THE FIRST CATIONIC INDENYL-*f*-METAL COMPLEXES WITH PENTAGONAL BIPYRAMIDAL GEOMETRY. CRYSTAL STRUCTURES OF $[C_9H_7UBr_2(CH_3CN)_4]^+{}_2$ $[UBr_6]^{2-}$ AND $[\{C_9H_7UBr(CH_3CN)_4\}_2O]^{2+}[UBr_6]^{2-}$ *

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Summary

Treatment of the octahedral complexes, $C_9H_7AnHal_3 \cdot 2C_4H_8O$ (An = U or Th) with very pure methyl cyanide leads to the formation of the novel complexes $[C_9H_7AnHal_2(CH_3CN)_4]^+{}_2$ $[AnHal_6]^{2-}$ (I). Reaction of $C_9H_7UHal_3 \cdot 2C_4H_8O$ with methyl cyanide containing dry oxygen gives the red complex $[\{C_9H_7UHal-(CH_3CN)_4\}_2O]^{2+}$ $[UHal_6]^{2-}$ (II).

Both uranium complexes with Hal = Br have been characterized by elemental analysis, vibration spectroscopy and X-ray structure analysis. The cation in I exhibits a pentagonal bipyramidal geometry and that in II consists of two pentagonal bipyramids bonded by an oxygen occupying the common apex. A series of analogous compounds containing the 1-ethylindenyl, 1, 4, 7-trimethylindenyl or 1,2,3,4,5,6,7-heptamethylindenyl anion has been prepared and characterized. The reactions of the octahedral compounds with butyronitrile and benzonitrile is discussed.

Introduction

The octahedral organometallic compounds, $C_9H_7AnHal_3 \cdot 2THF$, (An = actinide) undergo a wide range of reactions with various Lewis bases [1,2]; generally, the THF molecules are simply displaced by the stronger bases without fundamental modifications of the molecular geometry. We show below that with methyl cyanide under carefully chosen conditions it is possible to obtain indenyl compounds with a geometry previously unobserved in the organometallic chemistry of actinide elements.

After exposure to traces of oxygen, many cyclopentadienyl compounds exhibit infrared bands characteristic of U–O vibrations without major modifications of the other absorptions [3,4] but the structures of these compounds are unknown. The structure of an anionic complex containing U^{VI} and U^{IV}, viz. $[U(Cp)_3(CH_3CN)_2]^+_2$ $[UO_2Cl_2]^{2-} \cdot 2C_4H_6$, has been established [5] but, in this complex, there is no bond between uranium and oxygen in the organometallic part of the molecule. In this paper, indenyl compounds containing such a bond, viz. $[\{C_9H_7UHal(CH_3CN)_4\}_2O]^{2+} \cdot [UHal_6]^{2-}$, are described.

Experimental

All experiments were performed under pure nitrogen ($H_2O < 3$ ppm, $O_2 < 5$ ppm) in Schlenk-type glassware or in a glove box.

Tetrahydrofuran was distilled under argon from K-Na alloy. Methyl cyanide, butyronitrile, and benzonitrile were treated with calcium hydride and distilled under argon. Methyl cyanide containing oxygen (ca. 25 mg/l) was dried with P_2O_5 in an air atmosphere. Trimethylphosphine oxide was prepared by oxidation of trimethylphosphine using aqueous potassium permanganate [6] and purified by sublimation under high vacuum. 1-Ethylindene, 1,4,7-trimethylindene and 1,2,3,4,5,6,7-heptamethylindene were prepared by published methods [7,8].

Infrared spectra were recorded on a Perkin–Elmer 580B spectrophotometer and the VIS-NIR infrared spectra on a Cary 17 apparatus. The magnetic data was obtained between 1.5 and 300 K by the Faraday method; the observed susceptibilities were corrected for the diamagnetism of the constituents of the molecule.

X-ray analysis

X-ray studies were carried out on the complexes $[C_9H_7UBr_2(CH_3CN)_4]^+_2$ $[UBr_6]^{2-}$ (I) and $[\{C_9H_7UBr(CH_3CN)_4\}_2O]^{2+} \cdot [UBr_6]^{2-}$ (II). Single crystals mounted in thin-walled glass capillaries were set up on an Enraf-Nonius CAD4 diffractometer (Mo-K_α radiation, graphite monochromator). Cell dimensions were obtained by the least-squares method from angle data of 25 reflections. The intensities of 2607 and 4349 independent reflections were measured at 295 K for I and II respectively by a $\theta/2\theta$ scan in the range $4 \leqslant 2\theta \leqslant 50°$. Intensities were corrected for Lorentz-polarization and empirical absorption [9]. The structures were solved by direct methods and refined by the least-squares method in a full-matrix approximation. In I only the U and Br atoms were refined anisotropically. Isotropic H atoms, placed at calculated positions, were included in the final structure factor calculations.

Other relevant crystal and experimental data are given in Table 1. The coordi-

TABLE 1

CRYSTALLOGRAPHIC DATA AND EXPERIMENTAL DETAILS

	I	II
Space group	$P\bar{3}$	$P2/c$
a (Å)	24.465(6)	10.670(5)
b (Å)	24.465(6)	14.516(5)
c (Å)	8.944(4)	16.747(7)
β (°)	90.0	10.772(3)
V (Å^3)	4637(9)	2475(4)
D (Mg m^{-3})	2.226	2.587
Z	3	2
Linear absorption coefficient (cm^{-1})	138.648	157.145
Number of reflexions used in the final refinement	1454 $(I > 2\sigma(I))$	2793 $(I > 3\sigma(I))$
Final values: R	0.051	0.045
R_w	0.058	0.057

nates and temperature factors of non-hydrogen atoms are given in Table 2. Lists of structure factors may be obtained from the authors.

Preparative methods

Starting materials

The complexes [LAnHal$_3 \cdot$2THF], where An = U or Th and L = C$_9$H$_7^-$, 1-C$_2$H$_5$-C$_9$H$_6^-$, 1,4,7-(CH$_3$)$_3$C$_9$H$_4^-$ or 1,2,3,4,5,6,7-(CH$_3$)$_7$C$_9^-$, were all prepared by the following method.

