bond angle from 124.1 to 142.6°.

Figure 3B suggests that the "dimer" is stabilized by interactions between the planar ligands of the component molecules. The angle between the normals to the least-squares planes defined by the two ligands is 28.9° for the "monomer" and 7.0° for the "dimer". Coplanarity of the two ligands optimizes the π overlap. In the "dimer", the distance between the least-squares planes through all salicylideniminato atoms in the respective molecules is 3.47 Å, which is only slightly larger than the 3.31-Å[7] separation in naphthalene at room temperature and is in the range observed for many planar charge-transfer complexes.

Figure 3B also suggests that the small deviation from coplanarity of the two salicylaldimine ligands observed in the dimer could be the result of the weak iron–oxygen interaction. It is clear, however, that if a five-coordinate to six-coordinate transformation is to occur in the solid state, any significant shortening of the Fe–O′ bond must be accompanied by a drastic change in ligand orientation and at the expense of a significant amount of π stabilization.

A related Schiff base complex, Fe(salen)Cl, has been crystallized in both monomeric[8] and dimeric[2] forms. In this case the dimer is a true dimer with 2.18-Å Fe–O bonds linking the component molecules. This complex differs from the SANE analogue in that an ethylene bridge links the two salicylaldimine components, forcing the complex to adopt a square-pyramidal geometry with the oxygen atoms in adjacent (rather than opposite) basal sites. Figure 3C shows, however, that the potential for π overlap of the type observed in the "loose dimer" also exists in this complex. The distortion from coplanarity of the ligand ring systems observed for this compound is very similar to that required if the SANE dimer is to undergo the proposed transformation.

The anomalous temperature dependence of the magnetic moment of the dimeric form observed by Bertrand et al.[1] (from $\mu = 3.12\ \mu_B$ at 80 K to 5.95 μ_B at 298 K) is certainly consistent with the proposed "loose" dimer to "tight" dimer transformation. This interpretation is supported by the observation that the magnetic moment of the monomer is nearly constant over the same temperature range. There are, however, at least three possible types of transformations in accord with the limited amount of experimental data available. The first is an abrupt (first-order) transition. The second possibility is a continuous (second-order) transition in which at intermediate temperatures there exists an equilibrium mixture of "loose" and "tight" dimers. There is a large class of spin-equilibrium complexes in which processes of this type are known to occur. A third possibility is a continuous "displacive" transition in which there is a gradual decrease in the intermolecular distance with decrease in thermal energy. All molecular crystals in which planar molecules stack in a parallel fashion show a strong temperature dependence of the intermolecular separation. However, since formation of a strong Fe–O′ bond in this case requires major disruption of the ligand π interaction, a transition of the third type is somewhat difficult to envision. Further, the drastic rearrangement of ligands that must accompany Fe–O′ bond formation is likely to significantly alter the crystal-packing interactions. Such a change increases the probability of a first-order transition. A transition of this type might preclude the direct single-crystal characterization of this transformation by multiple-temperature X-ray structural analysis.[9]

Acknowledgment. This work was supported by the National Science Foundation (Grant CHE79-06343) and by the donors of the Petroleum Research Fund, administered by the American Chemical Society.

Registry No. Fe(SANE)$_2$Cl, 42294-92-8.

Supplementary Material Available: Listings of anisotropic thermal parameters, hydrogen positions, and observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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Uranyl Complexes of β-Polyketonates. Crystal and Molecular Structure of a Mononuclear Uranyl 1,3,5-Triketonate and a Novel Trinuclear Uranyl 1,3,5-Triketonate with a Trigonal-Planar Bridging Oxide

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Received September 18, 1981

Two uranyl complexes of 1,3,5-triketonate ligands have been crystallized and examined by X-ray diffraction techniques. The first is the mononuclear bis[1,5-diphenyl-1,3,5-pentanetrionato(1−)](methanol)dioxouranium(VI)–methanol, [UO$_2$(C$_{35}$H$_{30}$O$_7$)(CH$_3$OH)], UO$_2$(H(DBA))$_2$(CH$_3$OH)·CH$_3$OH, in which the uranium atom is bound to four enolic oxygens, two uranyl oxygens, and one methanolic oxygen. The triketonate ligands are in a cis configuration presumably due to the steric constraints of the methanol coordination. Crystal data are as follows: $P2_1/c$, $a = 9.932$ (4), $b = 30.29$ (4), $c = 11.671$ (4) Å; $\beta = 103.03°$, $V = 3421$ (2) Å^3; $Z = 4$, $R_1 = 0.048$, $R_2 = 0.050$. The second is a trinuclear UO$_2^{2+}$ anion containing a trigonal, tribridging oxide ion that results during attempts to prepare binuclear UO$_2^{2+}$ complexes of 1,3,5-triketonates. The compound bis(triethylammonium) tris(2,2′,8,8′-tetramethyl-3,5,7-nonanetrionato)-μ_3-oxo-tris(dioxouranate)(2−), [(C$_2$H$_5$)$_3$NH]$_2$[U$_3$O$_6$(C$_{39}$H$_{60}$O$_9$)O], [(C$_2$H$_5$)$_3$NH]$_2$[(UO$_2$)$_3$(DPA)$_3$O], contains a nearly equilateral triangle of UO$_2^{2+}$ ions with a central O^{2-} ion trigonally bonded to the three U atoms. One triketonate occupies each edge of the triangle with the central enolic oxygen bridging two U atoms and the terminal oxygens bound to one U atom. Each U is seven-coordinate in nearly pentagonal-bipyramidal geometry. Crystal data are as follows: $C2/c$, $a = 27.90$ (2), $b = 15.65$ (2), $c = 31.81$ (3) Å; $\beta = 107.8$ (1)°, $V = 13220$ (20) Å^3; $Z = 8$, $R_1 = 0.062$, $R_2 = 0.078$.

Introduction

During the past decade it has become increasingly apparent that the 1,3,5-triketones and their Schiff-base derivatives are an extremely versatile class of binucleating ligand. Part of our efforts during this period have been directed toward developing synthetic methods to produce pure samples of binu-

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clear complexes containing unusual combinations of two different metal ions (heterobinuclear complexes)[1] and unusual binuclear complexes containing the same metal ions (homobinuclear complexes).[2] A primary goal of this work is to design and characterize a class of metal complexes whose potential reactivity due to the presence of two metal ions may be enhanced or modified as compared to that of similar mononuclear complexes.

