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Contribution from the Materials and Molecular Research Division, Lawrence Berkeley Laboratory, and the Department of Chemistry, University of California, Berkeley, California 94720

Crystal Structure of Tetrakis[bis(*N*,*N*′-dimethylethylenediamido)uranium(IV)], a Tetrameric Globular Complex[1]

JOHN G. REYNOLDS, ALLAN ZALKIN,* DAVID H. TEMPLETON,* and NORMAN M. EDELSTEIN*

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The tetrameric compound $U_4(CH_3NCH_2CH_2NCH_3)_8$ is a minor product of the reaction of tetrakis(diethylamido)uranium(IV) with dimethylethylenediamine in pentane. The crystals are orthorhombic, space group *Fddd*, with $a = 12.02$ (2) Å, $b = 22.73$ (4) Å, and $c = 34.32$ (6) Å; $d_{\text{calcd}} = 2.32$ g/cm^3 for $Z = 8$. X-ray diffraction intensity data were collected by an automated diffractometer using graphite-monochromated Mo Kα radiation. For 399 reflections with $F^2 > 2\sigma$, $R_1 = 0.078$ and $R_2 = 0.060$. Four bis[*N*,*N*′-dimethylethylenediamido]uranium(IV) units are connected by bridging nitrogen atoms to form a closed tetrameric complex in which the four uranium atoms are 3.6 Å apart at the corners of a twisted square. Each uranium atom is bonded to six nitrogen atoms in a highly distorted trigonal prism. Attached to each uranium atom are two nitrogen atoms from a nonbridging dimethylethylenediamido ligand and four from two bridging ligands.

Introduction

We recently reported the synthesis, crystal structure, and magnetic and optical properties of a novel trimeric amide complex of uranium, $U_3(CH_3NCH_2CH_2NCH_3)_6$.[2] This compound was synthesized by the aminolysis reaction

$$3U(NEt_2)_4 + 6CH_3NHCH_2CH_2NHCH_3 \rightarrow U_3(CH_3NCH_2CH_2NCH_3)_6 + 12HNEt_2 \qquad (1)$$

The three uranium atoms in this compound form a linear chain and the center U atom is linked to each of the terminal U atoms by a triple nitrogen bridge. Each of the dimethylethylenediamido ligands has one N atom which acts as a bridge (four-coordinate) while the second N atom is bonded to a terminal U atom and two carbon atoms (three-coordinate) and is coplanar with these atoms. The uranium–uranium distance is 3.54 Å but even at this short distance the magnetic data show no evidence of metal–metal interaction down to 4.2 K. As a minor product of the above reaction we isolated some red-brown crystals which have now been shown to consist of tetrameric molecules. We report in this paper the characterization of this tetramer by determination of its crystal structure.

Experimental Section

N,*N*′-Dimethylethylenediamine was added to a solution of $U(NEt_2)_4$ in pentane at 77 K as previously described.[2] The reaction mixture was warmed to room temperature and after 24 h the precipitate which formed was filtered and vacuum-dried. Two types of crystals were grown from the filtrate, the major product (~95%) being the previously described trimer $U_3(CH_3NCH_2CH_2NCH_3)_6$ and the minor product being orthorhombic red-brown crystals, $U_4(CH_3NCH_2CH_2NCH_3)_8$. Crystals were obtained for x-ray diffraction by removing them from the walls of the flask with a tungsten needle in an argon-atmosphere box. The separation of the two types of crystals was achieved by noting their different shapes and colors. The crystals were placed in quartz capillaries which were then sealed with vacuum grease. The capillaries were fire-sealed immediately upon removal from the box. Only the yellow trimer crystals were found upon recrystallization from pentane of the initial precipitate.

