(861 and 475 cm^{-1}) are shifted to lower frequencies (830 and 460 cm^{-1}) in the adduct.[31]

Finally the new band observed at ~4300 Å in the electronic spectrum of solutions of the adduct may be attributed to what is commonly called an "intermolecular charge transfer" as defined by Mulliken.[29] All the points discussed until now indicate that the interaction between TCNQ as an electron acceptor and Cu(salphen) as a donor is extremely weak.

Although no definitive data regarding the orbital interactions are available, the overlap diagram in Figure 5 is instructive in illustrating possible intermolecular interactions. The overlap between TCNQ and Cu(salphen) mainly takes place between the dicyanomethylene groups of TCNQ and the ring O(1)–C(5)G1–C(6)G1–C(1)–N(1) and phenyl group G1 of Cu(salphen). The molecular overlap is not of the ring-to-ring type; this was already noticed concerning the TCNQ–bis(8-hydroxyquinolato)copper(II) complex.[17] One cyano group, C(5)T–N(1)T, lies just over the ring O(1)–C(5)G1–C(6)-G1–C(1)–N(1), while the other one, C(6)T–N(2)T, nearly overhangs one side of the phenyl group G1, C(4)Gl–C(3)Gl. Another phenyl group G1, related to the previous one by translation $+\vec{c}$, covers the ethylenic bond C(3)T–C(4)T, the bond C(4)T–C(5)T, and, partly, the bond C(4)T–C(6)T. From examination of the atom-to-plane distances given in Table V, distances of respectively 3.29 and 3.35 Å are observed from atoms C(5)T and N(1)T to the ring O(1)–C(5)G1–C-(6)G1–C(1)–N(1). With the idea that the electronic density of Cu(salphen) is most likely delocalized over the whole molecule, these relatively short distances could be indicative of interaction between both molecules. The distances to the plane of the cyanomethylene group of the overlying atoms (C1)G1 and C(2)G1 (3.35 and 3.31 Å) and of the underlying atoms C(5)G1 and C(4)G1 (3.30 and 3.35 Å) are also compatible with intermolecular interactions. The presumed interactions take place at both ends of the molecule of TCNQ linking the component molecules into infinite chains. This arrangement is compatible with the low but nonnegligible electrical conductivity that has been observed.

In conclusion, [Cu(salphen)]$_2$·TCNQ is a weak molecular adduct. There are, however, some hints that the charge transfer between the component molecules may not be totally negligible.

Acknowledgment. This work has been technically supported in part by the French CNRS, the DGRST, and the DESR. We thank Dr. R. Haran for recording the ESR spectra, Professor O. Kahn for the magnetic measurements and Dr. L. Interrante and Dr. J. Kasper for helpful comments on the manuscript. The helpful assistance of M. F. Bruniquel is also acknowledged.

Note Added in Proof. Since submission of this paper, the synthesis and structure of a 1:2 molecular complex of bis(*N*-isopropyl-2-oxy-1-naphthylidenaminato)copper(II) with TCNQ has been reported (Matsumoto, N.; Nonaka, Y.; Kida, S.; Kawano, S.; Ueda, I. *Inorg. Chim. Acta* **1979**, *37*, 27.). The crystal structure of this complex shows what these authors call "a typical Π–Π type molecular complex structure of alternately stacked donor and acceptor molecules."

Registry No. [Cu(salphen)]$_2$·TCNQ, 72121-31-4; Cu(salphen), 42490-12-0.

Supplementary Material Available: Listings of structure factor amplitudes and root-mean-square amplitudes of vibration (5 pages). Ordering information is given on any current masthead page.

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Crystal Structure of Uranium(IV) Tetraiodide by X-ray and Neutron Diffraction

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The crystal structure of uranium tetraiodide has been solved by a combination of X-ray and neutron diffraction techniques. UI_4 is monoclinic, of space group $C2/c$, with a = 13.967 (6) Å, b = 8.472 (4) Å, c = 7.510 (3) Å, and β = 90.54 (5)°. The uranium atom is at position 4(e) with y = 0.152 (2), and the iodine atoms are in general positions 8(f). There are two types of iodine atoms with I(1) at (0.123 (1), 0.118 (2), –0.086 (2)) and I(2) at (–0.134 (1), 0.382 (3), and 0.100 (2)). The structure, based on hexagonal close packing of the iodine atoms, consists of zigzag chains $UI_2I_{4/2}$, with the terminal iodine atoms in cis positions. The U–I(1) (bridging) distances are 3.08 (2) and 3.11 (2) Å, and the U–I(2) (terminal) distances are both 2.92 (2) Å. The parameters were determined by the neutron powder profile refinement technique, and $R = \sum(|y_o - y_c|)/\sum y_o = 0.13$, $R(\text{expected}) = ((\text{NO} - \text{NV})/\sum w y_o^2)^{1/2} = 0.11$, and $\chi^2 = \sum w(y_o - y_c)^2/(\text{NO} - \text{NV}) = 1.7$. UI_4 is not isostructural with any other known MX_4 halide and is the only actinide tetrahalide to have a chain structure, although chains are common in the transition-metal tetrahalide structures.

