GHOSH, M., BASAK, A. K., ROY, P. N., MAZUMDAR, S. K. & SHELDRICK, B. (1987). *Acta Cryst.* C**43**, 732–734.
KÁLMÁN, A., CZUGLER, M. & ARGAY, GY. (1981). *Acta Cryst.* B**37**, 868–877.
LEGER, J. M., ALBEROLA, S. & CARPY, A. (1977). *Acta Cryst.* B**33**, 1455–1459.
O'CONNELL, A. M. & MASLEN, E. N. (1977). *Acta Cryst.* **22**, 134–145.
RABINDRA ACHARYA, K., KUCHELA, K. N. & KARTHA, G. (1982). *J. Crystallogr. Spectrosc. Res.* **12**, 369–376.
SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
SINGH, T. P., PATEL, U. & HARIDAS, M. (1984). *Acta Cryst.* C**40**, 2088–2091.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

Acta Cryst. (1990). C**46**, 1226–1228

Structure of Dinuclear Bis(di-2-pyridylmethanone oximato)copper(II) Dihydrate

BY E. O. SCHLEMPER, J. STUNKEL AND C. PATTERSON

Department of Chemistry, University of Missouri, Columbia, MO 65211, *USA*

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Abstract. Bis-μ-(di-2-pyridyl ketone oximato-*O*,*N*)-bis(di-2-pyridyl ketone oximato)dicopper(II) dihydrate, $[Cu(C_{11}H_8N_3O)_2]_2.2H_2O$, $M_r = 956{\cdot}0$, monoclinic, $C2/c$, $a = 23{\cdot}619\ (4)$, $b = 11{\cdot}280\ (2)$, $c = 19{\cdot}155\ (3)$ Å, $\beta = 125{\cdot}24\ (2)°$, $V = 4168$ Å^3, $Z = 4$, $D_x = 1{\cdot}523\ (2)$ g cm^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}7107$ Å, $\mu = 10{\cdot}85$ cm^{-1}, $F(000) = 1960$, $T = 295\ (1)$ K, final $R = 0{\cdot}038$ for 1171 observed reflections $[F_o^2 > 2\sigma(F_o^2)]$. This structure consists of dinuclear complexes with twofold internal symmetry. The copper(II) coordination geometry is slightly distorted trigonal bipyramidal with each copper coordinated by two pyridine N atoms [av. Cu—N = 2·031 (13) Å], two oxime N atoms [av. Cu—N = 1·964 (6) Å], and one oxime O atom [Cu—O = 2·133 (5) Å]. One pyridine nitrogen of each ligand as well as the oxime oxygen of one ligand on each Cu atom are not involved in copper coordination. The angles of the trigonal plane are 100·4 (2), 123·1 (2) and 136·4 (2)° while the angle between axial ligand atoms is 179·0 (3)°. The water of hydration bridges two molecules by hydrogen bonding to the free oxime oxygen in one molecule and to one of the free pyridine nitrogens of the second molecule.

Introduction. Although metal complexes of the ligand di-2-pyridylmethanone oxime have been known for some time and used for analytical purposes (*e.g.* Holland & Bozic, 1968; Holland, Bozic & Gerard, 1968), no crystal-structure studies have been reported. Because of the four possible coordinating atoms of the ligand (two pyridine nitrogens, an oxime nitrogen and an oxime oxygen), we decided to investigate the structure of the complex isolated by reaction with $CuCl_2$ in aqueous media. This complex is different to the Cu^{II} complex from acetone media reported earlier (Blackmore, Sceney, O'Neill & Magee, 1974).

Experimental. The ligand was obtained by reaction of the commercial ketone with $NH_2OH.HCl$ in a fashion similar to that reported (Niemers & Hiltmann, 1976). Reaction of the ligand (1:2 *M*:*L* ratio) with $CuCl_2$(aq.) in slightly basic solution produced green crystals on slow evaporation of the solvent.

