Acta Crystallographica Section C
**Crystal Structure
Communications**
ISSN 0108-2701

# An ion pair formed by protonated $Fe(cp^*py)_2$ and the octanuclear cluster $U_8Cl_{24}O_4(cp^*py)_2$ [cp*py is tetramethyl-5-(2-pyridyl)cyclopentadiene]

**Lionel Moisan, Thierry Le Borgne, Pierre Thuéry* and Michel Ephritikhine**

CEA/Saclay, SCM (CNRS URA 331), Bâtiment 125, 91191 Gif-sur-Yvette, France
Correspondence e-mail: thuery@drecam.cea.fr

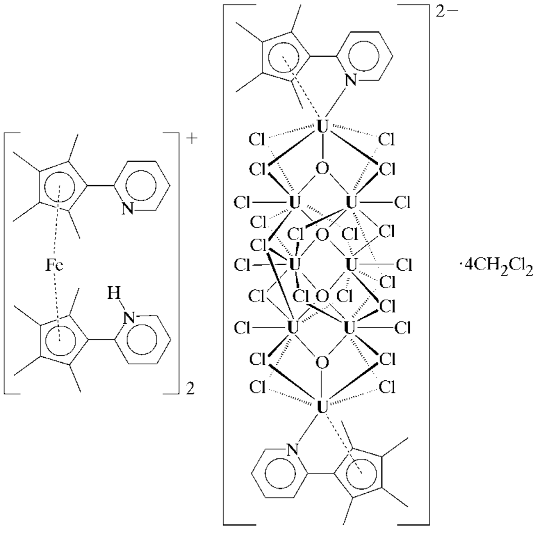
Received 31 August 2001
Accepted 20 November 2001
Online 23 January 2002

In bis[1,1′,2,2′,3,3′,4,4′-octamethyl-5-(2-pyridinio)-5′-(2-pyridyl)ferrocene] di-$\mu_3$-chloro-hexadeca-$\mu_2$-chloro-hexachloro-di-$\mu_4$-oxo-di-$\mu_3$-oxo-bis[($\eta^5$,$\kappa N$)-1,2,3,4-tetramethyl-5-(2-pyridyl)cyclopentadienyl]octauranium(IV) dichloromethane tetrasolvate, $[Fe(C_{14}H_{17}N)(C_{14}H_{16}N)]_2[U_8Cl_{24}O_4(C_{14}H_{16}N)_2]\cdot 4CH_2Cl_2$, (I), two protonated $Fe(cp^*py)_2$ units [cp*py is tetramethyl-5-(2-pyridyl)cyclopentadiene] form an ion pair with the dianionic centrosymmetric cluster $U_8Cl_{24}O_4(cp^*py)_2$. The latter is the highest nuclearity assemblage in the chemistry of uranium (non-uranyl) compounds reported to date.

## Comment

Although discrete molecular species including up to six (Thuéry, Nierlich, Souley *et al.*, 1999) and even eight (Thuéry, Nierlich, Baldwin *et al.*, 1999) uranyl ions are known, as well as a cluster comprising six uranium(V) centres (Duval *et al.*, 2001), only one compound with six U atoms in the +3 or +4 oxidation state has been structurally characterized, namely octa-$\mu_3$-hydroxo-dodeca-$\mu_2$-diphenylphosphato-hexauranium(III,IV) (Mokry *et al.*, 1996). In the course of our studies of the synthesis and structures of uranium complexes with the ligand tetramethyl-5-(2-pyridyl)cyclopentadiene, hereinafter denoted cp*py, we unintentionally obtained the title compound, (I), containing an octanuclear uranium(IV) cluster, and its structure is described here.

