125·7 (5)° both of which indicate sp^2 hybridization for C16.

(2) The coordinated N2 atom is part of a stable carbinolamine group HO2—C6H*R*—N2*R*′. The sp^3 hybridization of C6 is confirmed by the single-bond values for C6—C5, C6—O2 and C6—N2 of 1·503 (8), 1·408 (6) and 1·476 (7) Å together with the normal tetrahedral angles.

(3) Coordination of N22, a primary amine function of tren which has not condensed with the aldehyde. This is presumably a consequence of the steric requirements imposed by the coordination of the tertiary nitrogen of tren.

In contrast to our complex the tertiary nitrogen in [Ni(py$_3$tren)]$(\mathrm{PF}_6)_2$ (Kichner *et al.*, 1987) is not coordinated (Ni—N 3·235 Å) and all the primary amine groups can undergo Schiff-base condensation with an aldehyde. Thus whether the tertiary N atom is coordinated to the metal or not has an important impact on the nature of the tripodal ligand formed.

Fig. 2 is a packing diagram of the unit-cell contents. The O1···O*w* and O2···O*w* distances, 2·803 (6) and 2·708 (6) Å respectively, are indicative of hydrogen bonding; the formation of the latter may increase the stability of the carbinolamine intermediate. The O*w*···F3 distance of 2·887 (7) Å is greater than that reported by Zhou (1984).

References

Kichner, R. M., Mealli, C., Bailey, M., Howe, N., Torre, L. P., Wilson, L. J., Andrews, L. C., Rose, N. J. & Lingafelter, E. C. (1987). *Coord. Chem. Rev.* **77**, 89–163.

Mealli, C. & Lingafelter, E. C. (1970). *J. Chem. Soc. Chem. Commun.* pp. 885–886.

Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package.* MSC, 3200A Research Forest Drive, The Woodlands, TX77381, USA.

Orpen, A. G., Brammer, L., Allen, F. H., Kennard, O., Watson, D. G. & Taylor, R. (1989). *J. Chem. Soc. Dalton Trans.* pp. S1–83.

Patai, S. (1970). *The Chemistry of Carbon–Nitrogen Bond.* New York: Interscience.

Wilson, L. J. & Rose, N. J. (1968). *J. Am. Chem. Soc.* **90**, 6041–6045.

Zhou, G. (1984). *Inorganic Structure Chemistry.* (In Chinese.) Beijing: Science Press.

Acta Cryst. (1991). C**47**, 711–714

Structure of (Isothiocyanato)[3,3,9,9-tetramethyl-4,8-diazaundecane-2,10-dione dioximato(1 −)]copper(II) Monohydrate

By Tsong-Jen Lee, Tseng-Yuh Lee and Chung-Sun Chung

National Tsing Hua University, Hsinchu, Taiwan 30043

and Yun-Ming Wang

Institute of Nuclear Energy Research, PO Box 3, *Lung Tan* 32500, *Taiwan*

(*Received* 1 *May* 1990; *accepted* 12 *September* 1990)

Abstract. $[\mathrm{Cu}(\mathrm{C}_{13}\mathrm{H}_{27}\mathrm{N}_4\mathrm{O}_2)(\mathrm{NCS})].\mathrm{H}_2\mathrm{O}$, $M_r = 411{\cdot}02$, orthorhombic, $P2_12_12_1$, $a = 7{\cdot}236$ (2), $b = 13{\cdot}291$ (5), $c = 20{\cdot}802$ (3) Å, $U = 2000{\cdot}6$ (4) Å^3, $Z = 4$, $D_x = 1{\cdot}365$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}71069$ Å, $\mu = 1{\cdot}26$ mm^{-1}, $F(000) = 868$, $T = 297$ (5) K, $R = 0{\cdot}058$ for 1412 observed reflections $[I > 3\sigma(I)]$. The coordination about the Cu$^{\mathrm{II}}$ atom is a distorted square pyramid with the deprotonated diazadioxime molecule equatorial and the N atom of the isothiocyanato group axial. The Cu atom is significantly (0·349 Å) out of the basal plane of the four N atoms towards the isothiocyanato group. The central six-membered chelate ring is in a stable chair conformation; one of the two terminal five-membered rings is in a stable *gauche* conformation, while the other is in an unstable eclipsed conformation.

