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Structure of (2,2′-Bipyridine *N*,*N*′-dioxide)dichloro(methanol)copper(II), [Cu(bpyO$_2$)(MeOH)Cl$_2$]

By M. Koman, P. Baran and D. Valigura

Department of Inorganic Chemistry, Slovak Technical University, CS-81237 Bratislava, Czechoslovakia

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Abstract. [CuCl$_2$(C$_{10}$H$_8$N$_2$O$_2$)(CH$_4$O)], $M_r = 354{\cdot}68$, monoclinic, $P2_1/c$, $a = 16{\cdot}420\,(5)$, $b = 8{\cdot}545\,(2)$, $c = 19{\cdot}001\,(4)$ Å, $\beta = 90{\cdot}30\,(1)^\circ$, $V = 2665{\cdot}9\,(11)$ Å^3, $Z = 8$, $D_m = 1{\cdot}77$, $D_x = 1{\cdot}767$ g cm^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}54178$ Å, $\mu = 61{\cdot}33$ cm^{-1}, $F(000) = 1432$, room temperature, $R = 0{\cdot}0615$, $wR = 0{\cdot}0638$ for 4056 reflections with $I \geq 3\sigma(I)$. The crystal structure is formed by discrete [Cu(bpyO$_2$)(MeOH)Cl$_2$] complex molecules. The asymmetric unit contains two such molecules. The coordination polyhedron of each Cu$^{\mathrm{II}}$ atom is a highly distorted tetragonal pyramid defined by two Cl and three O atoms.

Introduction. Aromatic *N*-oxides such as 2,2′-bipyridine *N*,*N*′-dioxide (abbreviated to bpyO$_2$ throughout this paper) can exhibit a wide variety of bonding modes since they can act as both bridging and chelating ligands. We have recently synthesized and studied two isomeric dimeric [Cu$_2$(bpyO$_2$)$_2$Cl$_4$] complexes (Baran, Koman, Valigura & Mrozinski, 1991). The same synthetic route gives different products if the temperature or solvent mixture is altered. Thus we have now obtained single crystals of [Cu(bpyO$_2$)(MeOH)Cl$_2$] by addition of dioxane to the methanolic reaction mixture and have undertaken their X-ray diffraction analysis.

Experimental. Green prism-shaped crystals prepared from methanol/dioxane (1:2) solution of CuCl$_2$ with bpyO$_2$ in the appropriate stoichiometric ratio. Crystal dimensions $0{\cdot}81 \times 0{\cdot}29 \times 0{\cdot}13$ mm; density measured by flotation. Syntex $P2_1$ diffractometer; 15 reflections with $11{\cdot}60 \leq \theta \leq 20{\cdot}43^\circ$ used to determine lattice parameters; absorption and extinction ignored. Intensity measurements from θ–2θ scans carried out for $0 \leq 2\theta \leq 100^\circ$; h, k, l range: h −18 to 18, k 0 to 10, l 0 to 22. Two reflections re-estimated after every 98 measurements decreased in intensity by 15% during the course of the experiment; 4056 independent reflections with $I \geq 3\sigma(I)$ (1750 unobserved reflections); 439 refined parameters. Cu-atom positions from Patterson function, other non-H atoms from Fourier syntheses; H atoms from difference syntheses. Anisotropic full-matrix refinement for non-H atoms (H-atom refinement isotropic) based on F. $R = 0{\cdot}0615$, $wR = 0{\cdot}0638$, $S = 1.64$; $w = k/[\sigma^2(F_o) + g(F_o)^2]$, $k = 16{\cdot}7547$, $g = 0{\cdot}000257$; $|\Delta\rho| \leq 0{\cdot}71$ e Å^{-3}; $(\Delta/\sigma)_{\max}$ in final least-squares cycle 1·40. Calculations performed with *SHELX*76 program system (Sheldrick, 1976); scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

Discussion. Final coordinates of the non-H atoms are listed in Table 1* and selected interatomic distances and bond angles are in Table 2. The molecular structure and atomic numbering are shown in Fig. 1.