The crystal chosen for the X-ray study had approximate dimensions 0·1 × 0·15 × 0·2 mm and was placed in random orientation on an Enraf–Nonius CAD-4 diffractometer. After optical centering, 25 reflections ($2\theta = 18$–$35°$) were located by automatic search of reciprocal space and recentered twice. The setting angles of these reflections were used to determine the cell dimensions. θ–2θ scan. Three standard reflections were measured after every 7200 s of X-ray exposure (no significant variation), three orientation standards after every 200 reflections with recentering of all 25 if any significant angular error, three ψ scans to obtain an empirical absorption curve (relative transmission = 88·9–99·6%), *hkl* range (0,0,−19 to 22,10,19 and −13,−6,−11 to 0,0,11), agreement of Friedel pairs, statistics, and successful refinement confirmed the choice of space group $C2/c$. 2700 reflections from $2\theta = 4$–$40°$, 1945 independent reflections (internal agreement on $F_o^2 = 0{\cdot}035$), 1171 reflections with $F_o^2 > 2\sigma(F_o^2)$ used in structure solution and refinement: structure solved by Patterson and difference Fourier methods, full-matrix least squares minimized $\sum w(|F_o| - |F_c|)^2$ where $w = 4F_o^2/[\sigma^2_{\text{counting}} + (0{\cdot}040F_o^2)^2]$, H atoms from difference Fourier map and calculation were not refined, all other atoms

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Table 1. *Positional parameters with e.s.d.'s in parentheses*

	x	y	z	B(Å^2)
Cu	0·02456 (4)	0·06082 (9)	−0·14548 (5)	2·46 (2)
O*W*	0·2861 (3)	0·3787 (7)	−0·1743 (3)	8·4 (2)
O1	−0·0875 (2)	−0·0064 (4)	−0·3168 (3)	2·7 (1)
N1	−0·0522 (2)	−0·0374 (5)	−0·2347 (3)	2·3 (2)
C1	−0·0653 (3)	−0·1369 (6)	−0·2127 (4)	1·9 (2)
C2	−0·0201 (3)	−0·1627 (7)	−0·1216 (4)	2·1 (2)
N3	0·0284 (2)	−0·0782 (6)	−0·0744 (3)	2·4 (2)
C4	0·0760 (3)	−0·0966 (7)	0·0084 (4)	3·1 (2)
C5	0·0789 (4)	−0·1997 (8)	0·0482 (5)	4·0 (2)
C6	0·0294 (4)	−0·2850 (8)	0·0010 (4)	4·1 (3)
C7	−0·0210 (3)	0·2660 (7)	−0·0843 (4)	2·5 (2)
C8	−0·1198 (3)	−0·2202 (7)	−0·2764 (4)	2·6 (2)
C9	−0·1250 (4)	−0·2522 (7)	−0·3493 (4)	3·5 (2)
C10	−0·1763 (4)	−0·3308 (8)	−0·4066 (5)	4·5 (3)
C11	−0·2211 (4)	−0·3756 (8)	−0·3888 (5)	4·0 (3)
C12	−0·2124 (4)	−0·3403 (7)	−0·3162 (5)	3·6 (3)
N13	−0·1639 (2)	−0·2643 (6)	−0·2593 (3)	2·8 (2)
O1′	0·1607 (2)	0·1161 (5)	0·0029 (3)	3·2 (1)
N1′	0·1007 (3)	0·1611 (6)	−0·0578 (3)	2·6 (2)
C1′	0·0879 (3)	0·2752 (7)	−0·0628 (4)	2·2 (2)
C2′	0·0189 (3)	0·3091 (7)	−0·1342 (4)	2·5 (2)
N3′	−0·0233 (2)	0·2198 (5)	−0·1837 (3)	2·2 (2)
C4′	−0·0899 (3)	0·2437 (7)	−0·2488 (4)	3·2 (2)
C5′	−0·1146 (3)	0·3578 (8)	−0·2674 (5)	3·5 (2)
C6′	−0·0706 (4)	0·4485 (8)	−0·2192 (5)	4·0 (2)
C7′	−0·0033 (3)	0·4261 (7)	−0·1515 (4)	3·2 (2)
C8′	0·1392 (3)	0·3591 (6)	0·0018 (4)	2·3 (2)
C9′	0·2032 (3)	0·3729 (7)	0·0149 (4)	2·6 (2)
C10′	0·2503 (3)	0·4487 (8)	0·0777 (4)	3·4 (2)
C11′	0·2350 (4)	0·5056 (8)	0·1275 (5)	4·3 (3)
C12′	0·1690 (4)	0·4888 (8)	0·1089 (4)	4·1 (2)
N13′	0·1216 (3)	0·4176 (6)	0·0473 (3)	3·4 (2)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $\frac{4}{3}[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$