Introduction. It is now well established that copper(II) coordinates with a deprotonated diazadioxime and a monodentate ligand to form a five-coordinate square-pyramidal complex having a strong intramolecular hydrogen bond between *cis* oxime groups (Gavel & Schlemper, 1979). A comprehensive study of this hydrogen bond is in progress in order to examine the effect of the O···O distance on the H-atom position and the important factors that influence the O···O distance. Previously, three important factors have been reported (Lee, Chang, Chung & Wang, 1990; Pal, Murmann, Schlemper, Fair & Hussain, 1986); (1) the constraint imposed by the methylene C atoms bridging the amine N atoms; (2) changing from an sp^3 amine N atom to an sp^2 imine N atom; and (3) the steric effect of the C—

0108-2701/91/040711-04$03.00

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$U_{eq} = (U_{11} + U_{22} + U_{33})/3.$

	x	y	z	U_{eq} (× 1000)
Cu	0·0948 (2)	0·0259 (1)	0·94672 (7)	51 (1)
S	0·3828 (6)	−0·2122 (3)	0·8095 (2)	79 (3)
O(1)	0·269 (1)	0·1822 (6)	0·8656 (4)	61 (6)
O(2)	0·384 (1)	0·1677 (6)	0·9804 (4)	57 (5)
O(3)	0·250 (1)	0·3528 (6)	1·0065 (4)	63 (6)
N(1)	0·129 (1)	0·1122 (7)	0·8717 (4)	42 (6)
N(2)	−0·135 (1)	−0·0071 (7)	0·8975 (4)	54 (6)
N(3)	0·000 (1)	−0·0218 (7)	1·0301 (4)	44 (5)
N(4)	0·264 (2)	0·0989 (7)	1·0033 (5)	44 (6)
N(5)	0·254 (2)	−0·1158 (9)	0·9163 (6)	77 (10)
C(1)	0·027 (2)	0·1014 (10)	0·8233 (6)	48 (7)
C(2)	0·048 (2)	0·1651 (11)	0·7641 (11)	81 (10)
C(3)	−0·133 (2)	0·0270 (9)	0·8305 (5)	49 (7)
C(4)	−0·095 (2)	−0·0583 (9)	0·7814 (6)	73 (9)
C(5)	−0·318 (2)	0·0775 (10)	0·8158 (6)	67 (9)
C(6)	−0·230 (2)	−0·1014 (11)	0·9154 (8)	72 (11)
C(7)	−0·253 (2)	−0·1182 (12)	0·9819 (9)	83 (11)
C(8)	−0·114 (3)	−0·1123 (9)	1·0306 (6)	77 (10)
C(9)	0·129 (2)	−0·0039 (9)	1·0854 (5)	54 (8)
C(10)	0·244 (3)	−0·0973 (11)	1·0949 (9)	114 (14)
C(11)	0·028 (3)	0·0282 (16)	1·1450 (6)	144 (15)
C(12)	0·262 (2)	0·0793 (8)	1·0632 (6)	49 (8)
C(13)	0·381 (2)	0·1296 (10)	1·1139 (6)	81 (10)
C(14)	0·310 (2)	−0·1566 (9)	0·8704 (7)	55 (9)

Table 2. *Bond lengths* (Å) *and bond angles* (°)

Cu—N(1)	1·953 (9)	N(4)—C(12)	1·27 (2)
Cu—N(2)	2·000 (9)	N(5)—C(14)	1·17 (2)
Cu—N(3)	1·970 (8)	C(1)—C(2)	1·50 (2)
Cu—N(4)	1·957 (10)	C(1)—C(3)	1·53 (2)
Cu—N(5)	2·30 (1)	C(3)—C(4)	1·55 (2)
S—C(14)	1·56 (1)	C(3)—C(5)	1·53 (2)
O(1)—N(1)	1·38 (1)	C(6)—C(7)	1·41 (2)
O(2)—N(4)	1·35 (1)	C(7)—C(8)	1·43 (2)
N(1)—C(1)	1·26 (1)	C(9)—C(10)	1·51 (2)
N(2)—C(3)	1·47 (1)	C(9)—C(11)	1·50 (2)
N(2)—C(6)	1·48 (2)	C(9)—C(12)	1·54 (2)
N(3)—C(8)	1·46 (2)	C(12)—C(13)	1·52 (2)
N(3)—C(9)	1·50 (1)		