Synthetically the UO_2^{2+} ion in binuclear 1,3,5-triketonate complexes is of interest since its seven-coordinate, pentagonal-bipyramidal geometry imposes constraints on these chelating ligands that have not as yet been investigated. More significant, however, complexes of the UO_2^{2+} ion have possible applications in solar energy conversion systems[3] due to its spectral properties (absorption and luminescence), excited-state lifetimes, and excited-state electron-transfer properties. These properties together with the possibility of preparing compounds in which UO_2^{2+} is present in a heterobinuclear complex have encouraged us to investigate the structures of the two complexes discussed herein as a preliminary stage in the study of a variety of polynuclear complexes containing UO_2^{2+}.

Experimental Section

Ligand Synthesis. The ligands were prepared by the general method of Miles, Harris, and Hauser in which appropriate 1,3-diketones are condensed with an ester by using NaH in boiling THF.[4]

Bis[1,5-diphenyl-1,3,5-pentanetrionato(1−)](methanol)dioxouranium(VI)–Methanol, $UO_2(H(DBA))_2(CH_3OH)\cdot CH_3OH$. 1,5-Diphenyl-1,3,5-pentanetrione, H_2DBA (2.66 g, 10 mmol), was dissolved in 200 mL of boiling CH_3OH. An aqueous solution of 2.12 g (5 mmol) of $UO_2(C_2H_3O_2)_2\cdot 2H_2O$ in 50–60 mL of water was added to the boiling ligand solution. A dark red precipitate formed immediately. The mixture was boiled for 10 min, cooled in an ice bath for 2 h, and then filtered. The crude complex was dissolved in about 2 L of CH_3OH and left for slow evaporation, upon which small red crystals formed.

The red crystals melt at 113 °C and are soluble in common organic solvents such as $CHCl_3$, CH_3CH, and CH_3OH. Anal. Calcd for $UO_2(C_{17}H_{13}O_3)_2(CH_3OH)_2$: C, 50.00; H, 3.90; U, 27.55. Found: C, 49.46; H, 3.82; U, 27.80.

Bis(triethylammonium) Tris(1,5-diphenyl-1,3,5-pentanetrionato)-μ_3-oxo-tris(dioxouranate)(2−), $[(C_2H_5)_3NH]_2[(UO_2)_3(DBA)_3O]$, and Bis(triethylammonium) Tris(2,2′,8,8′-tetramethyl-3,5,7-nonanetrionato)-μ_3-oxo-tris(dioxouranate)(2−), $[(C_2H_5)_3NH]_2[(UO_2)_3(DPA)_3O]$. The ligand (5.0 mmol) was dissolved in 200 mL of refluxing acetone. An equimolar quantity (5.0 mmol) of $UO_2(C_2H_3O_2)_2\cdot 2H_2O$ was dissolved in 25 mL of H_2O and added to the ligand solution. An immediate, intensely red solution was obtained. Triethylamine (1.7 mL, 1.1 g, 10.5 mmol) was then added to the solution. This solution was refluxed and stirred for 6 h, after which it was stirred and cooled in an ice bath. The red microcrystalline compound was separated and dried in air. The filtrate was set aside for slow evaporation, which produced larger crystals. The combined yield was about 75–80%.

The red crystals of $[(C_2H_5)_3NH]_2[(UO_2)_3(DBA)_3O]$ are soluble in $CHCl_3$, $(CH_3)_2CO$, CH_3OH, CH_3CN, and C_6H_6 but are essentially insoluble in CCl_4. The compound decomposes at 256–258 °C. Anal. Calcd for $[(C_2H_5)_3NH]_2[U_3O_6(C_{17}H_{12}O_3)_3O]$: C, 41.49; H, 3.70; N, 1.54; U, 39.19. Found: C, 41.64; H, 3.50; N, 1.50; U, 38.34. The red crystals of $[(C_2H_5)_3NH]_2[(UO_2)_3(DPA)_3O]$ are soluble in most concern organic solvents but insoluble in CCl_4. The compound decomposes at 305 °C. Anal. Calcd for $[(C_2H_5)_3NH]_2[U_3O_6(C_{13}H_{20}O_3)_3O]$: C, 35.96; H, 5.40; N, 1.65; U, 41.95. Found: C, 35.98; H, 5.57; N, 1.62; U, 41.61.

Crystallography and Structure Determination. 1. $UO_2(H(DBA))_2(CH_3OH)\cdot CH_3OH$. A suitable crystal (0.19 × 0.19 × 0.27 mm) was mounted in a sealed, dry, thin-walled capillary and transferred to a Syntex $P2_1$ automated diffractometer (Mo Kα radiation, λ = 0.71069 Å, graphite monochromator). Partial rotation photographs and a sample data set proved consistent with the space group[5] assignment $P2_1/c$ (ref 5, No. 14, systematic absences $h0l$, l = odd, and $0k0$, k = odd) having the following monoclinic cell constants: $a = 9.932$ (4), $b = 30.29$ (4), $c = 11.671$ (4) Å; $\beta = 103.03$ (3)°, $V = 3421$ (2) Å^3, $Z = 4$, $\rho_{calcd} = 1.679$ g cm^{-3}, and $F_{000} = 1688$ e. Intensities were measured for 6794 reflections of the forms $h,k,\pm l$ in the region $2.5° \le 2\theta \le 50.0°$. From these, 2472 unique, observed ($I \le 2.5\sigma(I)$) reflections were obtained by averaging. Gaussian integration absorption corrections[6] were applied (μ 45.5 cm^{-1}), yielding transmission coefficients that varied from 1.99 to 2.22. Other details of data collection were as follows: scan method, $\theta/2\theta$; scan rate, 2.0–4.0°/min; scan range, 0.8° below Kα_1 to 0.9° above Kα_2 in 2θ; background/scan time, 0.5; max h, 13; max k, 35; max l, 15.

