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Reactivity of Dicyclopentadienylbis(diethylamido)uranium(IV). Reactions with Carboxylic and Thiocarboxylic Acids

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The reaction of $Cp_2U(NEt_2)_2$ with carboxylic and thiocarboxylic acids produced complexes of the type $Cp_2U(XYCR)_2$ (X = Y = O, R = Me, Ph, *t*-Bu; X = O, Y = S, R = Me, Ph). Solubility properties of the acetate and benzoate derivatives indicate polymeric behavior, whereas molecular weight measurements show that the pivalate complex is dimeric and the thiobenzoate compound is monomeric. The infrared spectra of all the complexes indicate η^5-cyclopentadienyl bonding and bidentate, chelating and/or bridging, carboxylate moieties. Assuming that the monomeric $Cp_2U(OSCPh)_2$ exhibits the expected pseudo-cis-octahedral geometry, it is shown that the variable-temperature ^1H NMR spectra of the molecule is only compatible with a combination of metal-centered rearrangement and C–Ph bond rotation. The simple and temperature-invariant nature of the spectrum for $Cp_2U(O_2CCMe_3)_2$ implies a symmetrical dimeric structure, and a possibility for this is proposed.

Introduction

Recent studies of dicyclopentadienyluranium(IV) compounds have emphasized ways of stabilizing these highly air- and moisture-sensitive compounds. One approach has been the use of persubstituted-cyclopentadienyl groups which resulted in sterically stabilized compounds such as $(\eta^5\text{-}C_5Me_5)_2UCl_2$[1] and $(\eta^5\text{-}C_5Me_4Et)_2UCl_2$.[2] Another approach, which we have used, is to achieve coordinative saturation through the use of chelating ligands which increase the coordination number around the uranium center. Starting from the uranium(IV) complex $Cp_2U(NEt_2)_2$, a compound shown previously to possess labile uranium–nitrogen bonds,[3] the carbamate complexes, $Cp_2U(XYCNEt_2)_2$ where X, Y = O or S and X = O, Y = S, have been formed.[4] The reactivity of the uranium–nitrogen bond in $Cp_2U(NEt_2)_2$ with reagents containing acidic protons can also be used to form stable Cp_2U^{IV} species. This method was employed to generate the uranium(IV) carboxylate compounds $Cp_2U(OXCR)_2$, where X = O, S and R = Me, Ph, or CMe_3, which will be discussed in this paper.

Complexes of uranium(IV) containing only the carboxylate ligand have been knwon for some time. These compounds are quite stable. In addition to the strength of the uranium–oxygen bond, the high coordination numbers achieved in these complexes through the bidentate carboxylate bonding mode undoubtedly contributes to this stability. A review by Bagnall discusses synthetic and structural aspects of a large number of carboxylate derivatives of both lanthanides and actinides.[5]

Although there are no previous reports of uranium complexes containing both the cyclopentadienyl and carboxylate moieties, among the transition metals a number of such derivatives are known. It is found that the monocyclopentadienyl compounds of the early transition metals contain bidentate carboxylate groups, with chelating coordination in $CpZr(O_2CMe)_3$[6] and bridging coordination in $[CpV(O_2CMe)_2]_2$[7] and $[CpV(O_2CCF_3)_2]_2$.[8] However when the transition-metal complex contains two cyclopentadienyl rings, then almost invariably and exclusively for $Cp_2M(O_2CR)_2$-type compounds the carboxylate groups are monodentate. This situation has been established in the compounds $Cp_2Zr(O_2CCF_3)_2$,[7] $Cp_2Ti(O_2CPh)_2$,[9] and recently $Cp_2Nb(O_2CCF_3)_2$ and $Cp_2Nb(O_2CCMe_3)$.[10] The seldom observed occurrence of a coordination number greater than 8 in transition-metal derivatives might be offered as a rationale for the monodentate behavior of the carboxylate ligands in the above complexes. The propensity of uranium for high coordination numbers, however, might lead to the stabilization of the bidentate bonding mode of the carboxylate ligands in the analogous $Cp_2U(O_2CR)_2$ complexes. The possibility of obtaining complexes which would exhibit novel stereochemistries gave us an extra impetus for the synthesis of these derivatives.

Experimental Section

All reactions and operations were performed with the use of Schlenk techniques under a static atmosphere of rigorously purified nitrogen. All solvents were dried by refluxing under nitrogen with the appropriate drying agent and were distilled just prior to use. The compound $Cp_2U(NEt_2)_2$ was synthesized and purified according to published procedures.[3]

Benzoic acid (Fisher), previously recrystallized, was pumped to dryness under vacuum. Trimethylacetic acid (pivalic acid) (Aldrich) was pumped to dryness under vacuum; however, this was only done for a short period of time as the compound sublimes at room temperature. Concentrated glacial acetic acid (Fisher) was used as received. Thiobenzoic acid (Aldrich) was dried by adding $MgSO_4$ to a solution of the acid dissolved in hexane. The slurry was stirred and filtered and the solvent removed under vacuum. The yellow liquid was then used without further purification. Thioacetic acid (Aldrich) was stirred over $MgSO_4$, filtered, and then distilled, resulting in a yellow liquid.

