C(1)—N(1)—C(2)	125 (2)	C(3)—N(2)—C(4)	123 (2)
C(9)—N(3)—C(10)	123 (2)	C(11)—N(4)—C(12)	121 (2)
N(1)—C(1)—C(4)	116 (2)	N(1)—C(1)—C(5)	120 (2)
C(4)—C(1)—C(5)	123 (2)	N(1)—C(2)—C(3)	116 (2)
N(1)—C(2)—C(6)	119 (2)	C(3)—C(2)—C(6)	125 (2)
N(2)—C(3)—C(2)	120 (2)	N(2)—C(3)—C(7)	120 (2)
C(2)—C(3)—C(7)	120 (2)	N(2)—C(4)—C(1)	120 (2)
N(2)—C(4)—C(8)	120 (2)	C(1)—C(4)—C(8)	120 (2)
N(3)—C(9)—C(12)	118 (2)	N(3)—C(9)—C(13)	117 (2)
C(12)—C(9)—C(13)	125 (2)	N(3)—C(10)—C(11)	119 (2)
N(3)—C(10)—C(14)	119 (2)	C(11)—C(10)—C(14)	122 (2)
N(4)—C(11)—C(10)	120 (1)	N(4)—C(11)—C(15)	117 (2)
C(10)—C(11)—C(15)	123 (2)	N(4)—C(12)—C(9)	119 (2)
N(4)—C(12)—C(16)	119 (2)	C(9)—C(12)—C(16)	122 (2)

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $x, 1 + y, z$.

Data collection and cell refinement used *CRYSTAL LOGIC Diffractometer Control Software* (Strouse, 1990). Structure solution was by direct methods and refinement by full-matrix least squares using *SHELXTL-Plus* (Sheldrick, 1990). The non-H atoms were refined anisotropically and H atoms were not located. Corrections were applied for absorption (empirical *via* ψ scans), Lorentz and polarization effects, and real and imaginary anomalous dispersion (Cromer, 1974). An isotropic extinction parameter was calculated by a method similar to Larson (1970). Structure solution, refinement and the calculation of derived results were performed using *SHELXTL-Plus*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SZ1036). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A Condensed Dialkoxide Complex of Copper(II), $[(CH_3)_2NCH_2CH_2N(CH_3)_2]$-$Cu[\{OC(CF_3)_2\}_2O]$

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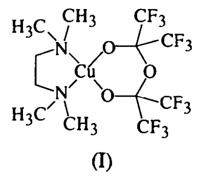
Abstract

The title complex, [1,1,1,5,5,5-hexafluoro-3-oxa-2,4-bis(trifluoromethyl)-2,4-pentanediolato-*O*,*O*′]-(*N*,*N*,*N*′,*N*′-tetramethylethylenediamine-*N*,*N*′)copper(II), $[Cu(C_6F_{12}O_3)(C_6H_{16}N_2)]$, contains a condensed dialkoxide ligand forming a markedly non-planar six-membered chelate ring with a skew-boat conformation. There are two independent molecules in the unit cell. In molecule 1, the absolute conformations of the tetramethylethylenediamine and dialkoxide rings are both λ and in molecule 2, they are δ and λ, respectively. The mean O—Cu—O angle is 92.6 (3)°, with a mean Cu—O bond length of 1.893 (3) Å.

Comment

We have developed a rational synthetic approach to complexes of the versatile *gem*-diol ligand $(CF_3)_2C(OH)_2$ (Bradford, Hynes, Payne & Willis, 1990). It can either coordinate as a monodentate alkoxide (Hynes, Payne & Willis, 1990) or act as the chelating dialkoxide $[\text{-O—C}(CF_3)_2\text{—O-}]^{2-}$ forming a four-membered ring (Bradford, Hynes, Payne & Willis, 1990; Hynes, Willis & Payne, 1992). Modinos & Woodward (1975) described the first complexes of the condensed dialkoxide $[\text{-O—C}(CF_3)_2\text{—O—C}(CF_3)_2\text{—O-}]^{2-}$ (OCOCO), each of which contained a six-membered chelate ring coordinated to Pt^{II}. We report herein the structure of $[(CH_3)_2NCH_2CH_2N(CH_3)_2]Cu(OCOCO)$, (I), the first example of a condensed dialkoxide complex of a first-row transition metal.



