shorter than that of Os—C(1) [1.82 (2) Å]. The Os—C(2) bond is strengthened by a strong electron donor in the *trans* position. Two Os—I bond lengths [2.698 (2), 2.705 (3) Å] are relatively short compared with that of other Os complexes. To our knowledge these are among the shortest Os—I bond lengths reported in the literature. We previously reported the crystal structure of $Os(CO)_3[NH_2C(CH_3)_3]I_2$ in which the ligands are also in a *cis* orientation to Os—I with distances of 2.735 (1) and 2.736 (1) Å (Lu, Chen, Lin & Peng, 1988). The structural difference between the two molecules is that, in (2), a triphenylphosphine ligand which is a better σ donor, replaces one of the carbonyl ligands of $Os(CO)_3(NH_2\text{-}i\text{Pr})I_2$. This causes remarkable shortening of the Os—I distance. Therefore the electronic effect is likely to be a key factor in determining the bond length. The shortest Os—I distance of 2.662 Å is found in tetraphenylarsonium nitridotetraiodoosmate(VI) which bears a negative charge on the Os metal center and has the same *cis* orientation for the I ligands (Phillips, Skapski & Withers, 1975). In our case, complex (2) is a neutral compound. Studies on the relationship between the Os—I distance and the Os coordinated environment are underway.

This work was supported by the National Science Council, Taiwan.

References

Dombek, B. D. (1981). *J. Am. Chem. Soc.* **103**, 6508–6510.

Gabe, E. J., Lee, F. L. & Le Page, Y. (1985). *Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Kruger & R. Goddard, pp. 167–174. Oxford: Clarendon Press.

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

Lu, K. L., Chen, J. L., Lin, Y. C. & Peng, S. M. (1988). *Inorg. Chem.* **27**, 1726–1730.

Morrison, E. D., Geoffroy, G. L. & Rheingold, A. L. (1985). *J. Am. Chem. Soc.* **107**, 254–255.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–354.

Phillips, F. L., Skapski, A. C. & Withers, M. J. (1975). *Transition Met. Chem.* **1**, 28–34.

Acta Cryst. (1992). C**48**, 35–40

Copper(I) Reoxygenation Products: the Structures of Di-μ-hydroxy-bis(di-2-pyridylamine)bis(tetrafluoroborato)dicopper(II) and μ-Aqua-di-μ-hydroxy-bis(di-2-pyridylamine)dicopper(II) Dichloride Dihydrate

By Liang-Ping Wu, Mary E. Keniry and Brian Hathaway

The Chemistry Department, University College, Cork, Ireland

(*Received* 6 *June* 1990; *accepted* 15 *July* 1991)

Abstracts. (I) $[Cu_2(FBF_3)_2(OH)_2(C_{10}H_9N_3)_2]$, $C_{20}H_{20}B_2Cu_2F_8N_6O_2$, $M_r = 677.11$, triclinic, $P\bar{1}$, $a = 9.686$ (2), $b = 9.429$ (2), $c = 7.414$ (3) Å, $\alpha = 69.90$ (1), $\beta = 97.53$ (2), $\gamma = 106.97$ (3)°, $V = 607.97$ (3) Å^3, $Z = 1$, $D_m = 1.70$ (4), $D_x = 1.85$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.781$ mm^{-1}, $F(000) = 338$, room temperature. (II) $[Cu_2(OH)_2(H_2O)(C_{10}H_9N_3)_2]Cl_2.2H_2O$, $C_{20}H_{22}Cu_2N_6O_3^{2+}.2Cl^-.2H_2O$, $M_r = 628.47$, orthorhombic, $Cmc2_1$, $a = 15.675$ (3), $b = 8.563$ (1), $c = 18.115$ (3) Å, $V = 2431.49$ Å^3, $Z = 4$, $D_m = 1.67$ (5), $D_x = 1.717$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.946$ mm^{-1}, $F(000) = 1280$, room temperature. With 1750 and 1045 unique reflections $R = 0.0474$ and 0.0309 for (I) and (II), respectively. Both complexes contain a dinuclear $[(dpyam)Cu(OH)_2Cu(dpyam)]^{2+}$ unit, dpyam = 2,2′-bipyridylamine, with near planar CuN_2O_2 chromophores. In (I) the centrosymmetric dinuclear unit is approximately planar, but each CuN_2O_2 chromophore has a tetrahedral twist, dihedral angle 24.0°. An F atom from a monodentate $[BF_4]^-$ anion completes a distorted square pyramidal CuN_2O_2F chromophore with a Cu—F distance of *ca* 2.745 (7) Å. In (II) the dinuclear unit has a roof-top structure (140.6°), with an additional single water molecule bridging both copper(II) cations at a Cu—O′ distance of 2.419 (5) Å, to give a square pyramidal CuN_2O_2O' chromophore. The Cu—Cu distances are 2.919 (5) and 2.799 (1) Å in (I) and (II), respectively. Both (I) and (II) are ESR silent, but while the room-temperature magnetic moment of (I) is normal (0.90 BM) that of (II) is slightly low (1.75 BM).

