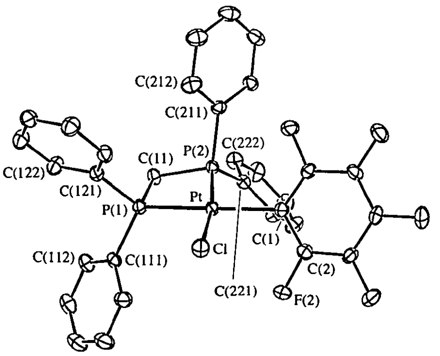

Fig. 1. Molecular structure and crystallographic numbering scheme employed for [PtCl(dppm)C_6F_5] (Johnson, 1971).

atom, a C atom from the pentafluoroaryl group and two P atoms from a bidentate dppm ligand. The deviations from the least-squares plane through the four donor atoms are significant: Cl −0·025 (1), P(1) 0·023 (1). P(2) −0·024 (1) and C(1) 0·346 (4) Å; the Pt atom lies 0·1099 (2) Å out of this plane. The distortion from ideal square-planar geometry may be related to the restricted bite distance of the bidentate ligand which imposes a P—Pt—P angle of 73·9 (1)°. As a consequence, the two angles P(1)—Pt—Cl and P(2)—Pt—C(1) are each opened up to approximately 99°. In the related complex, Pt(C_6H_5)$_2$(dppm), there is also a deviation from square-planar geometry [P—Pt—P 73 (1)°], but the Pt atom and the four donor atoms are coplanar (Braterman, Cross, Manojlovic-Muir, Muir & Young, 1975) by contrast with the present complex.

The Pt—P bond distances, Pt—P(1) 2·295 (1) and Pt—P(2) 2·224 (1) Å, are not equivalent with the shorter bond distance being *trans* to the Cl atom reflecting the greater *trans*-influence of the aryl C atom over that of the Cl atom; this effect has been reported previously for a related complex PtCl(dcy)-C_6F_5 (dcy = dicyclopentadiene) (Deacon *et al.*, 1989). The longer Pt—P bond distance is comparable to the Pt—P bond distances of 2·30 (1) Å found in Pt(C_6H_5)$_2$(dppm) (Braterman *et al.*, 1975). In order to relieve possible steric interactions between the phenyl groups bound to the dppm ligand and the C_6F_5 group, the latter is oriented such that the dihedral angle between it and the square plane about the Pt atom is 60·4°; the C_6F_5 group is perpendicular to the coordination plane in PtCl(dcy)C_6F_5 (Deacon *et al.*, 1989), where steric interactions are greater.

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Structure of Di-μ-cyanato-bis[cyanato(*N*,*N*-diethylethylenediamine)copper(II)], [Cu(NCO)$_2$(diEten)]$_2$

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Abstract. [$Cu_2(NCO)_4(C_6N_2H_{16})_2$], $M_r = 527·56$, monoclinic, $P2_1/c$, $a = 11·586$ (2), $b = 7·279$ (1), $c = 13·742$ (2) Å, $\beta = 96·02$ (2)°, $V = 1152·5$ (6) Å^3, $Z = 2$, $D_x = 1·520$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 18·87$ cm^{-1}, $F(000) = 548$, $T = 296$ *K*, $R = 0·033$ for 1393 observed reflections. The compound is in a

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dimeric form. Each metal atom is coordinated to five N atoms: two from one diEten group [Cu—N = 2·102 (3), 1·974 (3) Å], one from a terminal cyanate group [Cu—N = 1·938 (4) Å] and two belonging to bridging cyanate groups [Cu—N = 2·017 (3), 2·450 (4) Å], giving rise to a distorted, elongated square–pyramidal configuration. The Cu···Cu distance is 3·236 (1) Å. Dimers are linked through H bonds involving the O of the bridging cyanate and the NH_2 end of diEten [N(4)···O(1)($-x$, $-1-y$, $1-z$) = 2·943 (5) Å, N(4)—H(4)···O(1) = 165·2 (2)°].

Introduction. One of our research interests has been the solid-state structural characterization of copper compounds with nitrogen-based ligands (Zukerman-Schpector, Castellano, Oliva, Mauro & Roveri, 1985; Zukerman-Schpector, Castellano, Mauro & Roveri, 1986), because structural parameters from copper amine complexes may be related to those of biological systems such as copper-containing proteins (Chaudhuri, Oder, Wieghardt, Nuber & Weiss, 1986). As part of this study the title compound was synthesized and its structure determination carried out.

Experimental. To a solution 2·82 mmol of $Cu(NO_3)_2.3H_2O$ in methanol was added a 2·82 mmol solution of diEten, followed by a dropwise addition of a 6·47 mmol water solution of KCNO. The mixture was stirred for 15 min at room temperature and the compound obtained was filtered off, washed with Et_2O and dried in vacuo. Recrystallization from methanol yielded prismatic blue crystals.