N(1)—Cu—N(2)	79·9 (4)	C(2)—C(1)—C(3)	121·5 (10)
N(1)—Cu—N(3)	159·6 (4)	N(2)—C(3)—C(1)	107·5 (9)
N(1)—Cu—N(4)	96·3 (4)	N(2)—C(3)—C(4)	113·7 (10)
N(2)—Cu—N(3)	95·3 (4)	N(2)—C(3)—C(5)	108·5 (9)
N(2)—Cu—N(4)	159·5 (4)	C(1)—C(3)—C(4)	106·1 (9)
N(3)—Cu—N(4)	81·2 (4)	C(1)—C(3)—C(5)	111·0 (10)
Cu—N(1)—O(1)	124·2 (6)	C(4)—C(3)—C(5)	111·0 (10)
Cu—N(1)—C(1)	119·9 (8)	N(2)—C(6)—C(7)	116·0 (10)
O(1)—N(1)—C(1)	115·8 (9)	C(6)—C(7)—C(8)	126·9 (13)
Cu—N(2)—C(3)	114·3 (7)	N(3)—C(8)—C(7)	116·1 (11)
Cu—N(2)—C(6)	116·3 (8)	N(3)—C(9)—C(10)	108·2 (10)
C(3)—N(2)—C(6)	120·4 (10)	N(3)—C(9)—C(11)	112·2 (11)
Cu—N(3)—C(8)	117·9 (7)	N(3)—C(9)—C(12)	105·8 (9)
Cu—N(3)—C(9)	114·1 (7)	C(10)—C(9)—C(11)	113·2 (12)
Cu—N(4)—O(2)	121·7 (7)	C(10)—C(9)—C(12)	106·7 (11)
Cu—N(4)—C(12)	118·5 (8)	C(11)—C(9)—C(12)	110·3 (11)
O(2)—N(4)—C(12)	119·7 (10)	N(4)—C(12)—C(9)	116·8 (10)
Cu—N(4)—C(12)	118·5 (8)	N(4)—C(12)—C(13)	125·5 (11)
Cu—N(5)—C(14)	141·1 (11)	C(9)—C(12)—C(13)	117·7 (11)
N(1)—C(1)—C(2)	122·1 (11)	N(5)—C(14)—S	179·3 (12)
N(1)—C(1)—C(3)	116·1 (10)		

Intramolecular hydrogen bond lengths (Å) and angles (°)

	O···O	O—H	O—H···O
O(1)—H(302)···O(2)	2·54 (1)	0·965 (8)	158·1 (6)

methyl groups. In the current investigation, we have attempted to study the effect of the nature of the monodentate ligand. The crystal structure of perrhenato[3,3,9,9-tetramethyl-4,8-diazaundecane-2,10-dione dioximato(1−)]copper(II) has been reported (Liss & Schlemper, 1975). In this study, the title complex has been synthesized and the three-dimensional X-ray structure has been determined.

Experimental. The ligand, 3,3,9,9-tetramethyl-4,8-diazaundecane-2,10-dione dioxime ($pnaoH_2$), was prepared by using the procedure of Vassian & Murmann (1967). To a mixture of an acidic aqueous solution of $pnaoH_2$ and $CuSO_4.5H_2O$, sufficient NaOH was added to make this solution neutral. Addition of excess NaSCN solution gave dark-violet crystals which were recrystallized twice from water. Crystal of size 0·15 × 0·3 × 0·4 mm was used for data collection; CAD-4 diffractometer; unit-cell parameters from 24 reflections with $15 < \theta < 30°$; data collected by ω–2θ scans with scan width $2(0{\cdot}7 + 0{\cdot}35\tan\theta)°$ and with variable scan speed 2 to 7° min^{-1}, according to peak height measured; standard reflections 312, 267 and 157 checked every hour varied within $3\sigma(I)$. Max. $(\sin\theta)/\lambda = 0{\cdot}70354$ Å^{-1} ($0 < h < 8$, $0 < k < 15$, $0 < l < 23$). Intensity data for 3076 reflections collected; 1412 unique observed reflections with $I > 3\sigma(I)$. Empirical absorption correction based on azimuthal rotation from reflections 312, 267 and $0\bar{2}0$ (North, Phillips & Mathews, 1968); max., min. transmission coefficients 0·99, 0·95. Heavy-atom method located the position of the Cu atom. Other atoms were located by successive difference Fourier syntheses and full-matrix least-squares fits. The function minimized is $\sum w(|F_o| - |F_c|)$, where $w = 1/\sigma^2(F)$ from counting statistics.