Introduction. Copper metal reduction of the $[Cu^{II}(dpyam)_2][BF_4]_2$ complex, by refluxing in air in acetonitrile solution then reoxygenation in air, yields steel-blue crystals of $[Cu^{II}_2(dpyam)_2(OH)_2(FBF_3)_2]$, (I)

0108-2701/92/010035-06$03.00

Table 1. *Refinement data*

	(I)	(II)
Molecular formula	$[Cu_2(OH)_2(FBF_3)_2(dpyam)_2]$	$[Cu_2(OH)_2(H_2O)(dpyam)_2]Cl_2.2H_2O$
Measured reflections	1784	1075
Unique reflections used (*N*)	1759	1045
Number of parameters (*NP*)	216	170
N/*NP*	8.15	6.15
Number of anisotropic atoms	23	21
Final weighting: *k*, *g**	1.00, 0.00053	2.136, 0.0000
R	0.0474	0.0309
wR	0.0517	0.0338
Max. final shift/e.s.d.	0.001	0.001
Max. and min. residual electron density (e Å^{-3})	0.40, −0.53	0.52, −0.38

*$w = k[\sigma^2(F_o) + g(F_o)^2]^{-1}$.

(Wu, 1988). The copper metal reduction in air of $[Cu^{II}(Cl)(dpyam)_2]Cl$ in acetonitrile solution yields blue needles of $[Cu^{II}(CO_3)(H_2O)(dpyam)].2H_2O$ (Akhter, Fitzgerald & Hathaway, 1991), but in CO_2-free air yields purple crystals of $[Cu_2^{II}(OH)_2(H_2O)(dpyam)_2]Cl_2.2H_2O$ (II). As both complexes suggest evidence for the formation of the OH^- anion by the reoxygenation in air of these copper(I) complexes in solution, the X-ray crystal structures of (I) and (II) are reported.

Experimental. $[Cu^{II}(dpyam)_2][BF_4]_2$, (*A*), was prepared by adding 20 ml of a boiling methanol solution of $[Cu(OH_2)_6][BF_4]_2$ (0.35 g, 1.0 mmol), to 20 ml of a hot methanol solution of dpyam (0.35 g, 2.0 mmol). On slow evaporation (*A*) was deposited as purple crystals. 0.58 g (1.0 mmol) of (*A*) were dissolved in 25 ml of acetonitrile and 0.3 g of copper metal plate added. The solution was refluxed for 15 h in air. When the colour changed from green to pale yellow, removal of the heat source resulted in a reversal of the colour change and deposition of steel-blue crystals of (I). Found: C, 35.62; H, 2.82; N, 12.45; Cu, 18.20%. Calculated for $C_{20}H_{20}B_2Cu_2F_8N_6O_2$: C, 35.47, H, 2.96; N, 12.42; Cu, 18.77%. (II) was prepared by reoxygenation of $[Cu^I(dpyam)_2]Cl$, (*B*), which was prepared from a hot ethanol solution of dpyam (0.35 g, 2.0 mmol), $Cu(O_2CH)_2.3H_2O$ (0.21 g, 1.0 mmol), $NH_2OH.HCl$ (0.20 g, 2.88 mmol) in water (60 ml) and 1 ml of concentrated 0.88 aqueous ammonia. The green solution was heated to boiling, when it turned yellow, flushed with nitrogen and stoppered. After six days orange/red diamond-shaped crystals of (*B*) were deposited. Found: C, 54.45; H, 4.62; N, 19.00; Cu, 13.88; Cl, 7.43%. Calculated for $C_{20}H_{18}ClCuN_6$: C, 54.41; H, 4.12; N, 19.04; Cu, 14.39; Cl, 8.03%. 0.4 g (0.91 mmol) of (*B*) were dissoved in a 1:1 mixture of water and ethanol, heated with stirring in air and the resulting green solution flushed with methane gas and stoppered. After 5 d a crop of dark purple crystals of $[Cu_2^{II}(OH)_2(H_2O)(dpyam)_2]Cl_2.2H_2O$ (II) were deposited. Found: C, 38.07; H, 4.19; N, 13.05; Cu, 20.27; Cl, 11.14%. Calculated for $Cu_{20}H_{26}Cl_2Cu_2N_6O_5$: C, 38.22; H, 4.18; N, 13.37; Cu, 20.22; Cl, 11.28%.

The structure analyses of (I) and (II) are summarized in Table 1. The unit-cell dimensions (25 reflections) and intensities θ 3–25° were measured on a Philips PW 1100 four-circle diffractometer, with graphite-monochromatized Mo $K\alpha$ radiation. ω–2θ scan mode with a constant scan speed of 0.05° s^{-1} and a variable scan width of $(0.70 + 0.10\tan\theta)$°. With an acceptance criteria of $I > 2.5\sigma(I)$, 1784 observed reflections, 1759 unique (*h* −10–10, *k* −10–10, *l* 0–8) for (I) and 1075 observed reflections, 1045 unique (*h* 0–18, *k* 0–10, *l* 0–21) for (II) were retained. Lorentz and polarization corrections were applied, but no correction was made for absorption. The structures were solved using three-dimensional Patterson and Fourier techniques and refined by full-matrix least-squares minimization of $\sum w(|F_o| - |F_c|)^2$. Anisotropic temperature factors were refined for all non-H atoms. The $[BF_4]^-$ anion in (I) was refined as a disordered unit. Calculated H-atom positions were used, with fixed C—H and N—H bond lengths of 1.08 Å and a fixed U_{iso} of 0.07 Å^2; H atoms rode on the associated C, N or O atoms. Refined weighting scheme with $w = k/[\sigma^2(F_o) + g(F_o)^2]^{-1}$ (see Table 1 for final *k* and *g* values). Complex neutral-atom scattering factors for non-H atoms (Cromer & Waber, 1974). Absolute structure not determined for (II). All calculations were carried out with *SHELX76* and *SHELXS86* (Sheldrick, 1976, 1986), *XANADU* (Roberts & Sheldrick, 1979), *CHEM-X* (Davies, 1980) and *PUBTAB* (Hendrick, 1980) on the UCC mainframe IBM 4341 and VAX 11/780 or 6310 computers. The final non-H-atom coordinates are given in Table 2.* Bond lengths and angles are given

