

- BRITTON, D. (1972). *Acta Cryst.* A28, 296–297.
- BUERGER, M. J. (1960). *Crystal-Structure Analysis*, pp. 53–72. New York: John Wiley.
- CATTI, M. & FERRARIS, G. (1976). *Acta Cryst.* A32, 163–165.
- CULLEN, D. L. & LINGAFELTER, E. C. (1970). *Inorg. Chem.* 9, 1858–1864.
- DUBLER, E., MATTHIEU, J. P. & OSWALD, H. R. (1975). *Thermal Analysis*, Vol. 1, pp. 377–386. *Proc. 4th Int. Conf. Thermal Analysis*. Bayreuth: Birkhäuser Verlag.
- DUNITZ, J. D., GEHRER, H. & BRITTON, D. (1972). *Acta Cryst.* B28, 1989–1994.
- GRAINGER, C. T. (1969). *Acta Cryst.* A25, 427–434.
- GRAINGER, C. T. & MCCONNELL, J. F. (1969). *Acta Cryst.* B25, 1962–1970.
- HAWTHORNE, F. C. (1974). *Acta Cryst.* A30, 603–604.
- JAMESON, G. B. (1982). *Acta Cryst.* A38, 817–820.
- LOSMAN, D., KARLSSON, R. & SHELDRICK, G. M. (1977). *Acta Cryst.* B33, 1959–1962.
- MACKAY, D. J. (1977). *Aust. J. Chem.* 30, 281–284.
- MAREZIO, M., DERNIER, P. D. & SANTORO, A. (1973). *Acta Cryst.* A29, 618–621.
- MAZHAR-UL-HAQUE, CAUGHLAN, C. N. & EMERSON, K. (1970). *Inorg. Chem.* 9, 2421–2424.
- MITRA, S. N. & SENGUPTA, P. (1973). *Indian J. Phys.* 47, 79–88.
- MURRAY-RUST, P. (1973). *Acta Cryst.* B29, 2559–2566.
- NODA, Y., MORI, M. & YAMADA, Y. (1978). *J. Phys. Soc. Jpn.* 45, 954–966.
- PERENTHALER, E., SCHULZ, H. & BEYELER, H. U. (1981). *Acta Cryst.* B37, 1017–1023.
- PRATT, C. S., COYLE, B. A. & IBERS, J. A. (1971). *J. Chem. Soc. A*, pp. 2146–2151.
- REINEN, D., FRIEBEL, C. & REETZ, K. P. (1972). *J. Solid State Chem.* 4, 103–114.
- SABELLI, C., TANGOCCHI, P. & ZANAZZI, P. F. (1969). *Acta Cryst.* B25, 2231–2235.
- SANTORO, A. (1974). *Acta Cryst.* A30, 224–231.
- SUDARSANAN, K., YOUNG, R. A. & DONNAY, J. D. H. (1973). *Acta Cryst.* B29, 808–814.
- WEI, C. H. (1969). *Inorg. Chem.* 8, 2384–2397.
- WERNER, A. (1899). *Z. Anorg. Allg. Chem.* 21, 210.
- ZALKIN, A., FORRESTER, J. D. & TEMPLETON, D. H. (1964). *Acta Cryst.* 17, 1408–1412.

Acta Cryst. (1982). B38, 3020–3023

(*N*-Methylimidazole)(2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene)copper(II) Hexafluorophosphate

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(Received 22 February 1982; accepted 12 July 1982)

Abstract

$[\text{Cu}(\text{C}_4\text{H}_6\text{N}_2)(\text{C}_{14}\text{H}_{24}\text{N}_4)] \cdot (\text{PF}_6)_2$, $\text{C}_{18}\text{H}_{30}\text{CuN}_6^{2+} \cdot 2\text{PF}_6^-$, *Pna*2₁, $a = 17.535$ (4), $b = 18.527$ (3), $c = 8.569$ (2) Å, $V = 2784$ Å³, $Z = 4$, $d_{\text{exp}} = 1.64$ (2), $d_{\text{calc}} = 1.632$ g cm⁻³, $\text{Mo K}\alpha$, $\mu = 10$ cm⁻¹. The structure was refined by full-matrix least squares to $R = 0.051$ and $R_w = 0.037$, with 5718 F values in the $hk\pm l$ quadrant. The coordination of the copper atom is square pyramidal, the four nitrogen atoms of the macrocycle forming the basal plane and the unsubstituted *N*-methylimidazole nitrogen atom the apex. The copper atom is displaced out of the coordination plane toward the axial ligand by 0.44 (1) Å.