The asymmetric unit in (I) comprises one complete cationic iron complex (Fig. 1) and half the dianionic centrosymmetric polyuranium assemblage. The $Fe^{II}$ atom in the protonated octamethyl-5,5′-di(2-pyridyl)ferrocene moiety is in the same environment as described earlier by Siemeling *et al.* (1995) and Neumann *et al.* (1997), with a mean Fe—C distance of 2.05 (4) Å; the distances to the centroids are 1.651 Å for both ligands, and the angle around the Fe atom is 176.8°. The two $\eta^5$-cyclopentadienyl rings are nearly parallel, with a dihedral angle of 1.0 (5)° between them. Whereas octamethyl-5,5′-di(2-pyridyl)ferrocene is a neutral species, the N atom of one of the pyridyl moieties in (I) is protonated and involved in an intramolecular hydrogen bond with the N atom of the second pyridyl group, thus giving a cationic species with hydrogen-bonding geometry N3—H3 = 0.92 Å, H3···N2 = 1.80 Å, N3···N2 2.696 (14) Å and N3—H3···N2 164°. The dihedral angle between the two pyridyl moieties is 34.5 (5)°. Atoms C16, C19, C30 and C33 are slightly displaced out of the mean planes of the corresponding cyclopentadienyl rings, the maximum deviation being 0.52 (4) Å for C16. This deformation of the ligands is probably due to the presence of the hydrogen bond.



(I)

The $U_8Cl_{24}O_4(cp^*py)_2$ dianion is a large elongated assemblage (Fig. 2), roughly cylinder-shaped, with the two cp*py ligands as bases. The environment of atom U1 is the most unusual, whereas atoms U2, U3 and, to a lesser extent, U4, possess nearly similar coordination spheres. Atom U1 is bonded to the tetramethylcyclopentadienyl moiety, denoted cp*, in a $\eta^5$ fashion, with a mean U—C bond length of

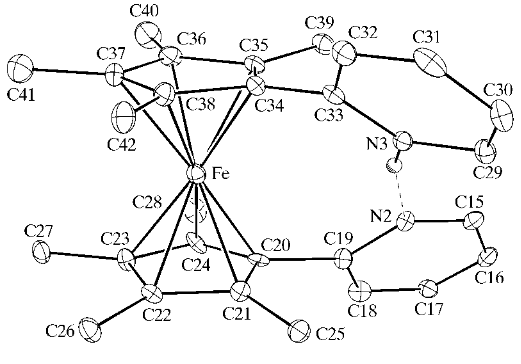


**Figure 1**
The cationic part of (I) with the atom-numbering scheme and displacement ellipsoids drawn at the 10% probability level. H atoms have been omitted for clarity, except for that involved in the intramolecular hydrogen bond, which is drawn as a small sphere of arbitrary radius. The hydrogen bond is shown as a dashed line.