Introduction

The existence of uranium tetraiodide has been known for many years, but it has remained structurally uncharacterized because single crystals and good X-ray photographs are very difficult to obtain, and UI_4 is not isostructural with ThI_4,[1] UBr_4,[2] or any other known actinide or transition-metal tetrahalide. The present work was undertaken to fill this gap in the MX_4 structure types.

Experimental Section

Approximately 25 g of UI_4 was prepared by reacting uranium metal turnings with iodine, according to the method of Bagnall et al.[3] In the final phases of this preparation, excess iodine was sublimed from the UI_4 within the evacuated vessel. The dissociation $UI_4 \rightarrow UI_3 + {}^1/_2I_2$ occurs to some extent depending on temperature conditions, generally resulting in a small amount of UI_3 contamination. The moisture-sensitive UI_4 was always handled by drybox methods.

Some needles of UI_4 were mounted with Kel-F grease in glass capillaries. The crystals appeared lathlike under the microscope, with

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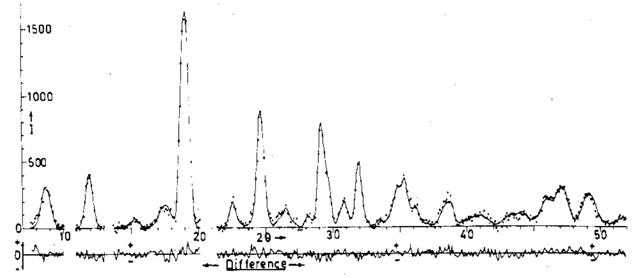

Figure 1. The observed and calculated neutron powder pattern profiles for UI_4.

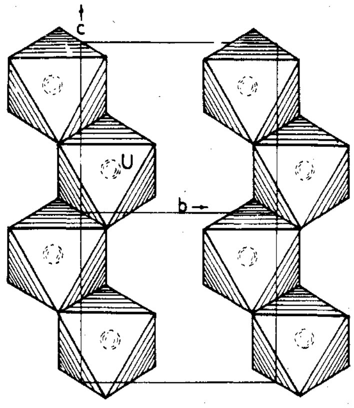

Figure 2. The structure of UI_4 viewed normal to the hexagonal close-packed iodine layers showing the zigzag chains of edge-sharing octahedra. The chains are at the same level, $x = 0$. The chains at $x = {}^1/_2$ are not shown.

much shearing and bending of the laths. Some needles gave no diffraction pattern at all, indicating a high degree of disorder. Finally, a lath was found which at one end gave diffraction spots corresponding to a single-crystal region. Rotation and Weissenberg photographs with Cu Kα radiation (λ = 1.5418 Å) identified UI_4 as monoclinic, space group $C2/c$. The intensities of 80 strong reflections were measured on a four-circle diffractometer with MoKα radiation (λ = 0.7107 Å).

A neutron powder pattern of a sample sealed in a cylindrical vanadium can (${}^1/_2 \times 1{}^1/_2$ in.) was collected on the AAEC research reactor HIFAR with the elastic diffraction technique,[4] the neutron wavelength being 1.085 Å.

Structure Determination

A Patterson synthesis of the 80 X-ray reflections showed the iodine atoms to be in hexagonal close packing. The only uranium position consistent with the map was 4(e), $(0, y, {}^1/_4)$, and the value of y was approximately ${}^1/_8$. An idealized structure was derived by placing the close-packed iodine array around the uranium atom.

The structure was refined with the neutron profile technique[5] ($b_U = 0.85$, $b_I = 0.53 \times 10^{-12}$ cm). Some (about 10%) UI_3 was found to be in the UI_4 sample. The strongest UI_3 line was resolved in the pattern; the UI_3 impurity contribution was removed by calculating a UI_3 pattern, scaling it, and subtracting it from the observed pattern. Because of the lath-shaped crystals, a preferred orientation correction was necessary ([100] perpendicular to the lath face). No absorption corrections were necessary. The observed and calculated neutron profiles, given in Figure 1, show that the observed and calculated patterns fit within the experimental errors.