Infrared spectra were recorded in the region 4000–250 cm^{-1} with a Perkin-Elmer 467 grating spectrometer. The complexes were studied as Nujol and Fluorolube mulls between potassium bromide plates. The samples were prepared in a glovebag filled with purified nitrogen.

Proton nuclear magnetic resonance spectra were recorded on the following spectrometers: Perkin-Elmer R-32 (35 °C), Varian HA-100 (32 °C), and Varian HA-100 Digilab (32 °C). Variable-temperature spectra were recorded on the Perkin-Elmer and Varian HA-100 Digilab machines with the use of sealed NMR tubes. Ambient-temperature NMR spectra were obtained with use of serum-stoppered NMR tubes.

Mass spectra were recorded on an AEI-MS12 mass spectrometer operating at 70 eV and at temperatures just sufficient to record the spectra. Each sample was sealed in a capillary under nitrogen and

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Table I. Analytical Data and Physical Properties of $Cp_2U(XYCR)_2$ Complexes

		yield,	anal. (exptl values in parentheses)					
compd	color	%	% C	% H	% O	% S	% U	mol wt
$Cp_2U(O_2CMe)_2$[a]	green	69	34.58 (33.81)	3.32 (3.38)	13.16 (12.75)		48.95 (48.50)	
$Cp_2U(OSCMe)_2$[b]	green	60	32.43 (32.17)	3.11 (3.21)	6.17 (5.98)	12.37 (12.14)	45.91 (46.20)	
$Cp_2U(OSCPh)_2$[c]	red	58	44.86 (44.65)	3.14 (3.26)	4.98 (5.15)	9.98 (10.03)	37.04 (36.86)	643 (619)[g]
$Cp_2U(O_2CPh)_2$[d]	green	52	47.22 (47.07)	3.30 (3.41)	10.48 (5.34)[f]			
$Cp_2U(O_2CCMe_3)_2$[e]	green	68	42.11 (41.95)	4.95 (5.10)	11.22 (5.71)[f]			571 (1151)[h]

[a] The compound is insoluble in benzene, acetone, dichloromethane, tetrahydrofuran, acetonitrile, and nitromethane but very soluble in pyridine. A molecular weight could not be obtained because of low solubility in common solvents. [b] This compound can be sublimed at 100 °C under mercury diffusion pump vacuum albeit with significant decomposition. A molecular weight could not be obtained because the compound decomposed at the temperature at which the measurements were made. [c] The compound is soluble in benzene, toluene, carbon disulfide, and dichloromethane. [d] The compound is soluble in tetrahydrofuran, and insoluble in benzene and hexane. [e] The compound is soluble in hexane, benzene, and dichloromethane. [f] The analytical laboratory mentioned that for procedural reasons in related organometallic compounds sometimes only one C-bonded oxygen atom is determined; on the basis of spectral results and correct C and H analyses we believe the complexes are pure. [g] Osmometry in CH_2Cl_2. [h] Osmometry in benzene.

admitted into the spectrometer by using the direct-probe technique.

Analyses and molecular weight determinations were performed by Analytische Laboratorien, D-5250 Engelskirchen, West Germany, on samples sent in glass tubes sealed under vacuum.

Abbreviations used were as follows: $Cp = \eta^5\text{-}C_5H_5$, $Et = CH_2CH_3$, $Me = CH_3$, $Ph = C_6H_5$.

Preparation of the Complexes. Since the syntheses of the reported complexes followed essentially similar procedures, only the preparation of a representative example, $Cp_2U(O_2CMe)_2$, and the attempted synthesis of $Cp_2U(NEt_2)(O_2CCMe_3)$ are given. The physical properties and analytic data on the compounds prepared in this study are listed in Table I.

$Cp_2U(O_2CMe)_2$. $Cp_2U(NEt_2)_2$ (2.26 g, 4.42 mmol) was dissolved in 70 mL of hexane, stirred, and filtered. To this solution at 0 °C was added a solution of MeCOOH (0.50 mL, 8.74 mmol) in 30 mL of hexane. There was an immediate color change from gold-brown to green-brown along with the observation of a faint cloudiness above the solution. As the addition proceeded, a green precipitate was formed. After 18 h of stirring at room temperature, the lime green supernatant liquid was decanted and the remaining pale green solid was dried under vacuum to give a yield of 69% of pure $Cp_2U(O_2CMe)_2$.

$Cp_2U(NEt_2)(O_2CCMe_3)$. $Cp_2U(NEt_2)_2$ (4.12 g, 8.03 mmol) was dissolved in 60 mL of hexane, stirred, and filtered. To this solution at room temperature was added through a transfer tube a solution of Me_3CCO_2H (0.813 g, 7.96 mmol) in 30 mL of hexane. The flask and transfer tube were rinsed with another 20 mL of hexane. The reaction mixture was stirred at room temperature for 22 h. A 5-mL aliquot of the solution was transferred to a small flask where the solvent was removed under vacuum, resulting in a gold-brown oily solid. NMR analysis of this material indicated that a mixture of $Cp_2U(NET_2)(O_2CCMe_3)$, $Cp_2U(O_2CCMe_3)_2$, and $Cp_2U(NEt_2)_2$ was present.