We examined several crystals with a Picker FACS-I automated diffractometer equipped with a graphite monochromator and molybdenum tube. We obtained cell dimensions by a least-squares procedure from the angular positions of seven manually centered reflections for which the 2θ values were between 15 and 20°. With one of the crystals we collected intensity data to $2\theta = 30°$, yielding 257 independent reflections with $I > \sigma$. From these data the uranium positions were determined, in good agreement with the final results described below, but we failed to find a satisfactory structure for the light atoms. In retrospect one can recognize a poorly resolved image of the final structure in the electron density maps, but other spurious features are also present. Later another crystal (which is described in Table I) permitted measurement of some reflections as high as $2\theta = 40°$. The space group and cell dimensions are also given in Table I with some other details of the experiment. The highly reactive nature of the crystals precluded a direct measurement of the density. ω scans of several low-angle reflections showed widths of half-peak height of about 0.20°. A total of 2102 scans were measured and later averaged to give a set of 1122 unique data of which only 421 had $F^2 > 2\sigma$. Three standard reflections were measured after each 200th scan to monitor for crystal decay, instrumental stability, and crystal alignment. No significant change occurred for 004 and 080. An abrupt increase for 400 suggested a change of alignment after 372 reflections in the range $h = -11$ to -6 had been measured, and on this basis these intensities were adjusted upward by about 5%, an amount less than the individual statistical errors.

Absorption corrections were calculated using an analytical algorithm.[3] The crystal shape was described by seven surface planes. Azimuthal scans of integrated intensities were performed for nine reflections in as diverse a region of reciprocal space as the instrument

Table I. Summary of Crystal Data and Intensity Collection

Compd	$U_4(CH_3NCH_2CH_2NCH_3)_8$
Formula wt	1641.2
a, Å	12.02 (2)
b, Å	22.73 (4)
c, Å	34.32 (6)
V, Å^3	9377
Z	8
Density (calcd), g/cm^3	2.32
Space group	*Fddd*
Crystal shape and size	Irregular shape with 7 faces 013, $01\bar{1}$, $0\bar{1}\bar{2}$, $0\bar{2}\bar{1}$, $0\bar{2}1$, 200, $\bar{2}00$; dimensions approximately 0.04 × 0.06 × 0.09 mm
Crystal vol, mm^3	0.0003
T, °C	23
Radiation	Mo Kα (λ 0.709 26 and 0.713 54 Å), monochromated from (002) face of mosaic graphite
Transmission factor	1.61–2.41
μ, cm^{-1}	130
Data collection	θ–2θ scan (2°/min along 2θ)
Scan range	1° below Kα_1 to 1° above Kα_2
Background counts	10 s; backgrounds offset from scan limits by 0.5°
2θ limits, deg	3–40
No. of variables	58
Unique data used ($F_o^2 > 2\sigma$; $(\sin\theta)/\lambda > 0.15$ Å^{-1})	399

would allow, and the dimensions of the crystal were adjusted to give the best consistency of corrected intensities for these scans. The data were processed, averaged, and given estimated standard deviations using formulae presented in the supplementary material. The factor $p = 0.03$ was used in the calculation of $\sigma(F^2)$.

Table II. Positional and Thermal Parameters[a]

Atom	x	y	z	B, Å^2
U	0.0134 (2)[b]	0.4478 (1)	0.3547 (1)	c
N(1)	0.089 (4)	0.400 (2)	0.416 (1)	5 (1)
N(2)	−0.082 (3)	0.487 (2)	0.414 (1)	4 (1)
N(3)	0.137 (4)	0.521 (2)	0.355 (2)	7 (1)
N(4)	0.067 (5)	0.475 (3)	0.292 (2)	10 (2)
C(1)	0.212 (5)	0.390 (3)	0.420 (2)	8 (2)
C(2)	0.063 (6)	0.430 (4)	0.452 (2)	10 (3)
C(3)	−0.053 (5)	0.456 (3)	0.451 (2)	6 (2)
C(4)	−0.083 (6)	0.551 (3)	0.423 (3)	11 (3)
C(5)	0.203 (5)	0.538 (3)	0.391 (2)	9 (2)
C(6)	0.189 (8)	0.539 (5)	0.319 (2)	12 (3)
C(7)	0.112 (9)	0.533 (4)	0.284 (3)	15 (3)
C(8)	0.045 (5)	0.461 (3)	0.251 (2)	9 (2)

[a] The anisotropic temperature factor has the form $\exp(-0.25(B_{11}h^2a^{*2} + 2B_{12}hka^*b^* + \ldots))$. The isotropic temperature factor has the form $\exp[-B((\sin\theta)/\lambda)^2]$. [b] The estimated standard deviations, indicated in parentheses, are the result of the least-squares refinement on a model with all bond distances restrained. [c] For U, $B_{11} = 3.6$ (1), $B_{22} = 4.2$ (1), $B_{33} = 6.1$ (1), $B_{12} = 0.1$ (1), $B_{13} = 0.1$ (2), and $B_{22} = -1.0$ (1).