---

* Lists of structure factors, anisotropic thermal parameters, calculated H-atom coordinates and mean-plane data have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54538 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Fractional atomic coordinates and thermal parameters* (Å^2) *with e.s.d.'s in parentheses*

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq} (Å^2)
(I)				
Cu(1)	0.02566 (4)	0.34511 (4)	0.06215 (6)	0.0325 (3)
O(1)	−0.0822 (3)	0.4555 (3)	0.1349 (4)	0.051 (1)
N(1)	−0.0824 (3)	0.1342 (3)	0.2181 (4)	0.044 (1)
C(1)	−0.2152 (4)	0.1196 (4)	0.2742 (6)	0.052 (2)
C(2)	−0.3054 (4)	−0.0184 (5)	0.3736 (6)	0.056 (2)
C(3)	−0.2598 (5)	−0.1542 (4)	0.4207 (6)	0.054 (2)
C(4)	−0.1284 (4)	−0.1431 (4)	0.3671 (5)	0.048 (2)
C(5)	−0.0418 (4)	0.0017 (4)	0.2650 (5)	0.045 (2)
N(3)	0.0903 (4)	0.0046 (4)	0.2136 (5)	0.050 (2)
C(6)	0.2016 (4)	0.1234 (4)	0.1149 (5)	0.049 (2)
C(7)	0.3279 (4)	0.0854 (5)	0.1020 (6)	0.058 (2)
C(8)	0.4387 (4)	0.1945 (5)	−0.0007 (6)	0.065 (2)
C(9)	0.4239 (4)	0.3458 (5)	−0.0928 (7)	0.067 (2)
C(10)	0.3009 (4)	0.3768 (4)	−0.0716 (7)	0.059 (2)
N(2)	0.1878 (3)	0.2686 (3)	0.0310 (4)	0.045 (1)
B(1)	0.2352 (5)	−0.3676 (6)	0.3618 (7)	0.057 (3)
F(1)*	0.2555 (9)	−0.4749 (10)	0.2771 (11)	0.112 (5)
F(2)*	0.1429 (8)	−0.2857 (7)	0.2425 (12)	0.097 (5)
F(3)	0.3612 (4)	−0.2876 (5)	0.4186 (7)	0.134 (3)
F(4)*	0.1503 (13)	−0.4576 (11)	0.5114 (11)	0.146 (7)
F(5)†	−0.1299 (10)	0.3142 (13)	−0.4212 (18)	0.130 (8)
F(6)†	−0.2309 (14)	0.2879 (12)	−0.1722 (12)	0.115 (7)
F(7)†	−0.2040 (13)	0.5091 (8)	−0.4185 (30)	0.161 (11)
(II)				
Cu(1)	0.41071 (4)	0.30885 (7)	0.79523 (10)	0.0276 (3)
Cl(1)	0.0000	0.3167 (2)	0.8044 (2)	0.039 (1)
Cl(2)	0.5000	0.1675 (3)	0.0208 (2)	0.056 (1)
N(1)	0.3255 (3)	0.4458 (5)	0.8472 (3)	0.028 (2)
C(1)	0.3545 (4)	0.5438 (7)	0.9015 (3)	0.035 (3)
C(2)	0.3036 (4)	0.6275 (8)	0.9473 (4)	0.035 (3)
C(3)	0.2153 (4)	0.6136 (7)	0.9395 (3)	0.035 (3)
C(4)	0.1838 (4)	0.5207 (7)	0.8853 (3)	0.035 (3)
C(5)	0.2409 (3)	0.4373 (6)	0.8389 (3)	0.029 (3)
N(3)	0.2055 (3)	0.3466 (7)	0.7842 (3)	0.035 (3)
C(6)	0.2409 (4)	0.2657 (7)	0.7253 (3)	0.030 (3)
C(7)	0.1840 (5)	0.2089 (9)	0.6730 (4)	0.043 (4)
C(8)	0.2153 (4)	0.1243 (9)	0.6138 (4)	0.045 (4)
C(9)	0.3034 (5)	0.1041 (9)	0.6075 (4)	0.044 (4)
C(10)	0.3551 (4)	0.1645 (8)	0.6608 (3)	0.039 (3)
N(2)	0.3252 (3)	0.2464 (6)	0.7210 (3)	0.031 (2)
O(1)	0.5000	0.3519 (7)	0.8678 (3)	0.035 (3)
O(2)	0.5000	0.1730 (6)	0.7566 (4)	0.034 (3)
O(3)	0.5000	0.4887 (7)	0.7272 (4)	0.040 (3)
O(4)	0.5000	0.1956 (8)	0.4891 (5)	0.062 (5)
O(5)	0.5000	0.4777 (10)	0.5772 (4)	0.077 (5)

* SOF = 0.55.
† SOF = 0.45.

in Table 3. Figs. 1 and 2 illustrate the molecular structures and atom-numbering schemes for (I) and (II), respectively.