(I)

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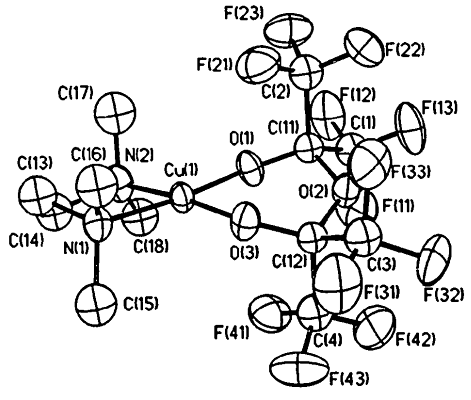
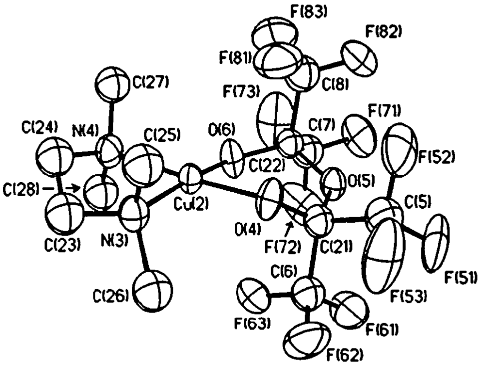
The crystal structure of (I) consists of discrete molecules, with two independent species in the unit cell. The shortest intermolecular distances are 2.45 between H(23*B*) and F(51)(1 + *x*, *y*, *z*), 2.93 between F(62) and F(83)(*x*, *y*, 1 + *z*), and 2.63 Å between H(17*C*) and H(28*B*)(*x*, *y*, 1 + *z*). Perspective views of both molecules showing the atom-numbering schemes are presented in Fig. 1.



Molecule 1



Molecule 2

Fig. 1. Perspective views of molecules 1 and 2 of (I), showing the atom-numbering schemes and 40% displacement ellipsoids.

Each Cu atom has a slightly distorted square-planar coordination geometry, with the O—Cu—O planes twisted by 5.5 (3) and 8.7 (4)° from the N—Cu—N planes in molecules 1 and 2, respectively. The tetramethylethylenediamine (TMED) chelate rings adopt *gauche* conformations and the OCOCO rings skew boat conformations. In molecule 1, the absolute conformations of the TMED and OCOCO rings are both λ and in molecule 2, they are δ and λ, respectively (IUPAC Information Bulletin No. 33, 1970). The geometries of the TMED rings are normal, with a mean Cu—N distance of 2.017 (4) Å and a mean bite angle of 86.2 (5)°.

The six-membered OCOCO chelate rings are nonplanar, with approximate twofold axes passing through the Cu and ethereal O atoms. The mean bite angle at the metal atom of 92.6 (3)° is noticeably larger than that of 86.5 (4)° found in the Pt complex (Modinos & Woodward, 1975). The mean Cu—O distance is 1.893 (3) Å. As found by Modinos & Woodward, the mean alkoxide O—C(CF$_3$)$_2$ bond length of 1.332 (9) Å is noticeably shorter than the mean ethereal O—C(CF$_3$)$_2$ value of 1.422 (5) Å (Δ/σ = 8.7), a difference ascribed to donation of the O-atom lone pair of electrons into the antibonding orbitals of the C(CF$_3$)$_2$ entity.

With constraints applied, the CF$_3$ groups behaved well during the refinement, giving C—F distances ranging from 1.293 (8) to 1.342 (8) Å. The F—C—F angles range from 105.3 (6) to 108.3 (7)° and are significantly smaller than the C—C—F angles, which range from 108.8 (6) to 115.7 (6)°.

Experimental

The title complex was prepared according to the method of Bradford, Hynes, Payne & Willis (1990). A sample was recrystallized from dichloromethane. Elemental analysis: calculated for $C_{12}H_{16}CuF_{12}N_2O_3$: C 27.32, H 3.04, N 5.31, Cu 11.95%; found: C 27.47, H 2.94, N 5.41, Cu 12.30%. The density D_m was measured by flotation in a 1,2-dibromoethane/hexanes solution.

