Acta Cryst. (1982). B**38**, 730–732

X-ray Structure of Aqua(5,7-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,7-diene)-(hexafluorophosphato)copper(II) Hexafluorophosphate

BY MARY JANE HEEG, JOHN F. ENDICOTT, MILTON D. GLICK* AND MOHAMED A. KHALIFA

The Department of Chemistry, Wayne State University, Detroit, MI 48202, *USA*

(*Received* 1 *December* 1980; *accepted* 17 *August* 1981)

Abstract

$[Cu(Me_2[14]4,7\text{-diene}N_4)(OH_2)(PF_6)]PF_6$ crystallizes in the monoclinic space group $C2/c$ with $a = 22{\cdot}394$ (8), $b = 16{\cdot}737$ (6), $c = 15{\cdot}560$ (3) Å, $\beta = 130{\cdot}97$ (2)°, $V = 4404$ (3) Å^3, $Z = 8$, $D_c = 1{\cdot}797$ Mg m^{-3}. The structure contains distorted tetragonal Cu^{II} cations with Cu coordinated to four N donor atoms from the diene macrocycle and to a water molecule and F atom of a PF_6 group at long axial lengths. Some disorder is evident in a special-position PF_6^- anion. The structure was refined to an R value of 0·072 for 2286 independent observed reflections.

Introduction

Macrocyclic-ligand complexes containing β-diimine moieties have been found to exhibit a remarkable variety of oxidation–reduction behavior (Endicott & Durham, 1979; Switzer & Endicott, 1980; Dabrowiak & McElroy, 1976; Weiss & Goedkin, 1976; Durham, Anderson, Switzer, Endicott & Glick, 1977). In the course of our continuing investigation of these systems, we found that there were no X-ray structural data of simple Cu^{II} complexes which could be used in direct comparisons with those of the Co^{II} and Ni^{II} homologs.

Experimental

The title compound was prepared as the β-diiminato-hexafluorophosphate salt following the literature procedure (Martin & Cummings, 1973). This salt was recrystallized from warm (333 K), dilute (1 *M*) HCl. The solution was cooled and crystals were formed over a period of two days.

A cube-shaped maroon crystal of approximate dimensions 0·30 × 0·30 × 0·30 mm was mounted on a glass fiber and intensity data were measured for 4280 reflections in the range $2{\cdot}5° \leq 2\theta < 50°$ using a Syntex $P2_1$ automated diffractometer (Mo $K\alpha$ radiation, graphite monochromator). After averaging, 2286 unique observed $[I \geq 3\sigma(I)]$ reflections were obtained. Systematic absences of the form hkl, $h + k =$ odd and $h0l$, $l =$ odd were consistent with the space groups $C2/c$ and Cc. The cell parameters were obtained by precisely centering upon 15 intense reflections. Other details of data collection were as follows: scan method, $\theta/2\theta$; scan rate 1·0–4·0° min^{-1}; scan range 0·8° below $K\alpha_1$ to 0·9° above $K\alpha_2$ in 2θ; ratio of background to scan time, 0·5. No absorption corrections were applied.