Results and Discussion

The carboxylate and monothiocarboxylate derivatives of dicyclopentadienyluranium(IV) were formed easily by the reaction of $Cp_2U(NEt_2)_2$ and 2 equiv of the appropriate acid as outlined in eq 1. An attempt to produce the monosubstituted carboxylate compound resulted in a mixture of both the mono- and disubstituted complexes according to eq 2. It is noteworthy that even though the pure mixed complex could not be obtained, no evidence of $Cp_3U(O_2CCMe_3)$ was found either. Redistribution reactions, to produce compounds containing the Cp_3U fragment, have been observed often in this area of chemistry.[4,11] It is evident that the coordination saturation or steric congestion around $Cp_2U(NEt_2)(O_2CCMe_3)$ is sufficient to stabilize the compound and to prevent a redistribution reaction from occurring. Alternative approaches are being explored to synthesize this potentially interesting complex and related derivatives.

$$Cp_2U(NEt_2)_2 + 2RCOXH \xrightarrow[\text{hexane or toluene}]{0\ °C} Cp_2U(OXCR)_2 \tag{1}$$

$$R = Me, Ph;\ X = O \text{ or } S$$

$$R = CMe_3;\ X = O$$

$$3Cp_2U(NEt_2)_2 + 3Me_3CCOOH \xrightarrow[\text{hexane}]{\text{room temperature}} Cp_2U(O_2CCMe_3)_2 + Cp_2U(NEt_2)(OCCMe_3) + Cp_2U(NEt_2)_2 \tag{2}$$

Molecular weight determinations could only be obtained for two compounds. $Cp_2U(OSCPh)_2$ was shown to be a monomer and $Cp_2U(O_2CCMe_3)_2$, a dimer. Determinations were not performed on $Cp_2U(OSCMe)_2$ or $Cp_2U(O_2CMe)_2$ due to thermal decomposition of the former and insolubility of the latter. It can be inferred from the solubility properties of $Cp_2U(O_2CMe)_2$ and $Cp_2U(O_2CPh)_2$ that these compounds are polymers since the dimeric $Cp_2U(O_2CMe_3)_2$ is soluble in hexane whereas the first two compounds are insoluble in hexane and even in aromatic solvents.

The mass spectral data of the compounds partially confirm the associated nature of some of these derivatives as determined by the molecular weight measurements. The data and the major fragmentation patterns are summarized in Tables II and III. The strong relative abundance of the molecular ion peak attests to the robust nature of the complexes. Peaks above the molecular ion are observed only for $Cp_2U(O_2CMe)_2$ and $Cp_2U(O_2CCMe_3)_2$. These peaks do not correspond to a dimer or a trimer but instead to losses of cyclopentadienyl ligand and carboxylate group fragments from high mass units. It is possible that some of the high-mass peaks are the result of recombination within the mass spectrometer caused by the direct-insertion method and the high ionizing energy used.[12] The base peak for the carboxylates, and for almost all other Cp_2U derivatives, results from loss of one cyclopentadienyl ligand form the parent ion. Loss of the carboxylate ligand is less favored although it is one of the major fragmentation processes observed. A comparison of the relative abundance of the fragment ions arising from this process also shows that the carboxylate ligand is more labile than the monothiocarboxylate moiety, 12.8% of $Cp_2U(O_2CPh)^+$ in $Cp_2U(O_2CPh)_2$ as opposed to only 1.4% of $Cp_2U(OSCPh)^+$ in $Cp_2U(OSCPh)_2$.

Now we wish to turn to an examination of the infrared spectral data listed in Table IV, as a guide for the assignment of the different metal–ligand bonding modes featured in the complexes.

The carboxylate moiety can exhibit monodentate or bidentate (chelating or bridging) ligating behavior. The different possibilities are shown. Diagrams a and b also indicate that the monothiocarboxylate ligand, when acting as a monodentate

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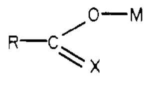

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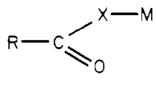

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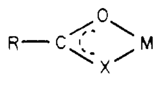

