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Structure of Diperchloratobis(2,2′,2″-tripyridylamine)copper(II)

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Abstract. $[Cu\{(C_5H_4N)_3N\}_2(ClO_4)_2]$, $M_r = 759.04$, monoclinic, $P2_1/n$, $a = 18.638$ (2), $b = 8.552$ (3), $c = 9.822$ (1) Å, $\beta = 91.44$ (1)°, $V = 1565.1$ (6) Å^3, $Z = 2$, $D_m = 1.61$ (1), $D_x = 1.611$ Mg m^{-3}, graphite monochromator, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 0.97$ mm^{-1}, $F(000) = 774$, $T = 293$ K, $R = 0.049$ and $wR = 0.063$ for 2495 unique observed reflections with $I > 3\sigma(I)$. The metal ion is six-coordinate and lies on a crystallographic centre of inversion so that the complex itself possesses inversion symmetry and is, therefore, a *trans* complex. The coordination geometry can be described as tetragonally distorted octahedral. The centrosymmetric tripyridylamine molecules, acting as bidentate ligands, coordinate in equatorial positions through the N atoms of two pyridyl rings of each molecule, with Cu—N bonds of 2.006 (3) and 1.992 (3) Å. The steric constraints imposed on the tripyridylamine molecules by the strictly planar equatorial coordination of the N atoms are manifested by an intraligand angle of 84.5 (1)° and a puckering of the two coordinated pyridyl rings in each molecule. The centrosymmetrically related perchlorate groups weakly coordinate in axial positions, with a small deviation of 6.4°, through one O atom, with Cu—O distances of 2.593 (8) Å and Cu—O—Cl angle of 136.9 (4)°.

Experimental. Dark yellowish-brown prismatic crystals, density measured by flotation in carbon tetrachloride/bromoform. Single crystal, prepared according to literature procedures (Wibaut & La Bastide, 1933; McWhinnie, Kulasingam & Draper, 1966), of average dimensions 0.3 × 0.3 × 0.2 mm used for X-ray data collection on a CAD-4 Nonius four-circle diffractometer, $\omega/2\theta$ scan mode. 4543 unique reflections measured within the range $0 \leq h \leq 26$, $0 \leq k \leq 12$, $-13 \leq l \leq 13$, up to $(\sin\theta)/\lambda = 0.7027$ Å^{-1}. Of these, 2495 considered observed with $I > 3\sigma(I)$. Three standard reflections showed statistical variations within 3%. Unit-cell parameters refined by least-squares fitting procedure using 25 reflections with $26.4 \leq 2\theta \leq 45.78°$. Lorentz–polarization and empirical absorption ($A_{\max} = 0.598$, $A_{\min} = 0.581$) corrections were applied. Structure solved using direct-methods program *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Full-matrix least-squares refinement on F for non-H atoms with anisotropic temperature factors. H atoms, in calculated positions (C—H = 0.89 Å), included in structure factor calculations with equivalent isotropic temperature factors of bonded C atoms, but not refined; 223 parameters varied, overdetermination ratio 9.2, $S = 2.52$, $R = 0.049$ and $wR = 0.063$ with $w = w_1w_2$ [$w_1 = 1$ if $\sin\theta > 0.40$, otherwise $w_1 = (\sin\theta)/0.40$, and $w_2 = 1$ if $|F_o| < 14.0$, otherwise $w_2 = 14.0/|F_o|$], $(\Delta/\sigma)_{\max} = 0.09$ for temperature factors, mean $\Delta/\sigma = 0.009$; final difference Fourier map excursions within -0.48 and 0.92 e Å^{-3}. Scattering factors for non-H atoms taken from Cromer & Mann (1968) and for H atoms from Stewart, Davidson & Simpson (1965). Dispersion corrections for scattering factors of Cu and Cl atoms taken from *International Tables for X-ray Crystallography* (1974, Vol IV). Calculations performed with *XRAY*76 (Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1976) on an IBM4361 computer at the Faculty Computer Centre. Final atomic coordinates and equivalent isotropic thermal parameters are listed in Table 1, with selected bond distances and angles in Table 2.* The atom-numbering scheme is given in the *ORTEP*II plot (Johnson, 1976) of the asymmetric unit in Fig. 1. The tetragonally distorted octahedral coordination of the metal ion

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* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond distances and angles, and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54830 (33 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. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic temperature factors* (Å^2 $\times$ 10^3), *with e.s.d.'s in parentheses*