The structure was solved by the heavy-atom (Patterson) technique. Hydrogen atoms were placed by a combination of observed and calculated positions (where calculated, C–H = 1.05 Å) and given arbitrary isotropic temperature factors of 4.0 Å^2.[6] It is difficult to locate the hydrogen atoms on both methanol molecules, so these were not included in the final model. All parameters associated with hydrogen were held fixed throughout refinement. Because of the smaller number of observation/number of variables ratio, the phenyl carbon atoms were refined isotropically while all other nonhydrogen atoms were refined with anisotropic temperature parameters. Full-matrix least squares[7] using our usual weighting scheme[8] reached convergence at $R_1 = 0.48$ and $R_2 = 0.050$.[9] In the final cycle, the maximum shift/error was less than 0.01, the number of variables was 304, and the number of observations was 2472. A final difference map showed a number of small peaks (representing up to 1.1 e/Å^3) occurring in the vicinity of the uranium atom (within approximately 1 Å) but was otherwise featureless. Neutral-atom scattering factors[10] were used and those for uranium were corrected[11] for anomalous dispersion. An examination of the error of fit over intervals of increasing F_o and $(\sin\theta)/\lambda$ showed only minor deviations. The error in an observation of unit weight was 1.18. The value of p in the calculation of $\sigma(I)$ is 0.05. Final atomic positional parameters are presented in Table I. Essential interatomic distances and angles are listed in Tables II and III, respectively. Tables containing anisotropic thermal parameters (Table A), isotropic thermal parameters (Table B), hydrogen positional parameters (Table C), hydrogen bond lengths (Table D), displacements (Table E), calculated and observed structure factors (Table F), nonessential bond distances (Table G) and bond angles (Table H), and least-squares planes and atomic deviations (Table I) are available.[12]

2. $[(C_2H_5)_3NH]_2[(UO_2)_3(DPA)_3O]$. A large bright red multifaceted crystal was mounted whose overall geometry approximated that of a sphere (dimensions 0.37 × 0.37 × 0.42 mm) and transferred to a Syntex $P2_1$ automated diffractometer (Mo Kα, λ = 71069 Å, graphite monochromator). The crystal was found to be monoclinic with cell constants $a = 27.90$ (2), $b = 15.65$ (2), and $c = 31.81$ (3) Å; $\beta = 107.8$ (1)°, $V = 13\,220$ (20) Å^3, $Z = 8$, $\rho_{calcd} = 1.711$ g cm^{-3}, and $F_{000} = 6528$ e. A sample data set indicated systematic absences of hkl, $h + k$ = odd, and $h0l$, l = odd, which is consistent with the space

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(8) $w = 1/(\sigma(F)^2$.

(9) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.

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(12) Supplementary material.

Table I. Atomic Coordinates[a] for $UO_2(H(DBA))_2(CH_3OH)\cdot CH_3OH$

atom	x	y	z
U	0.12652 (6)	0.15295 (2)	−0.19166 (5)
O1	0.3548 (12)	0.1433 (4)	−0.0997 (9)
O2	0.2310 (11)	0.1082 (4)	−0.3106 (8)
O3	0.3866 (15)	0.1197 (5)	−0.5221 (10)
O4	−0.0835 (12)	0.1834 (4)	−0.1925 (9)
O5	−0.0380 (11)	0.1268 (4)	−0.3548 (8)
O6	−0.0148 (11)	0.0738 (4)	−0.5167 (9)
C1	0.4617 (18)	0.1243 (5)	−0.1129 (14)
C2	0.4649 (15)	0.0984 (6)	−0.2146 (14)
C3	0.3497 (17)	0.0913 (5)	−0.3027 (14)
C4	0.3570 (16)	0.0588 (5)	−0.4045 (12)
C5	0.3514 (15)	0.0823 (6)	−0.5174 (14)
C6	−0.2089 (17)	0.1798 (5)	−0.2426 (13)
C7	−0.2584 (13)	0.1519 (6)	−0.3398 (12)
C8	−0.1692 (16)	0.1268 (5)	−0.3921 (12)
C9	−0.2261 (14)	0.1018 (5)	−0.4966 (12)
C10	−0.1501 (16)	0.0764 (5)	−0.5536 (12)
O7	0.1674 (10)	0.2007 (4)	−0.0167 (9)
C71	0.1518 (27)	0.1880 (7)	0.0967 (17)
O8	0.0913 (12)	0.1088 (3)	−0.1096 (9)
O9	0.1618 (12)	0.1990 (4)	−0.2689 (9)
C11	0.5929 (15)	0.1289 (5)	−0.0211 (13)
C12	0.5899 (15)	0.1564 (6)	0.0699 (13)
C13	0.7039 (18)	0.1625 (6)	0.1639 (15)
C14	0.8220 (18)	0.1405 (6)	0.1572 (14)
C15	0.8280 (18)	0.1128 (6)	0.0695 (16)
C16	0.7142 (17)	0.1074 (5)	−0.0222 (14)
C21	0.3006 (15)	0.0553 (5)	−0.6300 (13)
C22	0.2748 (16)	0.0115 (6)	−0.6289 (13)
C23	0.2282 (18)	−0.0117 (6)	−0.7361 (16)
C24	0.2048 (19)	0.0121 (7)	−0.8365 (17)
C25	0.2268 (20)	0.0536 (7)	−0.8400 (17)
C26	0.2782 (18)	0.0802 (6)	−0.7354 (16)
C31	−0.3065 (15)	0.2108 (5)	−0.2028 (12)
C32	−0.4420 (17)	0.2155 (5)	−0.2582 (14)
C33	−0.5261 (18)	0.2454 (6)	−0.2136 (15)
C34	−0.4743 (19)	0.2697 (6)	−0.1178 (16)
C35	−0.3365 (21)	0.2655 (7)	−0.0600 (17)
C36	−0.2552 (17)	0.2345 (6)	−0.1008 (14)
C41	−0.2069 (15)	0.0511 (5)	−0.6603 (12)
C42	−0.3429 (16)	0.0548 (5)	−0.7190 (13)
C43	−0.3933 (18)	0.0277 (6)	−0.8226 (15)
C44	−0.3044 (19)	−0.0003 (6)	−0.8573 (15)
C45	−0.1758 (18)	−0.0040 (6)	−0.8032 (15)
C46	−0.1218 (16)	0.0210 (5)	−0.7001 (13)
O10	0.1869 (22)	0.2859 (6)	−0.0171 (16)
C101	0.0834 (32)	0.3087 (8)	−0.0863 (21)

[a] The esd's are given in parentheses.