DOI: 10.1107/S0108270101020029

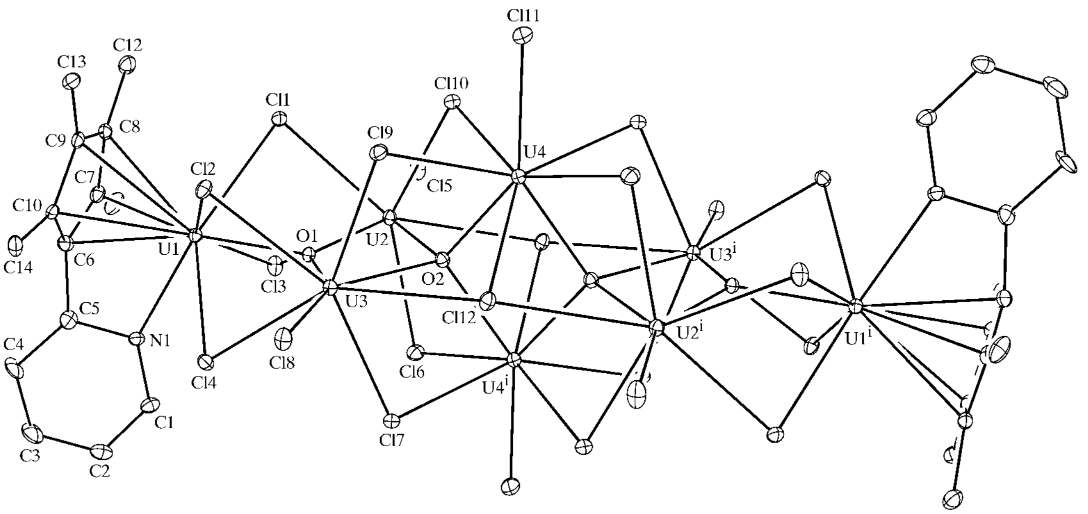


**Figure 2**
The anionic part of (I) with the atom-numbering scheme and displacement ellipsoids drawn at the 10% probability level. H atoms and solvent molecules have been omitted for clarity [symmetry code: (i) $-x$, $-y$, $-z$].

2.72 (9) Å (distance to the centroid = 2.43 Å), and also to the N atom of the pyridyl group. The cp*py ligand is distorted so that atom N1 comes closer to U1, atoms C2 and C5 being strongly displaced out of the mean plane of the cyclopentadienyl ring by 1.62 (3) and 0.42 (2) Å, respectively. The dihedral angle between the two rings is 71.7 (4)°, which indicates that the U–cp*py assemblage does not contain a pseudosymmetry plane due to the tilting of the pyridyl group. Several cases are known in which the Fe(cp*py)$_2$ complex is involved in the design of di- or trinuclear heterometallic complexes in which the ligand geometry is close to that observed in (I) and the N atoms of the pyridyl units are bonded to the second transition metal atom (Neumann *et al.*, 1997), but, to the best of our knowledge, there is only one other case in which the N atom of a cp*py moiety (or its equivalent without methyl substituents, cppy) is bonded to the same metal atom as the cp* (or cp) ring (Le Borgne *et al.*, 2002).

Atom U1 is further bonded to four $\mu_2$-chloro ions, with a mean U—Cl bond length of 2.80 (5) Å, and one $\mu_3$-oxo ion, O1, with a bond length of 2.244 (7) Å, in good agreement with the mean distance of 2.24 (7) Å for similar cases reported in the Cambridge Structural Database (CSD, Version 5.21; Allen & Kennard, 1993). The four Cl atoms define a plane to within 0.078 (2) Å, atoms U1 and O1 being 0.937 (2) and −1.307 (7) Å, respectively, from this mean plane, which is, further, roughly parallel to the cyclopentadienyl mean plane, with a dihedral angle of 10.2 (3)°. However, the four Cl atoms are far from defining a regular square, the Cl···Cl distances being in the range 2.271 (5)–4.456 (4) Å. The geometry of the uranium coordination sphere does not exactly match any of the polyhedra common in such seven-coordinate cases (Kepert, 1982). If the cp* ring is approximated to its centroid, this geometry may perhaps best be viewed as a distorted capped octahedron, with N1 in the capping position.

Atoms U2 and U3 share similar bonding features, each being bonded to a monodentate Cl atom directed towards the exterior of the 'cylinder', to the $\mu_3$-oxo ion O1, with bond lengths of 2.184 (7) and 2.159 (7) Å, respectively, slightly less than U1—O1, to the $\mu_4$-oxo ion O2, with larger bond lengths of 2.493 (8) and 2.454 (7) Å, and to four $\mu_2$- and one $\mu_3$-chloro ions. For both U2 and U3, two of these Cl atoms are shared with U1, while U2 shares two Cl atoms with U4$^{i}$ [symmetry code: (i) $-x$, $-y$, $-z$] and one with U4. Atom U3 exhibits the reverse pattern, sharing two Cl atoms with U4 and one with U4$^{i}$. Finally, U4 is bonded to two symmetrically related $\mu_4$-oxo ions, with a mean U—O bond length of 2.33 (4) Å, and to a monodentate Cl atom and five bridging Cl atoms, one shared with U2, one with U3, one with U2$^{i}$, one with U3$^{i}$ and one (Cl12) with both U3 and U2$^{i}$. The geometry of the coordination sphere of the three eight-coordinate atoms U2, U3 and U4 can be viewed as a distorted dodecahedron, if the difference in nature between O and Cl atoms is neglected.