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

	x	y	z	$U_{\rm eq}$
Cu	0	0	5000	37
N(1)	−1578 (1)	−958 (4)	5693 (3)	38
N(11)	−896 (2)	1276 (4)	5171 (3)	41
C(11)	−1540 (2)	583 (5)	5273 (4)	38
C(12)	−2172 (2)	1433 (6)	4981 (5)	53
C(13)	−2131 (3)	2982 (7)	4695 (6)	69
C(14)	−1469 (3)	3724 (6)	4727 (6)	65
C(15)	−870 (2)	2838 (5)	4947 (5)	53
N(12)	−386 (1)	−1220 (4)	6546 (3)	39
C(21)	−1073 (2)	−1702 (5)	6555 (3)	37
C(22)	−1279 (2)	−2911 (6)	7410 (5)	51
C(23)	−784 (3)	−3543 (6)	8318 (5)	57
C(24)	−95 (2)	−2955 (6)	8387 (4)	51
C(25)	80 (2)	−1828 (6)	7496 (4)	48
N(13)	−2718 (2)	−1588 (5)	6551 (4)	53
C(31)	−2271 (2)	−1732 (5)	5516 (4)	39
C(32)	−2413 (2)	−2545 (6)	4346 (4)	47
C(33)	−3059 (2)	−3345 (6)	4247 (5)	58
C(34)	−3523 (2)	−3269 (6)	5303 (6)	60
C(35)	−3337 (2)	−2378 (7)	6411 (5)	59
Cl	684.2 (5)	2543.2 (15)	7808.7 (11)	54
O(1)	684 (3)	2051 (12)	6481 (5)	164
O(2)	25 (2)	2770 (12)	8283 (6)	153
O(3)	1172 (3)	3722 (11)	8158 (7)	147
O(4)	1047 (7)	1378 (12)	8482 (14)	234

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

Metal coordination			
Cu—N(11)	2.006 (3)	N(11)—Cu—N(12)	84.5 (1)
Cu—N(12)	1.992 (3)	N(11)—Cu—O(1)	89.1 (2)
Cu—O(1)	2.593 (8)	N(12)—Cu—O(1)	96.2 (2)
Tripyridylamine molecule*			
N(1)—C(11)	1.383 (5)	C(11)—N(1)—C(21)	125.0 (3)
N(1)—C(21)	1.403 (4)	C(11)—N(1)—C(31)	116.6 (3)
N(1)—C(31)	1.458 (4)	C(21)—N(1)—C(31)	116.4 (3)

	$m = 1$	$m = 2$	$m = 3$
N(1*m*)—C(*m*1)	1.345 (5)	1.344 (4)	1.336 (5)
N(1*m*)—C(*m*5)	1.355 (6)	1.362 (5)	1.341 (6)
C(*m*1)—N(1*m*)—C(*m*5)	118.9 (3)	118.0 (3)	115.3 (4)
N(1*m*)—C(*m*1)—C(*m*2)	120.0 (4)	120.6 (3)	125.1 (3)
C(*m*4)—C(*m*5)—N(1*m*)	122.7 (4)	123.9 (4)	124.3 (4)
N(1)—C(*m*1)—N(1*m*)	119.6 (3)	118.8 (3)	115.8 (3)
N(1)—C(*m*1)—C(*m*2)	120.3 (3)	120.6 (3)	119.1 (3)

* m = 1,2,3 for pyridyl py(1), py(2), py(3) rings respectively; py(1) and py(2) are metal coordinated.

showing the main structural features of the complex is illustrated in Fig. 2.

Related literature. The tripod-like tripyridylamine [(py)$_3$N] molecule has been known to coordinate both as a bidentate or as a tridentate ligand, *via* the pyridyl N atoms (McWhinnie, Kulasingam & Draper, 1966; Kulasingam & McWhinnie, 1967; Dedert, Thompson, Ibers & Marks, 1982; Keene, Snow, Stephenson & Tiekink, 1988). In the perchlorate metal complexes [M(py)$_3$N].ClO$_4$ with M = Fe, Co, Kucharski, McWhinnie & White (1978) reported a preference of the (py)$_3$N molecule for a tridentate ligation and the perchlorate ion non-coordinated. The occurrence of the two isomers of the copper perchlorate analogue, in which the (py)$_3$N ligand coordinates in the bi- and tridentate modes, was suggested by McWhinnie, Kulasingam & Draper (1966) from spectroscopic studies. This work describes the structure of the isomer with the ligand in the bidentate mode and the perchlorate group entering the coordination sphere of the metal ion. The relatively large Cu—O bond of the unidentate weakly coordinated perchlorate ion can be compared with those reported for axial perchlorate O atoms in other Cu$^{\rm II}$ complexes with D_{4h} symmetry (Lewis & Hodgson, 1974; Tasker & Sklar, 1975; Fawcett, Rudich, Toby, Lalancette, Potenza & Schugar, 1980; Potenza, Potenza & Schugar, 1988).