Table III. Distances (Å)[a]

U-U′	3.59 (1)	N(2)–C(3)	1.49 (5)
-U″	3.61 (1)	–C(4)	1.48 (5)
-N(1)	2.53 (4)	N(3)–C(5)	1.50 (5)
-N(1)′	2.50 (4)	–C(6)	1.46 (5)
-N(2)	2.51 (4)	N(4)–C(7)	1.46 (5)
-N(2)″	2.44 (4)	–C(8)	1.47 (5)
-N(3)	2.23 (4)	C(2)–C(3)	1.51 (5)
-N(4)	2.32 (5)	C(6)–C(7)	1.52 (5)
N(1)-C(1)	1.50 (5)		
-C(2)	1.46 (5)		

[a] The estimated standard deviations in parentheses are the result of a least-squares refinement in which all of the above distances, with the exception of U–U, were restrained and do not represent the true error of these distances.

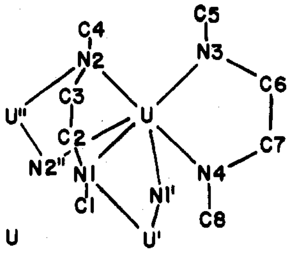


Figure 1. Schematic of part of the tetramer showing the numbering and coordination of each atom. Singly primed atoms are in positions x, $^3/_4 - y$, $^3/_4 - z$. Doubly primed atoms are in positions $^3/_4 - x$, y, $^3/_4 - z$.

A three-dimensional Patterson function revealed a pattern of strong peaks that was readily interpreted as a quartet of symmetry-related uranium atoms on the corners of a distorted square with an edge length of 3.6 Å. A Fourier function using the phases given by the uranium atom positions was calculated. This Fourier map, due to the paucity of high-angle data, showed a well-resolved uranium atom and a positive area of poorly resolved peaks where the light atoms were located. Several series of least-squares and difference-Fourier calculations were performed in which light atoms were introduced into the trial structure. The uranium atom was included with anisotropic thermal parameters and the light atoms were included with isotropic ones. The refinement converged, but the resultant structure retained some distances that were chemically unacceptable. To handle this problem of poor resolution we modified the least-squares program as suggested by Waser[4] to include restraints on interatomic distances. Interatomic distances between selected atoms are introduced into the calculations and treated as observations; estimated standard deviations of these distances are also introduced and used to calculate the weights. Except that the derivatives of these distances with respect to the positional parameters are calculated by a special patch and that these "observations" are not included in the R values reported here, these terms are included in the least-squares calculation in the same manner as observed structure factors. This procedure allows the structure to adjust to the electron density with a flexibility governed by the weighting. All the bond distances were restrained to the following values: U–N (bridging) to 2.50 ± 0.05 Å, other U–N to 2.25 ± 0.05 Å, N–C to 1.48 ± 0.05 Å, and C–C to 1.54 ± 0.05 Å. These distances were selected from the values obtained in previously determined uranium amide structures.[2,5,6] The resulting restrained structure refined to convergence by least-squares to R factors that were very little different from the unrestrained model. Some temperature parameters were slightly larger, but within a standard deviation of the values obtained in the unrestrained model refinements. A difference Fourier map calculated after the last least-squares cycle (restrained model) showed peaks of 2.9 e/Å^3 or less. The largest peak was near the intersection of three twofold axes at the center of the tetramer. Because of some large discrepancies in the low-angle data, 22 reflections below $(\sin\theta)/\lambda$ of 0.15 Å^{-1} were deleted. The majority of these data are in a region of very high backgrounds from the quartz capillary. The final least-squares statistics are given below for the restrained and unrestrained refinements (in parentheses). The final R factor, $\sum|\Delta F|/\sum|F_o|$, was 0.078 (0.076) for 399 data where $F^2 > 2\sigma$, $0.48 > (\sin\theta)/\lambda > 0.15$ Å^{-1}; R was 0.214 (0.213) for all 1122 data. The weighted R_w factor, $(\sum w(\Delta F)^2/\sum wF_o^2)^{1/2}$, was 0.060 (0.059). The standard deviation of an observation of unit weight was 1.21 (1.16). These refinement statistics show that the restrained model with its chemically acceptable geometry fits the data about as well as the unrestrained structure. The positions of C(7) and N(4) differ by 0.36 and 0.27 Å, respectively, between the two structures, while no other atom changed more than 0.12 Å.