A solution of LK or LNa (10 mmol) in THF was added dropwise under nitrogen to the actinide tetrahalide (10 mmol) in THF at 0°C. The solution was stirred for 2 d at room temperature, the KHal or NaHal was removed by centrifugation, and the supernatant liquid was kept at low temperature to deposit crystals. The yield was 60–80% (Table 3).

Adducts with methyl cyanide

A solution of [LAnHal$_3 \cdot$2THF] (1 mmol) in CH$_3$CN (100 ml) was made up at room temperature then rapidly centrifuged, and any solid was discarded. After a few minutes, precipitation of a crystalline product was observed. The crystals, yellow for thorium compounds and deep brown for uranium compounds, were carefully dried by pumping (10^{-3}–10^{-4} torr) at room temperature for 1–2 h (yield: 30–50% based on actinide) (Table 3).

Adducts with butyro- and benzo-nitrile

A solution of [LAnHal$_3 \cdot$2THF] (1 mmol) in the appropriate nitrile (100 ml) was made up at room temperature. A precipitate was slowly formed, and this isolated by centrifugation and dried at 50°C (10^{-3}–10^{-4} torr) for 1 h (yield 60–80% based on actinide) (Table 3).

TABLE 2

ATOMIC POSITIONAL AND THERMAL PARAMETERS (Å^2) FOR COMPOUNDS I AND II
($B_{eq} = 1/3[\Sigma_{i,j} B_{ij} a_i^\star a_j^\star (a_i a_j)]$)

Atom	x	y	z	B_{eq}
Compound I				
U(1)	0.36595(6)	0.16879(6)	0.3484(2)	3.37(3)
U(2)	0.0	0.0	0.0	2.97(6)
U(3)	0.333	0.667	0.0512(3)	3.25(5)
Br(1)	0.3522(2)	0.1511(2)	0.6583(5)	6.2(1)
Br(1′)	0.3029(2)	0.0387(2)	0.3326(5)	6.0(1)
Br(2)	0.1054(2)	0.0379(2)	0.1771(6)	7.0(1)
Br(3)	0.4391(2)	0.7040(2)	0.2294(5)	5.7(1)
Br(3′)	0.4003(2)	0.7718(2)	−0.1250	6.5(1)
C(1)	0.467(1)	0.279(1)	0.296(4)	4.3(9)
C(2)	0.454(1)	0.283(1)	0.443(4)	5(1)
C(3)	0.394(1)	0.285(1)	0.439(4)	4.3(9)
C(4)	0.328(2)	0.295(2)	0.225(5)	6(1)
C(5)	0.326(2)	0.297(2)	0.075(5)	7(1)
C(6)	0.373(2)	0.297(2)	−0.022(5)	7(1)
C(7)	0.422(2)	0.288(2)	0.029(4)	5(1)
C(8)	0.424(1)	0.284(1)	0.195(4)	4.1(9)
C(9)	0.374(2)	0.286(2)	0.289(5)	5(1)
N(1)	0.420(1)	0.155(1)	0.118(3)	4.3(7)
C(1′)	0.437(1)	0.142(1)	0.016(4)	3.8(9)
C(1″)	0.461(2)	0.126(2)	−0.116(4)	5(1)
N(2)	0.463(1)	0.164(1)	0.428(3)	4.8(8)
C(2′)	0.509(2)	0.168(2)	0.460(4)	6(1)
C(2″)	0.579(2)	0.172(2)	0.516(5)	7(1)
N(3)	0.259(1)	0.161(1)	0.404(3)	3.7(7)
C(3′)	0.216(2)	0.164(2)	0.424(5)	6(1)
C(3″)	0.158(2)	0.167(2)	0.455(5)	6(1)
N(4)	0.299(1)	0.150(1)	0.114(3)	4.5(7)
C(4′)	0.267(2)	0.145(2)	0.018(5)	7(1)
C(4″)	0.228(2)	0.147(2)	−0.110(6)	9(2)
Compound II				
U(1)	0.45866(5)	0.44927(4)	0.10386(3)	1.819(9)
U(2)	1.000	0.500	0.500	1.89(1)
Br(1)	0.1872(2)	0.4344(1)	0.0092(1)	3.63(4)
Br(2)	0.7730(2)	0.4104(1)	0.5026(1)	3.47(3)
Br(3)	1.0331(2)	0.5660(1)	0.6605(1)	4.19(4)
Br(4)	0.8576(2)	0.6552(1)	0.4355(1)	4.55(4)
O	0.500	0.500	0.000	2.5(3)
N(1)	0.439(1)	0.2940(9)	0.0295(8)	3.5(3)
C(1′)	0.422(2)	0.226(1)	−0.007(1)	3.2(4)
C(1″)	0.398(2)	0.138(1)	−0.055(1)	5.2(5)
N(2)	0.357(1)	0.6063(9)	0.1149(7)	2.8(3)
C(2′)	0.277(2)	0.654(1)	0.1178(9)	2.9(3)
C(2″)	0.165(2)	0.711(1)	0.123(1)	5.4(5)
N(3)	0.641(1)	0.5645(9)	0.1714(8)	3.1(3)
C(3′)	0.732(2)	0.611(1)	0.1865(9)	3.6(4)
C(3″)	0.849(2)	0.667(1)	0.204(1)	5.7(5)
N(4)	0.687(1)	0.3767(9)	0.1179(8)	3.3(3)
C(4′)	0.785(2)	0.356(1)	0.116(1)	3.1(4)
C(4″)	0.916(2)	0.330(2)	0.114(1)	5.6(5)
C(1)	0.573(2)	0.397(1)	0.2680(9)	3.3(4)

TABLE 2 (continued)

Atom	x	y	z	B_{eq}
C(2)	0.504(2)	0.319(1)	0.226(1)	4.4(4)
C(3)	0.366(2)	0.336(1)	0.204(1)	4.3(4)
C(4)	0.235(2)	0.472(1)	0.241(1)	4.0(4)
C(5)	0.250(2)	0.554(1)	0.285(1)	4.0(4)
C(6)	0.380(2)	0.589(1)	0.3258(9)	3.4(4)
C(7)	0.489(2)	0.546(1)	0.3206(9)	3.4(4)
C(8)	0.478(2)	0.463(1)	0.2774(8)	2.6(3)
C(9)	0.346(1)	0.423(1)	0.2357(8)	2.7(3)