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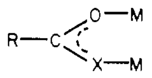

d

X = S or O

group, has the option to bond through either the oxygen or the sulfur atom. It is apparent from the diagrams that as the coordination mode changes from monodentate to bidentate (chelating or bridging) there is a decrease in the double bond character of the C=O or C=S bond, and consequently changes in the infrared stretching frequencies of the O–C–X moieties are expected. The difference between the asymmetric O–C–O and symmetric O–C–O stretching frequencies, $\Delta\nu$(OCO), has been used as a guide to the ligation of the carboxylate group.[13,14] It was noted that if this number was approximately 100 cm^{-1} or less, there was a strong possibility of chelating coordination; bridging coordination was likely when $\Delta\nu$(OCO) was between 100 and 200 cm^{-1}, and values greater than 200 cm^{-1} were indicative of monodentate coordination. These guidelines have been utilized previously to predict the bonding mode of the carboxylate groups in a series of titanium complexes containing both the cyclopentadienyl and carboxylate moieties. These complexes, $Cp_2Ti(O_2CR)$,[15] were assumed to have chelating carboxylate group based on $\Delta\nu$(OCO) values which were below 115 cm^{-1}. The corresponding value for the complexes $CpTi(O_2CR)_2$[16] was 168 ± 3 cm^{-1} and suggested to the authors the presence of bridging carboxylate ligands. This assumption was further supported by the dimeric nature of the complexes on the basis of molecular weight measurements and proven conclusively by the X-ray structural determination of the benzoate derivative $CpTi(O_2CPh)_2$.[17]

Although useful in assigning coordination modes, the $\Delta\nu$(OCO) criterion does have some problems associated with it. First, there is some overlap in the ranges associated with the different bonding modes. Catterick and Thornton[14] in their review show a spread of 80–250 cm^{-1} for the bridging configuration. Robinson and Uttley,[18] studying a series of Ru, Os, Rh, and Ir derivatives containing triphenylphosphine and carboxylate moieties, found that both the asymmetric and symmetric carboxylate band positions varied extensively. Meaningful interpretation of their data followed only if both the position of the asymmetric stretch and the differences in the carboxylate stretching frequencies were monitored. It thus appears that although the monodentate bonding mode is usually indicated by a combination of high frequency of the asymmetric C–O stretch and large splitting between two ν(OCO) modes, the prediction of chelating or bridging coordination based on infrared considerations alone is not as reliable.

In the case of the tetracarboxylate compounds of uranium reported to date, almost all contain at least chelating ligands. This is not surprising considering the tendency of uranium toward high coordination numbers as well as its predisposition toward oxygen bonding.[19,20] The difference between the asymmetric and symmetric stretching modes are less than 200 cm^{-1} but tend to be greater than 100 cm^{-1}. For instance, the compound $U(O_2CMe)_4$, known to be a polymer with bridging and chelating moieties,[21] has $\Delta\nu$(OCO) values of 160 and 170 cm^{-1}.

For the uranium carboxylate compounds studied here, the assignments of some of the bands in the infrared spectra proved difficult because of overlap between vibrations arising from the cyclopentadienyl ring, the alkyl or aryl groups, and the carboxylate functions.

The infrared pattern of the cyclopentadienyl ring in the present complexes consists of strong bands at around 1020 and 800 cm^{-1} assigned to the in-plane ($\delta(C-H)_{Cp}$) and out-of-plane ($\gamma(C-H)_{Cp}$) C–H bending modes, respectively. Another vibration associated with the C–C stretching of the cyclopentadienyl ring at 1410–1450 cm^{-1} is obscured by the strong asymmetric C–O stretch of the carboxylate ligand also occurring in this area (vide infra). The simplicity of the pattern is indicative of a η^5 bonding mode for the cyclopentadienyl moieties.[22]

The asymmetric and symmetric stretching modes for the alkyl carboxylates have been assigned to the strong bands which occur in the regions normally associated with these vibrations. As mentioned before, the symmetric C–O stretching mode at ~1420 cm^{-1} is in the same region as the ν(C–C) of the Cp ring and could have some contribution from the latter. In the case of the acetate $Cp_2U(O_2CMe)_2$ and to a lesser extent the pivalate compound $Cp_2U(O_2CCMe_3)_2$, these bands are quite broad. The cause of this broadness is not apparent unless it is related to the associated nature of the complexes.

The spectrum of the benzoate complex poses a different problem. The strong bands at 1494 and 1488 cm^{-1} are probably due to the asymmetric C–O stretch; the low value for this frequency is not totally unexpected since the corresponding vibration in $Cp_2Ti(O_2CPh)$ is found at 1505 cm^{-1}.[15] The benzoate complex also possesses two medium intensity bands at 1602 and 1591 cm^{-1}, but these we have assigned to a phenyl vibration.[23] A similar medium intensity band in the spectrum of $Cp_2U(OSCPh)_2$ is observed at 1596 cm^{-1}, and a band at 1602 cm^{-1} has also been assigned to a phenyl vibration in the $CpTi(O_2CPh)_2$[16] complex. Although it is possible that one of the two bands of $CpU(O_2CPh)_2$ is due to a phenyl vibration and the other to a high-frequency asymmetric C–O stretch, the almost invariably high intensity found for the latter vibration seems to mitigate against such an assignment.