Final positional and thermal parameters are given in Table II. Because of the restraints imposed on the model, the standard deviations which are obtained represent an estimate of the confidence one can have in the atomic coordinates if one accepts the imposed distances. In the model without restraints we obtained standard deviations which were either similar in magnitude or up to 65% larger. Distances and angles are listed in Tables III and IV and a sketch of a portion of the molecule to indicate the numbering scheme is given in Figure 1. A stereoscopic view of the globular complex is shown in Figure 2. A structural schematic diagram of the tetramer is shown in Figure 3.

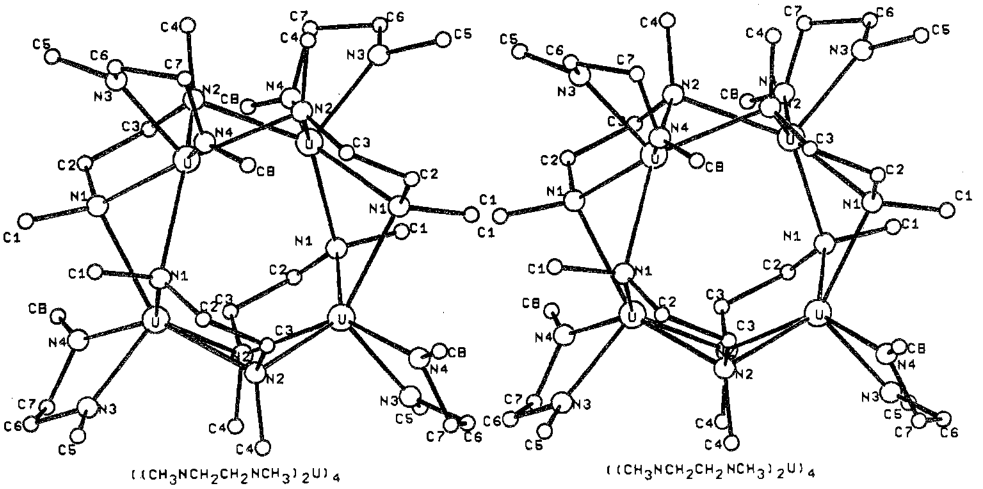


Figure 2. Stereogram of the tetramer.

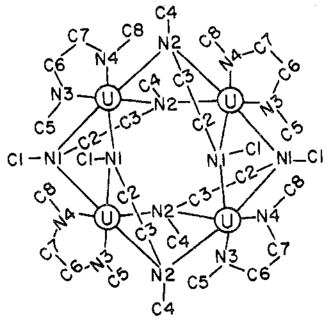


Figure 3. Structural formula of the tetramer.

Table IV. Selected Angles (deg)

U'-U-U''	81.4 (1)	U'-N(1)-C(1)	121 (4)
N(1)-U-N(1)'	74 (2)	U-N(1)-C(2)	115 (4)
N(1)'-U-N(2)	135 (2)	C(1)-N(1)-C(2)	102 (4)
N(1)'-U-N(2)''	125 (2)	U-N(2)-U''	93 (2)
N(1)-U-N(2)	69 (2)	U-N(2)-C(3)	114 (4)
N(1)-U-N(2)''	135 (2)	U-N(2)-C(4)	121 (4)
N(1)'-U-N(3)	115 (2)	U''-N(2)-C(3)	106 (3)
N(1)-U-N(3)	94 (2)	U''-N(2)-C(4)	114 (4)
N(1)'-U-N(4)	83 (2)	C(3)-N(2)-C(4)	107 (5)
N(1)-U-N(4)	141 (2)	U-N(3)-C(5)	124 (4)
N(2)-U-N(2)''	71 (2)	U-N(3)-C(6)	119 (6)
N(2)-U-N(3)	92 (2)	C(5)-N(3)-C(6)	113 (6)
N(2)''-U-N(3)	109 (2)	U-N(4)-C(7)	121 (6)
N(2)-U-N(4)	142 (2)	U-N(4)-C(8)	142 (5)
N(2)''-U-N(4)	84 (2)	C(7)-N(4)-C(8)	94 (6)
N(3)-U-N(4)	68 (3)	N(1)-C(2)-C(3)	112 (7)
U-N(1)-U'	91 (2)	N(2)-C(3)-C(2)	115 (6)
U'-N(1)-C(1)	105 (4)	N(3)-C(6)-C(7)	113 (8)
U'-N(1)-C(2)	125 (4)	N(4)-C(7)-C(6)	100 (8)