Table 3. *Bond lengths* (Å) *and angles* (°)

(I)			
Cu(1)—O(1)	1.906 (2)	Cu(1)—N(1)	1.977 (3)
Cu(1)—N(2)	1.977 (3)	Cu(1)—Cu(1)	2.917 (1)
N(1)—C(1)	1.358 (5)	N(1)—C(5)	1.337 (4)
C(1)—C(2)	1.358 (5)	C(2)—C(3)	1.392 (6)
C(3)—C(4)	1.348 (6)	C(4)—C(5)	1.389 (5)
C(5)—N(3)	1.373 (5)	N(3)—C(6)	1.375 (5)
C(6)—C(7)	1.394 (5)	C(6)—N(2)	1.333 (4)
C(7)—C(8)	1.349 (6)	C(8)—C(9)	1.395 (6)
C(9)—C(10)	1.347 (6)	C(10)—N(2)	1.361 (5)
B(1)—F(1)	1.430 (8)	B(1)—F(2)	1.380 (7)
B(1)—F(3)	1.335 (6)	B(1)—F(4)	1.346 (8)
Cu(1)—O(1′)	1.921 (2)		
N(1)—Cu(1)—O(1)	95.5 (1)	N(2)—Cu(1)—O(1)	161.4 (1)
N(2)—Cu(1)—N(1)	92.7 (1)	C(1)—N(1)—Cu(1)	117.2 (2)
C(5)—N(1)—Cu(1)	126.6 (3)	C(5)—N(1)—C(1)	116.1 (3)
C(2)—C(1)—N(1)	124.2 (4)	C(3)—C(2)—C(1)	118.3 (4)
C(4)—C(3)—C(2)	118.8 (4)	C(5)—C(4)—C(3)	119.9 (4)
C(4)—C(5)—N(1)	122.7 (4)	N(3)—C(5)—N(1)	120.3 (3)
N(3)—C(5)—C(4)	117.0 (3)	C(6)—N(3)—C(5)	132.9 (3)
C(7)—C(6)—N(3)	117.4 (3)	N(2)—C(6)—N(3)	121.2 (3)
N(2)—C(6)—C(7)	121.4 (3)	C(8)—C(7)—C(6)	120.6 (4)
C(9)—C(8)—C(7)	118.5 (4)	C(1)—C(9)—C(8)	118.4 (4)
N(2)—C(10)—C(9)	124.1 (4)	C(6)—N(2)—Cu(1)	125.7 (3)
C(10)—N(2)—Cu(1)	117.0 (2)	C(10)—N(2)—C(6)	117.0 (3)
F(2)—B(1)—F(1)	108.3 (5)	F(3)—B(1)—F(1)	111.2 (5)
F(3)—B(1)—F(2)	118.7 (5)	F(4)—B(1)—F(1)	104.8 (6)
F(4)—B(1)—F(2)	100.9 (7)	F(4)—B(1)—F(3)	111.6 (6)
Cu(1)—O(1)—Cu(1′)	99.3 (2)	I(1)—Cu(1)—O(1′)	80.7 (2)
(II)			
Cu(1)—N(1)	2.012 (4)	Cu(1)—N(2)	1.973 (5)
Cu(1)—O(1)	1.955 (4)	Cu(1)—O(2)	1.949 (4)
Cu(1)—O(3)	2.419 (5)	Cu(1)—Cu(1)	2.799 (1)
N(1)—C(1)	1.370 (7)	N(1)—C(5)	1.337 (7)
C(1)—C(2)	1.356 (9)	C(2)—C(3)	1.396 (9)
C(3)—C(4)	1.357 (9)	C(4)—C(5)	1.420 (8)
C(5)—N(3)	1.376 (8)	N(3)—C(6)	1.388 (9)
C(6)—C(7)	1.389 (9)	C(6)—N(2)	1.334 (8)
C(7)—C(8)	1.384 (11)	C(8)—C(5)	1.395 (10)
C(9)—C(10)	1.363 (9)	C(10)—N(2)	1.378 (8)
N(2)—Cu(1)—N(1)	91.5 (2)	O(1)—Cu(1)—N(1)	92.9 (2)
N(2)—Cu(1)—N(1)	91.5 (2)	O(1)—Cu(1)—N(1)	92.9 (2)
O(1)—Cu(1)—N(2)	174.8 (2)	O(2)—Cu(1)—N(1)	172.9 (2)
O(2)—Cu(1)—N(2)	94.7 (2)	O(2)—Cu(1)—O(1)	80.8 (2)
O(3)—Cu(1)—N(1)	104.6 (2)	O(3)—Cu(1)—N(2)	102.6 (2)
O(3)—Cu(1)—O(1)	79.0 (2)	O(3)—Cu(1)—O(2)	77.4 (2)
Cu(1)—O(1)—Cu(1″)	91.4 (3)	Cu(1)—O(2)—Cu(1′)	91.8 (2)
Cu(1)—O(3)—Cu(1″)	70.7 (2)	C(1)—N(1)—Cu(1)	118.2 (4)
C(5)—N(1)—Cu(1)	125.1 (4)	C(5)—N(1)—C(1)	116.3 (5)
C(2)—C(1)—N(1)	124.6 (5)	C(3)—C(2)—C(1)	118.4 (6)
C(4)—C(3)—C(2)	119.9 (6)	C(5)—C(4)—C(3)	119.5 (5)
C(4)—C(5)—N(1)	122.1 (5)	N(3)—C(5)—N(1)	120.7 (5)
N(3)—C(5)—C(4)	117.1 (5)	C(6)—N(3)—C(5)	132.4 (5)
C(7)—C(6)—N(3)	116.2 (6)	N(2)—C(6)—N(3)	120.3 (5)
N(2)—C(6)—C(7)	123.5 (6)	C(8)—C(7)—C(6)	119.0 (7)
C(9)—C(8)—C(7)	118.6 (6)	C(10)—C(9)—C(8)	118.9 (7)
N(2)—C(10)—C(9)	123.4 (6)	C(6)—N(2)—Cu(1)	126.7 (4)
C(10)—N(2)—Cu(1)	116.5 (4)	C(10)—N(2)—C(6)	116.6 (5)