Crystal data

[Cu(C$_6$F$_{12}$O$_3$)(C$_6$H$_{16}$N$_2$)]
M_r = 527.80
Triclinic
$P\bar{1}$
a = 9.9019 (14) Å
b = 12.2972 (15) Å
c = 8.9716 (12) Å
α = 108.28 (2)°
β = 110.66 (2)°
γ = 86.16 (2)°
V = 969.4 (2) Å^3
Z = 2
D_x = 1.808 Mg m^{-3}
D_m = 1.828 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 20 reflections
θ = 15–17°
μ = 1.255 mm^{-1}
T = 293 (2) K
Block
0.38 × 0.21 × 0.19 mm
Violet

Data collection

Enraf–Nonius CAD-4*F* diffractometer
$\theta/2\theta$ scans with moving backgrounds
Absorption correction: by integration from crystal shape
T_{min} = 0.729, T_{max} = 0.886
6781 measured reflections

6781 independent reflections
5802 observed reflections [$I > 2\sigma(I)$]
θ_{max} = 24.97°
$h = -11 \rightarrow 11$
$k = -14 \rightarrow 14$
$l = -10 \rightarrow 10$
4 standard reflections frequency: 180 min intensity decay: 10.3%

Refinement

Refinement on F^2
$R(F)$ = 0.0401
$wR(F^2)$ = 0.1022
S = 1.035

Extinction correction: *SHELXL*93
Extinction coefficient: 0.0098 (9)

6780 reflections
423 parameters
H atoms riding with C—H = 0.95 Å
$w = 1/[\sigma^2(F_o^2) + (0.0446P)^2 + 1.0987P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.024$
$\Delta\rho_{\max} = 0.448$ e Å^{-3}
$\Delta\rho_{\min} = -0.464$ e Å^{-3}

Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983) parameter = 0.200 (13)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