Discussion

The structure of UI_4 seen down the a axis (perpendicular to the hexagonal close-packed layers) is shown in Figure 2. A side-on view is shown in Figure 3. The layer sequence in the unit cell is |ABAB|. The coordinates in Table I show that the iodine atoms are in nearly perfect close packing, while the uranium atom deviates slightly from the idealized position because of U–U repulsions. Thus, the contraction around occupied holes and expansion around vacant holes, which is so marked in UCl_6[6] and UF_6,[7] are not found in UI_4. In fact, the unit cell dimensions may be obtained from the iodine ionic radius R (2.16 Å) as follows: $a = 4(8/3)^{1/2}R = 14.1$ Å; $b = 4R = 8.6$ Å; $c = 2(3^{1/2})R = 7.5$ Å ($\beta = 90°$ ideally).

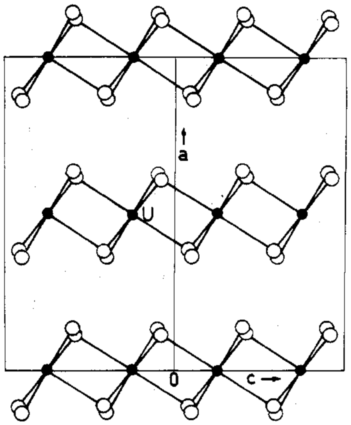

Figure 3. A side-on view of the $UI_2I_{4/2}$ chains normal to the hexagonal close-packed iodine layers ABAB. The chains at $x = {}^1/_2$ are displaced by $y = {}^1/_2$ relative to the chains at $x = 0$.

Table I. Crystal Data and Parameters for Uranium Tetraiodide

monoclinic
space group $C2/c$ ($C_{2h}{}^6$)
$a = 13.967$ (6) Å
$b = 8.472$ (4) Å
$c = 7.510$ (3) Å
$\beta = 90.54$ (5)°
$V = 888.7$ Å^3
$D_{calcd} = 5.57$ g cm^{-3}
$Z = 4$

preferred orientation parameter: $G^f = 0.201$ (4)
half-width parameters (deg $2\theta^2$):[c] $U = 8.2$ (11), $V = -4.0$ (5), $W = 0.74$ (6)
R factor over neutron pattern points:[a] $\Sigma(|y_o - y_c|)/\Sigma y_o = 0.129$
R factor (expected): $((NO - NV)/\Sigma w y_o{}^2)^{1/2} = 0.111$
$\chi^2 = \Sigma w(y_o - y_c)^2/(NO - NV) = 1.7$

atom	position	10^3x	10^3y	10^3z	B Å^2
U	4(e)	0	152 (2)	250	2.9 (3)
U idealized		0	125	250	
I(1)	8(f)	123 (1)	118 (2)	−086 (2)	1.9 (4)[d]
I(1) idealized		125	125	−083	
I(2)	8(f)	−134 (1)	382 (3)	100 (2)	4.7 (5)[e]
I(2) idealized		−125	375	083	

[a] NO and NV are the number of observations and variables and y_o and y_c are the background-corrected pattern intensities. [b] B is the Debye-Waller isotropic temperature factor (TF = $\exp[-B \times (\sin^2\theta)/\lambda^2]$). [c] The half-width H is defined by $H^2 = U \tan^2\theta + V \tan\theta + W$. [d] Bridging. [e] Terminal. [f] Reference 5.

The structure explains the fibrous nature of the crystals. The endless zigzag UI_4 chains (terminal iodine atoms in cis positions) run parallel to c and form layers parallel to (011), and the I–I distances between chains are van der Waals contacts (~4.30 Å). Thus faults in the stacking of the chains cause the poor X-ray patterns given by this substance.

Figure 2 shows an off-center displacement of the U atom which is caused by U–U repulsions (U–U = 4.55 Å). The U–I(1) (bridging) distances are 3.08 (2) and 3.11 (2) Å, and the U–I(2) (terminal) distances are both 2.92 (2) Å. The temperature factor of the terminal iodine atom is significantly larger than that of the bridging iodine (Table I). The U–I

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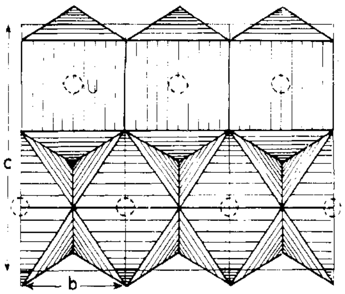

Figure 4. The sheet structure of UI_3, formed when adjacent UI_4 chains fuse and liberate one terminal iodine atom per octahedron.

distances are not much shorter than the sum of the ionic radii of U^{4+} and $I^- = 3.16$ Å. The bond angles in the octahedra are consistent with the uranium repulsions.