Symmetry code: (′) $-x, -y, -z$; (″) $1-x, y, z$.

Discussion. *Crystal structure.* The structure of (I) consists of a centrosymmetric dinuclear $[Cu_2(OH)_2(dpyam)_2]^{2+}$ cation and two weakly coordinating $[BF_4]^-$ anions. The cation is approximately planar with symmetrically bridging OH^- anions and terminal chelate dpyam ligands (Fig. 1). The CuN_2O_2 chromophores are non-planar, with a distinct tetrahedral twist, evident from the dihedral angle of 24.0° between the CuO(1)O(1′) and CuN(1)N(2) planes. The fifth axial coordination site of each copper(II) ion is occupied by an F atom from one of the two separate tetrafluoroborate anions, at a Cu(1)—F(1) distance of 2.745 (7) Å, to complete an approximate square pyramidal CuN_2O_2F chromophore. However, the Cu—F distances are too long for even weak semi-coordination, 2.4 Å is the upper limit for such bonding (Tomlinson, Hathaway, Billing & Nicholls, 1969). This is reflected in the small displacement of 0.022 Å for the Cu(1) atom from the mean N_2O_2 plane, towards the axial F atom. The CuN_2O_2 chromophores involve Cu—O distances of 1.906 (2) and 1.921 (2) Å, and Cu—N(1) and Cu—N(2) distances of 1.977 (3) Å. The bridging Cu(1)—O(1)—Cu(1′) angle is 99.3 (2)°, significantly greater than 90°, and the O(1)—Cu(2)—O(1′) angle of 80.7 (2)° is significantly less than 90°. The bite angle of the dypyam ligands [N(1)—Cu—N(2) 92.7 (1)°] is only slightly greater than 90°. The Cu—Cu distance is 2.919 (5) Å. There are no unusual bond lengths or bond angles in the dpyam ligand (Ray & Hathaway, 1978) (Table 3) and the individual pyridine rings are essentially planar, r.m.s.d. 0.022 and 0.076 Å, respectively. The dpyam ligand is not planar, but involves an angle of 6.59° between the individual pyridine rings.

The structure of (II) (Fig. 2) consists of a dinuclear $[Cu_2(OH)_2(H_2O)(dpyam)_2]^{2+}$ cation, two Cl^- anions and an H_2O molecule. The cation is located on a mirror plane through the two bridging OH^- ligands and the bridging water molecule of the cation. Both the Cl^- anion and the non-coordinated H_2O molecule are located on mirror planes, and are not even involved in semi-coordination to the copper(II) cations (Procter, Hathaway & Nicholls, 1968). Each Cu atom involves an essentially planar CuN_2O_2 chromophore, through the two bridging OH^- ligands and a terminal bipyam ligand. The bridging water molecule occupies a fifth coordinate position at a distance of 2.414 (6) Å, to give two square pyramidal CuN_2O_2O' chromophores. Owing to the mirror plane there is an angle of 140.6° between the corresponding CuN_2O_2 planes, to give a roof-top structure, held in place by the bridging H_2O molecule. The Cu—Cu distance is 2.800 (8) Å. The Cu—O distances are not significantly different at 1.957 (4) and 1.947 (3) Å, respectively, but the two Cu—N distances are significantly different at 2.014 (4) and 1.982 (4) Å, respectively. The Cu—OH_2 distance of 2.414 (6) Å is considerably longer than the four in-plane distances, but is within significant bonding distance of the Cu atoms [the upper limit for such bonding is 2.7 Å (Procter *et al.*, 1968)]. The CuN_2O_2 chromphore is planar to within 0.0019 Å, with only a slight tetrahedral twist, 3.91°. The Cu atom is lifted 0.049 Å above the CuN_2O_2 plane towards the H_2O ligand, as is normally found for the square pyramidal copper(II) stereochemistry (Hathaway, 1987).