TABLE 3. ANALYTICAL RESULTS

Compound [a]	MW	Found (calcd.) (%)				
		C	H	N	Hal	An
$[L^1UCl_3 \cdot 2THF]$	631.812	36.02 (36.12)	4.39 (4.31)		16.83 (16.83)	37.81 (37.67)
$[L^1ThCl_3 \cdot 2THF]$	625.831	36.29 (36.47)	4.29 (4.35)		16.95 (17.00)	37.17 (37.08)
$[L^2UCl_3 \cdot 2THF]$	645.839	36.57 (37.20)	4.90 (4.53)		16.72 (16.47)	36.49 (36.86)
$[L^2ThCl_3 \cdot 2THF]$	639.848	37.59 (37.54)	4.48 (4.57)		16.77 (16.62)	36.12 (36.26)
$[L^3ThCl_3 \cdot 2THF]$	695.956	41.19 (41.42)	5.50 (5.36)		15.41 (15.28)	33.81 (33.34)
$[C_9H_7ThCl_2(CH_3CN)_4]^+_2 \cdot [ThCl_6]^{2-}$	1609.376	25.49 (25.37)	2.38 (2.38)	7.00 (6.96)	22.13 (22.03)	43.30 (43.25)
$[C_9H_7UCl_2(CH_3CN)_4]^+_2 \cdot [UCl_6]^{2-}$	1627.349	24.87 (25.09)	2.43 (2.35)	7.01 (6.89)	21.87 (21.79)	43.62 (43.88)
$[C_9H_7UBr_2(CH_3CN)_4]^+_2 \cdot [UBr_6]^{2-}$	2071.859	19.79 (19.71)	1.99 (1.85)		38.31 (38.57)	34.27 (34.47)
$[L^1ThCl_2(CH_3CN)_4]^+_2 \cdot [ThCl_6]^-$	1665.484	27.68 (27.40)	2.70 (2.78)	6.55 (6.73)	22.21 (21.29)	40.95 (41.80)
$[L^1UCl_2(CH_3CN)_4]^+_2 \cdot [UCl_6]^{2-}$	1683.454	27.01 (27.11)	2.87 (2.75)	6.72 (6.66)	21.40 (21.06)	43.06 (42.42)
$[L^2ThCl_2(CH_3CN)_4]^+_2 \cdot [ThCl_6]^{2-}$	1693.538	28.00 (28.37)	2.87 (2.98)	6.32 (6.62)	20.78 (20.93)	40.94 (41.10)
$[L^2UCl_2(CH_3CN)_4]^+_2 \cdot [UCl_6]^{2-}$	1711.511	29.01 (28.07)	2.90 (2.94)	6.34 (6.55)	20.71 (20.71)	42.02 (41.72)
$[L^3ThCl_2(CH_3CN)_4]^+_2 \cdot [ThCl_6]^{2-}$	1805.754	30.99 (31.93)	3.78 (3.68)	6.40 (6.21)	19.43 (19.63)	38.27 (38.55)
$[\{C_9H_7UBr(CH_3CN)_4\}_2O]^{2+} \cdot [UBr_6]^{2-}$	1928.050	21.15 (21.18)	1.87 (1.99)	5.98 (5.81)	33.52 (33.15)	27.34 (37.04)
$C_9H_7UBr_3 \cdot 2CH_3CH_2CH_2CN$	731.109	28.54 (27.93)	3.01 (2.90)	3.71 (3.83)	32.90 (32.79)	32.00 (32.56)
$L^1UBr_3 \cdot 2CH_3CH_2CH_2CN$	759.163	29.08 (30.06)	3.12 (3.32)	3.60 (3.69)	31.18 (31.58)	31.07 (31.35)
$L^1UCl_3 \cdot 2CH_3CH_2CH_2CN$	625.810	36.70 (36.47)	4.28 (4.03)	4.30 (4.48)	17.00 (17.00)	38.53 (38.04)
$L^1ThCl_3 \cdot 2CH_3CH_2CH_2CN$	619.819	37.12 (36.82)	4.23 (4.07)	4.70 (4.52)	17.00 (17.16)	36.98 (37.44)
$L^1UCl_3 \cdot 2C_6H_5CN$	693.844	42.79 (43.28)	3.00 (3.05)	4.17 (4.04)	15.80 (15.33)	34.72 (34.31)
$L^3ThCl_3 \cdot 2CH_3CH_2CH_2CN$	689.954	41.57 (41.78)	5.22 (5.11)	4.21 (4.06)	15.80 (15.42)	34.02 (33.63)
$L^3ThCl_3 \cdot 2C_6H_5CN$	757.988	48.12 (47.54)	4.29 (4.11)	3.52 (3.70)	13.72 (14.03)	30.02 (30.61)

[a] $L^1 = 1\text{-}C_2H_5C_9H_6$; $L^2 = 1,4,7\text{-}(CH_3)_3C_9H_4$; $L^3 = 1,2,3,4,5,6,7\text{-}(CH_3)_7C_9$.

Reaction with CH_3CN in presence of dry oxygen

A solution of [LAnHal$_3$ · 2THF] (1 mmol) in $CH_3CN(O_2)$ (100 ml) was centrifuged, and the supernatant liquid was slowly evaporated to give red crystals (yield: 50% based on actinide). After a few days, deep brown crystals began to separate, indicating that most of dissolved oxygen had been consumed in the formation of the red compound (Table 3).

Reaction with trimethylphosphine oxide

To a solution of [LUHal$_3$ · 2THF] (1 mmol) in THF (50 ml) a solution of trimethylphosphine oxide in THF (2 mmol in 100 ml) was added dropwise at 0°C. The brown-red solution turned gradually green with precipitation of UHal$_4$ · $n(CH_3)_3PO$ [10]. No organometallic compound was isolated.

Results and discussion

The new indenyl thorium compounds are yellow while the uranium analogs are brown to deep red. The octahedral compounds are soluble in common organic solvents such as THF, dichloromethane, acetone, and dimethoxyethane but the substituted indenyl compounds slowly disproportionate in benzene. In general, heating of the solutions or addition of small amounts of n-pentane induces decomposition.