Discussion

The complexing of four uranium atoms into a globular tetrameric cluster is unique. The four uranium atoms are at the corners of a square 3.6 Å on an edge which is severely twisted so that each uranium is 0.7 Å from a mean plane. The uranium atoms are chemically and crystallographically equivalent, and each is bonded to six nitrogen atoms. Four of these nitrogen atoms act as double bridges to two neighboring uranium atoms in the ring. The other two nitrogen neighbors are bonded only to a single uranium. The six neighbors define an irregular polyhedron which can be described as a distorted trigonal prism. The entire tetramer has symmetry 222 and conforms approximately to the higher symmetry $\bar{4}2m$.

Half of the dimethylethylenediamido ligands are singly coordinated to uranium at each nitrogen, while the other half of the ligands participate in bridging with both nitrogen atoms. This is in contrast to the trimer structure[2] in which each ligand is singly coordinated at one nitrogen and acts as a bridge at the other. As observed in other uranium amides[2,5,6] and amides of other metals[7] each nitrogen atom bonded to a single metal atom is coplanar with its three bonding atoms, while no bridging nitrogen atom is coplanar with any three of its four neighbors.

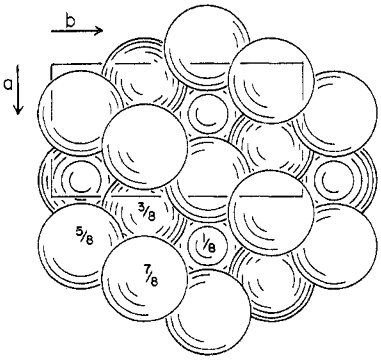
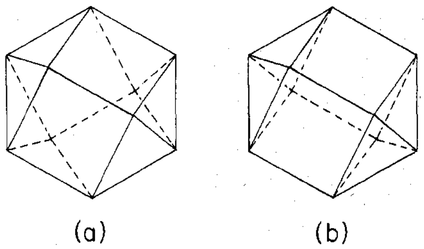


Figure 4. Packing of the tetramer molecules, each represented by a sphere. The fractions indicate z coordinates of tetramer centers, and the rectangle outlines, one unit cell.

The bonds from U to N(3) and N(4) are regarded as single bonds and those to N(1) and N(2) as half-bonds, in the terminology we have used before.[2] The bond distances are consistent with this description, but because of the manner in which they were restrained in the calculation they do not represent independent determinations.

The globular tetramer molecules pack in a manner appropriate for approximately spherical molecules (Figure 4). Molecules lie in close-packed triangular arrays in planes parallel with the a and b axes, each with two neighbors at 12.02 Å and four at 12.86 Å (measured between centers of the tetramers). These layers stack in such a way that each molecule has two neighbors above and two below, all at 10.72 Å. The relation between adjacent layers is the same as that in protactinium metal[8] and in two other globular uranium complexes which we recently studied.[9,10] However, the pattern of further stacking is different. The tetragonal protactinium structure repeats every second layer, while in this orthorhombic structure the pattern repeats only every fourth layer. In each case the coordination polyhedron defined by the ten nearest neighbors (Figure 5) is a dodecahedron with four rectangular and eight triangular faces, but the symmetry of these dodecahedra is 222 for the orthorhombic structure and $4/mmm$ for the tetragonal structure. We had not seen this orthorhombic packing described before, but a brief literature search



(a) (b)

Figure 5. Coordination polyhedra for the ten nearest molecular neighbors (a) in the orthorhombic structure, symmetry 222, and (b) in tetragonal protactinium metal, symmetry 4/*mmm*.

revealed that it exists in one of the forms of 1,2,3,4-tetrabromocyclohexane[11] and in one polymorph of cyclotetramethylenetetranitramine.[12]

The synthesis of $U_4(dmed)_8$ probably proceeds with a stepwise replacement of the diethylamide groups by dimethylethylenediamine. There is evidence from the color changes observed during the formation of $U(N(C_6H_5)_2)_4$ for this type of stepwise addition.[6] Changing the reaction conditions might result in a greater yield of the tetramer. The U–U distance in the tetramer is slightly longer than in the trimer; so, as in the trimer molecule, it is unlikely that there will be any magnetic interactions above 4.2 K. A remarkable characteristic of these uranium–amide systems is their tendency toward oligomerization. Further work on f-electron and d-electron metal amide complexes is necessary to determine the generality of this oligomerization reaction.