Table 2. *Bond distances* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Cu—O1	2·133 (5)	C11—C12	1·34 (1)
Cu—N1	1·965 (6)	C12—N13	1·35 (1)
Cu—N3	2·044 (6)	O1′—N1′	1·311 (7)
Cu—N1′	1·962 (6)	N1′—C1′	1·312 (9)
Cu—N3′	2·018 (6)	C1′—C2′	1·46 (1)
O1—N1	1·333 (7)	C1′—C8′	1·47 (1)
N1—C1	1·298 (9)	C2′—N3′	1·347 (9)
C1—C2	1·46 (1)	C2′—C7′	1·39 (1)
C1—C8	1·49 (1)	N3′—C4′	1·356 (9)
C2—N3	1·358 (9)	C4′—C5′	1·37 (1)
C2—C7	1·37 (1)	C5′—C6′	1·37 (1)
N3—C4	1·329 (9)	C6′—C7′	1·38 (1)
C4—C5	1·37 (1)	C8′—C9′	1·39 (1)
C5—C6	1·37 (1)	C8′—N13′	1·334 (9)
C6—C7	1·37 (1)	C9′—C10′	1·37 (1)
C8—C9	1·38 (1)	C10′—C11′	1·36 (1)
C8—N13	1·352 (9)	C11′—C12′	1·40 (1)
C9—C10	1·39 (1)	C12′—N13′	1·33 (1)
C10—C11	1·38 (1)		

O1—Cu—N1	88·8 (2)	C8—C9—C10	119·7 (8)
O1—Cu—N3	100·4 (2)	C9—C10—C11	118·9 (9)
O1—Cu—N1′	91·2 (2)	C10—C11—C12	117·7 (8)
O1—Cu—N3′	123·1 (2)	C11—C12—N13	125·6 (9)
N1—Cu—N3	79·1 (3)	C8—N13—C12	117·0 (7)
N1—Cu—N1′	179·0 (3)	Cu—N1′—O1′	121·6 (5)
N1—Cu—N3′	98·2 (3)	Cu—N1′—C1′	116·5 (6)
N3—Cu—N1′	101·9 (3)	O1′—N1′—C1′	122·1 (6)
N3—Cu—N3′	136·4 (2)	N1′—C1′—C2′	114·4 (7)
N1′—Cu—N3′	80·9 (3)	N1′—C1′—C8′	121·8 (7)
Cu—O1—N1	114·2 (4)	C2′—C1′—C8′	123·7 (8)
Cu—N1—O1	120·9 (5)	C1′—C2′—N3′	116·0 (7)
Cu—N1—C1	118·6 (5)	C1′—C2′—C7′	122·7 (8)
O1—N1—C1	120·4 (6)	N3′—C2′—C7′	121·3 (8)
N1—C1—C2	114·5 (7)	Cu—N3′—C2′	112·2 (5)
N1—C1—C8	122·3 (7)	Cu—N3′—C4′	128·3 (6)
C2—C1—C8	123·1 (8)	C2′—N3′—C4′	119·5 (7)
C1—C2—N3	114·2 (7)	N3′—C4′—C5′	121·3 (7)
C1—C2—C7	124·9 (8)	C4′—C5′—C6′	118·9 (7)
N3—C2—C7	120·8 (7)	C5′—C6′—C7′	120·9 (8)
Cu—N3—C2	113·6 (5)	C2′—C7′—C6′	118·1 (8)
Cu—N3—C4	126·6 (6)	C1′—C8′—C9′	120·3 (8)
C2—N3—C4	119·5 (7)	C1′—C8′—N13′	117·0 (8)
N3—C4—C5	122·2 (7)	C9′—C8′—N13′	122·7 (7)
C4—C5—C6	118·5 (7)	C8′—C9′—C10′	118·5 (8)
C5—C6—C7	119·9 (8)	C9′—C10′—C11′	120·0 (7)
C2—C7—C6	119·2 (8)	C10′—C11′—C12′	117·9 (8)
C1—C8—C9	121·6 (9)	C11′—C12′—N13′	123·5 (8)
C1—C8—N13	117·2 (8)	C8′—N13′—C12′	117·5 (7)
C9—C8—N13	121·4 (8)		