The centrosymmetric group $C2/c$ was assumed and gave satisfactory refinement. The position of the heavy atom (Cu) was obtained from a Patterson synthesis. All other non-H atoms were located from a series of Fourier maps and their parameters refined by least-squares techniques. All atoms occupy general positions in the unit cell except for P(2) and P(3) which lie on the twofold rotation axis. H atoms were placed in observed positions according to peaks on a ΔF map and given arbitrary isotropic temperature factors of $B = 4{\cdot}0$ Å^2. Full-matrix least squares, holding all H parameters invariant, yielded a conventional unweighted $R = 0{\cdot}077$ and $R' = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2} = 0{\cdot}104$. An examination of a difference map at this point indicated some disorder around the special-position PF_6 group, P(3). In order to improve the model, two partial F atoms were substituted in the disordered region with occupancy factors calculated on the basis of peak heights in a Fourier synthesis: F(33) and F(34) were assigned multiplicities of 0·662 and 0·338 respectively. The model then refined to $R = 0{\cdot}072$ and $R' = 0{\cdot}097$ which represents significant improvement at the 99·5% confidence level (Hamilton, 1965). The choice of $C2/c$ as an acceptable space group is supported by the chemically reasonable parameters of the model. In the final cycle of least squares, the maximum shift/error was less than 0·4, the number of variables was 299 and the number of observations was 2286. In a final difference map the largest peak represented 0·7e Å^{-3} and was in the vicinity of the disordered PF_6^- anion. Neutral-atom scattering factors of Cromer & Mann (1968) were used with Cu and P atoms corrected for anomalous dispersion (*International Tables for X-ray Crystallography*, 1974). The value of p in the cal-

* To whom correspondence should be addressed.

0567-7408/82/030730-03$01.00

Table 1. *Atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses*

$$B_{eq} = \tfrac{4}{3}\sum_i \sum_j \beta_{ij}\, \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	B_{eq} (Å^2)
Cu	0·33132 (6)	−0·34786 (6)	0·19067 (9)	3·6 (1)
P(1)	0·1651 (2)	−0·1761 (2)	0·1539 (2)	4·2 (1)
P(2)	0·5000	0·0120 (2)	0·2500	5·3 (2)
P(3)	0	0·0088 (3)	0·2500	6·9 (2)
N(1)	0·3301 (5)	0·3326 (5)	−0·0670 (7)	4·5 (2)
N(7)	0·3997 (4)	0·2556 (5)	−0·1487 (7)	4·2 (2)
N(10)	0·3296 (5)	0·3579 (5)	−0·3202 (6)	4·5 (2)
N(14)	0·2607 (5)	0·4421 (4)	−0·2340 (7)	4·4 (2)
F(11)	0·2265 (6)	−0·1355 (6)	0·1520 (10)	10·2 (3)
F(12)	0·1038 (6)	−0·2174 (6)	0·1583 (8)	9·7 (3)
F(13)	0·1306 (5)	−0·0921 (4)	0·1444 (10)	9·4 (3)
F(14)	0·2018 (5)	−0·2605 (4)	0·1672 (7)	8·4 (2)
F(15)	0·2241 (5)	−0·1659 (5)	0·2859 (6)	9·3 (3)
F(16)	0·1053 (5)	−0·1885 (5)	0·0248 (6)	9·5 (3)
F(21)	0·4369 (6)	−0·0511 (6)	0·2071 (8)	11·4 (3)
F(22)	0·4748 (6)	0·0143 (5)	0·1285 (7)	10·6 (3)
F(23)	0·4366 (6)	0·0795 (6)	0·2075 (10)	10·8 (3)
F(31)	0·0874 (5)	0·0124 (6)	−0·1951 (10)	10·8 (3)
F(32)	0·0145 (7)	0·0750 (9)	−0·1671 (10)	13·6 (4)
F(33)	−0·0146 (15)	−0·0724 (11)	−0·3006 (18)	12·5 (5)
F(34)	0·0286 (42)	−0·0286 (17)	−0·1387 (30)	10·1 (14)
C(2)	0·3665 (6)	0·2795 (7)	0·0117 (8)	4·7 (2)
C(3)	0·3665 (9)	0·2711 (8)	0·1053 (10)	6·8 (3)
C(4)	0·4146 (7)	0·2159 (7)	0·0123 (10)	5·7 (3)
C(5)	0·4287 (5)	0·2091 (6)	−0·0632 (9)	4·4 (2)
C(6)	0·4842 (7)	0·1391 (7)	−0·0367 (12)	6·3 (4)
C(8)	0·4202 (7)	0·2496 (6)	−0·2204 (9)	5·0 (2)
C(9)	0·3507 (7)	0·2815 (6)	−0·3377 (9)	5·3 (3)
C(11)	0·2596 (7)	0·3959 (7)	−0·4291 (9)	5·6 (3)
C(12)	0·2331 (7)	0·4721 (7)	−0·4149 (9)	5·3 (3)
C(13)	0·2006 (6)	0·4651 (7)	−0·3574 (10)	5·5 (3)
C(15)	0·2249 (8)	0·4279 (7)	−0·1850 (12)	6·0 (3)
C(16)	0·2841 (7)	0·3964 (8)	−0·0658 (10)	5·9 (3)
O(1)	0·0499 (6)	0·0709 (6)	0·0666 (9)	9·1 (3)