The assignment of the bands for the monothiocarboxylate complexes was based on works by Nyquist et al.[24] on thiol esters and related compounds, by Patal et al.[25] on metal derivatives of thiobenzoate, and by Coutts and Wailes[26] on Cp_2Ti(OSCR)-type compounds. The position of the $\nu(C\overset{\cdots}{-}O)$ stretch and the $\nu(C\overset{\cdots}{-}S)$ stretch seem to indicate that bidentate coordination has occurred in these complexes also. The low carbonyl frequency is also in apparent accord with this bonding mode. The variety of bonding modes available to the monothiocarboxylate ligand has been diagramed before (a–d). The

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Table II. Summary of Mass Spectral Data for $Cp_2U(XYCR)_2$[a] Complexes

	$Cp_2U(O_2CPh)_2$			$Cp_2U(OSCPh)_2$		$Cp_2U(OSCMe)_2$		$Cp_2U(O_2CMe)_2$		$Cp_2U(O_2CCMe_3)_2$	
	m/e	rel abund[b]	rel abund[c]	*m/e*	rel abund[d]	*m/e*	rel abund[e]	*m/e*	rel abund[f]	*m/e*	rel abund[g]
P^+	610	24.5	21.0	642	28.6	518	39.6	486	25.3	570	19.7
$P - Cp^+$	545	100	100	577	100	453	100	421	100	505	100
$P - (XYCR)^+$	489	12.8	14.3	505	1.4	443	4.6	427	5.9	469	15.7
$P - Cp - (XYCR)^+$	424	1.1	0.7	440	1.0	378	1.0	362	0.6	404	0.9
$[P - Cp - (XYCR)]SH^+$				473	0.5	411	12.3				
$[P - Cp - (XYCR)]OH^+$	441	2.3	0.6	457	1.2	395	22.7	379	40.0	421	4.3
$[P - Cp - (XYCR)]S^+$				472	1.8	410	0.6				
$[P - Cp - (XYCR)]O^+$	440	4.9	3.6	456	6.8	394	2.2	378	3.3	420	2.3
$CpU(XYCR)(R)^+$	501	0.7	0.7	517	0.9	393	0.3	377	0.2	461	0.0
Cp_2UO^+	384	3.5	1.8	384	0.8	384	0.8	384	2.6	384	3.2
$CpUO^+$	319	23.4	16.2	319	21.8	319	39.7	319	27.7	319	12.3
UOS^+	286			286	4.1	286	12.9				
UO_2^+	270	21.3	11.8	270	16.3	270	12.3	270	22.0	270	5.7
US_2^+	302			302	0.9	302	1.7				
peaks higher than P^+	no			no	no	no		yes		yes[h]	

[a] Not corrected for ^{13}C, relative abundance given in percent. [b] $T = 130$ °C. [c] $T = 150$ °C. [d] $T = 125$ °C. [e] $T = 120$ °C. [f] $T = 120$–150 °C. [g] $T = 100$ °C. [h] At high temperatures only.

Table III. Major Fragmentation Processes for $Cp_2U(XYCR)_2$ Complexes

	metastable peaks									
	$Cp_2U(O_2CPh)_2$		$Cp_2U(OSCPh)_2$		$Cp_2U(O_2CMe)_2$		$Cp_2U(OSCMe)_2$		$Cp_2U(O_2CCMe_3)_2$	
process	calcd	found	calcd	found	calcd	found	calcd	found	calcd	found
$P^+ \rightarrow P\text{-}Cp^+ + Cp$	486.9	487.0	518.6	519.0	364.7	365.0	396.2	396.0	447.4	447.5
$P^+ \rightarrow [P\text{-}XYCR]^+ + XYCR$	392.0	392.0	397.2	not seen	375.2	375.0	278.9	not seen	385.9	386.0
$P\text{-}Cp^+ \rightarrow [P\text{-}Cp\text{-}XYCR]O^+ + XCR$	355.2	355.3	360.4	360.5						
$P\text{-}Cp^+ \rightarrow [P\text{-}Cp\text{-}XYCR]OH^+ + XCR\text{-}H$					341.2	341.5	344.4	344.5	351.0	351.0
$P\text{-}Cp^+ \rightarrow [P\text{-}Cp\text{-}XYCR]SH^+ + YCR\text{-}H$							372.9	373.0		

Table IV. Characteristic Infrared Absorptions (cm^{-1})[a] of $Cp_2U(XYCR)_2$ Complexes

assignt	$Cp_2U(OSCPh)_2$	$Cp_2U(O_2CPh)_2$	$Cp_2(OSCMe)_2$	$Cp_2U(O_2CMe)_2$	$Cp_2U(O_2CCMe_3)_2$
$\nu(C\text{-}C)_{phenyl}$	1596 m	1602 m			
		1591 m			
$\nu_{asym}(OCO)$ or $\nu(C{\cdots}O)$		1494 s		1523 s vbr	1564 vs br
	1465 s	1488 s	1487 s		1484 s
$\nu_{sym}(OCO)$		1423 s		1463 s br	1424 s
				1416 s br	
	1226 vs	1179 m	1157 vs		1223 s
$\delta(C\text{-}H)_{Cp}$	1016 m	1022 s	1016 s	1016 s	1017 s
$\nu(C{\cdots}S)$	963 s		974 m		
$\gamma(C\text{-}H)_{Cp}$	797 s	785 s	797 vs	789 s	786 s
$\Delta(\nu_{asym} - \nu_{sym})$[b]		65, 71		60, 107	60, 140

[a] In Nujol and Fluorolube mulls. [b] Refers to the OCO stretching frequencies.