The 12 Cl atoms of the repeat unit can be divided into three groups, corresponding to $\eta^1$-, $\mu_2$- and $\mu_3$-coordination modes. The mean U—Cl bond lengths are 2.60 (5), 2.79 (5) and 3.0 (1) Å, respectively, showing the expected bond lengthening. The mean U—Cl—U angles are 88 (5)° for the $\mu_2$-chloro ions. In the case of the $\mu_3$-chloro ion Cl12, two U—Cl—U angles have a comparable mean value, 82 (2)°, while the third, U2$^{i}$—Cl12—U3, is much larger at 147.7 (1)°. The bonding mode of Cl12 appears to be strongly asymmetric, the U3—Cl12 bond length in particular [3.183 (3) Å] being so large that it can hardly be considered as indicative of a true coordinative bond. There is only one other example of a $\mu_3$-chloro bridge in U$^{IV}$ chemistry (Arliguie *et al.*, 1994), in which the mean U—Cl bond length is 2.91 (1) Å, in good agreement with the present results, particularly for the bond lengths involving U2 and U4.

As previously indicated, the two oxo ions have different bonding patterns: O1 is a $\mu_3$-oxo bridge, with a mean U—O bond length of 2.20 (4) Å [in good agreement with the literature mean value of 2.24 (7) Å, as indicated above] and a mean U—O—U angle of 120 (4)°, whereas O2 is a $\mu_4$-oxo bridge, with a mean U—O of 2.40 (9) Å, the bond length involving U4 and U4$^{i}$ being about 0.15 Å smaller than those of U2 and U3, and a mean U—O—U angle of 110 (5)°. A search of the CSD indicates that this is the first occurrence of a $\mu_4$-oxo ion in uranium chemistry.

The eight U atoms in the cluster can be viewed as located in two planes, one defined by U1, U2, U3, U1$^{i}$, U2$^{i}$ and U3$^{i}$ [maximum deviation 0.0282 (3) Å], and the second by U1, U4, U1$^{i}$ and U4$^{i}$. These two planes are nearly orthogonal [dihedral angle 85.70 (1)°] and the four O atoms are located close to their intersection [maximum distance from the planes 0.151 (8) Å]. If the cp*py ligands are disregarded, the intersection of the two planes defines a pseudo-binary axis. The mean U$\cdots$U distance between U atoms bridged by O or Cl ions is 3.9 (1) Å. In the hexanuclear uranium(III,IV) cluster previously described (Mokry *et al.*, 1996), the six U atoms were held together by $\mu_3$-hydroxo and $\mu_2$-diphenylphosphato bridges, with a mean U$\cdots$U distance of 3.854 (9) Å, and were octahedrally arranged. The novelty of the structure of (I) is the variety of bonding modes exhibited by the constituent atoms, and the unprecedented elongated shape of the molecule that contains two terminal organic ligands.

## Experimental

Octamethyl-5,5′-di(2-pyridyl)ferrocene was synthesized according to the procedure described by Siemeling *et al.* (1995) and was mixed in a 1:1 ratio with $UCl_4$ in $CH_2Cl_2$. Adventitious traces of oxygen probably entered the flask during prolonged heating. Single crystals of (I) formed upon standing at room temperature.

### *Crystal data*

$[Fe(C_{14}H_{17}N)(C_{14}H_{16}N)]_2[U_8Cl_{24}O_4(C_{14}H_{16}N)_2]\cdot 4CH_2Cl_2$
$M_r = 4462.13$
Triclinic, $P\overline{1}$
$a = 14.3894\ (8)$ Å
$b = 15.9758\ (7)$ Å
$c = 16.0646\ (9)$ Å
$\alpha = 61.128\ (3)°$
$\beta = 70.648\ (2)°$
$\gamma = 83.316\ (3)°$
$V = 3047.0\ (3)$ Å$^3$