Table II. Bond Distances (Å) in $UO_2(H(DBA))_2(CH_3OH)\cdot CH_3OH$

U–O1	2.30 (1)	U–O7	2.46 (1)
U–O2	2.34 (1)	U–O8	1.73 (1)
U–O4	2.28 (1)	U–O9	1.84 (1)
U–O5	2.35 (1)		
O1–C1	1.25 (2)	O5–C8	1.28 (2)
O2–C3	1.27 (2)	O6–C10	1.32 (2)
O3–C5	1.19 (2)	O7–C71	1.42 (2)
O4–C6	1.26 (2)		
C1–C2	1.43 (2)	C6–C7	1.41 (2)
C2–C3	1.37 (2)	C7–C8	1.41 (2)
C3–C4	1.56 (2)	C8–C9	1.44 (2)
C4–C5	1.49 (2)	C9–C10	1.35 (2)

Table III. Bond Angles (Deg) in $UO_2(H(DBA))_2(CH_3OH)\cdot CH_3OH$

O1–U–O2	71.4 (4)	O4–U–O5	70.4 (4)
O1–U–O4	149.3 (4)	O4–U–O7	75.2 (4)
O1–U–O5	140.2 (4)	O4–U–O8	90.9 (5)
O1–U–O7	74.1 (4)	O4–U–O9	88.0 (5)
O1–U–O8	86.8 (5)	O5–U–O7	145.6 (3)
O1–U–O9	93.0 (5)	O5–U–O9	89.8 (5)
O2–U–O4	139.3 (4)	O5–U–O9	92.0 (4)
O2–U–O5	69.2 (4)	O7–U–O8	90.7 (4)
O2–U–O7	145.0 (3)	O7–U–O9	86.8 (4)
O2–U–O8	93.0 (4)	O8–U–O9	177.4 (6)
O2–U–O9	89.3 (5)		
U–O1–C1	141 (1)	U–O5–C8	138.3 (9)
U–O2–C3	136 (1)	U–O7–C71	126 (1)
U–O4–C6	141 (1)		
O1–C1–C2	122 (1)	C2–C3–C4	120 (1)
O1–C1–C11	120 (2)	O2–C3–C2	127 (1)
C2–C1–C11	118 (2)	O2–C3–C4	114 (1)
C1–C2–C3	122 (1)		

groups $C2/c$ and Cc. The centrosymmetric space group $C2/c$ was chosen and the correctness of the choice is verified by the successful refinement of the structure.

Intensities were measured for 11 086 reflections of the form $h,k,\pm l$ in the region $2.5° \leq 2\theta \leq 45°$. From these, 5972 unique observed ($I \geq 3\sigma(I)$) reflections were obtained by averaging. Because of the difficulty in indexing the large number of crystal faces and the approximate spherical shape of the crystal no absorption corrections were applied. Other details of data collections were as follows: scan method, $\theta/2\theta$; scan rate 2.0–4.0°/min.; scan range, 0.9° below Kα to 0.9° above Kα_2 in 2θ; background/scan time, 0.5; $\mu = 70.0$ cm^{-1}.

The structure was solved by the heavy-atom (Patterson) technique. Hydrogen atoms were placed in a combination of observed and calculated positions (where calculated, C–H = 1.0 Å in trigonal or tetrahedral geometry) and given isotropic temperature factors of 6.0 Å^2.[6] Full-matrix least-squares[7] calculations were contained with use of our usual weighting scheme,[8] with hydrogen parameters held invariant. Refinement was terminated when the maximum shift ($\sim 1\sigma$) did not decrease for three cycles. The final R values[9] were $R_1 = 0.062$ and $R_2 = 0.078$ with all nonhydrogen atoms described anisotropically, with the exception of the methyl groups on the DPA ligands (labeled C1m through C18m), which remained isotropic throughout. The number of variables was 559, and the error in observation of unit weight was 2.2. A final difference map showed a significant amount of electron density about the uranium atoms was unaccounted for. The six highest peaks each representing ~ 3 e/Å^3 were all within 1.0 Å of one of the uranium atoms. Neutral-atom scattering factors[10] were used, with uranium corrected[11] for anomalous dispersion. The value of ρ in the calculation of $\sigma(I)$ was 0.05. Final atomic positional parameters are presented in Table IV. Essential interatomic distances and angles are listed in Tables V and VI, respectively. Tables containing anisotropic thermal parameters (Table SI), isotropic thermal parameters (Table SII), hydrogen positional parameters (Table SIII), hydrogen bond lengths (Table SIV), calculated and observed structure factors (Table SV), nonessential interatomic distances (Table SVI) and angles (Table SVII), and least-squares planes and atomic deviations (Table SVIII) are available.[12]

Results and Discussion

1. Structure of $UO_2(H(DBA))_2(CH_3OH)\cdot CH_3OH$. The structure of $UO_2(H(DBA))_2(CH_3OH)\cdot CH_3OH$ (where H(DBA) refers to the monoanion of 1,5-diphenyl-1,3,5-pentanetrionate) consists of discrete neutral molecules in which the uranium atom is seven-coordinate in a pentagonal-bipyramidal arrangement. The coordination sphere is comprised of two uranyl oxygen atoms, two DBA ligands each acting as a bidentate chelate, and one methanol. The additional solvent molecule is not located in the primary coordination sphere, the oxygen atom of this solvent methanol being over 4 Å from the uranium atom. The apex positions in the pentagonal bipyramid are occupied by the uranyl oxygen atoms and are essentially perpendicular to the pentagonal base. The least-squares plane of the pentagonal base[12] shows only small deviations (0.1 Å or less) of the equatorial donor atoms from this plane with a slightly ruffled arrangement in which U or O4 share the mean plane while the other consecutive donor atoms lie on alternating sides of the plane. The oxygen-uranium-oxygen equatorial bond angles range from 69.2 to 75.2° and are indicative of a fairly regular pentagon (the ideal angle is 72°). Pentagonal-bipyramidal geometry is not unusual for