TABLE 4

SELECTED BOND DISTANCES (Å) AND ANGLES (°)

In [C$_9$H$_7$UBr$_2$(CH$_3$CN)$_4$]$^+$

U(1)–Br(1)	2.800(5)	Br(1)–U(1)–Br(1')	85.3(3)
U(1)–Br(1')	2.761(4)	Br(1)–U(1)–N(2)	76.0(7)
U(1)–N(1)	2.56(3)	Br(1)–U(1)–N(3)	76.0(6)
U(1)–N(2)	2.53(3)	Br(1')–U(1)–N(1)	80.3(7)
U(1)–N(3)	2.57(3)	Br(1')–U(1)–N(2)	87.4(7)
U(1)–N(4)	2.57(3)	Br(1')–U(1)–N(3)	87.8(6)
U(1)–C(1)	2.63(4)	Br(1')–U(1)–N(4)	79.0(7)
U(1)–C(2)	2.67(4)	N(1)–U(1)–N(2)	70.3(10)
U(1)–C(3)	2.69(4)	N(1)–U(1)–N(4)	69.2(9)
U(1)–C(8)	2.81(4)	N(3)–U(1)–N(4)	66.8(9)
U(1)–C(9)	2.82(4)		

In [{C$_9$H$_7$UBr(CH$_3$CN)$_4$}$_2$O]$^{2+}$

U(1)–Br(1)	2.861(2)	Br(1)–U(1)–O	90.06(4)
U(1)–O	2.057(1)	Br(1)–U(1)–N(1)	75.1(3)
U(1)–N(1)	2.55(1)	Br(1)–U(1)–N(2)	74.0(3)
U(1)–N(2)	2.56(1)	N(1)–U(1)–N(4)	67.9(4)
U(1)–N(3)	2.56(1)	N(2)–U(1)–N(3)	70.7(4)
U(1)–N(4)	2.60(1)	N(3)–U(1)–N(4)	69.9(4)
U(1)–C(1)	2.75(1)	O–U(1)–N(1)	84.9(3)
U(1)–C(2)	2.72(2)	O–U(1)–N(2)	87.0(3)
U(1)–C(3)	2.75(1)	O–U(1)–N(3)	79.0(3)
U(1)–C(8)	2.86(1)	O–U(1)–N(4)	77.5(3)
U(1)–C(9)	2.85(1)		
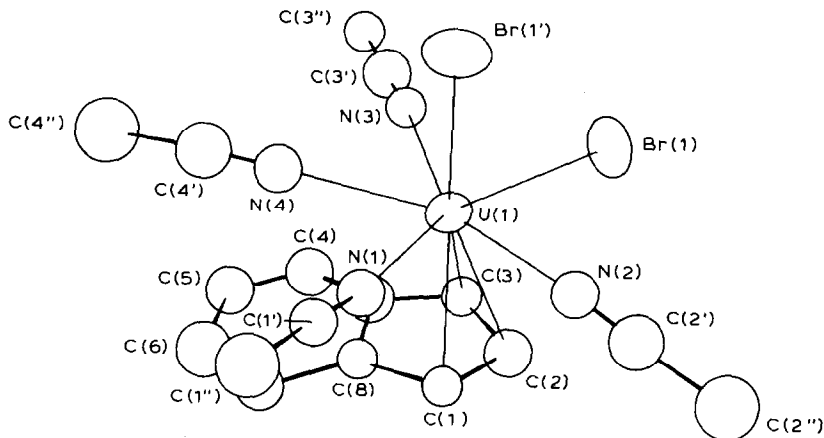
Fig. 1. Molecular structure of $[C_9H_7UBr_2(CH_3CN)_4]^+$.

The reactions of the octahedral compounds, $[C_9H_7AnHal_3 \cdot 2THF]$, with an appropriate oxygen donor compound (L) such as a phosphine oxide [1,2] have been used to prepare a number of actinide indenyls, $[C_9H_7AnHal_3 \cdot 2L]$; the reaction with pure acetonitrile did not involve a simple replacement of the THF ligands. Chemical analysis of the solids suggested a more complicated composition than that corresponding to classical octahedral geometry (Table 3).

As single crystals of the uranium bromide derivative could be grown an X-ray structure analysis was undertaken. The complex must be formulated as $[C_9H_7UBr_2(CH_3CN)_4]^+_2$ $[UBr_6]^{2-}$, two complex cations being associated with an octahedral hexabromouranium anion. Selected bond distances and angles are listed in Table 4. The cation is illustrated in Fig. 1. The coordination polyhedron about the uranium(IV) ion is a distorted pentagonal bipyramid, with the four acetonitrile nitrogens and one bromide lying in the equatorial plane. The two apexes are occupied by the second bromide and the indenide ligand respectively.

The degree of distortion of the coordination geometry is shown by the angles subtended at the uranium atom (Table 4).

A series of analogous compounds was successfully prepared (Table 3). The new compounds are almost insoluble in common organic solvents. The lability of the indenyl ligand was revealed by the following reaction:

$$(C_9H_7)_3UCl + 2UCl_4 \cdot 4CH_3CN \xrightarrow[\text{room temp.}]{THF} 3C_9H_7UCl_3 \cdot 2THF + 8CH_3CN$$
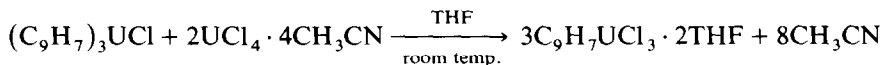
The reaction was complete after 6–8 d of agitation at room temperature. The monoindenyl complex was obtained in a pure state by concentrating the solution at low temperature (0°C). Its purity is unaffected by the presence of the small amount of methyl cyanide and spectrophotometric examination of the monoindenyl complex in THF in the presence of increasing quantities of methyl cyanide reveals that a substantial volume of methyl cyanide ($V_{CH_3CN}/V_{THF} > 1$) must be added before significant changes are observed in the electronic spectrum (400–2200 nm).