Table V. ^1H NMR Data for $Cp_2U(XYCR)_2$ Complexes

	chemical shift[a,b]				
compd	Cp	CH_3	CMe_3	other	
$Cp_2U(OSCPh)_2$	−6.0 (s)[c,d]			−7.8 (br, *p*)	−5.64 (t, *m*)[d]
$Cp_2U(OSCMe)_2$	−6.2 (s)	[illegible].5 (s)			
$Cp_2U(O_2CCMe_3)_2$	−3.5 (s)		4.5 (s)		
$Cp_2U(NEt_2)(O_2CCMe_3)$	25.2 (s)		7.0 (s)	−39.4 (q, CH_2)	−21.9 (t, CH_3)

[a] Negative shift is a downfield shift; $T = 35$ °C; solvent = C_6D_6. [b] Chemical shift recalculated to Me_4Si from internal benzene (−7.24 ppm); s = singlet, t = triplet, q = quartet, br = broad; *p* = para, *m* = meta. [c] Overlapping resonances of Cp and ortho protons. [d] See text for explanation.

position of the $\nu(C{\cdots}O)$ and $\nu(C{\cdots}S)$ bands have been used by Patal et al.[25] to determine which of these coordination modes are present in a series of transition-metal–thiobenzoate complexes. Variation in the carbonyl or thiocarbonyl band positions as compared to sodium thiobenzoate was used to assign preferential coordination to sulfur or oxygen in the series of complexes. Applying this procedure to the present complexes, the $\nu(C{\cdots}O)$ band at 1465 and 1487 cm^{-1} is seen to be lower than 1500 cm^{-1} whereas the $\nu(C{\cdots}S)$ band at 963 and 974 cm^{-1} is comparable to the value of 960 cm^{-1} found in the sodium salt. Such results may indicate that although there is bidentate coordination, a slight bonding preference toward oxygen is exhibited. In compounds where there are S-bonded monothiocarboxylate groups, the $\nu(C{=}O)$ frequency is above 1630 cm^{-1}.[27,28]

In summary then, the positions and the $\Delta\nu(OCO)$ values for the symmetric and asymmetric C–O stretching vibrations

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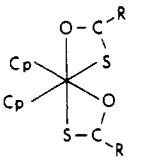
(27) J. Weidlein, *J. Organomet. Chem.*, **32**, 181 (1971).

(28) J. Otera and R. Okawara, *J. Organomet. Chem.*, **17**, 353 (1969).

given in Table IV for the uranium carboxylate complexes are indicative of chelating and/or bridging coordination modes for the carboxylate groups. The presence of bridging carboxylates would of course be consistent with the low solubility of the complexes which also suggest polymeric behavior.

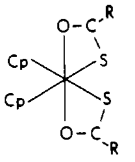
The proton NMR spectra of the soluble complexes have been recorded and the data are listed in Table V. As expected for paramagnetic uranium(IV) complexes, the resonances are displaced from the usual diamagnetic positions. There is very little that can be said about the magnitude of the shifts in the absence of structural and magnetic studies. It is, nevertheless, worth pointing out that for the mixed amido–carboxylate complex, $Cp_2U(NEt_2)(O_2CCMe_3)$, the shifts are much larger than usually found for Cp_2U-type complexes. This may be the result of some unique stereochemistry exhibited by the complex or could arise also from the increased magnetic anisotropy due to the low molecular symmetry of the complex.

As a first step in discussing the NMR data, the coordination geometry of the compounds must be set. Monomeric $Cp_2U(\text{chelate})_2$-type compounds possessing the pseudooctahedral structure (Cp ligand considered as occupying one coordination site) can, in principle, exist as the cis and trans geometrical isomers.[4] The structures of a few related complexes [$(\eta^5\text{-}MeC_5H_4)_2Hf(BH_4)_2$,[29] $Cp_2U(BH_4)_2$,[30] and $Cp_2U[cis\text{-}(OCMe)_2Re(CO)_4]_2$[31]] have been determined, and they all show the angular cisoid arrangement of the Cp_2M fragment. The cis-octahedral geometry will be assumed in the present context also, in order to discuss the ^1H NMR spectra of the monomeric thiocarboxylate derivatives. Although it must be admitted that the trans form cannot be rigorously excluded based on the present set of spectral data.