Introduction

As part of an effort to model and understand copper proteins, we have undertaken the determination of the

structures of a series of four- and five-coordinated compounds of divalent copper with the macrocycle 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene which we call TIM, see Fig. 1. The crystals of the present compound, royal blue in color, were provided by M. J. Maroney. The cation is five-coordinate square pyramidal, the apical ligand being *N*-methylimidazole, and the TIM nitrogen atoms forming the basal plane.

Oscillation, Weissenberg, and precession photographs indicated orthorhombic symmetry; the systematic absences, $0kl$ for $k + l = 2n + 1$ and $h0l$ for $h = 2n + 1$, suggested that the space group is *Pna*2₁ or *Pnam*; and the Wilson statistics narrowed the choice to *Pna*2₁. The cell parameters were determined by a least-squares fit of the parameters of the orientation matrix to the setting angles of 12 reflections with 2θ between 35 and 43°. The experimental density was measured by flotation in a solution of chloroform and 1,3-dibromopropane.

Intensity data: 0.4 × 0.4 × 0.5 mm crystal; $\theta/2\theta$ scans, 2° min⁻¹ in 2θ , 20 s background counts fore
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* From a dissertation submitted to the Graduate School, University of Washington, Seattle, Washington, in partial fulfillment of the requirements for the PhD degree in chemistry.

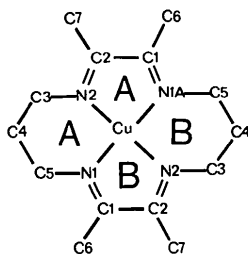


Fig. 1. The numbering scheme of the macrocycle.

and aft, FACS-1 computer-controlled four-circle diffractometer, graphite-monochromatized Mo $K\alpha$ radiation; 7200 $hk\pm l$ reflections out to $2\theta = 55^\circ$, including 820 systematic absences dropped from the data file; three standard reflections counted after each 100 measurements [3% overall deterioration, 'instability constant' $P = 0.4$ (2)%]; corrections made for coincidence and deterioration, but not absorption ($\mu = 10 \text{ cm}^{-1}$, $A_{\text{max}} 0.66$, $A_{\text{min}} 0.48$).

Data reduction: $F_o = (kI/Lp)^{1/2}$ [scale factor k , Lorentz and polarization factor Lp , $I = S - rB$ with scan counts S , (total) background count B , and scan/(total) background time ratio r]; $\sigma(I) = (S + r^2 B + P^2 I^2)^{1/2}$, $\sigma(F_o) = \sigma(I)/(2LpF)$, for large F 's, and $\sigma(F_o) = [F_o^2 + \sigma(F_o^2)]^{1/2} - F_o$, for small F 's; final $k = 0.358$. At each stage of the structure refinement reflections with both F_o and F_c less than $3\sigma(F_o)$ were excluded.

Of the three copper positions suggested by the Patterson map the one chosen for smaller R value, 0.408, on Cu-only F_c calculation led to the full structure, by way of F_c calculations, Fourier maps, and full-matrix F least squares, at first with unit weights and later $1/\sigma^2 F$ weights. At $R = 0.070$, the hydrogen atoms were included, six at C-H distance 1.0 Å and suitable angles and the rest from a difference density map, and their positions and Gaussian amplitudes were refined to convergence, followed by refinement of the non-hydrogen atoms to convergence. Anomalous dispersion was applied, the polarity of the structure being chosen as given in Tables 1 and 2 (it was checked by recalculation after the final cycle of refinement). Finally, disordered hexafluorophosphate anions were adjusted to fit the electron density in a difference Fourier map. The statistics of fit for the final model (Tables 1 and 2)* are $\text{GOF} = 5.0$, $R_w = 0.037$, and $R = 0.051$.