$Z = 1$
$D_x = 2.432$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 20 837 reflections
$\theta = 3.0$–$25.7°$
$\mu = 11.57$ mm$^{-1}$
$T = 100\ (2)$ K
Parallelepiped, dark brown
$0.20 \times 0.20 \times 0.15$ mm

### *Data collection*

Nonius KappaCCD area-detector diffractometer
$\varphi$ scans
Absorption correction: empirical (*MULABS* in *PLATON*; Spek, 2000)
$T_{min} = 0.082$, $T_{max} = 0.176$
20 837 measured reflections

10 693 independent reflections
7972 reflections with $I > 2\sigma(I)$
$R_{int} = 0.057$
$\theta_{max} = 25.7°$
$h = -15 \rightarrow 17$
$k = -18 \rightarrow 18$
$l = -19 \rightarrow 19$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.097$
$S = 1.03$
10 693 reflections
680 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0201P)^2 + 11.4271P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.19$ e Å$^{-3}$
$\Delta\rho_{min} = -1.16$ e Å$^{-3}$

**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| U1—O1 | 2.244 (7) | U4—O2 | 2.303 (7) |
| U1—N1 | 2.553 (9) | U4—O2$^{i}$ | 2.354 (8) |
| U1—C6 | 2.596 (12) | U4—Cl6$^{i}$ | 2.793 (3) |
| U1—C7 | 2.671 (13) | U4—Cl7$^{i}$ | 2.808 (3) |
| U1—C8 | 2.795 (12) | U4—Cl9 | 2.786 (3) |
| U1—C9 | 2.816 (11) | U4—Cl10 | 2.785 (3) |
| U1—C10 | 2.700 (10) | U4—Cl11 | 2.650 (3) |
| U1—Cl1 | 2.798 (3) | U4—Cl12 | 2.901 (3) |
| U1—Cl2 | 2.764 (3) | U1$\cdots$U2 | 3.7668 (6) |
| U1—Cl3 | 2.758 (3) | U1$\cdots$U3 | 3.7800 (6) |
| U1—Cl4 | 2.867 (3) | U2$\cdots$U3 | 3.8256 (6) |
| U2—O1 | 2.184 (7) | U2$\cdots$U4$^{i}$ | 3.9156 (7) |
| U2—O2 | 2.493 (8) | U2$\cdots$U4 | 4.0600 (6) |
| U2—Cl1 | 2.833 (3) | U3$\cdots$U4 | 3.9269 (6) |
| U2—Cl3 | 2.848 (3) | U3$\cdots$U4$^{i}$ | 4.0503 (6) |
| U2—Cl5 | 2.571 (3) | U4$\cdots$U4$^{i}$ | 3.7281 (9) |
| U2—Cl6 | 2.713 (3) | Fe—C20 | 1.969 (11) |
| U2—Cl10 | 2.734 (3) | Fe—C21 | 2.028 (14) |
| U2—Cl12$^{i}$ | 2.985 (3) | Fe—C22 | 2.061 (12) |
| U3—O1 | 2.159 (7) | Fe—C23 | 2.042 (12) |
| U3—O2 | 2.454 (7) | Fe—C24 | 2.063 (15) |
| U3—Cl2 | 2.847 (3) | Fe—C34 | 2.038 (12) |
| U3—Cl4 | 2.822 (3) | Fe—C35 | 2.025 (12) |
| U3—Cl7 | 2.712 (3) | Fe—C36 | 2.090 (13) |
| U3—Cl8 | 2.566 (3) | Fe—C37 | 2.086 (15) |
| U3—Cl9 | 2.711 (3) | Fe—C38 | 2.070 (15) |
| U3—Cl12 | 3.183 (3) | | |
| | | | |
| U1—Cl1—U2 | 83.96 (9) | U2$^{i}$—Cl12—U3 | 147.69 (10) |
| U1—Cl2—U3 | 84.69 (7) | U1—O1—U2 | 116.6 (3) |
| U1—Cl3—U2 | 84.40 (8) | U2—O1—U3 | 123.5 (3) |
| U1—Cl4—U3 | 83.28 (8) | U1—O1—U3 | 118.3 (3) |
| U2—Cl6—U4$^{i}$ | 90.65 (9) | U2—O2—U3 | 101.3 (3) |
| U3—Cl7—U4$^{i}$ | 94.40 (9) | U2—O2—U4 | 115.6 (3) |
| U3—Cl9—U4 | 91.18 (9) | U2—O2—U4$^{i}$ | 107.7 (3) |
| U2—Cl10—U4 | 94.72 (9) | U3—O2—U4 | 111.2 (3) |
| U2$^{i}$—Cl12—U4 | 83.38 (7) | U3—O2—U4$^{i}$ | 114.8 (3) |
| U3—Cl12—U4 | 80.24 (7) | U4—O2—U4$^{i}$ | 106.4 (3) |