anisotropically, scattering factors including f' and f'' from *International Tables for X-ray Crystallography* (1974); computation on PDP 11/24 and PDP 11/34 computers using Enraf–Nonius (1984) *SDP* programs, 289 variables, $R = 0{\cdot}038$, $wR = 0{\cdot}042$, $S = 1{\cdot}20$, no extinction correction, max. shift/e.s.d. = 0·01, max. and min. $\Delta\rho$ on final difference Fourier map 0·6 and −0·4 e Å^{-3}.

Discussion. Final parameters for non-H atoms are in Table 1.* Bond distances and angles are in Table 2. The crystal structure is made up of discrete binuclear Cu$^{\text{II}}$ complexes with distorted trigonal bipyramidal coordination of the copper (Fig. 1). The crystallographic twofold axis repeats one half of the complex into the other. The Cu atoms are chelated by the oxime nitrogen and one pyridine nitrogen of each ligand, and the deprotonated oxime oxygen of one of the two ligands bridges to the second Cu atom to form the doubly bridged binuclear complex. The other deprotonated oxime oxygen is not bonded to a Cu atom, and each ligand has a pyridine nitrogen which is not bonded to a Cu atom. As can be seen from Fig. 1, the oxime nitrogen atoms (N1 and N1′) occupy the axial positions of the distorted trigonal bipyramid [N1—Cu—N1′ = 179·0 (3)°]. The trigonal plane is much more distorted with a tendency toward square pyramidal with the pyridine nitrogen—Cu—pyridine nitrogen angle (N3—Cu—N3′) opened to 136·4 (2)° while the other two 'ideal' 120° angles are O1—Cu—N3 = 100·4 (2) and O1—Cu—N3′ = 123·1 (2)°. The 'ideal' 90° angles range from the bite angle of 79·1 (3)° (N1—Cu—N3) to 98·2 (3)° (N1—Cu—N3′). The Cu—N (oxime) distance of 1·965 (6) Å is similar to those observed in other amine oximes [*e.g.* 1·96 (1) Å (Liss & Schlemper, 1975) and 1·965 (11) Å (Pal, Murmann, Schlemper & Fair, 1986)] while the Cu—N (amine) distance of 2·031 (13) Å is considerably longer that of 1·986 (5) Å in the recently reported pyridyl-substituted propanolato copper(II) complex (Schlemper, Patterson & Stunkel, 1989). The present Cu—N (aromatic amine) distance is similar to the Cu—N (aliphatic amine) distance found in other

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* Lists of structure factors, H-atom parameters, torsion angles and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52665 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

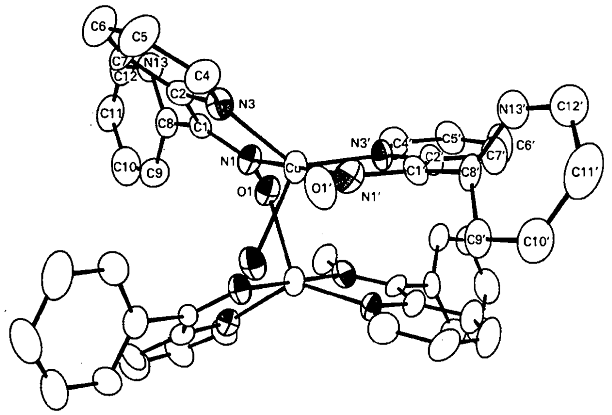

Fig. 1. A perspective view of the molecule (50% probability ellipsoids) showing the atom labeling and thermal ellipsoids. The bottom half of the dinuclear complex is related to the top half by a horizontal twofold axis.

amine oximes [*e.g.* 2·037 (5) Å (Pal *et al.*, 1986)]. In this previous study there is a bridging oxime oxygen with a Cu—O distance of 2·300 (4) Å compared with the much shorter distance [2·133 (5) Å] observed here. In the previous study, the Cu^{II} atom was in square-pyramidal coordination.