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* 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 54373 (28 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters for non-*H *atoms with e.s.d.'s in parentheses*

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

	x	y	z	U_{eq}(Å^2)
Cu1	−0·0648 (1)	0·5818 (1)	0·3540 (1)	0·0336 (4)
Cl1	−0·1944 (1)	0·6427 (3)	0·3820 (1)	0·0496 (7)
Cl2	−0·0686 (1)	0·6278 (3)	0·3701 (1)	0·0486 (7)
O1	−0·0723 (3)	0·4147 (6)	0·4254 (2)	0·0343 (16)
O2	−0·0643 (3)	0·3789 (6)	0·2801 (2)	0·0363 (17)
O5	−0·0661 (3)	0·7444 (7)	0·2795 (3)	0·0452 (20)
N1	−0·0204 (4)	0·2921 (7)	0·4226 (3)	0·0340 (19)
N2	−0·1256 (4)	0·2807 (8)	0·2945 (3)	0·0369 (20)
C1	0·0476 (5)	0·2970 (9)	0·4623 (4)	0·0360 (24)
C2	0·0976 (5)	0·1679 (9)	0·4645 (4)	0·0419 (28)
C3	0·0780 (5)	0·0345 (9)	0·4275 (4)	0·0446 (29)
C4	0·0094 (5)	0·0352 (9)	0·3867 (4)	0·0415 (25)
C5	−0·0409 (5)	0·1645 (9)	0·3835 (2)	0·0355 (24)
C6	−0·1167 (5)	0·1713 (9)	0·3439 (4)	0·0377 (25)
C7	−0·1771 (5)	0·0625 (9)	0·3547 (5)	0·0490 (30)
C8	−0·2499 (5)	0·0755 (8)	0·3146 (5)	0·0537 (32)
C9	−0·2583 (5)	0·1914 (9)	0·2681 (5)	0·0570 (35)
C10	−0·1958 (5)	0·2939 (9)	0·2577 (4)	0·0429 (28)
C21	−0·1295 (6)	0·7576 (9)	0·2284 (4)	0·0561 (34)
Cu2	0·5772 (1)	0·5292 (1)	0·1149 (1)	0·0367 (4)
Cl3	0·4512 (1)	0·6067 (3)	0·1458 (1)	0·0475 (6)
Cl4	0·7117 (1)	0·5689 (3)	0·1319 (1)	0·0555 (8)
O3	0·5808 (3)	0·3529 (6)	0·1816 (3)	0·0402 (18)
O4	0·5665 (3)	0·3425 (6)	0·0356 (3)	0·0398 (18)
O6	0·5723 (4)	0·6829 (7)	0·0377 (3)	0·0440 (20)
N3	0·5215 (4)	0·2482 (8)	0·1739 (3)	0·0368 (20)
N4	0·6233 (4)	0·2309 (8)	0·0441 (3)	0·0432 (24)
C11	0·4520 (5)	0·2581 (9)	0·2111 (4)	0·0474 (31)
C12	0·3936 (6)	0·1463 (9)	0·2056 (5)	0·0546 (36)
C13	0·4063 (7)	0·0207 (9)	0·1648 (6)	0·0600 (38)
C14	0·4774 (6)	0·0061 (9)	0·1262 (5)	0·0561 (35)
C15	0·5351 (5)	0·1217 (9)	0·1316 (4)	0·0387 (26)
C16	0·6121 (5)	0·1188 (9)	0·0937 (4)	0·0373 (25)
C17	0·6695 (6)	0·0033 (9)	0·1000 (5)	0·0522 (38)
C18	0·7388 (7)	0·0076 (8)	0·0611 (7)	0·0709 (42)
C19	0·7494 (6)	0·1239 (9)	0·0146 (6)	0·0712 (45)
C20	0·6908 (6)	0·2346 (9)	0·0055 (5)	0·0582 (35)
C22	0·6312 (6)	0·6912 (9)	−0·0176 (5)	0·0559 (36)