The replacement of the indenyl ligand by 1-ethylindenyl, 1,4,7-trimethylindenyl, or 1,2,3,4,5,6,7-heptamethylindenyl does not significantly modify the stoichiometry
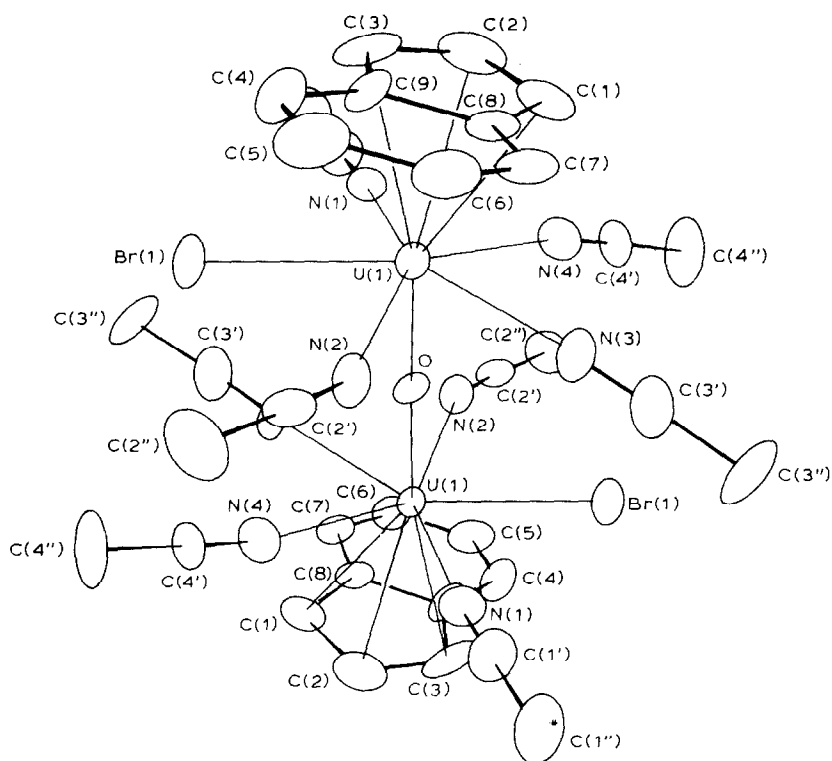
Fig. 2. Molecular structure of $[\{C_9H_7UBr(CH_3CN)_4\}_2O]^{2+}$.

of the compounds as indicated by the chemical analysis (Table 3). On the other hand, replacement of methyl cyanide by butyronitrile and benzonitrile yields products which correspond to an octahedral structure in which two nitriles occupy the THF positions (Table 3) [11]. These two organic nitriles are presumably too bulky to be accomodated within a pentagonal bipyramidal geometry. Because of the somewhat restricted space available around the cation, it might be expected that only small ligands would form pentagonal bipyramidal complexes, and so the reaction between octahedral compounds and trimethylphosphine oxide, another small base, was examined, but for a range of molar ratios of Lewis base to octahedral compound only $AnHal_4 \cdot n(CH_3)_3PO$ coming from disproportionation, was identified.

It is well known that methyl cyanide readily dissolves small amount of oxygen [6] and this property can be used in preparing new compounds. Thus the reaction between $C_9H_7UBr_3 \cdot 2THF$ and methyl cyanide containing dry oxygen gave a new type of compound; $[\{C_9H_7UBr(CH_3CN)_4\}_2O]^{2+}$ $[UBr_6]^{2-}$ (II) which was characterized by X-ray crystallography. The structure analysis showed II to be a complex dimerized cation in which two uranium atoms are bridged via one oxygen atom lying on a center of symmetry (see Fig. 2) Each uranium atom is seven-coordinated in a slightly distorted pentagonal bipyramid. The bridging oxygen occupies the common apex of the bipyramids. Bond distances and angles are listed in Table 4.
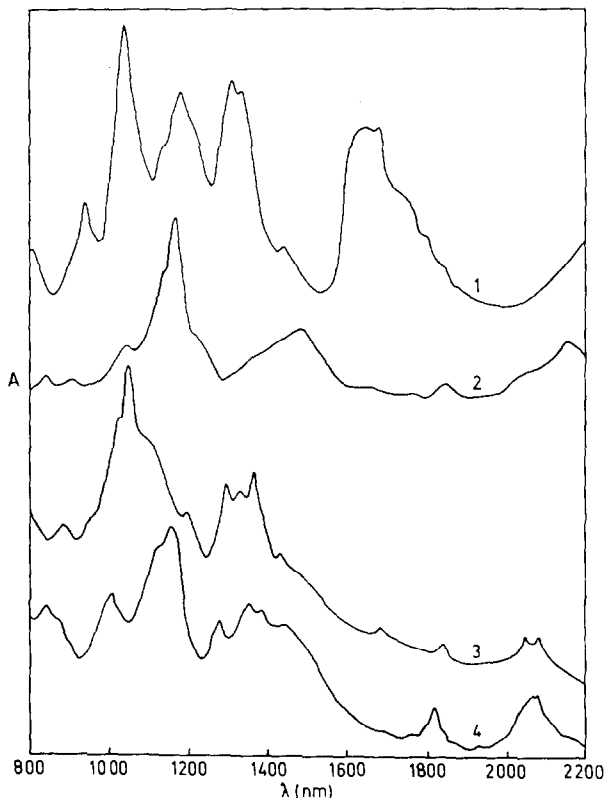
Fig. 3. Electronic spectra of: (1) [(C$_9$H$_7$)$_3$UBr] (THF solution); (2) [C$_9$H$_7$UBr$_3$·2THF] (THF solution); (3) [{C$_9$H$_7$UBr(CH$_3$CN)$_4$}$_2$O]$^{2+}$·[UBr$_6$]$^{2-}$ (KBr pellet); (4) [C$_9$H$_7$UBr$_2$(CH$_3$CN)$_4$]$^+_2$·[UBr$_6$]$^{2-}$ (KBr pellet).

The U–O (bridge) bond of 2.057(1) Å is quite short relative to the usual U–O (ligand) distances (e.g. the uranium alkoxide–oxygen bond of 2.17(1) Å in U(OC$_6$H$_5$)$_4$·2[(CH$_3$)$_2$P(CH$_2$)P(CH$_3$)$_2$] [12] is among the shortest U–O (ligand) previously reported); this short bond, associated with an U–O–U angle of 180°, probably reflects a strong metal–oxygen interaction.