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

	x	y	z	$U_{\rm eq}$
Cu(1)	−0.00002 (5)	0.00000 (4)	−0.00003 (6)	0.0390 (2)
Cu(2)	0.05195 (5)	−0.48537 (5)	−0.51427 (6)	0.0410 (2)
O(1)	0.1729 (4)	−0.0025 (4)	0.1779 (5)	0.0490 (10)
O(2)	0.3367 (5)	0.0437 (4)	0.0670 (5)	0.0461 (10)
O(3)	0.1001 (4)	0.0334 (3)	−0.1269 (5)	0.0479 (9)
O(4)	−0.0586 (4)	−0.5778 (3)	−0.4620 (5)	0.0530 (10)
O(5)	−0.2902 (5)	−0.5158 (4)	−0.5872 (6)	0.0507 (11)
O(6)	−0.1154 (4)	−0.4256 (4)	−0.6397 (5)	0.0581 (11)
N(1)	−0.1885 (5)	−0.0102 (4)	−0.1912 (6)	0.0514 (12)
N(2)	−0.1196 (6)	−0.0242 (5)	0.1286 (7)	0.0607 (14)
N(3)	0.2368 (6)	−0.5289 (4)	−0.3621 (7)	0.0512 (12)
N(4)	0.1805 (5)	−0.4036 (5)	−0.5814 (6)	0.0550 (13)
C(11)	0.2987 (6)	−0.0211 (5)	0.1533 (7)	0.0434 (13)
C(12)	0.2300 (6)	0.0866 (4)	−0.0522 (7)	0.0407 (13)
C(13)	−0.2967 (8)	−0.0627 (6)	−0.1527 (8)	0.070 (2)
C(14)	−0.2727 (8)	−0.0102 (7)	0.0294 (9)	0.075 (2)
C(15)	−0.2233 (8)	0.1044 (6)	−0.2050 (9)	0.075 (2)
C(16)	−0.1781 (7)	−0.0858 (6)	−0.3531 (8)	0.070 (2)
C(17)	−0.0951 (9)	−0.1382 (7)	0.1484 (11)	0.096 (2)
C(18)	−0.0807 (8)	0.0615 (6)	0.2943 (9)	0.084 (2)
C(21)	−0.1868 (7)	−0.5468 (5)	−0.4526 (8)	0.051 (2)
C(22)	−0.2461 (7)	−0.4799 (5)	−0.7006 (8)	0.049 (2)
C(23)	0.3550 (9)	−0.4593 (7)	−0.3513 (9)	0.077 (2)
C(24)	0.3312 (9)	−0.4362 (7)	−0.5069 (10)	0.079 (2)
C(25)	0.2547 (8)	−0.6520 (6)	−0.4262 (9)	0.076 (2)
C(26)	0.2359 (8)	−0.5067 (6)	−0.1898 (9)	0.076 (2)
C(27)	0.1390 (7)	−0.4359 (6)	−0.7656 (8)	0.073 (2)
C(28)	0.1685 (8)	−0.2792 (6)	−0.5154 (9)	0.079 (2)
C(1)	0.4208 (6)	0.0174 (5)	0.3280 (7)	0.0604 (14)
F(11)	0.4192 (5)	0.1279 (4)	0.4029 (5)	0.099 (2)
F(12)	0.4069 (4)	−0.0361 (4)	0.4309 (5)	0.0910 (14)
F(13)	0.5509 (4)	−0.0014 (5)	0.3194 (5)	0.0881 (14)
C(2)	0.3102 (6)	−0.1486 (5)	0.0646 (7)	0.0575 (14)
F(21)	0.1970 (4)	−0.1859 (3)	−0.0776 (5)	0.0830 (11)
F(22)	0.4246 (5)	−0.1721 (4)	0.0221 (7)	0.097 (2)
F(23)	0.3110 (5)	−0.2139 (3)	0.1562 (6)	0.0952 (13)
C(3)	0.2961 (6)	0.0739 (5)	−0.1889 (7)	0.0563 (13)
F(31)	0.2097 (5)	0.1069 (4)	−0.3151 (5)	0.0942 (13)
F(32)	0.4220 (5)	0.1320 (4)	−0.1319 (6)	0.0832 (13)
F(33)	0.3228 (5)	0.0345 (3)	−0.2519 (5)	0.0782 (12)
C(4)	0.2179 (7)	0.2157 (5)	0.0374 (7)	0.0629 (15)
F(41)	0.1424 (4)	0.2280 (3)	0.1375 (5)	0.0843 (11)
F(42)	0.3433 (5)	0.2720 (4)	0.1298 (7)	0.105 (2)
F(43)	0.1482 (6)	0.2698 (4)	−0.0721 (6)	0.106 (2)
C(5)	−0.2634 (7)	−0.6500 (6)	−0.4492 (9)	0.076 (2)
F(51)	−0.3887 (5)	−0.6303 (4)	−0.4264 (8)	0.108 (2)
F(52)	−0.2911 (6)	−0.7342 (4)	−0.5940 (7)	0.108 (2)
F(53)	−0.1835 (6)	−0.6917 (5)	−0.3289 (9)	0.137 (2)
C(6)	−0.1731 (7)	−0.4441 (5)	−0.2925 (8)	0.065 (2)
F(61)	−0.2982 (5)	−0.4025 (4)	−0.2855 (6)	0.097 (2)
F(62)	−0.1055 (5)	−0.4706 (5)	−0.1546 (5)	0.1035 (15)
F(63)	−0.0938 (4)	−0.3584 (3)	−0.2858 (5)	0.0810 (11)
C(7)	−0.3621 (7)	−0.3942 (6)	−0.7473 (8)	0.074 (2)
F(71)	−0.4962 (5)	−0.4382 (4)	−0.8171 (6)	0.100 (2)
F(72)	−0.3601 (6)	−0.3101 (4)	−0.6131 (7)	0.126 (2)
F(73)	−0.3411 (6)	−0.3489 (6)	−0.8543 (8)	0.139 (2)
C(8)	−0.2633 (8)	−0.5847 (6)	−0.8585 (9)	0.077 (2)
F(81)	−0.1524 (5)	−0.6524 (4)	−0.8224 (6)	0.113 (2)
F(82)	−0.3809 (6)	−0.6470 (5)	−0.9105 (7)	0.120 (2)
F(83)	−0.2566 (7)	−0.5557 (6)	−0.9827 (6)	0.136 (2)