Table IV. Fractional Atomic Coordinates[a] of $[(C_2H_5)_3NH]_2[(UO_2)_3(DPA)_3O]$

atom	*x*	*y*	*z*
U1	0.33257 (3)	0.33897 (5)	0.18253 (3)
U2	0.29762 (3)	0.12294 (5)	0.12245 (3)
U3	0.19452 (3)	0.29318 (5)	0.11676 (3)
O1	0.4098 (5)	0.3323 (9)	0.2326 (5)
O2	0.3685 (5)	0.1951 (8)	0.1826 (5)
O3	0.3720 (6)	0.0553 (10)	0.1261 (6)
O4	0.2617 (6)	0.0108 (10)	0.0785 (6)
O5	0.2030 (5)	0.1359 (8)	0.1012 (5)
O6	0.1163 (5)	0.2370 (10)	0.0832 (5)
O7	0.1515 (5)	0.4192 (10)	0.1092 (5)
O8	0.2542 (5)	0.4190 (8)	0.1419 (5)
O9	0.3459 (5)	0.4799 (9)	0.1997 (5)
O10	0.3549 (5)	0.3548 (8)	0.1356 (4)
O11	0.3101 (5)	0.3256 (9)	0.2295 (4)
O12	0.2924 (5)	0.0640 (9)	0.1682 (5)
O13	0.3040 (5)	0.1766 (9)	0.0753 (5)
O14	0.2022 (5)	0.3119 (8)	0.0645 (4)
O15	0.1865 (5)	0.2764 (9)	0.1693 (5)
O16	0.2743 (5)	0.2478 (8)	0.1439 (4)
C1	0.4557 (12)	0.3057 (17)	0.3096 (12)
C2	0.4301 (8)	0.2760 (15)	0.2612 (8)
C3	0.4287 (9)	0.1890 (14)	0.2506 (8)
C4	0.4052 (8)	0.1551 (14)	0.2096 (7)
C5	0.4239 (8)	0.0755 (14)	0.2008 (8)
C6	0.4097 (9)	0.0336 (13)	0.1586 (10)
C7	0.4407 (12)	−0.0389 (18)	0.1460 (13)
C8	0.2303 (12)	−0.1330 (22)	0.0665 (19)
C9	0.2295 (12)	−0.0373 (16)	0.0792 (10)
C10	0.1819 (11)	−0.0104 (16)	0.0887 (10)
C11	0.1692 (8)	0.0747 (13)	0.0959 (8)
C12	0.1214 (9)	0.0892 (14)	0.0984 (8)
C13	0.0979 (8)	0.1668 (16)	0.0933 (8)
C14	0.0429 (11)	0.1753 (21)	0.0952 (11)
C15	0.1126 (10)	0.5288 (18)	0.0579 (11)
C16	0.1566 (8)	0.4871 (14)	0.0906 (8)
C17	0.2038 (10)	0.5255 (15)	0.0925 (9)
C18	0.2514 (8)	0.4934 (14)	0.1260 (7)
C19	0.2914 (9)	0.5515 (13)	0.1339 (9)
C20	0.3351 (10)	0.5414 (14)	0.1665 (11)
C21	0.3817 (12)	0.6095 (21)	0.1808 (19)
C1m	0.4165 (18)	0.3451 (29)	0.3261 (16)
C2m	0.4829 (16)	0.3854 (29)	0.3067 (15)
C3m	0.4677 (19)	0.2423 (36)	0.3451 (17)
C4m	0.4180 (25)	−0.0800 (45)	0.1115 (23)
C5m	0.4435 (24)	−0.1072 (42)	0.1803 (22)
C6m	0.4926 (24)	−0.0209 (39)	0.1615 (19)
C7m	0.2700 (18)	−0.1416 (28)	0.0444 (16)
C8m	0.1885 (25)	−0.1652 (38)	0.0368 (21)
C9m	0.2503 (29)	−0.1764 (46)	0.1050 (25)
C10m	0.0222 (16)	0.0966 (27)	0.1037 (14)
C11m	0.0138 (16)	0.2163 (28)	0.0576 (15)
C12m	0.0460 (17)	0.2370 (30)	0.1328 (15)
C13m	0.0889 (15)	0.4640 (27)	0.0249 (14)
C14m	0.1182 (19)	0.6043 (33)	0.0346 (16)
C15m	0.0764 (19)	0.5334 (32)	0.0883 (17)
C16m	0.3802 (12)	0.6513 (21)	0.1353 (11)
C17m	0.4262 (20)	0.5605 (33)	0.1900 (18)
C18m	0.3721 (22)	0.6694 (36)	0.2095 (19)
N1	0.3541 (8)	0.3296 (16)	0.0448 (6)
C22	0.3052 (12)	0.3542 (21)	0.0118 (9)
C23	0.2803 (14)	0.4232 (22)	0.0290 (11)
C24	0.3753 (11)	0.2492 (24)	0.0263 (9)
C25	0.4207 (13)	0.2122 (27)	0.0605 (12)
C26	0.3891 (13)	0.4025 (22)	0.0607 (10)
C27	0.4090 (14)	0.4360 (27)	0.0234 (15)
N2	0.2848 (12)	0.0477 (16)	0.2536 (8)
C28	0.2952 (13)	0.1410 (27)	0.2608 (10)
C29	0.2893 (18)	0.1693 (30)	0.3038 (11)
C30	0.3235 (36)	−0.0045 (47)	0.2850 (20)
C31	0.3484 (21)	−0.0625 (50)	0.2703 (18)
C32	0.2334 (21)	0.0180 (36)	0.2506 (14)
C33	0.1988 (18)	0.0111 (58)	0.2117 (17)

[a] The esd's are given in parentheses.