UI_4 is converted by gentle heating into UI_3. Presumably the layers of UI_4 chains at $x = 0$ and $x = {}^1/_2$ then become the sheets of the UI_3 structure shown in Figure 4. It is likely that in the conversion one of the two terminal iodine atoms in every octahedron is liberated, adjacent chains fuse, and cross-linked, linear -U-U-U- chains are formed with the same U-U separation as in UI_4. The U coordination polyhedron changes from an octahedron to a bicapped trigonal prism.

The structures of the actinide halides have been reviewed recently,[8] and UI_4 is the only actinide tetrahalide to show a chain structure ($UI_2I_{4/2}$). However, the chain structure, either linear with trans terminal halide atoms or zigzag with cis terminal atoms, is common in the transition-metal tetrahalides. Although none of these are isostructural with UI_4. Zigzag chains are found in $ZrCl_4$ and $HfCl_4$,[9] $TcCl_4$,[10] $PtCl_4$, $PtBr_4$, and α-PtI_4[11] and linear chains in $NbCl_4$,[12] α-$MoCl_4$,[13] $OsCl_4$,[14] and α-NbI_4.[15] The zigzag chain is found where there is no metal-metal attraction, while the linear chain generally signifies a metal-metal interaction. An unusual chain (corner-linked bioctahedra Re_2Cl_9) is found in $ReCl_4$.[16] TeI_4 shows a Te_4I_{16} tetramer.[17] UI_4 is thus a new variant of the infinite-chain structure $MX_2X_{4/2}$, previously found only in the halides of the transition metals.

Registry No. UI_4, 13470-22-9.

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Crystal Structure at -35 °C of (Cyclobutadiene)(1,2-bis(diphenylphosphino)ethane-*P*,*P'*)iron Carbonyl and an Examination of Stereochemical Distortions in Cyclobutadiene-ML_3 Complexes

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The structure of $(C_4H_4)[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]Fe(CO)$ has been determined by single-crystal X-ray diffraction techniques with three-dimensional data gathered at -35 °C by counter methods. Yellow, platelike single crystals form in triclinic space group $P\bar{1}$ with unit cell constants at -35 °C $a = 9.608$ (8) Å, $b = 14.694$ (3) Å, $c = 9.473$ (2) Å, $\alpha = 103.30$ (1)°, $\beta = 102.54$ (2)°, and $\gamma = 92.73$ (2)°. The calculated density of 1.414 (4) g cm^{-3} for two molecules per unit cell of the complex agrees with the measured value of 1.45 g cm^{-3}. Full-matrix least-squares refinement of the structure has converged with an R index (on $|F|$) of 0.049 for the 4890 symmetry-independent reflections within the Mo Kα shell defined by $4 < 2\theta < 55°$ which have $I_o/\sigma(I_o) > 2$. The iron atom is bonded to the cyclobutadiene ring in a symmetric manner, to the two phosphorus atoms of the diphosphine ligand, and to the CO ligand. As a consequence of the electron-donating capacity of the diphosphine ligand, the electron-withdrawing CO group is more firmly bound to Fe than in the corresponding $Fe(CO)_3$ complex, as indicated by the Fe-C and C-O bond lengths (1.742 (3) and 1.165 (4) Å) and by the lower frequency of the CO symmetric stretch (1880 cm^{-1}), as compared to the values for the $Fe(CO)_3$ complex. Stereochemical results for ten cyclobutadiene-transition-metal complexes of the form $(C_4R_4)ML_3$, which have been characterized by X-ray diffraction methods, have been analyzed in terms of distortions from two idealized symmetrical structures, one in which an M-L bond eclipses a ring carbon atom and one in which an M-L bond bisects a ring C-C bond. The observation that torsion parameters for these structures are distributed over the entire range between those of the two idealized structures supports the experimental results and theoretical suggestions of a low barrier in such complexes.

Introduction

As part of an investigation in our laboratory of the structural and spectroscopic consequences of the systematic substitution of phosphine ligands in metal complexes of the form $[(\pi\text{-}C_nH_n)Fe(PR_3)_m(CO)_{3-m}]^{p+}$ ($n = 4$ or 5, $m = 0$-2, $p = 0$ or 1), we have determined the crystal structure of $(C_4H_4)Fe(P(C_6H_5)_2CH_2\text{-})_2(CO)$, a species obtained by photolysis of the parent tricarbonyl complex in the presence of $(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$.[1] This structural study also affords an examination of the geometry of an unsubstituted cyclobutadiene ligand for which only a few examples have been reported[2-4] and for which a very low barrier of rotation about the metal-C_4 axis has been predicted by Hoffmann and co-workers.[5]

In addition to reporting the details of this crystal structure, this paper provides the opportunity for an assessment of the

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