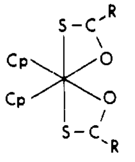
e

2 Cp
2 R



f

1 Cp
1 R



g

1 Cp
1 R

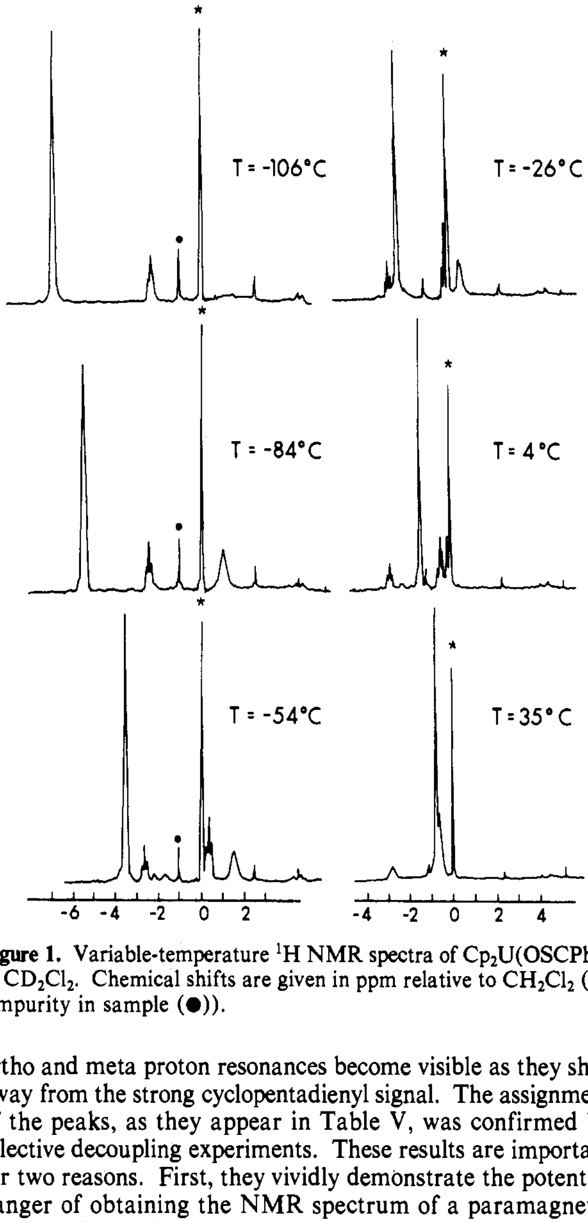


Figure 1. Variable-temperature ^1H NMR spectra of $Cp_2U(OSCPh)_2$ in CD_2Cl_2. Chemical shifts are given in ppm relative to CH_2Cl_2 (*) (impurity in sample (●)).

For the thiocarboxylate complexes three isomers are possible as outlined in diagrams e, f, and g. Indicated in parentheses are the number of Cp and R group resonances expected for each isomer. If all three isomers were present in solution, then a complicated NMR spectrum should be observed. The ambient-temperature ^1H NMR spectrum in C_6D_6 of the thioacetate complex exhibited only two singlets in a 5:3 ratio due to the cyclopentadienyl ring and methyl group, respectively. The spectrum of the thiobenzoate derivative gave a singlet for the η^5-cyclopentadienyl moiety and showed only the para- and meta-proton peaks of the phenyl ring. The simple spectra may be the result of accidental chemical shift equivalence or some nonrigid behavior akin to the metal-centered rearrangement processes postulated in the carbamate complexes $Cp_2U(XYCNEt_2)_2$.[4] In order to distinguish between the two possibilities the ^1H NMR spectrum of $Cp_2U(OSCPh)_2$ was recorded in CD_2Cl_2 at different temperatures. The results are shown in Figure 1. It is clear from the figure that the spectrum at 35 °C shows only two peaks. However, the integration of the peaks is 8.8:1, indicating that the major signal arises from the fortuitous overlap of the Cp, ortho, and meta phenyl proton resonances. As the temperature is lowered, the ortho and meta proton resonances become visible as they shift away from the strong cyclopentadienyl signal. The assignment of the peaks, as they appear in Table V, was confirmed by selective decoupling experiments. These results are important for two reasons. First, they vividly demonstrate the potential danger of obtaining the NMR spectrum of a paramagnetic compound at only one temperature since troublesome and unexpected overlap of resonances can sometimes occur. However, they also clearly show that such accidental overlap can be established easily from a variable-temperature study since the temperature dependence of the chemical shifts for different protons or isomers are usually different. This last point seems to indicate that the observation of a single cyclopentadienyl resonance and one set of phenyl peaks for $Cp_2U(OSCPh)_2$ at −54 °C is not due to accidental overlap of the resonances from different isomers but to some metal-centered rearrangement that apparently interconverts the isomers even at this low temperature. As with the similar thiocarbamate complex $Cp_2U(OCSNEt_2)_2$,[4] it is not knwon whether this is a simple trigonal-twist type motion which would interconvert isomers f and g only or a more complicated process which would cause exchange among all three isomers. It is also important to realize that a metal-centered rearrangement alone cannot produce the simple phenyl proton pattern observed at −54 °C. Although interconverting isomers and R groups, such a motion does not exchange the two ortho and meta protons of the same phenyl ring. To do this, C–Ph bond rotation must also be occurring. Further lowering of the temperature causes the ortho and meta protons to broaden considerably, and by −106 °C both peaks have disappeared into the base line. In the same temperature interval, the

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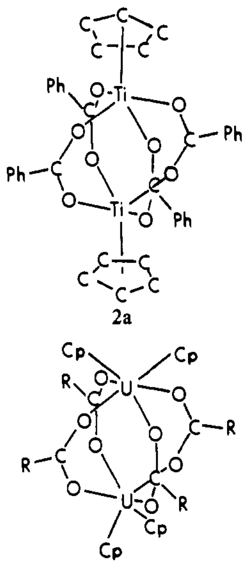
(29) P. J. Johnson, S. A. Cohen, T. J. Marks, and J. M. Williams *J. Am. Chem. Soc.*, **100**, 2709 (1978).