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

Cu1—Cl1	2·258 (3)	Cu2—Cl3	2·253 (2)
Cu1—Cl2	2·245 (2)	Cu2—Cl4	2·256 (3)
Cu1—O1	1·973 (5)	Cu2—O3	1·969 (6)
Cu1—O2	2·230 (5)	Cu2—O4	2·200 (6)
Cu1—O5	1·984 (6)	Cu2—O6	1·970 (5)
O1—N1	1·351 (8)	O3—N3	1·330 (8)
O2—N2	1·341 (8)	O4—N4	1·343 (9)
N1—C1	1·346 (10)	N3—C11	1·349 (11)
C1—C2	1·376 (11)	C11—C12	1·354 (14)
C2—C3	1·376 (12)	C12—C13	1·340 (16)
C3—C4	1·365 (11)	C13—C14	1·388 (15)
C4—C5	1·380 (11)	C14—C15	1·373 (13)
N1—C5	1·359 (10)	N3—C15	1·366 (10)
C5—C6	1·454 (10)	C15—C16	1·459 (11)
N2—C6	1·331 (10)	N4—C16	1·356 (10)
C6—C7	1·376 (12)	C16—C17	1·369 (12)
C7—C8	1·418 (13)	C17—C18	1·361 (15)
C8—C9	1·334 (14)	C18—C19	1·339 (18)
C9—C10	1·365 (13)	C19—C20	1·361 (15)
N2—C10	1·350 (10)	N4—C20	1·332 (12)
O5—C21	1·426 (10)	O6—C22	1·433 (12)
Cl1—Cu1—Cl2	147·9 (1)	Cl3—Cu2—Cl4	144·9 (1)
Cl1—Cu1—O2	109·5 (2)	Cl3—Cu2—O4	108·7 (2)
Cl2—Cu1—O2	102·4 (2)	Cl4—Cu2—O4	106·4 (2)
O1—Cu1—O5	175·3 (2)	O3—Cu2—O6	171·9 (2)
O1—Cu1—Cl1	86·7 (2)	O3—Cu2—Cl3	94·7 (2)
O1—Cu1—Cl2	95·6 (2)	O3—Cu2—Cl4	89·8 (2)
O1—Cu1—O2	82·6 (2)	O3—Cu2—O4	83·6 (2)
O5—Cu1—Cl1	90·0 (2)	O6—Cu2—Cl3	87·9 (1)
O5—Cu1—Cl2	88·9 (2)	O6—Cu2—Cl4	92·4 (1)
O5—Cu1—O2	95·4 (2)	O6—Cu2—O4	88·3 (2)
Cu1—O1—N1	119·5 (4)	Cu2—O3—N3	115·1 (4)
Cu1—O2—N2	110·7 (4)	Cu2—O4—N4	112·3 (4)
Cu1—O5—C21	123·2 (5)	Cu2—O6—C22	123·6 (4)
O1—N1—C5	119·3 (6)	O3—N3—C15	118·4 (6)
N1—C5—C6	117·3 (7)	N3—C15—C16	116·7 (7)
C5—C6—N2	118·9 (7)	C15—C16—N4	116·9 (7)
C6—N2—O2	120·2 (6)	C16—N4—O4	119·3 (6)
O1—N1—C1	118·4 (6)	O3—N3—C11	121·4 (6)
O2—N2—C10	118·8 (6)	O4—N4—C20	119·7 (7)