The H-atom peak between the oximes was found in the difference Fourier maps; other H atoms were geometrically calculated and not refined (Doherty & Stewart, 1988). The B values of H atoms were initially assigned as 5·0 Å^2 and refined. Other atoms refined anisotropically. In the last stage of least-squares calculation, the R factor reduced to 0·058, $wR = 0{\cdot}056$, $S = 2{\cdot}113$, $(\Delta/\sigma)_{max} = 0{\cdot}009$, $(\Delta\rho)_{max} = 0{\cdot}858$, $(\Delta\rho)_{min} = 0{\cdot}250$ e Å^{-3}. Atomic scattering factors are from *International Tables for X-ray Crystallography* (1974, Vol. IV). All calculations were carried out using *XTAL*88 (Hall & Stewart, 1988) and *ORTEP*II (Johnson, 1976) on a CDC Cyber 840 computer.

Discussion. The atomic coordinates are listed in Table 1, bond lengths and bond angles in Table 2.*

---

* 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 53556 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Fig. 1 shows the molecular structure with the atom-numbering scheme and the deviations of the atoms from the N_4 basal plane. A stereoscopic view of the packing of the molecules in a unit cell is plotted in Fig. 2.

The coordination around the Cu^{II} atom is a slightly distorted square pyramid with the deprotonated diazadioxime equatorial and the N atom of the isothiocyanato group axial as shown in Fig. 1. The four donor N atoms of the deprotonated diazadioxime lie almost in a plane. The Cu^{II} atom is significantly (0·349 Å) out of this plane towards the axial isothiocyanato group. The two H atoms of the amine groups are on the same side of the N_4 basal plane.

The unidentate ligand $—NCS^-$ is N-bonded to the metal ion on the opposite side of the plane to the two H atoms of the NH groups. The thiocyanate $N—Cu^{II}$ bond is slightly distorted from the normal to the N_4 basal plane as evidenced by the N(5)—Cu—N_4 angles, 101·4 (4), 95·6 (4), 98·8 (4), 104·9 (4)°. The *M*—NCS group is bent, Cu—N(5)—C(14) is 141 (1)°. This bond angle and the bond lengths in Table 2 suggest that the resonance structure *M*—N=C=S is predominant in this crystal.

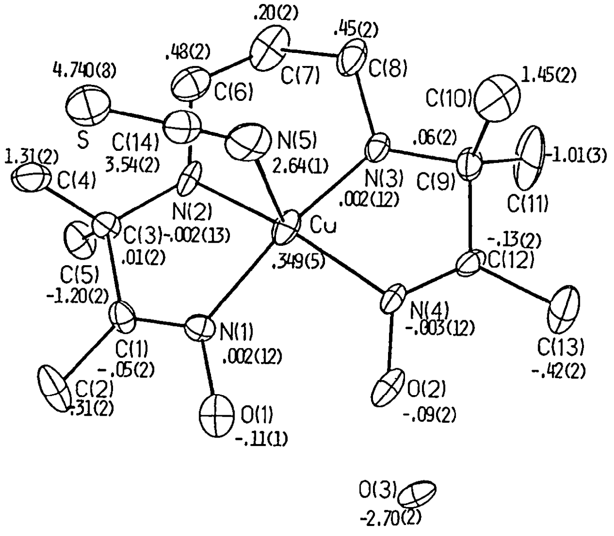

Fig. 1. Perspective view showing the atom-numbering scheme of the molecule; the deviations of the atoms from the N_4 basal plane are also indicated (Å) (Johnson, 1976).