Symmetry code: (i) $-x, -y, -z$.

The H atom bonded to N3 was found in a difference Fourier map and was constrained to ride on its parent atom with $U_{iso}(H) = 1.2U_{eq}(N)$. All other H atoms, except those of the solvent molecules, were introduced at calculated positions and refined as riding atoms [C—H = 0.93 (CH) and 0.96 Å ($CH_3$)] with $U_{iso}(H) = 1.2$ (CH) or 1.5 ($CH_3$) times $U_{eq}(C)$. Both dichloromethane solvent molecules in the asymmetric unit are disordered, one with two positions for one Cl atom and the second with two positions for the C atom. Both were refined with constraints on bond lengths and displacement parameters. The bond between the two C atoms linking one tetramethylcyclopentadienyl and one pyridyl species is longer than usual [C19—C20 1.552 (9) Å]. The highest residual electron-density peak is located 0.86 Å from U4.

Data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL* and *PARST*97 (Nardelli, 1995).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TR1004). Services for accessing these data are described at the back of the journal.

## References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 1, 31–37.

Arliguie, T., Ephritikhine, M., Lance, M., Vigner, J. & Nierlich, M. (1994). *J. Organomet. Chem.* **484**, 195–201.

Bruker (1999). *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.

Duval, P. B., Burns, C. J., Clark, D. L., Morris, D. E., Scott, B. L., Thompson, J. D., Werkema, E. L., Jia, L. & Andersen, R. A. (2001). *Angew. Chem. Int. Ed.* **40**, 3357–3361.

Kepert, D. L. (1982). *Inorganic Stereochemistry*, pp. 117–151. Heidelberg: Springer-Verlag.

Le Borgne, T., Thuéry, P. & Ephritikhine, M. (2002). *Acta Cryst.* C**58**, m8–m9.

Mokry, L. M., Dean, N. S. & Carrano, C. J. (1996). *Angew. Chem. Int. Ed. Engl.* **35**, 1497–1498.

Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.

Neumann, B., Siemeling, U., Stammler, H. G., Vorfeld, U., Delis, J. G. P., van Leeuwen, P. W. N. M., Vrieze, K., Fraanje, J., Goubitz, K., Fabrizi de Biani, F. & Zanello, P. (1997). *J. Chem. Soc. Dalton Trans.* pp. 4705–4711.

Nonius (1997). *KappaCCD Server Software*. Nonius BV, Delft, The Netherlands.

Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter & R. M. Sweet, pp. 307–326. London: Academic Press.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Siemeling, U., Vorfeld, U., Neumann, B. & Stammler, H. G. (1995). *Chem. Ber.* **128**, 481–485.

Spek, A. L. (2000). *PLATON*. University of Utrecht, The Netherlands.

Thuéry, P., Nierlich, M., Baldwin, B. W., Komatsuzaki, N. & Hirose, T. (1999). *J. Chem. Soc. Dalton Trans.* pp. 1047–1048.

Thuéry, P., Nierlich, M., Souley, B., Asfari, Z. & Vicens, J. (1999). *J. Chem. Soc. Dalton Trans.* pp. 2589–2594, and references therein.