Similar linear or nearly linear M–O–M units are found in several transition metal oxide bridged dimers [13]. In the actinide series the existence of oxygen-bridged dimer complexes has been proposed, but no structural data have been presented. Thus [(C$_5$R$_5$)$_3$U]$_2$O [14,15] is mentioned in the literature but without structural characterization, and Gilje et al. [16] obtained preliminary structural data on a new organometallic oxide complex (CH$_3$(C$_6$H$_5$)$_2$PCH$_2$)$_2$MgCl$_2$(C$_5$Me$_5$)$_2$U$_2$O$_2$((CH$_3$)$_2$-

TABLE 5

ELECTRONIC SPECTRA (KBr pellets)

Compound	Main features (nm)
[{C$_9$H$_7$UCl(CH$_3$CN)$_4$}$_2$O]$^{2+}$·[UCl$_6$]$^{2-}$	1050, 1295, 1360
[{1-C$_2$H$_5$-C$_9$H$_6$UCl(CH$_3$CN)$_4$}$_2$O]$^{2+}$·[UCl$_6$]$^{2-}$	1050, 1285, 1365
[{1,4,7-(CH$_3$)$_3$C$_9$H$_4$UCl(CH$_3$CN)$_4$}$_2$O]$^{2+}$·[UCl$_6$]$^{2-}$	1051, 1288, 1362

TABLE 6
ANALYTICAL RESULTS

Compound	MW	Found (calcd.) (%)				
		C	H	N	Hal	An
$[\{(C_9H_7UCl(CH_3CN)_4\}_2O]^{2+}\cdot[UCl_6]^{2-}$	1572.442	26.38	2.30	7.01	18.00	47.02
		(25.97)	(2.44)	(7.13)	(18.04)	(45.41)
$[\{1\text{-}C_2H_5\text{-}C_9H_6UCl(CH_3CN)_4\}_2O]^{2+}\cdot[UCl_6]^{2-}$	1628.55	27.37	2.71	7.01	17.88	43.08
		(28.03)	(2.85)	(6.88)	(17.42)	(43.85)
$[\{1,4,7\text{-}(CH_3)_3C_9H_4UCl(CH_3CN)_4\}_2O]^{2+}\cdot[UCl_6]^{2-}$	1656.604	29.10	3.13	6.84	17.80	44.08
		(29.00)	(3.04)	(6.76)	(17.12)	(43.10)

$(C_6H_5)_2P)_2$ which probably contains an U–O–U bridge with bond distances of 2.13 and 2.16 Å [17]. To our knowledge, $[\{Th(Phense)\text{-}(NO_3)(H_2O)\}_2O]\cdot(NO_3)_4\cdot H_2O$ [18] is the only example of an actinide oxo-bridged dimer whose structure has been reported.

The reaction with $[L\text{-}UCl_3\cdot 2THF]$, where L is indenyl or substituted indenyl ligand, with $CH_3CN(O_2)$ was also examined. The electronic spectra of the products were recorded and compared with those of I and II (Fig. 3), and this comparison (Table 5) and the elemental analysis (Table 6) suggest that a U–O–U bond is present in all of them.

The complexes of actinide halides with organic nitriles are known to be weak [19]. They are readily dissociated into their components by applying a high vacuum at room temperature or heat. The new organometallic compounds including organic nitriles appear to be relatively stable, and the actinide–nitrogen bond is not broken at 10^{-4} torr at room temperature.

Infrared spectra

A positive shift in the carbon nitrogen stretching frequency, γ_2 of free CH_3CN on going to coordinated methyl cyanide has been observed frequently [20–26], and is characteristic of coordination via the lone pair of the nitrogen atom [22]. The value of the shift is nearly the same for all the new compounds (Table 4), and is comparable to the values for other acetonitrile complexes [20,21,26]. However, although Evans and Lo [27] predicted an increase in the C–N stretching force constant by calculations based on a simple CH_3CN-Me picture with Urey-Bradley force field, the rise in γ_2 cannot be unambiguously interpreted in terms of the C–N bond strength. A second intense band at about 2305 cm^{-1} is assigned, as previously [20,21,23], to a combination band of the γ_3 CH_3 deformation and the γ_4 C–C stretching bands enhanced by a Fermi resonance with γ_2, though it must be noted that it has also been assigned to an overtone [28]. These two bands are sometimes splitted, as in $UCl_4\cdot 4CH_3CN$ and $UBr_4\cdot 4CH_3CN$ (Table 7), and it has been postulated [21,25] that this splitting is associated with the non-equivalence of the position of the methyl cyanide in the coordination sphere of the metal. The most recent X-ray structure of $UCl_4\cdot 4CH_3CN$ [29] effectively demonstrates that there are two different U–N distances in the complex 2.567 and 2.599 Å. In general, such splitting of the infrared bands was not observed in the new organometallic compounds (Fig. 4, Table 7).

Table 7 lists the observed infrared bands for the new complexes and tentative assignments [30]. As noticed by Reedijk et al. [20], there is increase in the γ_2, γ_4, γ_8

TABLE 7

C≡N FREQUENCIES (cm^{-1})

Compound[a]	$2\nu_4 + \nu_3$	$\nu_2 + \nu_4$	$\nu_3 + \nu_4$	C≡N stretching ν_2	CH$_3$ deform. ν_3	CH$_3$ rocking ν_7	C–C stretching ν_4	C–C≡N bending ν_8	Me–N
CH$_3$CN (liq.)	3203	3165	2293	2254	1376	1047	917	379	
[UCl$_4$·4CH$_3$CN]	3243	3210	2316	2283	1377	1035	937	408	197
	3233	3200	2308	2277	1368			400	190
[UBr$_4$·4CH$_3$CN]	3240	3210	2313	2287	1369	1030	938		
	3235	3200	2305	2277					
[IndThCl$_2$(CH$_3$CN)$_4$]$^+{}_2$·[ThCl$_6$]$^{2-}$	3235	3200	2303	2274	1365	1032	937	390	197
[IndUCl$_2$(CH$_3$CN)$_4$]$^+{}_2$·[UCl$_6$]$^{2-}$	3237	3202	2307	2279	1367	1028	938	390	189
[IndUBr$_2$(CH$_3$CN)$_4$]$^+{}_2$·[UBr$_6$]$^{2-}$	3235	3201	2305	2278	1365	1028	938	392	
[{IndUBr(CH$_3$CN)$_4$}$_2$O]$^{2+}$·[UBr$_6$]$^{2-}$			2306	2278	1365	1032	940	391	
[L^{1}UCl$_2$(CH$_3$CN)$_4$]$^+{}_2$·[UCl$_6$]$^{2-}$			2304	2276	1363	1036 1025	939		
[L^{1}ThCl$_2$(CH$_3$CN)$_4$]$^+{}_2$·[ThCl$_6$]$^{2-}$			2313 2306	2278	1370	1037	938		
[L^{3}ThCl$_2$(CH$_3$CN)$_4$]$^+{}_2$·[ThCl$_6$]$^{2-}$			2306	2278	1366	1037 1026	937		198

