B*) = 2.155 (10) Å, O(*wA*)—H(*w1*)—O(1*B*) = 167 (2)°]; O(*wB*)—H(*w3*)...O(1*A*) = 2.973 (7) Å [H(*w3*)...O(1*A*) = 2.327 (9) Å, O(*wB*)—H(*w3*)—O(1*A*) = 171 (2)°]; O(*wB*)—H(*w4*)...N(1*B*ⁱ) = 3.369 (9) Å [H(*w4*)...N(1*B*ⁱ) = 2.404 (10) Å, O(*wB*)—H(*w4*)—N(1*B*ⁱ) = 139 (2)°] [(i) = *x*, 0.5 - *y*, 0.5 + *z*] are established.

We thank Professor Lj. Golić (University of Ljubljana, Yugoslavia) for the collection of the X-ray intensities.

References

- CHUNDAK, S. YU., GERBELEU, N. V. & BUTSKO, S. S. (1984). *Zh. Neorg. Khim.* **29**, 1481–1485.
 KATYAL, M. & DUTT, Y. (1975). *Talanta*, **22**, 151–166.
 KITAEV, YU. P. (1977). Editor. *Khimiya Gidrazonov*. Moscow: Nauka.
 LEOVAC, V. M., BJELICA, L. J., JOVANOVIĆ, LJ. S. & CHUNDAK, S. YU. (1986). *Polyhedron*, **5**, 983–990.
 OBADOVIĆ, D. Z., PETROVIĆ, A. F., LEOVAC, V. M. & CHUNDAK, S. YU. (1990). *J. Phys. Condens. Matter*, **2**, 3611–3617.
 ROBERTSON, I. & TRUTER, M. R. (1967). *J. Chem. Soc. A*, pp. 309–313.
 SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
 SHELDRICK, G. M. (1985). *SHELXS86*. In *Crystallographic Computing 3*, edited by G. M. SHELDRICK, C. KRÜGER & R. GODDARD, pp. 175–179. Oxford Univ. Press.
 SMEETS, W. J. J. & SPEK, A. L. (1987). *Acta Cryst.* **C43**, 870–873.
 VICKOVIĆ, I. (1988). *Crystal Structure Utility*. Univ. of Zagreb, Yugoslavia.

Acta Cryst. (1991). **C47**, 716–719

Structure of Acetonitrile(dichloro)(phenyl)bis(triphenylstibine)rhodium(III)

BY RENZO CINI, GIANLUCA GIORGI AND ELDA PERICCIOLI

Dipartimento di Chimica dell' Università di Siena, Pian dei Mantellini 44, 53100 Siena, Italy

(Received 9 April 1990; accepted 12 September 1990)

Abstract. [Rh(C₄₄H₃₈Cl₂NSb₂)], *M_r* = 998.1, monoclinic, *C2/c*, *a* = 13.816 (2), *b* = 13.472 (2), *c* = 22.075 (3) Å, β = 95.61 (2)°, *V* = 4089 Å³, *Z* = 4, *D_x* = 1.62 Mg m⁻³, λ(Mo *Kα*) = 0.7107 Å, μ = 18.75 cm⁻¹, *F*(000) = 1960, *T* = 295 K, *R* = 0.051 for 2718 unique observed reflections. The structure consists of neutral complex molecules with an octahedral coordination sphere containing two chlorine ligands, two antimony atoms from triphenylstibine (SbPh₃), a nitrogen atom from acetonitrile (MeCN) and a

carbon atom from phenyl (Ph). The two chlorine ligands are *trans* to each other and the Rh—Cl bond distances are 2.360 (2) Å. The Rh—N bond length of 2.163 (9) Å is somewhat large, indicating a significant *trans* influence of the Ph ligand. The Rh—Sb distance is 2.588 (1) Å.

Introduction. The chemistry of transition metal ions is very important for processes of biological significance. The study of inorganic, organic and organo-