A single crystal with approximate dimensions 0·13 × 0·30 × 0·35 mm was used for data collection and cell determination on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. Unit-cell parameters were obtained from a least-squares refinement of the setting angles of 25 reflections in the θ range 12 to 24°. Intensity data were collected in the $\omega/2\theta$ scan mode up to θ_{max} = 25°; 2106 reflections were measured, of which 2002 were independent (R_{int} = 0·013, $-13 \leq h \leq 13$, $0 \leq k \leq 8$, $0 \leq l \leq 16$) and 1393 with $I \geq 4\sigma(I)$ were employed in the refinement procedure (137 parameters refined). Data were corrected for Lp and absorption, maximum and minimum transmission factors were 1·16, 0·81 (Walker & Stuart, 1983). The intensities of two standard reflections (029, 606) were essentially constant throughout the experiment.

The structure was solved using the heavy-atom Patterson method and difference Fourier techniques. In the final cycles of least-squares refinement, on F's, all non-H atoms were treated anisotropically. H atoms were included as fixed contributors at positions found in a difference synthesis, slightly modified, when possible, on stereochemical grounds, all with a common isotropic temperature factor that refined to U = 0·073 Å^2. The function minimized was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(F_o) + 0{\cdot}003F_o^2$, resulting in R = 0·033, wR = 0·036 and S = 0·63. The maximum shift/e.s.d. ratio was 0·001 and the maximum and minimum electron densities in the final difference map were 0·8 and −0·46 e Å^{-3} respectively. Scattering factors for non-H atoms were taken from Cromer & Mann (1968) with corrections for anomalous dispersion from Cromer & Liberman (1970); scattering factors for H atoms were from Stewart, Davidson & Simpson (1965). Programs used: *SHELX*76 (Sheldrick, 1976) and *ORTEP* (Johnson, 1965).

Table 1. *Final fractional atomic coordinates and isotropic temperature factors* (Å^2) *with e.s.d.'s in parentheses*

$*B_{iso} = \frac{4}{3}\sum_i\sum_j B_{ij}(\mathbf{a}_i.\mathbf{a}_j)$.

	x	y	z	B_{iso}*
Cu	0·1259 (1)	−0·0935 (1)	0·5274 (1)	2·53 (1)
N(1)	−0·0205 (3)	−0·1940 (5)	0·4541 (3)	3·6 (1)
N(2)	0·1882 (3)	−0·0104 (6)	0·4095 (3)	4·0 (1)
N(3)	0·2890 (3)	−0·0939 (5)	0·6103 (2)	2·78 (9)
N(4)	0·0677 (3)	−0·1639 (5)	0·6521 (2)	2·90 (9)
O(1)	−0·0868 (3)	−0·4329 (5)	0·3478 (3)	5·9 (1)
O(2)	0·3011 (5)	0·1976 (9)	0·3340 (4)	10·2 (2)
C(1)	−0·0513 (3)	−0·3141 (5)	0·4036 (3)	3·1 (1)
C(2)	0·2437 (4)	0·0922 (7)	0·3724 (3)	4·3 (1)
C(3)	0·1528 (3)	−0·1144 (7)	0·7345 (3)	3·5 (1)
C(4)	0·2697 (3)	−0·1720 (7)	0·7068 (3)	3·9 (1)
C(5)	0·3729 (4)	−0·2077 (7)	0·5608 (3)	4·1 (1)
C(6)	0·3291 (3)	0·1002 (6)	0·6191 (3)	3·7 (1)
C(7)	0·4479 (4)	0·1318 (8)	0·6750 (4)	5·3 (2)
C(8)	0·3239 (5)	−0·3880 (8)	0·5234 (5)	5·9 (2)

Table 2. *Interatomic distances* (Å) *and angles* (°)