Table 2. *Interatomic distances* (Å)

Cu–N(1)	1·960 (9)	C(12)–C(13)	1·480 (17)
Cu–N(7)	1·961 (8)	N(13)–N(14)	1·502 (13)
Cu–N(10)	2·001 (8)	N(14)–C(15)	1·443 (15)
Cu–N(14)	2·012 (8)	C(15)–C(16)	1·500 (17)
Cu–O(1^{i})	2·433 (9)	P(1)–F(11)	1·552 (8)
Cu–F(14^{ii})	2·652 (7)	P(1)–F(12)	1·578 (8)
N(1)–C(16)	1·492 (13)	P(1)–F(13)	1·564 (8)
N(1)–C(2)	1·282 (12)	P(1)–F(14)	1·578 (7)
C(2)–C(3)	1·477 (15)	P(1)–F(15)	1·560 (7)
C(2)–C(4)	1·511 (15)	P(1)–F(16)	1·530 (8)
C(4)–C(5)	1·404 (15)	P(2)–F(21)	1·522 (9)
C(5)–C(6)	1·554 (14)	P(2)–F(22)	1·579 (9)
C(5)–N(7)	1·292 (12)	P(2)–F(23)	1·582 (8)
N(7)–C(8)	1·462 (13)	P(3)–F(31)	1·541 (9)
C(8)–C(9)	1·521 (14)	P(3)–F(32)	1·565 (11)
C(9)–N(10)	1·477 (13)	P(3)–F(33)	1·495 (15)
N(10)–C(11)	1·488 (13)	P(3)–F(34)	1·532 (32)
C(11)–C(12)	1·483 (17)		

Symmetry code: (i) $\frac{1}{2}-x, \frac{1}{2}-y, \bar{z}$; (ii) $x, \bar{y}, 1\frac{1}{2}+z$.

Table 3. *Selected bond angles* (°)

N(1)–Cu–N(7)	94·7 (3)	C(4)–C(5)–N(7)	125·2 (9)
N(1)–Cu–N(10)	177·7 (3)	C(6)–C(5)–N(7)	120·1 (1·0)
N(1)–Cu–N(14)	85·3 (3)	C(5)–N(7)–C(8)	123·3 (9)
N(7)–Cu–N(10)	84·7 (3)	N(7)–C(8)–C(9)	107·8 (8)
N(7)–Cu–N(14)	179·7 (3)	C(8)–C(9)–N(10)	106·8 (8)
N(10)–Cu–N(14)	95·3 (4)	C(9)–N(10)–C(11)	112·2 (8)
C(16)–N(1)–C(2)	119·8 (9)	N(10)–C(11)–C(12)	114·0 (9)
N(1)–C(2)–C(3)	126·6 (1·1)	C(11)–C(12)–C(13)	115·1 (9)
N(1)–C(2)–C(4)	119·8 (9)	C(12)–C(13)–N(14)	114·2 (9)
C(3)–C(2)–C(4)	113·5 (1·0)	C(13)–N(14)–C(15)	112·1 (9)
C(2)–C(4)–C(5)	127·1 (9)	N(14)–C(15)–C(16)	111·4 (1·0)
C(4)–C(5)–C(6)	114·8 (1·0)	C(15)–C(16)–N(1)	107·1 (9)

culation of $\sigma(I)$ was 0·05. Final atomic positional parameters are presented in Table 1. Interatomic distances and selected bond angles are listed in Tables 2 and 3 respectively.*