[a] Ind = Indenyl; L^1 = 1-C$_2$H$_5$C$_9$H$_6$; L^3 = 1,2,3,4,5,6,7-(CH$_3$)$_7$C$_9$.
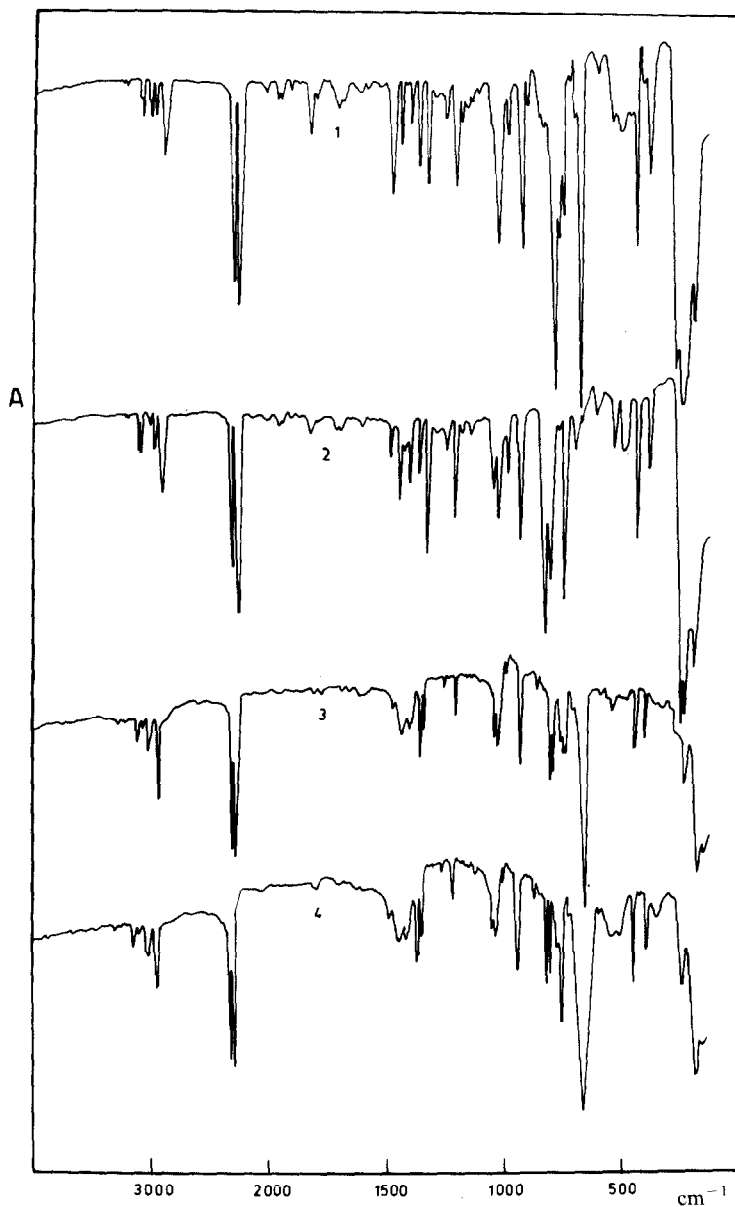
Fig. 4. Infrared spectra of: (1) $[C_9H_7ThCl_2(CH_3CN)_4]^+_2 \cdot [ThCl_6]^{2-}$; (2) $[C_9H_7UCl_2(CH_3CN)_4]^+_2 \cdot [UCl_6]^{2-}$; (3) $[C_9H_7UBr_2(CH_3CN)_4]^+_2 \cdot [UBr_6]^{2-}$; (4) $[\{C_9H_7UBr(CH_3CN)_4\}_2O]^{2+} \cdot [UBr_6]^{2-}$. (A = Transmission).

and $(\gamma_3 + \gamma_4)$ frequencies, in contrast with the slight decrease in the γ_3 and γ_7 frequencies of the coordinated methyl cyanide.

The infrared spectra of very similar compounds are rather different in the 700–800 cm^{-1} range. Such behavior has been observed for many indenyl com-
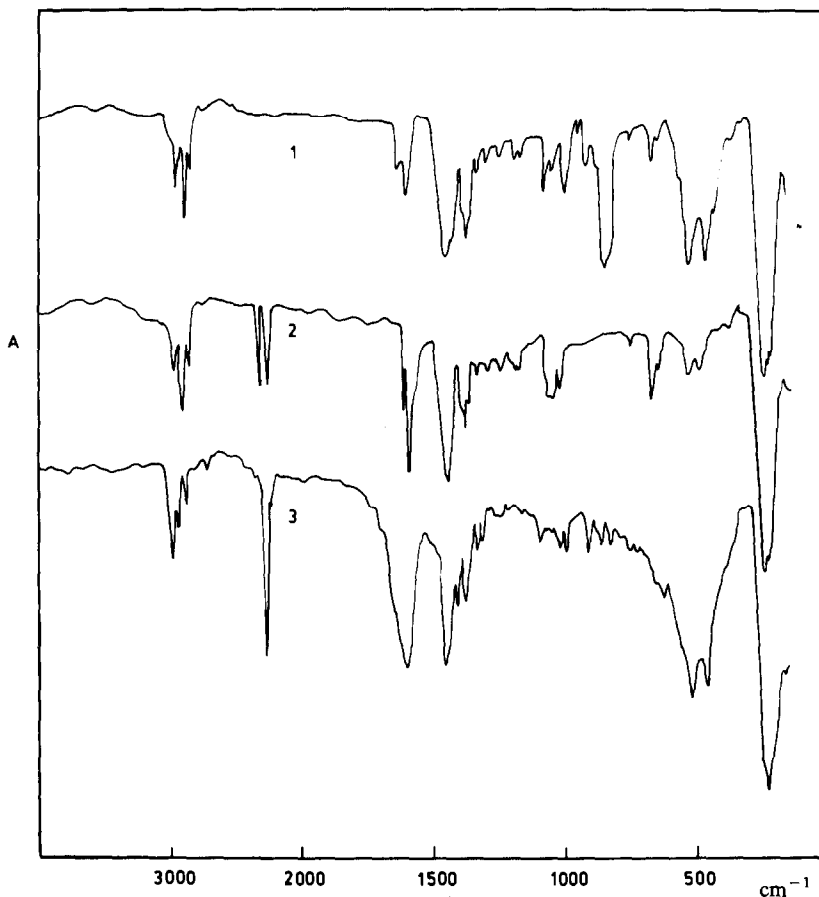
Fig. 5. Infrared spectra of: (1) [HMI ThCl$_3$·2THF]; (2) [HMIThCl$_2$(CH$_3$CN)$_4$]$^+_2$·[ThCl$_6$]$^{2-}$; (3) [HMI ThCl$_3$·2CH$_3$CH$_2$CH$_2$CN]. (A = Transmission).