Table V. Interatomic Distances (Å) for $[(C_2H_5)_3NH]_2[(UO_2)_3(DPA)_3O]$

U1· · ·U2	3.859 (4)	O1–C2	1.27 (2)
U1· · ·U3	3.847 (5)	O2–C4	1.28 (2)
U2· · ·U3	3.884 (3)	O3–C6	1.28 (3)
U1–O1	2.26 (1)	O4–C9	1.18 (3)
U1–O2	2.46 (1)	O5–C11	1.32 (2)
U1–O8	2.51 (1)	O6–C13	1.30 (3)
U1–O9	2.28 (1)	O7–C16	1.25 (3)
U1–O10	1.80 (1)	O8–C18	1.26 (2)
U1–O11	1.80 (1)	O9–C20	1.39 (3)
U1–O16	2.23 (1)	C2–C3	1.40 (3)
U2–O2	2.56 (1)	C3–C4	1.37 (3)
U2–O3	2.30 (1)	C4–C5	1.41 (3)
U2–O4	2.28 (2)	C5–C6	1.44 (3)
U2–O5	2.52 (1)	C9–C10	1.51 (4)
U2–O12	1.76 (1)	C10–C11	1.41 (3)
U2–O13	1.77 (1)	C11–C12	1.38 (3)
U2–O16	2.23 (1)	C12–C13	1.37 (3)
U3–O5	2.54 (1)	C16–C17	1.43 (3)
U3–O6	2.29 (1)	C17–C18	1.51 (3)
U3–O7	2.28 (1)	C18–C19	1.40 (3)
U3–O8	2.54 (1)	C19–C20	1.35 (3)
U3–O14	1.76 (1)		
U3–O15	1.77 (1)		
U3–O16	2.24 (1)		

Table VI. Interatomic Angles (Deg) for $[(C_2H_5)_3NH]_2[(UO_2)_3(DPA)_3O]$

O1–U1–O2	69.9 (5)	O8–U1–O9	72.1 (4)
O1–U1–O8	151.7 (5)	O8–U1–O10	88.4 (5)
O1–U1–O9	79.9 (5)	O8–U1–O11	90.9 (5)
O1–U1–O10	95.4 (6)	O8–U1–O16	70.2 (4)
O1–U1–O11	87.8 (6)	O9–U1–O10	89.6 (5)
O1–U1–O16	137.5 (5)	O9–U1–O11	89.2 (6)
O2–U1–O8	138.3 (4)	O9–U1–O16	142.3 (5)
O2–U1–O9	148.1 (4)	O10–U1–O11	178.8 (7)
O2–U1–O10	83.2 (5)	O10–U1–O16	90.6 (5)
O2–U1–O11	97.9 (6)	O11–U1–O16	90.1 (5)
O2–U1–O16	69.1 (4)		
O2–U2–O3	71.7 (5)	O4–U2–O5	70.7 (5)
O2–U2–O4	153.5 (5)	O4–U2–O12	88.4 (6)
O2–U2–O5	132.2 (5)	O4–U2–O13	89.1 (6)
O2–U2–O12	81.6 (6)	O4–U2–O16	138.4 (5)
O2–U2–O13	99.7 (6)	O5–U2–O12	85.4 (6)
O2–U2–O16	67.3 (4)	O5–U2–O13	95.9 (6)
O3–U2–O4	84.1 (6)	O5–U2–O16	68.5 (4)
O3–U2–O5	154.6 (5)	O12–U2–O13	176.6 (6)
O3–U2–O12	91.0 (6)	O12–U2–O16	95.7 (6)
O3–U2–O13	86.5 (6)	O13–U2–O16	87.6 (6)
O3–U2–O16	136.9 (5)		
O5–U3–O6	70.7 (5)	O7–U3–O8	68.7 (5)
O5–U3–O7	153.6 (5)	O7–U3–O14	88.2 (6)
O5–U3–O8	136.1 (4)	O7–U3–O15	90.8 (6)
O5–U3–O14	86.1 (5)	O7–U3–O16	137.9 (5)
O5–U3–O15	95.0 (6)	O8–U3–O14	84.9 (5)
O5–U3–O16	68.1 (4)	O8–U3–O15	94.5 (5)
O6–U3–O7	83.6 (5)	O8–U3–O16	69.3 (4)
O6–U3–O8	151.9 (5)	O14–U3–O15	178.9 (6)
O6–U3–O14	89.8 (6)	O14–U3–O16	91.3 (5)
O6–U3–O15	90.3 (6)	O15–U3–O16	89.2 (6)
O6–U3–O16	138.6 (5)		
U1–O1–C2	131 (1)	U3–O6–C13	127 (1)
U1–O2–C4	133 (1)	U3–O7–C16	131 (1)
U2–O2–C4	124 (1)	U3–O8–C18	129 (1)
U1–O2–U2	100.5 (5)	U1–O8–C18	127 (1)
U2–O3–C6	132 (2)	U3–O8–U1	99.2 (5)
U2–O4–C9	133 (2)	U1–O9–C20	120 (1)
U2–O5–C11	129 (1)	U1–O16–U2	119.9 (5)
U3–O5–C11	129 (1)	U1–O16–U3	118.7 (5)
U2–O5–U3	100.3 (5)	U2–O16–U3	120.4 (5)

uranium complexes and seems to be the preferred geometry for seven-coordinate uranyl compounds. X-ray structures have confirmed this geometry both in complexes containing che-

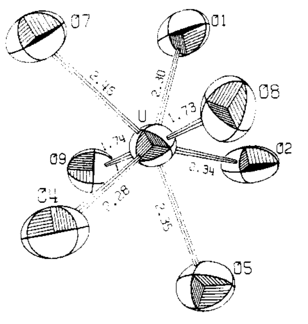


Figure 1. ORTEP drawing of the uranium coordination sphere in $UO_2(H(DBA))_2(CH_3OH)$. Ellipsoids represent 50% probability.