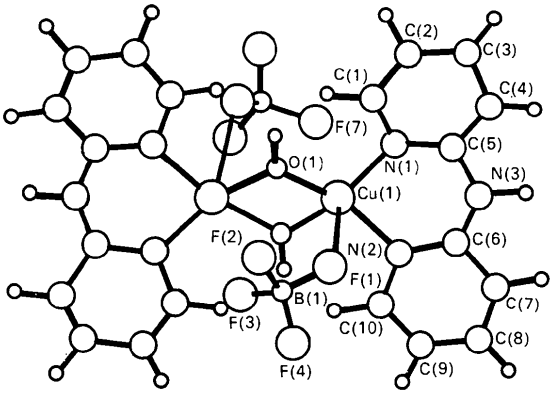

Fig. 1. The molecular structure of $[Cu_2(OH)_2(FBF_3)_2(dpyam)_2]$ (I) and the atom-numbering system used.

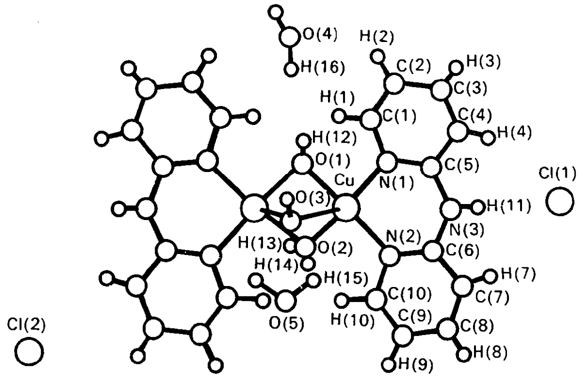

Fig. 2. The molecular structure of $[Cu_2(OH)_2(H_2O)(dpyam)_2]Cl_2 \cdot 2H_2O$ (II) and the atom-numbering system used.

Structural comparisons. (I) and (II) represent the first known structures of a dihydroxy-bridged copper(II) dimer involving the dpyam ligand (see Hathaway, 1987, p. 660, Table 43, for a recent summary). In the known dimer structures, three copper environments are observed: rhombic coplanar, CuN_2O_2 (Arcus, Fivizzani & Pavkovic, 1977), square-based pyramidal, CuN_2O_2X (Casey, Hoskins & Whillans, 1970, 1975; McGregor, Watkins, Lewis, Drake, Hodgson & Hatfield, 1973; Majeste & Meyers, 1970), and elongated rhombic octahedral, $CuN_2O_2X_2$ (Toofan, Boushehri & Ul-Haque, 1976). Thus the square-based pyramidal CuN_2O_2F chromophores of (I) are not exceptional and are typical of a weakly interacting $[BF_4]^-$ anion in the fifth ligand position (Foley, Kennefick, Phelan, Tyagi & Hathaway, 1983). However, the marked tetrahedral twist of the CuN_2O_2 chromophore of (I) (dihedral angle 24.0°) is less usual. The Cu—Cu separation of 2.919 (5) Å is typical of the range previously observed 2.87–3.00 Å (Hathaway, 1987, Table 43). The dihyroxy-bridged structure or (II), with the additional longer bonded bridging water molecule, is a novel structure. The triply bridged dimer is unusual in copper(II) chemistry (Hathaway, 1987), but does occur with $Cs_3[Cu_2Cl_7(H_2O)_2]$ (III) (Vogt & Haas, 1971) involving three bridging Cl^- anions and in $[Cu_2(C_{18}H_{14}N_6)Cl_3(OH)].1.5H_2O$ (IV) (Marongiu & Lingafelter, 1982) involving a short bonded OH^-

bridge, an N_2 bridge and a longer bonded Cl^- anion bridge. In (III) the large bridging Cl^- anions result in a longer Cu—Cu distance of 3.45 Å, significantly larger than in (II) (2.80 Å), while in (IV) a more comparable distance of 3.00 Å is observed. The most interesting feature of (II) is the roof-top CuO_2Cu angle of 140.6°, introduced into the structure by the bridging OH_2 group, but even this significant roof-top angle also occurs in other dihydroxy-dibridged copper(II) complexes. In $[Cu_2(OH)_2(cyclohexamine)_4][ClO_4]_2$ (Charlot, Jeannin, Jeannin, Kahn, Lucrece-Abaul & Martin-Frere, 1979) and in $[Cu_2(OH)_2(MeNH_2)_4][SO_4].H_2O$ (Iitaka, Shimuzu & Kwan, 1966) roof-top CuO_2Cu angles of 147.5 and 132.9°, respectively, span the angle of 140.6° in (II). The bridging water molecule of (II) is also unusual, it occurs in $[Cu(tsglyH)_2(4\text{-}Mepy)_2(OH_2)]$, tsglyH = *N*-tosylglycinato and 4-Mepy = 4-methylpyridine (Battaglia, Corradi & Menabue, 1983), with a long symmetrical bridging OH_2 group, Cu—O distance of 2.76 Å and also in $[Cu_2(OH_2)_{10}][Cu(OH_2)_6][Zr_4F_7]_2$ (Fisher & Weiss, 1973), where an asymmetric bridging OH_2 group occurs, with Cu—O distances of 1.96 and 2.66 Å, respectively.