* Lists of structure factors and their standard deviations, the anisotropic Gaussian amplitudes of the non-hydrogen atoms, and the final coordinates and isotropic amplitudes of the hydrogen atoms, as well as the bond lengths for the anion have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38053 (33 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atomic coordinates and equivalent isotropic Gaussian amplitudes of the non-hydrogen atoms of the cation (with e.s.d.'s in parentheses)

$$U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq} (Å ²)
Cu	0.15880 (2)	0.23935 (2)	0	0.0478 (2)
N(1A)	0.0637 (2)	0.1826 (2)	0.0282 (5)	0.063 (2)
N(2A)	0.1570 (2)	0.1855 (2)	-0.2023 (4)	0.054 (2)
C(1A)	0.0435 (2)	0.1476 (2)	-0.0872 (6)	0.064 (3)
C(2A)	0.0966 (3)	0.1471 (2)	-0.2224 (5)	0.056 (3)
C(3A)	0.2183 (3)	0.1910 (3)	-0.3162 (5)	0.078 (3)
C(4A)	0.2512 (3)	0.2600 (3)	-0.3350 (7)	0.105 (4)
C(5A)	0.2799 (3)	0.3027 (3)	-0.2090 (5)	0.100 (4)
C(6A)	-0.0303 (3)	0.1062 (3)	-0.1046 (7)	0.115 (5)
C(7A)	0.0783 (3)	0.1055 (2)	-0.3670 (6)	0.093 (3)
N(1B)	0.2219 (2)	0.3193 (2)	-0.0841 (4)	0.061 (2)
N(2B)	0.1271 (2)	0.3172 (2)	0.1447 (4)	0.066 (2)
C(1B)	0.2112 (3)	0.3782 (2)	-0.0220 (6)	0.068 (3)
C(2B)	0.1552 (3)	0.3804 (3)	0.1076 (6)	0.078 (4)
C(3B)	0.0695 (3)	0.3075 (4)	0.2628 (7)	0.104 (4)
C(4B)	0.0534 (4)	0.2324 (5)	0.2935 (7)	0.132 (6)
C(5B)	0.0164 (3)	0.1889 (4)	0.1679 (8)	0.107 (4)
C(6B)	0.2522 (3)	0.4490 (2)	-0.0619 (6)	0.109 (4)
C(7B)	0.1306 (3)	0.4487 (3)	0.1840 (8)	0.134 (5)
N(1C)	0.2463 (2)	0.1833 (2)	0.1248 (4)	0.052 (2)
C(2C)	0.2760 (2)	0.1195 (2)	0.0891 (5)	0.061 (3)
N(3C)	0.3357 (2)	0.1045 (2)	0.1806 (4)	0.060 (2)
C(4C)	0.3444 (3)	0.1616 (3)	0.2799 (6)	0.077 (3)
C(5C)	0.2893 (3)	0.2094 (2)	0.2450 (5)	0.066 (2)
C(3C)	0.3850 (3)	0.0420 (2)	0.1633 (7)	0.098 (4)

Table 2. Atomic coordinates and equivalent isotropic Gaussian amplitudes of the anion (with e.s.d.'s in parentheses)