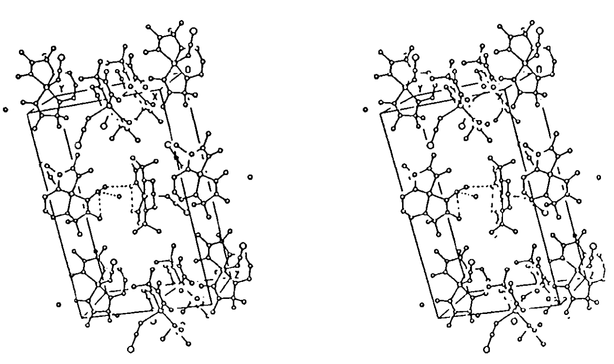

Fig. 2. Stereoscopic view of the molecular packing in a unit cell.

As observed in other amine oxime complexes (Lee, Chang, Chung & Wang, 1990), the average Cu—N(oxime) bond distance, 1·96 (1) Å, is slightly shorter than the average Cu—N(amine) bond distance, 1·99 (1) Å. The apical Cu—N bond is longer than those normally found in five-coordinate Cu^{II}-atom complexes with square-pyramidal configuration. Its length of 2·30 (1) Å, 0·3–0·4 Å longer than the equatorial Cu—N(amine) bond distance, is definitely in the range of Cu–N interactions. There is no weak coordination of the Cu atoms on the other side of the basal plane; the nearest atom in this direction is more than 4 Å away. The configuration of the two chiral amine N-atom centres is 4*RS* and 8*SR*. The central six-membered chelate ring is in a stable chair conformation; one of the two terminal five-membered rings, the CuN(3)C(9)C(12)N(4) ring, is in a stable *gauche* conformation, while the other, the CuN(1)C(1)C(3)N(2) ring, is in an unstable eclipsed conformation. The formation of such an unstable chelate ring is unusual. The reason for this is probably to reduce the steric interaction between the isothiocyanate group and the $—C(4)H_3$ group as shown in Fig. 1.

Both [Cu(pnaoH)(NCS)] and [Cu(pnaoH)(ReO_4)] (Liss & Schlemper, 1975) consist of discrete five-coordinate square-pyramidal Cu^{II} neutral comlexes. Comparing the crystal structure of these two compounds, we find the following significant differences: (1) the latter has C_s symmetry while the former does not contain such a symmetry plane; (2) the three chelate rings in the latter are in stable conformations, while one of the five-membered rings in the former has an unstable eclipsed conformation; (3) the O···O hydrogen bond in the former [2·54 (1) Å] is longer than that in the latter [2·46 (2) Å]; the former is asymmetric while the latter is symmetric.

The authors thank Mr Yian Chang for checking the crystal structure analysis and editing the manuscript. We also thank the National Science Council of the Republic of China for financial support of this work.

References

Doherty, R. & Stewart, J. (1988). *BONDAT. XTAL2.4 Users Manual*, edited by S. R. Hall & J. M. Stewart. Univs of Western Australia, Australia, and Maryland, USA.

Gavel, D. P. & Schlemper, E. O. (1979). *Inorg. Chem.* **18**, 283–286.

Hall, S. R. & Stewart, J. M. (1988). Editors. *XTAL2.4 Users Manual*. Univs. of Western Australia, Australia, and Maryland, USA.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Lee, T.-J., Chang, Y., Chung, C.-S. & Wang, Y.-M. (1990). *Acta Cryst.* C**46**, 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.* A**24**, 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). C**47**, 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($C_{16}H_{14}N_2O_2$)(H_2O)], M_r = 347·9, monoclinic, $P2_1/c$, a = 26·871 (5), b = 8·113 (2), c = 14·575 (3) Å, β = 101·95 (2)°, V = 3108·6 (1) Å^3, Z = 8, D_x = 1·49, D_m = 1·50 g cm^{-3}, μ = 14·0 cm^{-1}, λ(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-naphthoylhydrazones (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)(H_2O)], where L is the dianion of the mentioned ligand.

Experimental. Single crystals were obtained by slow evaporation (at room temperature) of the methanolic solution prepared by disolving 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–2θ scan technique; lattice parameters from setting angles of 20 reflections with $\theta_{\max}$ = 25°; 8990 independent reflections measured to $(\sin\theta)/\lambda$ = 0·70 Å^{-1}, 2$\theta_{\max}$ = 60°. 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 *SHELXS*86 (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 (*SHELX*76; 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

---

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

† To whom correspondence should be addressed.

0108-2701/91/040714-03$03.00