Spectroscopic properties. The infrared spectrum of (I) has two sharp peaks at 3340 and 3580 cm^{-1}, the latter is associated with the bridging OH^- group and the former with F—H hydrogen bonding, by comparison with a corresponding peak in $[Cu(dpyam)_2][BF_4]_2$ and $[Cu(dpyam)_2][PF_6]_2$ (Wu, Field, Akhter & Hathaway, 1991). The ν_3 mode of the $[BF_4]^-$ anion appears as a strong band, slightly split, at 1020 and 1085 cm^{-1}, consistent with its long bonding Cu—F distance of *ca* 2.75 Å (Foley *et al.*, 1983). The infrared spectrum of (II) has a strong band at 3400 cm^{-1} owing to the bridging OH^- group, and two weaker bands at 3160 and 3240 cm^{-1}, owing to the symmetric and asymmetric stretches of the water molecule (Nakamoto, 1978). Both complexes (I) and (II) are ESR silent, but while (I) has a normal room-temperature magnetic moment of 1.90 BM, that of (II) is significantly lower at 1.75 BM. The former result is surprising, as $[Cu^{II}_2(chelate)_2(OH)_2]X_2$ complexes are generally antiferromagnetic; however, the marked tetrahedral twist of the CuN_2O_2 chromophore may reduce the orthogonality of the copper(II) $d_{x^2-y^2}$ (or d_{xy}) orbital with the bridging OH^- orbitals. If this is the case than it is surprising that (I) is ESR silent. The electronic reflectance spectrum of (I) shows a broad band at 15 650 cm^{-1}, while (II) has a broad band at 17 500 cm^{-1}. The relatively low energy of the former may also be associated with the tetrahedral twist of the CuN_2O_2 chromophore (Foley *et al.*, 1983). The higher energy of (II) suggests that the single bridging OH_2 ligand is not very effective as a fifth ligand, not withstanding the short Cu—OH_2 distance of 2.44 Å, and may be associated with the bridging role of the water molecule.

Reoxygenation of Cu^I *to* Cu^{II} *complexes.* A significant feature of (I) and (II) is not just their structures but their method of preparation by reoxygenation of a copper(I) complex. This involves atmospheric O_2 as the most probable source of the OH^- anion by the following reactions.

$$[Cu^{II}(dpyam)_2][BF_4]_2 + Cu^0 \rightarrow 2[Cu^I(BF_4)(dpyam)]$$

$$2[Cu^I(BF_4)(dpyam)] + 1/2O_2 \rightarrow 2[Cu^{II}(BF_4)(dpyam)] + O^{2-}$$

$$O^{2-} + H_2O \rightarrow 2OH^-$$

$$2[Cu^{II}(dpyam)(BF_4)] + 2OH^- \rightarrow [Cu^{II}(OH)_2(FBF_4)_2(dpyam)_2].$$

In the reoxidized acetonitrile solution the Cu^{II}:-dpyam:OH^-:$[BF_4]^-$ ratio of 1:1:1:1 is then correct for the formation of (I) immediately. In the preparation of (II) the initial formation of a carbonate complex $[Cu^{II}(CO_3)(dpyam)].2H_2O$ (Akhter *et al.*, 1991) is understandable, as the OH^- generated reacts with CO_2 in the atmosphere by the reaction

$$HO^- + CO_2 \rightarrow [HCO_3]^-$$

$$[HCO_3]^- + HO^- \rightarrow [CO_3]^{2-} + H_2O.$$

Hence the need to use CO_2-free air in the preparation of (II).

The authors acknowledge the award of an EOLAS grant (to MK), a UCC senior studentship (to LPW and MK), help in data collection by Dr M. McPartlin and Mr A. Bashall (Department of Applied Chemistry and Life Sciences, Polytechnic of North London, Holloway Road, London), the Computer Bureau (UCC) for computing facilities, Professor G. M. Sheldrick, Drs P. Roberts, S. Motherwell, K. Henrick and K. Davies for the use of their programs and the Microanalysis Section (UCC) for analysis.

References

Akhter, P., Fitzgerald, P. & Hathaway, B. J. (1991). *Acta Cryst.* **C47**, 308–310.

Arcus, C., Fivizzani, K. P. & Pavkovic, S. F. (1977). *J. Inorg. Nucl. Chem.* pp. 285–287.

Battaglia, L. P., Corradi, A. B. & Menabue, L. (1983). *Inorg. Chem.* **33**, 3251–3255.

Casey, A. T., Hoskins, B. F. & Whillans, F. D. (1970). *J. Chem. Soc. Chem. Commun.* pp. 904–905.

Casey, A. T., Hoskins, B. F. & Whillans, F. D. (1975). *J. Chem. Soc. Dalton Trans.* pp. 1267–1272.

Charlot, M. F., Jeannin, S., Jeannin, Y., Kahn, O., Lucrece-Abaul, L. & Martin-Frere, J. (1979). *Inorg. Chem.* **18**, 1675–1681.

Cromer, D. T. & Waber, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, pp. 71, 148. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Davies, K. (1980). *CHEMX-X*. Molecular graphics program, developed and distributed by Chemical Design Ltd, Oxford.

Fisher, J. & Weiss, R. (1973). *Acta Cryst.* **29**, 1963–1967.

Foley, J., Kennefick, D., Phelan, D., Tyagi, S. & Hathaway, B. J. (1983). *J. Chem. Soc. Dalton Trans.* pp. 2333–2338.