Cu—N(1)	2·017 (3)	Cu—N(2)	1·938 (4)
Cu—N(3)	2·102 (3)	Cu—N(4)	1·974 (3)
Cu—N(1′)	2·450 (4)	Cu—Cu′	3·236 (1)
N(1)—C(1)	1·149 (5)	N(2)—C(2)	1·140 (6)
N(3)—C(4)	1·481 (5)	N(3)—C(5)	1·494 (6)
N(3)—C(6)	1·488 (6)	N(4)—C(3)	1·466 (5)
C(1)—O(1)	1·199 (6)	C(2)—O(2)	1·176 (8)
C(3)—C(4)	1·504 (6)	C(5)—C(8)	1·499 (8)
C(6)—C(7)	1·522 (7)		
N(1)—Cu—N(2)	93·6 (2)	N(1)—Cu—N(3)	158·7 (1)
N(1)—Cu—N(4)	89·6 (1)	N(1)—Cu—N(1′)	87·7 (1)
N(2)—Cu—N(3)	93·5 (1)	N(2)—Cu—N(4)	176·1 (1)
N(2)—Cu—N(1′)	93·1 (1)	N(3)—Cu—N(4)	84·2 (1)
N(3)—Cu—N(1′)	112·0 (1)	N(4)—Cu—N(1′)	85·0 (1)
Cu—N(1)—C(1)	140·3 (3)	Cu—N(1)—Cu′	92·3 (1)
C(1)—N(1)—Cu′	125·9 (3)	Cu—N(2)—C(2)	148·8 (4)
Cu—N(3)—C(4)	105·9 (2)	Cu—N(3)—C(5)	110·2 (2)
Cu—N(3)—C(6)	107·3 (2)	C(4)—N(3)—C(5)	111·2 (3)
C(4)—N(3)—C(6)	111·5 (3)	C(5)—N(3)—C(6)	110·5 (3)
Cu—N(4)—C(3)	110·1 (2)	N(1)—C(1)—O(1)	176·5 (5)
N(2)—C(2)—O(2)	179·8 (6)	N(4)—C(3)—C(4)	106·6 (3)
N(3)—C(4)—C(3)	110·1 (3)	N(3)—C(5)—C(8)	113·6 (4)
N(3)—C(6)—C(7)	116·3 (4)		

Symmetry operation: (′) $-x$, $-y$, $1-z$.

The infrared (IR) spectrum was recorded as a Nujol mull between CsI plates on a Nicolet 720-FT spectrophotomer.

Discussion. The final atomic parameters are given in Table 1* and bond distances and angles in Table 2. A projection of the dimer is shown in Fig. 1.

The compound is in a dimeric form with the two halves related by a center of symmetry; the Cu···Cu distance of 3·236 (1) Å is sufficiently long to preclude any significant interaction. The dimers are H bonded through the NH_2 end of the diEten group and the O of the bridging cyanate group: N(4)···O(1)-($-x$, $-1-y$, $1-z$) = 2·943 (5), N(4)—H(N4) = 0·941 (3) Å, N(4)—H(N4)···O(1) = 165·2 (2)°.

The Cu atom exhibits a distorted square-pyramidal coordination. The equatorial positions are occupied by four N atoms: two from the diEten group, one from the terminal and one from a bridging cyanate; the apical position is occupied by the N atom of the symmetry-related bridging cyanate group. As a result of the steric constraints imposed by the bite of the diEten residue the equatorial plane is distorted. The Cu atom lies out of the basal plane by 0·158 (1) Å towards the apical N atom.

As in other Cu(diEten) and Cu(diMeen) (diMeen = *N,N*-dimethylethylenediamine) complexes (Casagrande, Klein, Mauro & Tomita, 1989; Mauro, Klein, Saldaña, De Simone, Zukerman-Schpector & Castellano, 1990), the longest Cu—N bond length involves the most substituted N atom. The Cu—N(1) distance of 2·017 (3) Å is essentially equal to those found in other cyanate-bridged binuclear copper(II) complexes (Valach, Dunaj-Jurco, Garaj & Hvastijová, 1975; Boillot, Kahn, O'Connor, Gouteron, Jeannin & Jeannin, 1985).

The coordination chemistry of the cyanate anion has been extensively considered (Kepert, Kucharski & White, 1980) and a list of cyanate dimensions of structurally characterized cyanate-containing molecules can be found in Cortés, Arriortua, Rojo, Mesa, Solans & Beltran (1988). In agreement with the general aspects found for coordinated cyanate groups, both terminal and bridging cyanates are essentially linear [N(1)—C(1)—O(1) = 176·5 (5), N(2)—C(2)—O(2) = 179·8 (6)°]. They are, however, asymmetric, the longest N—C and C—O bonds being those of the bridging cyanate. Cortés *et al.* (1988) suggest that in agreement with the shorter N(2)—C(2) bond length, the shortening of the Cu—N(2) bond length, which is 0·079 Å shorter than that of the Cu—N(1), can be ascribed to a larger π-donor character in the Cu—N(2) bond.

The IR spectrum shows the absorption bands corresponding to N-bonded NCO ions (Nelson & Nelson, 1969; Burmeister & O'Sullivan, 1969): at 2206(w), 2187(s) cm^{-1}, νCN; 1214(m) cm^{-1}, νCO; 646(m), 618(m) cm^{-1}, δ(NCO).

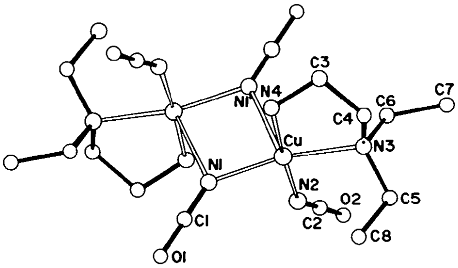

Fig. 1. Projection of a dimer showing the atom labeling. N(1') = N(1)($-x$, $-y$, $1-z$).

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* Lists of H-atom positions, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53651 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.