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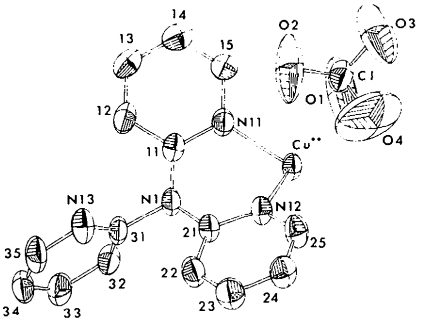

Fig. 1. Asymmetric unit [Cu{(py)$_3$N}ClO$_4$] with numbering scheme and thermal ellipsoids at 50% probability level. H atoms omitted.

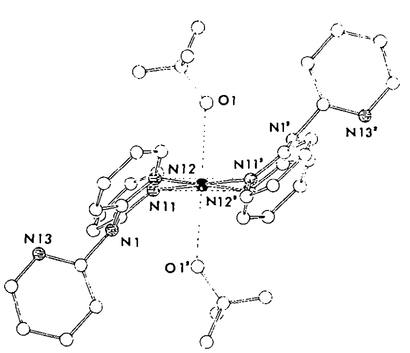

Fig. 2. Formula unit showing the tetragonally distorted octahedral coordination about the metal ion. Primed numbers denote centrosymmetrically related atoms.

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Structure of (Benzo[*c*]cinnoline-*N'*)pentacarbonyltungsten

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Abstract. $[W(C_{12}H_8N_2)(CO)_5]$, $M_r = 504.11$, triclinic, $P\bar{1}$, $a = 7.152$ (3), $b = 10.124$ (4), $c = 12.170$ (6) Å, $\alpha = 92.91$ (4), $\beta = 99.49$ (3), $\gamma = 107.62$ (3)°, $V = 823.7$ (6) Å^3, $Z = 2$, $D_x = 2.03$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 71.9$ cm^{-1}, $F(000) = 476$, $T = 298$ K, $R = 0.043$, $wR = 0.049$ for 3060 reflections with $I > 3\sigma(I)$. The compound is a mononuclear complex of benzo[*c*]cinnoline involving the coordination of the W metal to the lone pair of one N atom (N1). The W···N2 separation is 3.01 Å. The N1—N2 distance is 1.31 (1) Å, intermediate between that of a double bond (1.25 Å) and a single bond (1.40 Å). The benzo[*c*]cinnoline ligand is essentially planar with a 1° twist angle between the phenyl rings.

Experimental. The title compound was obtained as an unexpected product from the reaction of the Fischer carbene complex $(CO)_5W{=}C(OMe)(Me)$ with benzo[*c*]cinnoline which can be viewed as a rigidly fixed form of *cis*-azobenzene. Red prisms of the complex, recrystallized from a concentrated solution of CH_2Cl_2 at 253 K, had NMR data identical to an authentic sample prepared independently *via* a previously published route (Kooti & Nixon, 1976). A single crystal of dimensions 0.15 × 0.31 × 0.25 mm was mounted on a glass fiber and coated with epoxy cement. Data collection was performed on a Nicolet–Siemens $P2_1$ diffractometer (Mo $K\alpha$ radiation, graphite monochromator). From the least-squares fit of the angular settings of 25 reflections ($20 < 2\theta < 25°$) final unit-cell parameters were obtained. The intensities were collected at 298 K using the θ–2θ scan technique with a variable rate of 1 to 15° min^{-1} in the range $3 \leq 2\theta \leq 55°$. The index ranges were $10 \leq h \leq 0$, $-19 \leq k \leq 19$, $-21 \leq l \leq 21$. The three standard reflections measured every 97 reflections showed only 0.5% loss in intensity during the total exposure time of 255 h. Of 4095 reflections collected,

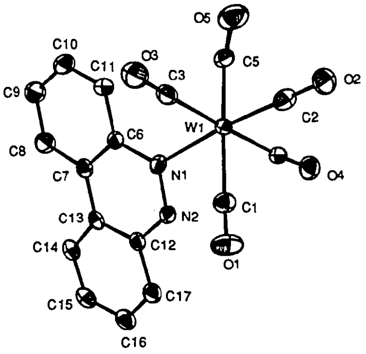

Fig. 1. *ORTEP* (Johnson, 1965) drawing of the title compound with the atom-numbering scheme. H atoms omitted. Ellipsoids are drawn at the 50% probability level.

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