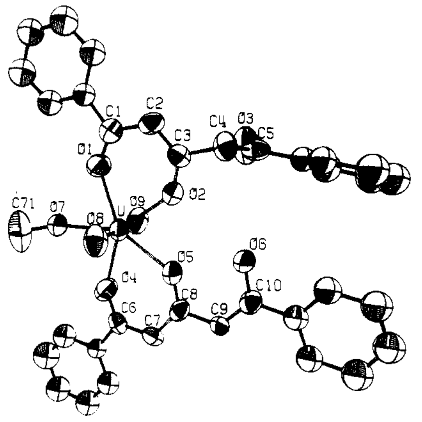
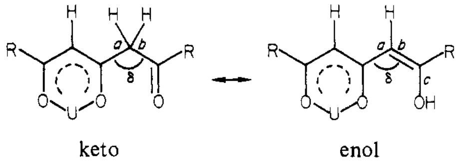


Figure 2. ORTEP drawing of molecule $UO_2(H(DBA))_2(CH_3OH)$ illustrating the atom numbering. Ellipsoids represent 50% probability.

lating ligands[13-19] and in complexes with exclusively monodentate ligands.[20,21]

This structure provides the opportunity to observe the bond lengths for three different types of U–O bonds within the same complex (see Figure 1). The U–O(uranyl) bond lengths (1.73 (1) and 1.74 (1) Å) are well within the range of those previously reported[13-20] and no doubt reflect the multiple bond order. The U–O(ketonate) bond lengths average 2.32 (6) Å and are slightly shorter than the U–O(ketonate) lengths found in $UO_2[(CF_3CO)_2CH]_2{\cdot}THF$[16] (average U–O(ketonate) = 2.38 (7) Å), which may be due to the increased electron-withdrawing power of the CF_3 groups. Further, this laboratory has examined[1,2] a number of metal triketonate complexes and has remarked[22] on the fact that the M–O bond length involving the oxygen bonded to the central carbon of the 1,3,5-triketone backbone is always longer than the M–O bond length involving the oxygens bound to the terminal backbone carbons. Even though this is the first seven-coordinate triketonate structure to be examined, the average bond lengths $U–O_{2,5}$(central) = 2.35 (1) and $U–O_{1,4}$(terminal) = 2.29 (1) Å support the aforementioned trend, reinforcing the notion that the hybridization of the central oxygen atom is slightly different from that of the terminal oxygen atoms. As expected on the basis of hybridization, the longest U–O bond within the title complex is U–O(methanol) at 2.46 (1) Å.

This structure also illustrates two different tautomers and geometries for the DBA ligand (see Figure 2). Since this complex is mononuclear, there are two possible tautomers:



Albeit the assignment of keto and enol forms is somewhat arbitrary, i.e., there is probably an equilibrium mixture present throughout the crystal, the DBA ligand containing O1, O2, O3 is best described as exhibiting the keto form (since *b* = 1.49 (2) Å, *c* = 1.19 (2) Å, *δ* = 112 (1)°) while the opposite DBA ligand containing O4, O5, O6 is probably primarily present as the enol form (*b* = 1.35 (2) Å, *c* = 1.32 (2) Å, *δ* = 124 (1)°). The enolic proton H(O6) is involved in intramolecular hydrogen bonding (O2–H(O6) = 2.35 (1) Å; O5–H(O6) = 2.41 (1) Å).

The geometry of these two ligands is also different with respect to rotation about bond *a* above. The atoms O4, O5, O6 belong to the DBA ligand whose geometry is similar to that of the metal–DBA structures[1,2] previously published in which the backbone carbon atoms (C6–C10) are coplanar with the three oxygen atoms. However, in the opposite DBA ligand (containing O1, O2, O3) there has been a torsional rotation about bond *a* such that C4, C5, O3 no longer lie in the plane described by O1, C1, C2, C3, O2. This conformation is probably due to the increased coordination of U relative to Ni and Co in the previous DBA structures. With the addition of a fifth equatorial group, the angle O2–U–O5 (69.2 (4)°) is significantly smaller than the analogous angle in the Ni (78.5°) and Co (77.3°) complexes. This induces the conformational change to a nonplanar arrangement to avoid steric interactions between the pendent oxygen atom O3 and O6.

Although the hydrogen atoms were not found for either methanol group, there are a number of close oxygen–oxygen contacts, some of which certainly describe hydrogen bonding of the methanolic protons (O10···O7 = 2.59 (2) Å, O10···O9 = 3.00 (2) Å, O7···O1 = 2.87 (2) Å, O7···O1 = 2.87 (2) Å, O7···O4 = 2.90 (1) Å).

2. Structure of $[(C_2H_5)_3NH]_2[(UO_2)_3(DPA)_3O]$. The uranium atoms of this compound are found in discrete triangular arrangements within the anions. Each of these uranium atoms is linked to two others through a dinegative oxygen atom located at the center of the uranium triangle. This triangular metal arrangement about a central O^{2-} atom has been observed in the basic acetates of other metals,[23-25] but to our knowledge this is the first example of this type of cluster coordination for uranium. The identification of the central bridge as O^{2-} rather than OH^- cannot be unambiguously made on the basis of X-ray data but rather is inferred by the very nearly planar trigonal geometry of the heavy atoms about the central oxygen.[12] The trigonal, bridging O16 lies 0.13 Å out of the plane of the three uranium atoms. The uranium atoms are additionally linked by bridging DPA^{2-} ligands external to the central triangle resulting in pentagonal equatorial coordination about each uranium. The uranyl oxygen atoms lie above and

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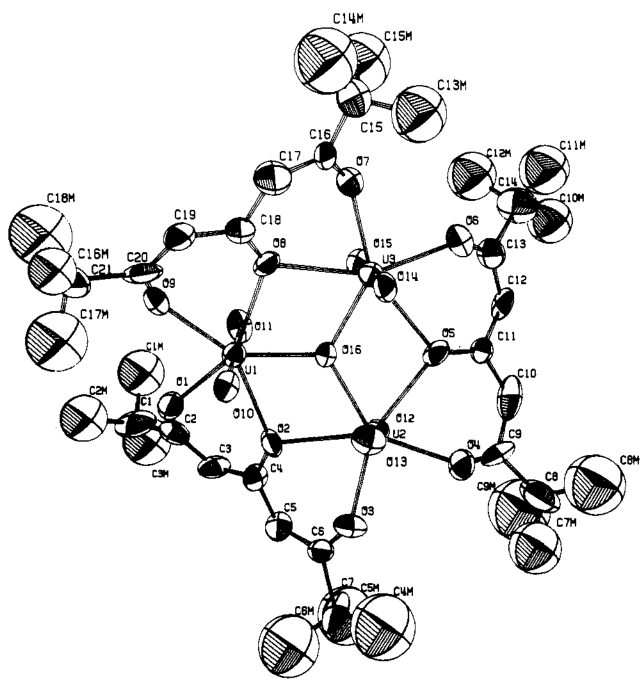

Figure 3. ORTEP drawing of the $[(UO_2)_3(DPA)_3O]^{2-}$ anion illustrating the atom numbering. Ellipsoids represent 50% probability.

below the pentagonal base, providing the preferred bipyramidal-pentagonal coordination for uranium. The U–U distances (3.847 (5), 3.859 (4), and 3.884 (3) Å) are long enough to preclude any direct metal–metal interaction. Figure 3 illustrates the trinuclear dianion with hydrogen atoms omitted for clarity.