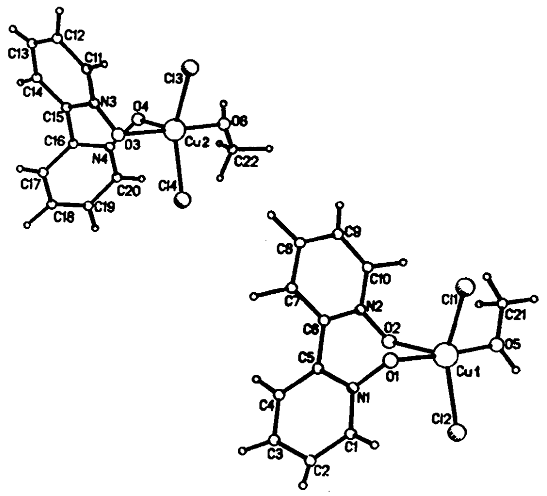

Fig. 1. The structures of the two symmetrically independent molecules of $[Cu(bpyO_2)(MeOH)Cl_2]$.

The asymmetric unit contains two symmetrically independent molecules of $[Cu(bpyO_2)(MeOH)Cl_2]$. The coordination polyhedron of each Cu^{II} atom is formed by two Cl atoms, two O atoms from a bidentate $bpyO_2$ ligand and one methanol O atom and can be described either as distorted trigonal bipyramidal (with respective equatorial planes formed by the Cl1, Cl2, O2 and Cl3, Cl4, O4 atoms and with apical positions occupied by the O1, O5 and O3, O6 atoms or as distorted tetragonal pyramidal (having the Cl1, Cl2, O1, O5 and Cl3, Cl4, O3, O6 atoms in respective basal planes, and the O2 and O4 atoms in apical positions). The distortion of a square pyramid toward a trigonal bipyramid can be characterized by τ-parameter values (Addison, Rao, Reedijk, van Rijn & Verschoor, 1984). The τ values of 45·7% and 45·0% for Cu1 and Cu2 indicate coordination polyhedra almost exactly intermediate between square pyramidal and trigonal bipyramidal. Similar deformations were found in $[CuCl_2(dmp)(H_2O)]$, dmp = 2,9-dimethyl-1,10-phenanthroline (Preston & Kennard, 1969) and $[Cu(terpy)X_2]$, $X = Br^-$, NCS^-, terpy = 2,6-bis(2-pyridyl)pyridine (Arriortua, Mesa, Rojo, Debaerdemaeker, Beltran-Porter, Stratemeier & Reinen, 1988). The Cu—Cl distances in Table 2 lie in the range from 2·209 (4) Å (Harlow, Wells, Watt & Simonsen, 1974) to 2·271 (10) Å (Anderson & Willett, 1971) found for $CuCl_4^{2-}$ anions and are close to corresponding values in the isomers of $[Cu_2Cl_4(bpyO_2)_2]$ (Baran, Koman, Valigura & Mrozinski, 1991).

The structure is held together by van der Waals interactions and hydrogen bonds; short intermolecular contacts Cl3···C8, Cl4···C22 and O5···O2 correspond to the sum of van der Waals radii of the atoms involved (Huheey, 1983).

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A Comparison of Phosphido-Bridged Triangular Rhenium Carbonyl Derivatives with 44, 46 and 48 Valence Electron Counts

By Hans-Jürgen Haupt, Ulrich Flörke and Harald Schnieder

*Anorganische und Analytische Chemie, Universität-GH-Paderborn, D-*4790 *Paderborn,*
Warburger Straße 100, *Germany*