$$U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	<i>x</i>	<i>y</i>	<i>z</i>	U/U_{eq} (Å ²)	p.p.*
P(1)	0.34634 (7)	0.43608 (7)	0.4143 (2)	0.0625 (7)	1.00
F(11)	0.3105 (1)	0.5072 (1)	0.3364 (3)	0.089 (2)	0.99 (1)
F(12)	0.3826 (1)	0.3651 (1)	0.4904 (4)	0.111 (2)	1.00 (1)
F(13)	0.4306 (2)	0.4558 (2)	0.3563 (6)	0.085 (2)	0.71 (4)
F(14)	0.3317 (3)	0.3945 (2)	0.2532 (5)	0.102 (3)	0.71 (4)
F(15)	0.2644 (2)	0.4155 (4)	0.4761 (11)	0.141 (5)	0.69 (4)
F(16)	0.3643 (4)	0.4750 (4)	0.5778 (6)	0.159 (6)	0.70 (4)
F(17)	0.3876 (9)	0.4329 (8)	0.2632 (17)	0.152 (5)	0.31 (6)
F(18)	0.3002 (11)	0.4505 (8)	0.5618 (18)	0.132 (6)	0.30 (5)
F(19)	0.3956 (8)	0.4931 (7)	0.4933 (2)	0.131 (5)	0.31 (6)
F(110)	0.2765 (8)	0.3909 (7)	0.3597 (17)	0.110 (4)	0.29 (5)
P(2)	-0.01928 (6)	0.35484 (6)	0.7349 (2)	0.0564 (7)	1.00
F(21)	-0.0522 (3)	0.2914 (3)	0.6321 (6)	0.143 (4)	0.79 (4)
F(22)	-0.0064 (3)	0.4043 (2)	0.5845 (5)	0.111 (4)	0.80 (3)
F(23)	0.0640 (2)	0.3295 (3)	0.7041 (6)	0.144 (4)	0.80 (3)
F(24)	-0.1026 (2)	0.3837 (2)	0.7672 (6)	0.116 (3)	0.81 (4)
F(25)	0.0369 (3)	0.3064 (3)	0.8796 (7)	0.141 (4)	0.81 (4)
F(26)	0.0103 (4)	0.4217 (3)	0.8380 (6)	0.137 (4)	0.80 (3)
F(27)	-0.100 (1)	0.361 (1)	0.680 (3)	0.115 (8)	0.20 (5)
F(28)	-0.009 (1)	0.278 (1)	0.683 (2)	0.112 (7)	0.20 (5)
F(29)	-0.030 (1)	0.374 (1)	0.571 (2)	0.074 (5)	0.19 (6)
F(210)	0.053 (2)	0.352 (2)	0.825 (4)	0.209 (12)	0.20 (5)
F(211)	-0.001 (1)	0.321 (1)	0.909 (3)	0.083 (8)	0.21 (6)
F(212)	-0.012 (2)	0.417 (2)	0.417 (4)	0.129 (13)	0.19 (6)

* p.p. is the partial population of the atoms.

Discussion

The structure of Cu(TIM)(*N*-Me-imid)(PF₆)₂ consists of discrete complex cations and disordered hexafluorophosphate anions. The copper(II) ion is five-

coordinate square pyramidal with the macrocyclic nitrogen atoms as the basal ligands, and the unsubstituted nitrogen atom of the *N*-methylimidazole at the apex (see Tables 3 and 4 and Figs. 1 and 3). The equatorial N—Cu distances range from 1.982 (4) to 2.000 (3) Å [average 1.988 (3) Å], slightly longer than the 1.942 (1) to 1.960 (1) Å reported by Morehouse, Polychronopoulou & Williams (1980) for the bis-(2,3-butanedione dioximato)imidazolecopper(II) complex, but well within the range 1.924 (7) to 2.035 (8) Å of other published (imine)N—Cu distances. Also, our results for four other copper(II)—TIM complexes fall well within this range. The axial N—Cu distance is 2.139 (3) Å, in agreement with the 2.141 (1) Å observed by Morehouse, Polychronopoulou & Williams (1980), but significantly shorter than previously reported results for axial N—Cu distances varying from 2.31 to 2.36 Å, and even 2.593 (3) Å for the axial ligands of the hexakis-(imidazole)copper(II) cation (McFadden, McPhail, Garner & Mabbs, 1975), and only slightly longer than results for equatorial N—Cu distances, 1.913 (7) to 2.049 (2) Å. The four macrocycle nitrogen atoms deviate only ±0.01 (1) Å from their mean plane, the copper atom by 0.44 (1) Å toward the axial ligand, and some of the TIM atoms even more, as given in Table 5.

Table 3. Bond lengths of the cation (with *e.s.d.*'s in parentheses)

Cu—N(1C)	2.139 (3)	N(2B)—C(3B)	1.441 (7)
Cu—N(1A)	1.986 (3)	C(1A)—C(2A)	1.486 (7)
Cu—N(2A)	2.000 (3)	C(1A)—C(6A)	1.512 (6)
Cu—N(1B)	1.984 (4)	C(2A)—C(7A)	1.494 (6)
Cu—N(2B)	1.982 (4)	C(1B)—C(2B)	1.483 (7)
N(1A)—C(1A)	1.234 (6)	C(1B)—C(6B)	1.534 (7)
N(2A)—C(2A)	1.288 (6)	C(2B)—C(7B)	1.487 (8)
N(1B)—C(1B)	1.229 (6)	C(3A)—C(4A)	1.412 (8)
N(2B)—C(2B)	1.309 (6)	C(4A)—C(5A)	1.429 (8)
N(1A)—C(5B)	1.461 (7)	C(3B)—C(4B)	1.443 (11)
N(2A)—C(3A)	1.454 (6)	C(4B)—C(5B)	1.494 (10)
N(1B)—C(5A)	1.508 (6)		