Hathaway, B. J. (1987). *Comprehensive Coordination Chemistry. The Synthesis, Reactions, Properties & Applications of Coordination Compounds.* Editor in Chief G. Wilkinson, FRS; Executive Editors R. D. Gillard & J. A. McCleverty, Vol. 5, section 53, pp. 533–774. Oxford: Pergamon Press.

Hendrick, K. (1980). *PUBTAB*. Program to prepare and print crystallographic tables for publication. Polytechnic of North London, England.

Iitaka, Y., Shimuzu, K. & Kwan, T. (1966). *Acta Cryst.* **20**, 803–807.

Majeste, R. J. & Meyers, E. A. (1970). *J. Phys. Chem.* **74**, 3497–3503.

Marongiu, G. & Lingafelter, E. C. (1982). *Acta Cryst.* B**38**, 620–622.

McGregor, K. T., Watkins, N. T., Lewis, D. L., Drake, R. F., Hodgson, D. J. & Hatfield, W. E. (1973). *Inorg. Nucl. Chem. Lett.* **9**, 423–429.

Nakamoto, K. (1978). *Infra-red and Raman Spectra of Inorganic and Coordination Compounds*, 3rd ed. New York: John Wiley.

Procter, I. M., Hathaway, B. J. & Nicholls, P. (1968). *J. Chem. Soc.* (*A*), pp. 1678–1684.

Ray, N. & Hathaway, B. J. (1978). *Acta Cryst.* B**34**, 3224–3229.

Roberts, P. & Sheldrick, G. M. (1979). *XANADU*. Program for crystallographic calculations. Univ. of Cambridge, England.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Sheldrick, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.

Tomlinson, A. A. G., Hathaway, B. J., Billing, D. E. & Nicholls, P. (1969). *J. Chem. Soc.* (*A*), pp. 65–71.

Toofan, M., Boushehri, A. & Ul-Haque, M. (1976). *J. Chem. Soc. Dalton Trans.* pp. 217–219.

Vogt, V. W. & Haas, H. (1971). *Acta Cryst.* B**27**, 1528–1532.

Wu, L.-P. (1988). PhD Thesis, Nat. Univ. Ireland.

Wu, L.-P., Field, P., Akhter, P. & Hathaway, B. J. (1991). *J. Chem. Soc. Dalton Trans.* Submitted.

Acta Cryst. (1992). C**48**, 40–42

Structure of (Diethylamino){1-[(2-hydroxyphenyl)iminomethyl]naphthalen-2-olato-*O*,*O*′,*N*}nickel(II)

By Yalcin Elerman*

Department of Engineering Physics, Faculty of Sciences, University of Ankara, Besevler, Ankara, Turkey

and Hartmut Fuess and Helmut Paulus

Fachgebiet Strukturforschung, FB Materialwissenschaft, Technische Hochschule, 6100 *Darmstadt, Germany*

(*Received* 2 *October* 1990; *accepted* 12 *April* 1991)

Abstract. $[\mathrm{Ni(C_4H_{11}N)(C_{17}H_{11}NO_2)}]$, $M_r = 393.11$, monoclinic, $P2_1/n$, $a = 12.233\,(4)$, $b = 8.846\,(3)$, $c = 17.155\,(6)$ Å, $\beta = 96.04\,(1)°$, $V = 1846.2$ Å^3, $Z = 4$, $D_x = 1.414\ \mathrm{g\,cm^{-3}}$, $\lambda(\mathrm{Mo}\,K\alpha) = 0.71069$ Å, $\mu = 10.41\ \mathrm{cm^{-1}}$, $F(000) = 824$, $T = 298$ K, final $R = 0.035$, $wR = 0.030$ for 2181 unique reflections with $F > 2\sigma(F)$. The coordination of the Ni atom is square planar with Ni—O distances 1.820 (3) and 1.842 (3) Å, Ni—N distances 1.849 (3) and 1.955 (4) Å; the angles between the neighbouring ligands are in the range 86.8 to 94.8 (1)°. The diethylamino ligand is fully extended perpendicular to the Ni coordination plane.

Introduction. Metal derivatives of Schiff bases have been extensively studied and the copper(II) and nickel(II) complexes play a major role in both synthesis and structural research. Copper(II) and nickel(II) ions react with tridentate anionic Schiff bases and form dimer complexes with square-planar configurations as described by Maggio, Pizzino & Romano (1974). They report that *N*-(2-hydroxyphenyl)salicylaldimine reacts with nickel(II) ions giving a pseudo-octahedral complex by polymerization. We have investigated the reaction of nickel(II) with the monodentate ligand diethylamine and the tridentate ligand *N*-(2-hydroxyphenyl)-2-hydroxy-1-naphthaldimine; the structure of the reaction product is reported in this paper.

Experimental. Suitable crystals were obtained directly from the synthesis of the compound. A solution of 0.01 mol *N*-(2-hydroxyphenyl)-2-hydroxy-1-naphthaldimine in 200 ml pure methanol was prepared and heated to boiling temperature. 1.5 ml diethylamine was slowly added to the solution, 0.01 mol $\mathrm{Ni(CH_3COO)_2.4H_2O}$ was dropwise dissolved in 25 ml hot methanol. The mixture of the

---

* Alexander von Humbolt fellow.