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Abstract. Hexacarbonyl-tris(μ-cyclohexylphosphido)-bis(μ_3-hydrido)-*triangulo*-trirhenium(3*Re*–*Re*), $C_{42}H_{68}O_6P_3Re_3$, $Re_3(CO)_6(\mu_3\text{-}H)_2[\mu\text{-}P(C_6H_{11})_2]_3$ (I), M_r = 1320·5, monoclinic, $P2_1/n$, a = 10·361 (2), b = 19·729 (4), c = 23·254 (5) Å, β = 92·85 (2)°, U = 4747·5 Å^3, Z = 4, D_x = 1·847 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 7·88 mm^{-1}, F(000) = 2552, T = 298 (1) K, R = 0·0688 for 4169 unique reflections. The molecular structure has a central Re_3 ring which has three edge-bridging μ-PCy_2 groups (Cy = cyclohexyl) and two μ_3-H ligands. The mean value of the metal–metal bonds is 2·756 (2) Å, the corresponding angles 60·0°. Hexacarbonyl-tris(μ-diphenylmethylphosphido)-(μ_3-hydrido)-*triangulo*-rhenium(3*Re*–*Re*), $C_{27}H_{25}O_6P_4Re_3$, $Re_3(CO)_6(\mu_3\text{-}H)(\mu_3\text{-}P)[\mu\text{-}P(C_6H_5)(CH_3)]_3$ (II), M_r = 1129·0, monoclinic, $P2_1/a$, a = 15·477 (6), b = 12·553 (4), c = 18·109 (6) Å, β = 114·22 (2)°, U = 3208·6 Å^3, Z = 4, D_x = 2·337 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 11·68 mm^{-1}, F(000) = 2084, T = 296 (1) K, R = 0·0741 for 3008 unique reflections. The central Re_3 ring is edge bridged by three μ-PPhMe groups (Ph = phenyl, Me = methyl) and capped by one μ_3-H and one μ_3-P ligand. The mean Re—Re bond distance is 2·804 (2) Å and the enclosed angles are 58·8, 60·5 and 60·7°. Hexacarbonyl-tris(μ-dicyclohexylphosphido)-(μ_3-hydrido)-(μ_3-phosphino)-*triangulo*-rhenium(3*Re*–*Re*), $C_{42}H_{67}O_6P_4Re_3$, $Re_3(CO)_6(\mu_3\text{-}H)(\mu_3\text{-}P)[\mu\text{-}P(C_6H_{11})_2]_3$ (III), M_r = 1351·5, monoclinic, $P2_1/n$, a = 10·083 (2), b = 21·220 (6), c = 22·441 (7) Å, β = 100·43 (2)°, U = 4722·2 Å^3, Z = 4, D_x = 1·901 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 7·95 mm^{-1}, F(000) = 2612, T = 298 (1) K, R = 0·0645 for 4766 unique reflections. The central molecular fragment is an Re_3 ring capped by one μ_3-H and one μ_3-P ligand, the Re—Re bonds are bridged by three μ-PCy_2 groups. The mean Re—Re bond distance is 2·815 (1) Å and the enclosed angles are 59·6, 60·1 and 60·3°. Nonacarbonyl-tris(μ-dicyclohexylphosphido)-*triangulo*-rhenium(3*Re*–*Re*), $C_{45}H_{66}O_9P_3Re_3$, $Re_3(CO)_9[\mu\text{-}P(C_6H_{11})_2]_3$ (IV), M_r = 1402·5, orthorhombic, $Pbcn$, a = 11·790 (3), b = 24·005 (8), c = 17·833 (4) Å, U = 5046·8 Å^3, Z = 4, D_x = 1·846 Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, μ = 7·42 mm^{-1}, F(000) = 2712, T = 296 (1) K, R = 0·0595 for 2869 unique intensities. The central Re_3 ring is edge bridged by three μ-PCy_2 groups, each Re atom has three CO ligands. The mean Re—Re bond distance is 2·913 (1) Å and the angles are 59·9 (×2) and 60·3°.

Introduction. As a requirement of the so-called effective atomic number (EAN) rule, Re atoms need, in a three-membered ring of three σ Re—Re bonds, 48 valence electrons (VE) (Lauher, 1978). Furthermore, this means that such a rhenium ring is unifold unsaturated with 46 and twofold unsaturated with 44 VE. The last VE count for a three-membered transition metal ring was obtained for the first time in $Re_3(CO)_6(\mu_3\text{-}H)_2(\mu\text{-}PPh_2)_3$ (Haupt, Flörke & Balsaa,

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