Table 4. Bond angles of the cation (°) (with *e.s.d.*'s in parentheses)

N(1A)—Cu—N(2A)	80.1 (1)	N(1B)—Cu—N(2B)	80.8 (2)
N(2A)—Cu—N(1B)	93.8 (1)	N(2B)—Cu—N(1A)	94.2 (2)
N(1A)—Cu—N(1B)	155.2 (1)	N(2A)—Cu—N(2B)	154.3 (1)
Cu—N(1A)—C(1A)	114.9 (3)	Cu—N(1B)—C(1B)	114.9 (3)
N(1A)—C(1A)—C(6A)	126.2 (5)	N(1B)—C(1B)—C(6B)	126.3 (5)
Cu—N(2A)—C(2A)	113.8 (3)	Cu—N(2B)—C(2B)	113.2 (3)
N(2A)—C(2A)—C(7A)	124.9 (4)	N(2B)—C(2B)—C(7B)	123.0 (5)
N(1A)—C(1A)—C(2A)	116.6 (4)	N(1B)—C(1B)—C(2B)	116.7 (4)
N(2A)—C(2A)—C(1A)	114.1 (4)	N(2B)—C(2B)—C(1B)	114.0 (4)
C(2A)—C(1A)—C(6A)	117.1 (4)	C(2B)—C(1B)—C(6B)	117.0 (4)
C(1A)—C(2A)—C(7A)	121.0 (4)	C(1B)—C(2B)—C(7B)	123.0 (4)
Cu—N(2A)—C(3A)	122.4 (3)	Cu—N(2B)—C(3B)	123.0 (4)
N(2A)—C(3A)—C(4A)	116.2 (4)	N(2B)—C(3B)—C(4B)	112.7 (5)
C(3A)—C(4A)—C(5A)	123.9 (5)	C(3B)—C(4B)—C(5B)	118.3 (6)
C(4A)—C(5A)—N(1B)	114.3 (4)	C(4B)—C(5B)—N(1A)	112.7 (5)
C(5A)—N(1B)—Cu	118.8 (3)	C(5B)—N(1A)—Cu	122.3 (3)
N(1C)—Cu—N(1A)	106.5 (1)	N(1C)—Cu—N(1B)	98.3 (1)
N(1C)—Cu—N(2A)	101.7 (1)	N(1C)—Cu—N(2B)	104.0 (1)

Table 5. Distances of atoms from the least-squares coordination plane (Å × 100)

The *e.s.d.*'s are 0.01 Å and 0.3°.

Cu	44	C(6A)/C(6B)	−97/−78
N(1A)/N(1B)	1/1	C(7A)/C(7B)	−92/−105
N(2A)/N(2B)	−1/−1	C(3A)/C(3B)	12/−3
C(1A)/C(1B)	−43/−39	C(4A)/C(4B)	−25/64
C(2A)/C(2B)	−44/−46	C(5A)/C(5B)	26/5
Dihedral angle (°)		41.0/57.8	

The dihedral angle given is between the coordination plane and the C(3A)—C(4A)—C(5A)/C(3B)—C(4B)—C(5B) arms.

The copper atom apparently interacts weakly with one of the hexafluorophosphate anions at the sixth coordination site. Two fluorine atoms of occupancy 0.2 at distances 3.276 (23) and 3.166 (34) Å from the copper atom make respective N(1C)—Cu—F angles of 163 (1) and 167 (1)°, and two other fluorine atoms of occupancy 0.8 at distances of 3.462 (5) and 3.793 (6) Å both make the angle 161 (1)°. These distances are considerably longer than the 2.652 (7) Å weak Cu—F bond of the aqua(12,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,11-diene)copper(II) hexafluorophosphate complex (Heeg, Endicott, Glick & Khalifa, 1982), but our Cu—N(1C) axial bond, 2.139 (3) Å, is shorter than their Cu—O axial bond, 2.433 (9) Å.