Discussion

The Cu atom of the title complex lies in the N_4 donor-atom plane of the Me_2[14]4,7-dieneN_4 macrocycle and is coordinated to two amine and two imine N atoms. In addition, Cu is involved in two long axial contacts, to a water molecule [Cu–O 2·433 (9) Å] and to a F atom of the general-position PF_6 group [Cu–F 2·652 (7) Å] making the overall geometry distorted tetragonal about Cu.

The average Cu–N distances of Cu–N(imine) 1·96 (1) Å and Cu–N(amine) 2·01 (1) Å are well within the range of Cu–N bond lengths noted in similar complexes: Cu–N(amine) 1·99–2·07; Cu–N(imine) 1·88–2·035 Å (Bauer, Robinson & Margerum, 1973;

* Lists of structure factors, H coordinates, anisotropic thermal parameters, H-bond lengths, additional bond angles and least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36139 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

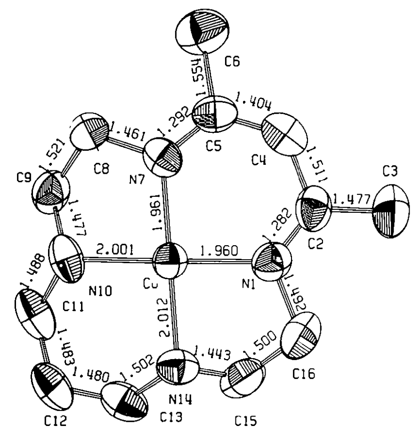

Fig. 1. Molecular geometry and bond lengths (Å) of 5,7-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,7-diene copper(II) fragment.

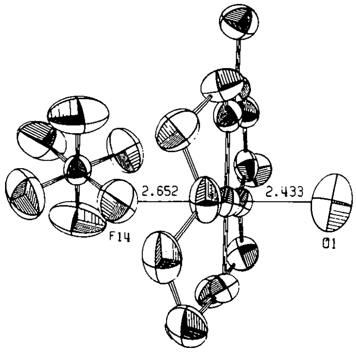

Fig. 2. View of the axial framework. (Distances in Å.)

Caira, Nassimbeni & Woolley, 1975; Cook, 1976; Jungst & Stucky, 1974). A shorter *M*—N(imine) length relative to the *M*—N(amine) length is a general feature of these types of macrocyclic complexes (see, for example, Bailey & Maxwell, 1972; Cunningham & Sievers, 1973; Endicott *et al.*, 1981; Roberts, Cummings & Cunningham, 1976) and results from the hybridizations of the N atom. Fig. 1 illustrates the geometry of the $Cu(Me_2[14]4,7\text{-diene}N_4)$ complex, labelled with bond lengths. The averaged bond lengths within the macrocycle are as follows: N(amine)—C 1·48 (3); N(imine)—C 1·48 (2); N=C 1·29 (2); C—C 1·49 (4) Å.

The long Cu—O axial bond is shown in Fig. 2. Cu is virtually in the mean N_4 equatorial plane (the maximum N deviation from the plane is 0·017 Å; the deviation of the Cu atom is 0·022 Å) unlike that usually seen in five-coordinate Cu^{II} structures (Blake & Fraser, 1974; Caria *et al.*, 1975; Lintvedt, Glick, Tomlonovic, Gavel & Kuszaj, 1976; Sinn, 1976). This implies some significant interaction between the *trans* F atom and the Cu atom resulting in a six-coordinate Cu^{II} species even though the Cu—F distance is fairly long [2·652 (7) Å].