(30) P. Zanella, G. De Paoli, G. Bombieri, G. Zanotti, and R. Rossi, *J. Organomet. Chem.*, **142**, C21 (1977).

(31) A. L. Arduini, J. Takats, C. M. Lukehart, L. T. Warfield, and V. W. Day, submitted for publication.



2a

2b

Figure 2. Schematic diagrams of the dimeric $CpTi(O_2CPh)_2$ structure and the proposed structure for $Cp_2U(O_2CCMe_3)_2$.

cyclopentadienyl signal remains a relatively sharp singlet and the para proton resonance maintains its triplet appearance. Since the low-temperature limiting spectrum could not be obtained, a definitive answer as to the stereochemistry of the complex remains elusive as does the exact nature of the metal-centered rearrangement. An intriguing possibility which would account for the variable-temperature spectral changes is that in this complex the C–Ph bond rotation is a higher energy process than the metal-centered rearrangement which interconverts the different isomers and gives, even at −106 °C, only one set of Cp and Ph resonances.

The only carboxylate complex that dissolved sufficiently in nondonor solvents for ^1H NMR investigation was the pivalate derivative, $Cp_2U(O_2CCMe_3)_2$. The other carboxylates dissolved only in pyridine. However, this solvent or small amounts of residual water in the solvent seemed to be reacting with the complexes and hampered the interpretation of the spectra. Consequently, we will only discuss the spectral features of the pivalate derivative.

A molecular weight determination in benzene for $Cp_2U(O_2CCMe_3)_2$ indicated dimeric behavior, and infrared data were consistent with bidentate carboxylate groups. It was of interest to see whether more information about the coordination geometry around the uranium could be gathered from the solution NMR data. Surprisingly, the ^1H NMR spectrum at room temperature showed only two singlets in a 5:9 ratio due to the η^5-cyclopentadienyl rings and the *tert*-butyl groups, respectively. The simple spectrum can be rationalized in at least three ways: the molecule possesses a highly symmetric carboxylate–bridged dimeric structure, some of the resonances are accidentally chemical shift equivalent at room temperature, or there is a rapid dimer–monomer equilibrium which averages the different resonances. So that these possibilities could be sorted out, a variable-temperature ^1H NMR sutdy on the complex was carried out. As indicated before, the chemical shifts of paramagnetic complexes are temperature dependent, thus it is highly unlikely that peaks which are overlapping at room temperature will remain so as the temperature is varied; an excellent illustration has just been provided by the $Cp_2U(OSCPh)_2$ complex. Of course, the dimer–monomer equilibrium is expected to be temperature dependent, and thus the study could shed some light on its presence or absence.

The NMR spectrum of $Cp_2U(O_2CCMe_3)_2$ was recorded over the temperature range −90 to +90 °C. The spectrum remained constant except for a slight broadening of the resonances and shifting of the peaks with temperature as expected for a paramagnetic compound. The temerature-invariant nature of the NMR spectra clearly rules out accidental chemical shift equivalence as being responsible for the simple two line spectrum. Although rapid equilibrium at all temperatures with a small concentration of monomeric $Cp_2U(O_2CCMe_3)_2$ is possible, it is more likely that the simple spectrum is a result of a symmetric dimeric structure of the type already established for $CpTi(O_2CPh)_2$.[17] A schematic diagram of the Ti structure and the proposed geometry of the uranium complex are shown in Figure 2. Recognizing the larger size of uranium and its propensity for high coordination number, we think **2b** is not an unreasonable proposal for the structure of $[Cp_2U(O_2CCMe_3)_2]_2$.

We are continuing our efforts to grow single crystals of some of the reported complexes in order to verify the geometrical predictions put forth in this article and to establish the extent of aggregate formation and the details of the bonding modes of the carboxylate or thiocarboxylate moieties.

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Registry No. $Cp_2U(O_2CMe)_2$, 77495-63-7; $Cp_2U(OSCMe)_2$, 77495-53-5; $Cp_2U(OSCPh)_2$, 77495-54-6; $Cp_2U(O_2CPh)_2$, 77495-65-9; $[Cp_2U(O_2CCMe_3)_2]_2$, 77495-55-7; $Cp_2U(NEt_2)O_2CCMe_3)$, 77495-56-8; $Cp_2U(NEt_2)_2$, 54068-37-0.