Registry No. $U_4(dmed)_8$, 62743-74-2.

Supplementary Material Available: Data processing formulae and listing of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Local and Internuclear Carbonyl Scrambling in Pentacarbonyl-7*H*-indenediiron, $(C_9H_8)Fe_2(CO)_5$, and Tetracarbonyl-7*H*-indene(triethylphosphine)diiron, $(C_9H_8)Fe_2(CO)_4(PEt_3)$

F. ALBERT COTTON* and BRIAN E. HANSON

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The molecule $(C_9H_8)Fe_2(CO)_5$ is observed to undergo two fluxional processes. Localized scrambling in the $Fe(CO)_3$ moiety has a coalescence temperature of −134 °C, one of the lowest known for such a process. On the other hand, internuclear carbonyl scrambling occurs with a higher activation energy than in other similar molecules. Coalescence is observed at ca. 120 °C, and the activation parameters for internuclear scrambling have been estimated to be $E_a = 17.7$ (3) kcal mol^{-1} and log $A = 12.3$. Crystals of $(C_9H_8)Fe_2(CO)_5$ belong to the orthorhombic system, space group *Pbca*. Unit cell parameters are $a = 14.968$ (5), $b = 13.576$ (5), and $c = 13.124$ (7) Å. The Fe–Fe bond length is 2.782 (1) Å. In the triethylphosphine derivative, $(C_9H_8)Fe_2(CO)_4PEt_3$, selective internuclear scrambling involving three of the four carbonyl ligands is observed, in close analogy to our earlier observations on (guaiazulene)$Fe_2(CO)_4PEt_3$.

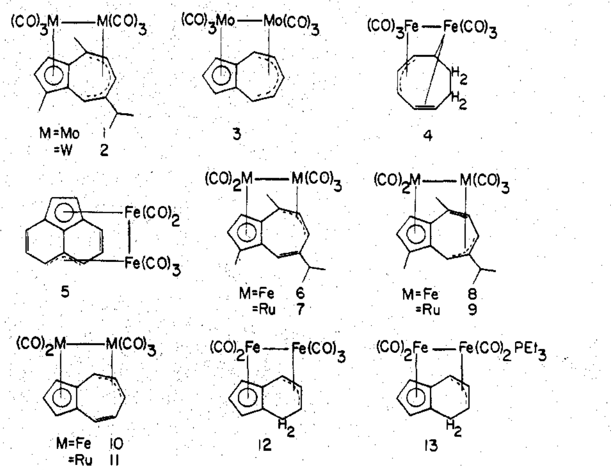
Introduction

In a recent paper[1] we have discussed conditions governing internuclear carbonyl scrambling in binuclear compounds having an $(OC)_nM-M'(CO)_m$ moiety bonded to a polyene or polyenyl group. On the basis of facts known at the present time, the following rules may be suggested.

(1) *n* should not be equal to *m*. Thus, for $(C_{15}H_{18})Mo_2(CO)_6$ (**1**),[2] $(C_{15}H_{18})W_2(CO)_6$ (**2**),[3] $(C_8H_{10})Fe_2(CO)_6$ (**4**),[4] and $(C_{10}H_{12})Fe_2(CO)_6$,[5] a bicyclic homologue of **4**, in all of which $n = m = 3$, only localized scrambling is observed.

(2) The π-electron density of the polyene ligand must be capable of a redistribution to allow for the transfer of a carbonyl ligand from one metal atom to the other. Thus no internuclear scrambling is observed in $(C_{12}H_8)Fe_2(CO)_5$,[6] **5**, at 75 °C.

The molecules that have been observed, **6–11**, to undergo internuclear exchange in this class of compounds have guaiazulene[1] or azulene[6] as the polyene ligand, with $n = 2$ and $m = 3$. In the iron derivatives of azulene and guaiazulene internuclear exchange is sufficiently facile that it is observed at room temperature.



Another molecule in this class of compounds, i.e., one that meets our empirical requirements for internuclear scrambling, is (7*H*-indene)$Fe_2(CO)_5$ (**12**). A recent carbon-13 NMR study[8] of this compound failed to show internuclear scrambling