Unlike the four-coordinate square-planar cation of Cu(TIM)(BPh₄)₂ (Elia, Lingafelter & Schomaker, 1983) and the hexacoordinate TIM complexes, in which, except for C(4), the macrocycle deviates very little from planarity, the macrocycle in the *N*-methylimidazole complex is significantly non-planar (Table 5), one of the six-membered chelate rings being a chair and the other a boat. The five-membered rings are domed away from the axial ligand, as shown in Fig. 2.

The N—C and C—C bond distances of the *N*-methylimidazole are all within 2σ of the weighted means of the bond lengths in previously reported imidazole structures, and the bond angles are all within

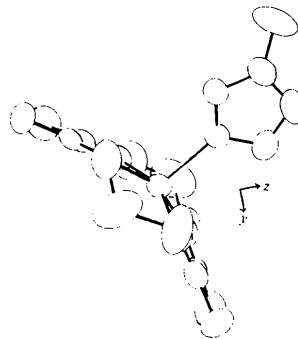


Fig. 2. A view of the complex cation showing the doming away from the axial ligand.

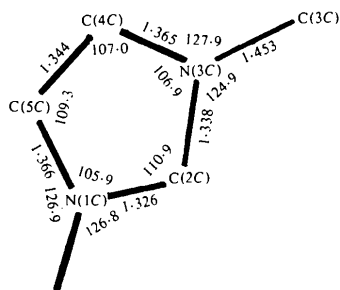


Fig. 3. Bond lengths and angles of *N*-methylimidazole and the numbering scheme. E.s.d.'s are 0.006 Å and 0.4°.

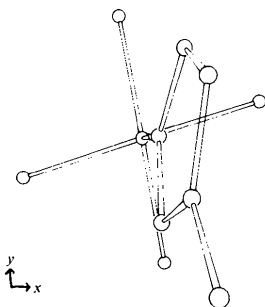


Fig. 4. Projection of *N*-methylimidazole on the coordination plane.

2.5 σ , see Fig. 3. The imidazole ring atoms deviate negligibly from planarity, and the methyl carbon atom is 0.15 (1) Å from the least-squares imidazole plane.

Contacts of the methyl carbon atom with F(22), F(26), F(212) at 3.395 (7), 3.256 (8), and 3.124 (36) Å, respectively, C(2C) with N(2A) at 3.476 (5) Å, and C(5C) with N(2B) at 3.581 (6) Å cause the imidazole plane to make an angle of 7.2 (10)° with the Cu—N(1C) bond, which makes an additional angle of 4.4 (10)° with the normal to the coordination plane, a total of 11.7 (10)° toward N(1B). Also, the *N*-methylimidazole is rotated so that the N(1A)—Cu—N(1C)—C(2C) and the N(1A)—Cu—N(1C)—C(5C) torsion angles are +68.3 (4) and -120.5 (4)°, respectively, and the projection of the C(2C) atom on the coordination plane is closest to N(2A), and of C(5C) to N(2B), as shown in Fig. 4.

Both hexafluorophosphate anions are disordered. One of them has ten partial fluorine atoms around P(1), the two axial ones at full occupancy, four equatorial ones of occupancy 0.70 and four of 0.30. The other anion has 12 partial fluorine atoms around P(2), forming two octahedra, one of occupancy 0.80 and the other of 0.20.

References

- ELIA, A. E., LINGAFELTER, E. C. & SCHOMAKER, V. (1983). In preparation.
- HEEG, M. J., ENDICOTT, J. F., GLICK, M. D. & KHALIFA, M. A. (1982). *Acta Cryst.* **B38**, 730–732.
- McFADDEN, D. L., MCPHAIL, A. T., GARNER, C. D. & MABBS, F. E. (1975). *J. Chem. Soc. Dalton Trans.* pp. 263–268.
- MOREHOUSE, S. M., POLYCHRONOPOULOU, A. & WILLIAMS, G. J. B. (1980). *Inorg. Chem.* **19**, 3558–3561.