Table 2. *Selected geometric parameters (Å, °)*

Cu(1)—O(1)	1.891 (4)	O(6)—C(22)	1.344 (7)
Cu(1)—O(3)	1.895 (4)	N(1)—C(13)	1.476 (8)
Cu(1)—N(2)	2.012 (5)	N(2)—C(14)	1.493 (9)
Cu(1)—N(1)	2.019 (5)	N(3)—C(23)	1.454 (9)
Cu(2)—O(4)	1.890 (4)	N(4)—C(24)	1.489 (9)
Cu(2)—O(6)	1.895 (4)	C(11)—C(2)	1.537 (8)
Cu(2)—N(3)	2.016 (5)	C(11)—C(1)	1.554 (8)
Cu(2)—N(4)	2.022 (5)	C(12)—C(3)	1.546 (8)
O(1)—C(11)	1.334 (7)	C(12)—C(4)	1.557 (8)
O(2)—C(11)	1.417 (7)	C(13)—C(14)	1.493 (10)
O(2)—C(12)	1.422 (7)	C(21)—C(5)	1.535 (9)
O(3)—C(12)	1.327 (6)	C(21)—C(6)	1.557 (9)
O(4)—C(21)	1.325 (7)	C(22)—C(7)	1.543 (9)
O(5)—C(21)	1.420 (7)	C(22)—C(8)	1.553 (9)
O(5)—C(22)	1.429 (7)	C(23)—C(24)	1.447 (10)
O(1)—Cu(1)—O(3)	92.8 (2)	C(14)—N(2)—Cu(1)	106.1 (4)
N(2)—Cu(1)—N(1)	86.6 (2)	C(23)—N(3)—Cu(2)	107.9 (4)
O(4)—Cu(2)—O(6)	92.3 (2)	C(24)—N(4)—Cu(2)	107.2 (4)
N(3)—Cu(2)—N(4)	85.9 (2)	O(1)—C(11)—O(2)	118.0 (5)
C(11)—O(1)—Cu(1)	121.1 (3)	O(3)—C(12)—O(2)	118.1 (4)
C(11)—O(2)—C(12)	121.6 (5)	N(1)—C(13)—C(14)	108.2 (6)
C(12)—O(3)—Cu(1)	120.8 (3)	N(2)—C(14)—C(13)	109.0 (6)
C(21)—O(4)—Cu(2)	120.8 (4)	O(4)—C(21)—O(5)	118.8 (5)
C(21)—O(5)—C(22)	120.8 (5)	O(6)—C(22)—O(5)	117.2 (5)
C(22)—O(6)—Cu(2)	121.7 (4)	C(24)—C(23)—N(3)	112.1 (6)
C(13)—N(1)—Cu(1)	106.0 (4)	C(23)—C(24)—N(4)	112.1 (6)

Cu(1)—O(1)—C(11)—O(2)	49.1 (6)
O(1)—C(11)—O(2)—C(12)	−27.9 (7)
C(11)—O(2)—C(12)—O(3)	−24.1 (7)
O(2)—C(12)—O(3)—Cu(1)	49.7 (6)
C(12)—O(3)—Cu(1)—O(1)	−25.8 (4)
O(3)—Cu(1)—O(1)—C(11)	−22.3 (4)
Cu(2)—O(4)—C(21)—O(5)	50.8 (7)
O(4)—C(21)—O(5)—C(22)	−21.4 (8)
C(21)—O(5)—C(22)—O(6)	−30.6 (8)
O(5)—C(22)—O(6)—Cu(2)	49.2 (7)
C(22)—O(6)—Cu(2)—O(4)	−20.3 (5)
O(6)—Cu(2)—O(4)—C(21)	−28.3 (5)

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *SDP-Plus* (Frenz, 1985). Program(s) used to solve structure: *MULTAN*11/82 (Main *et al.*, 1982). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990). Software used to prepare material for publication: *SHELXL*93.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, least-squares-planes data and torsion angles have been deposited with the IUCr (Reference: FG1118). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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catena-Poly[{di-μ-nitrato-1:2κ^4*O*-bis[(triphenylphosphine-*P*)copper(I)]}-μ-4,4′-bipyridyl-*N*:*N*′] Tetrahydrofuran Solvate