pounds [7], and has been attributed to the effect of the molecular environment on the carbon–hydrogen out-of-plane vibrations.

The actinide–chloride vibrations appear around 260 cm^{-1}, the actinide–bromide vibrations around 175 cm^{-1} and the actinide–indenyl vibrations at 235–240 cm^{-1} (Figs. 4 and 5). The assignment of the An–nitrogen vibration is to be difficult. Walton [31,32], in a study of the complexes MeX$_2$·2RCN (Me = Pt, Pd, Rh; X = Cl, Br) concluded that no band above 200 cm^{-1} could be unambiguously assigned to pure metal–ligand vibrations since their positions were not independent of the halide. Calculation performed by Evans and Lo [27] on ZnCl$_2$·2CH$_3$CN led to the prediction of a Zn–N mode at 174 cm^{-1}. Reedijk et al. [33] showed that these frequencies are little affected by anionic species, but depend merely on the nature of the metal. The proposed values range from 330 to 200 cm^{-1} for the Me–N stretching modes and from 240 to 180 cm^{-1} for the Me–NCC wagging mode.

In the spectra of the new organometallic compounds, a band at 198 cm^{-1} is observed for the thorium chloride complexes and one at about 190 cm^{-1} for the
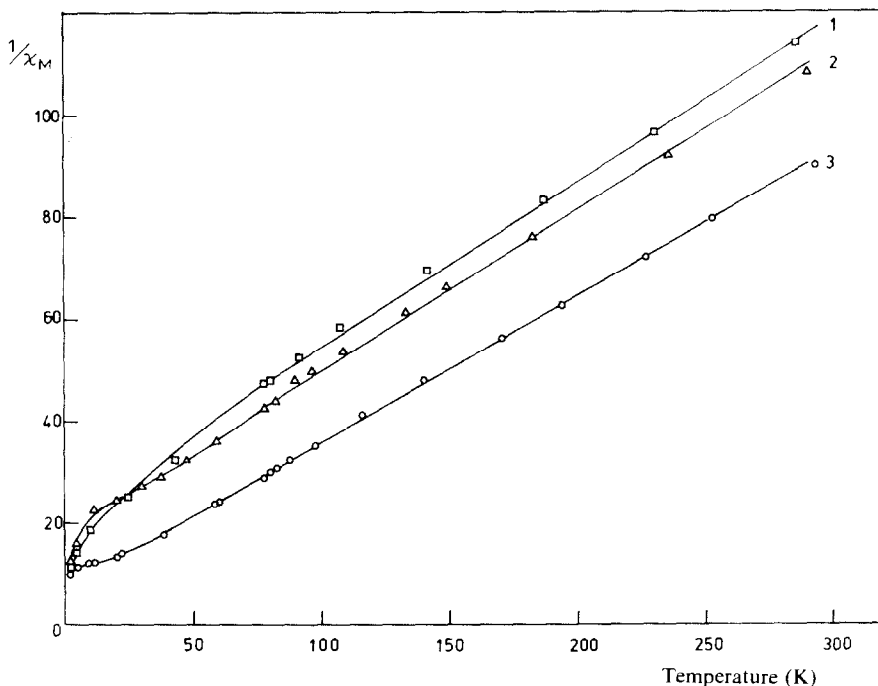
Fig. 6. Magnetic susceptibility of: (1) $[C_9H_7UBr_2(CH_3CN)_4]^+_2 \cdot [UBr_6]^{2-}$ (2) $[\{C_9H_7UBr(CH_3CN)_4\}_2O]^{2+} \cdot [UBr_6]^{2-}$ (3) $[C_9H_7UCl_2(CH_3CN)_4]^+_2 \cdot [UCl_6]^{2-}$

uranium chloride complexes (Table 7). In the case of the bromide complexes, these bands seem to be obscured by the metal bromide vibration or lie at very low frequencies ($< 170 \ cm^{-1}$). We tentatively assign the bands at 198 and 190 cm^{-1} to the An–N vibrations.

Plots of the molar paramagnetic susceptibilities of these new uranium compounds against the temperature are shown in Fig. 6. Since the anion is the octahedral $[UHal_6]^{2-}$, which has temperature independent paramagnetism [34,35], it is possible to calculate the magnetism of the uranium engaged in the organometallic compound. The magnetism of the compounds obeys the Curie–Weiss law between 50 and 300 K with $\theta = -31$ K ($\mu = 2.84$), $\theta = -30$ K ($\mu = 2.98$) and $\theta = -6.7$ K ($\mu = 3.27$), respectively for $[C_9H_7UBr_2(CH_3CN)_4]^+$, $1/2[\{C_9H_7UBr(CH_3CN)_4\}_2$-$O]^{2+}$ and $[C_9H_7UCl_2(CH_3CN)_4]^+$. The magnetic moments agree with those observed for U^{IV} organometallic compounds [36].

Conclusion

The synthesis and the complete characterization of $[L-AnHal_2(CH_3CN)_4]^+_2 \cdot$ $[UHal_6]^{2-}$ and $[\{L-AnHal(CH_3CN)_4\}_2O]^{2+} \cdot [UHal_6]^{2-}$ establish the existence of some new types of compounds in 5 f-organometallic chemistry. The formation of an oxide-bridged dimer can be related with confidence to one of the initial steps in the oxidation of the actinide indenyl compounds.

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