The water of hydration (O*W*) is 2·757 (9) Å from $O1'(\frac{1}{2}-x;\ \frac{1}{2}-y;\ -z)$ and 2·978 (9) Å from $N13(\frac{1}{2}+x;\ \frac{1}{2}+y;\ z)$ with an O1'—O*W*—N13 angle of 127·6 (3)°, allowing for hydrogen-bond formation with these ligand Lewis base atoms which are not involved in metal bonding. H-atom location for the water O atoms from difference Fourier summations was not satisfactory, and those positions reported are in reasonable hydrogen-bonding positions but are questionable.

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References

Blackmore, M. W., Sceney, C. G., O'Neill, D. R. & Magee, R. J. (1974). *J. Inorg. Nucl. Chem.* **36**, 1170–1171.

Enraf–Nonius (1984). *Structure Determination Package*. Enraf–Nonius, Delft, The Netherlands.

Holland, W. G. & Bozic, J. (1968). *Anal. Chem.* **40**, 433–434.

Holland, W. G., Bozic, J. & Gerard, J. T. (1968). *Anal. Chim. Acta*, **43**, 417–422.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Liss, I. B. & Schlemper, E. O. (1975). *Inorg. Chem.* **14**, 3035–3039.

Niemers, E. & Hiltmann, R. (1976). *Synthesis*, pp. 593–595.

Pal, J., Murmann, R. K., Schlemper, E. O. & Fair, C. K. (1986). *Inorg. Chim. Acta*, **115**, 153–162.

Schlemper, E. O., Patterson, C. & Stunkel, J. (1989). *Acta Cryst.* C**45**, 199–201.

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Structure of 10,11-μ-[(Triphenylphosphine)aurio]-9-dimethylsulfido-7,8-dicarba-*nido*-undecaborane(10) Methylene Chloride Solvate

By Ewan J. M. Hamilton and Alan J. Welch

Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ, Scotland

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Abstract. $C_{22}H_{31}AuB_9PS.CH_2Cl_2$, $M_r = 737·72$, monoclinic, $P2_1/n$, $a = 15·323$ (6), $b = 12·291$ (3), $c = 17·023$ (11) Å, $\beta = 112·45$ (4)°, $V = 2962·8$ Å^3, $Z = 4$, $D_x = 1·654$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 5·273$ mm^{-1}, $F(000) = 1440$, $T = 185$ (1) K, $R = 0·0310$ for 4710 independent observed reflections. Replacement of the μ-H atom in the precursor [10,11-μ-H-9-SMe_2-*nido*-$C_2B_9H_{10}$] by μ-$AuPPh_3$ results in depression (> 5°) of the SMe_2 function from its preferred inclination to the open C_2B_3 face. However, near eclipsing of the sulfur lone pair and C(8) is retained. The Au atom bridges the B(10)—B(11) connectivity in an asymmetric manner, Au—B(10) 2·233 (6), Au—B(11) 2·357 (6) Å.

Introduction. We are currently developing the transition-metal chemistry of the monoanionic carbaborane ligand [9-SMe_2-*nido*-7,8-$C_2B_9H_{10}$]$^-$ (carb'$^-$), with particular reference to similarities and differences that occur with respect to the chemistry of the $[C_5H_5]^-(Cp^-)$ ligand. As part of this program we are interested in complexes in which carb' is ligated to metal fragments that are formally one-orbital donors, and thus we have synthesized and structurally characterized the title compound, the results of which are presented here.

Experimental. Addition of a solution of Ph_3PAuCl in CH_2Cl_2 to an equimolar suspension of Tl[9-SMe_2-

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