The configuration of the diene macrocycle is *meso* and contains a near mirror plane which bisects the molecule and C(4) and C(12). The configuration of the ethylenediamine linkages is δ and λ, and the amine H atoms are *cis* with respect to each other and are oriented toward the coordinated water molecule. The saturated six-membered ring is in the chair conformation.

The structural similarities between this complex $Cu(Me_2[14]4,7\text{-diene}N_4)(OH_2)(PF_6)PF_6$ and the low-spin Co^{II} analog, $Co(Me_2[14]4,7\text{-diene}N_4)(OH_2)(PF_6)PF_6$ (Roberts *et al.*, 1976) are remarkable. Both structures report the same space group, similar lattice constants, special positioning of a PF_6^- anion, same metal coordination sphere, and nearly identical macrocycle geometries. As expected, the Co—ligand bond lengths are shorter than the corresponding Cu—ligand lengths due to additional antibonding electrons in the Cu orbitals [Co—N(imine) 1·916; Co—N(amine) 1·988; Co—O_w 2·283; Co—F 2·559 Å]. The $C(sp^2)$—$C(sp^3)$—$C(sp^2)$ bond angle in the imine ring has increased in deviation from the idealized sp^3 value of 109·5° [121·9° in the Co^{II} complex to 127·1° in the Cu^{II} complex] implying greater strain in this part of the molecule for the title complex.

Partial support of this research by the National Institutes of Health and by the National Science Foundation is gratefully acknowledged.

References

Bailey, M. F. & Maxwell, I. E. (1972). *J. Chem. Soc. Dalton Trans.* pp. 938–944.
Bauer, R. A., Robinson, W. R. & Margerum, D. W. (1973). *J. Chem. Soc. Chem. Commun.* pp. 289–290.
Blake, A. B. & Fraser, L. R. (1974). *J. Chem. Soc. Dalton Trans.* pp. 2554–2558.
Caira, M. R., Nassimbeni, L. R. & Woolley, P. R. (1975). *Acta Cryst.* B**31**, 1334–1338.
Cook, D. (1976). *Inorg. Nucl. Chem. Lett.* **12**, 103–105.
Cromer, D. T. & Mann, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
Cunningham, J. A. & Sievers, R. E. (1973). *J. Am. Chem. Soc.* **95**, 7183–7185.
Dabrowiak, J. C. & McElroy, F. L. (1976). *J. Am. Chem. Soc.* **98**, 7112.
Durham, B., Anderson, T. J., Switzer, J. A., Endicott, J. F. & Glick, M. D. (1977). *Inorg. Chem.* **16**, 271–278.
Endicott, J. F. & Durham, B. (1979). *Coordination Chemistry of Macrocyclic Compounds*, edited by G. A. Melson, pp. 393–460. New York: Plenum.
Endicott, J. F., Durham, B., Glick, M. D., Anderson, T. J., Kuszaj, J., Schmonsees, W. & Balakrishnan, K. P. (1981). *J. Am. Chem. Soc.* **103**, 1431.
Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502–510.
International Tables for X-ray Crystallography (1974). Vol. IV, pp. 148–150. Birmingham: Kynoch Press.
Jungst, R. & Stucky, G. (1974). *Inorg. Chem.* **13**, 2404–2408.
Lintvedt, R. L., Glick, M. D., Tomlonovic, B. K., Gavel, D. P. & Kuszaj, J. M. (1976). *Inorg. Chem.* **15**, 1633–1645.
Martin, J. G. & Cummings, S. C. (1973). *Inorg. Chem.* **12**, 1477–1482.
Roberts, G. W., Cummings, S. C. & Cunningham, J. A. (1976). *Inorg. Chem.* **15**, 2503–2510.
Sinn, E. (1976). *Inorg. Chem.* **15**, 2698–2712.
Switzer, J. A. & Endicott, J. F. (1980). *J. Am. Chem. Soc.* **102**, 1181–1183.
Weiss, M. C. & Goedkin, V. L. (1976). *J. Am. Chem. Soc.* **98**, 3389–3391.