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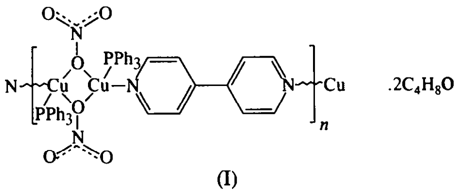
Abstract

A copper(I) complex with triphenylphosphine and 4,4′-bipyridine results in a one-dimensional polymer, $\{[Cu_2(NO_3)_2(C_{18}H_{15}P)_2(C_{10}H_8N_2)].2C_4H_8O\}_n$. The Cu centers are alternately bridged by nitrate counterions and bipyridine ligands. The four-membered Cu_2O_2 ring lies on an inversion center ($\frac{1}{2}-x$, $\frac{1}{2}-y$, $-z$) and the bipyridyl ligand lies on another inversion center ($\frac{1}{2}-x$, $\frac{3}{2}-y$, $-z$). The triphenylphosphine ligand coordinates to copper providing a distorted tetrahedral coordination environment, with bond lengths Cu1—P 2.168 (1), Cu—N 2.013 (3) and Cu—O 2.177 (2) and 2.147 (2) Å. The cavities between the chains contain tetrahydrofuran solvent molecules.

Comment

Copper(I) complexes of 4,4′-bipyridine have been studied with regard to the construction of supramolecular networks (MacGillivray, Subramanian & Zaworotko, 1994; Yaghi & Li, 1995). Copper(I) is an interesting metal to study due to its well defined tetrahedral coordination geometry, high lability, and potential catalytic and magnetic capabilities (Cotton & Wilkinson, 1988). A study was initiated on the role of the counterion and ancillary ligand on the network motif.

The X-ray analysis of the crystal that resulted from the complexation of nitratobis(triphenylphosphine)copper(I) with 4,4′-bipyridine in tetrahydrofuran, (I), shows that the copper(I) ions are linked by bridging nitrate anions and 4,4′-bipyridine ligands to form stair–step undulating polymer chains.



(I)

Copper(I) adopts a distorted tetrahedral geometry, with one bond to triphenylphosphine, one to 4,4′-bipyridine and two to separate bridging nitrato O atoms (Fig. 1). The tetrahydrofuran solvent molecule is disordered over two positions and occupies the space between the triphenylphosphine ligands and adjacent chains. The four-membered Cu_2O_2 ring lies about an inversion center ($\frac{1}{2}-x$, $\frac{1}{2}-y$, $-z$) and the bipyridyl ligand lies on another inversion center ($\frac{1}{2}-x$, $\frac{3}{2}-y$, $-z$). The chains run along the *b* axis and stack along a twofold screw axis antiparallel to one another (Fig. 2).

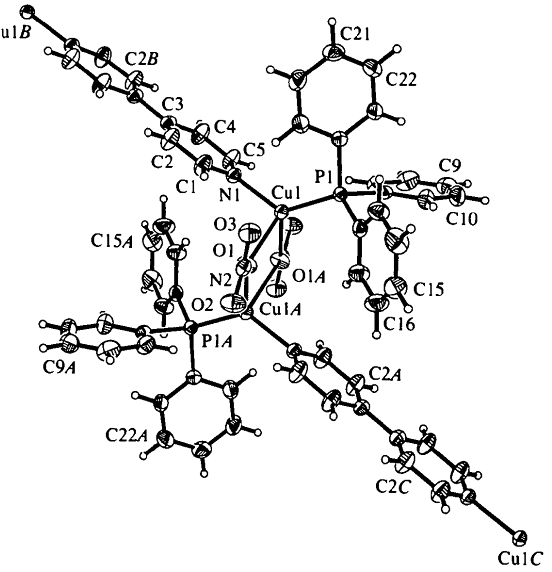


Fig. 1. An *ORTEP*II (Johnson, 1971) view of (I) showing 50% probability displacement ellipsoids for non-H atoms and circles of arbitrary size for H atoms. Symmetrically related equivalent positions for *A*, *B* and *C* are ($\frac{1}{2}-x$, $\frac{1}{2}-y$, $-z$), ($\frac{1}{2}-x$, $\frac{1}{2}-y$, $-z$) and (x, $y-1$, z), respectively.