The DPA^{2-} ligands are shown to coordinate in the usual manner of triketonate ligands with the outer oxygen atoms coordinating to one metal and the inner oxygen atoms serving as bridging ligands between two metals. The shorter U–O outer bond length relative to the U–O bridging length is a trend already noted[22] for related triketonate structures. Spatial crowding may also contribute to the bond length discrepancies in this structure. However, all the U–O bond distances are within the normal ranges seen in other uranyl complexes.[26-32] Unlike most other triketonate structures, this complex does not exhibit planarity of the backbone carbon atoms with the ketonate oxygen atoms and metal atoms. This is no doubt due to steric interaction between adjacent *tert*-butyl groups. Further consequence of this steric repulsion is seen in the distortion of the equatorial plane about uranium: the O–U–O angle involving two different DPA groups is significantly larger than predicted by ideal pentagonal geometry (O1–U1–O9 = 79.9°, O3–U2–O4 = 84.1°, O6–U3–O7 = 83.6°, ideal angle = 72°), and the five equatorial oxygen atoms about each uranium assume a slightly puckered arrangement wwith respect to their mean plane.[12]

The trimethylammonium cations are probably linked to the anion through hydrogen bonding between the ammonium proton and uranyl oxygen. Close contacts are H1N1–O10 = 2.08 (1) Å and H1N2–O12 = 1.84 (1) Å.

In our earlier work on heterobinuclear complexes with the diamine Schiff bases of the 1,3,5-triketones we developed a systematic synthetic approach to the preparation of the mixed-metal complexes.[1] The method that proved to be useful depends upon the coordinative selectivity afforded by ligands with two distinctly different coordination sites. As the result of such selectivity, certain metal ions can be quanitatively bound in one site, leaving the other for a second, different, metal ion. This approach depends, of course, on designing an extremely unsymmetric ligand since the selectivity is due to difference in coordination sites.

The strong tendency of the UO_2^{2+} ion to be seven-coordinate and pentagonal bipyramidal affords another approach to the synthesis of heterobinuclear complexes and, in this case, even those with symmetric ligands. As the structure of $[UO_2(H(DBA))(CH_3OH)]$ shows, the seventh ligand, which is the CH_3OH, has the effect of directing the orientation of the two 1,3,5-triketonates into a cis arrangement. It is obvious from the structure that this is the preferred and most likely the only arrangement expected for similar mononuclear UO_2^{2+} complexes. A trans configuration would be highly strained. A result of the cis arrangement is that the remaining coordination sites in the ligands are like poised claws available to chelate a second metal ion. Inasmuch as the potentially dianionic triketones are only monoanionic in $[UO_2(H(DBA))_2(CH_3OH)]$, reaction with an M(II) ion in the presence of a base can be expected to yield neutral molecules of the type $[(UO_2)M(DBA)_2(CH_3OH)]$. Recently several heterobinuclear complexes of this general class have been prepared and characterized in our laboratories.[33]

The preparation of the trinuclear $[(UO_2)_3(DBA)_3O]^{2-}$ and $[(UO_2)_3(DPA)_3O]^{2-}$ complexes was the result of attempts to introduce a second UO_2^{2+} ion into the mononuclear $[UO_2(H(DBA))_2(CH_3OH)]$. Although the seven-coordination requirement for the second UO_2^{2+} made the chances for success small due to excessive strain, attempts were made with the belief that unusual structures would result if the compounds could be prepared. It was subsequently found that identical products result from the reaction of $[UO_2(H(DBA))_2(CH_3OH)]$ with 1 equiv of $UO_2(CH_3CO_2)_2(H_2O)_2$ and 2 equiv of $(C_2H_5)_3N$ and the reaction of 1:1:2 H_2DBA:$UO_2(CH_3CO_2)_2(H_2O)_2$:$(C_2H)_5N$ molar ratios. The product, of course, is the trinuclear anionic cluster containing the trigonal-planar bridging oxide ion.

Polynuclear complexes of uranyl ions are not unusual, but most consist of polymeric chains[34-39] in which the U···U distances are much longer than that found in the discrete anions of the present structure. There is a report of a tetranuclear UO_2^{2+} complex that contains bridging trigonal O^{2-} ligands $[(UO_2)_4O_2Cl_8(H_2O)_2]^{4-}$ and exists as a discrete molecular anion.[40] The U–$O_{trigonal}$ distances of 2.203, 2.289, and 2.268 Å and U···U distances of 3.997, 3.986, and 3.682 Å are in good agreement with the distances in $[(UO_2)_3(DPA)_3O]^{2-}$. We know of no other polynuclear UO_2^{2+} complexes containing trigonal bridging O^{2-}, although it is reasonably common in the so-called basic carboxylates of the transition metals.[23-25] It is interesting to note the similarities and differences between the trinuclear O^{2-}-bridged carboxylates of the transition metals and the 1,3,5-triketonates of UO_2^{2+}. The main similarity is, of course, the planar triangle of metal atoms with an O^{2-} in

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the center. In the case of the transition metals, the lower coordination number is accommodated by straightforward bonding to the two oxygens in each carboxylate anion, thereby forming normal carboxylate bridging. In the case of UO_2^{2+}, the higher coordination number could not be entirely satisfied by carboxylates but requires the third oxygen of a triketonate to fulfill this requirement while maintaining the same general structure. The result is that the dianionic triketonate is present in its normal bridging mode in this unusual structure and shows a remarkably efficiency for using its oxygen donor atoms.

The present study supports the belief that the 1,3,5-triketonates and its derivatives are remarkably versatile in their ability to bind metal ions in close proximity to one another. It is now well established that they can easily accommodate metal ions that require coordination numbers of 4, 5, 6, and 7 and that they can accommodate a large variation in ion size.[1,2] It is also well established that these ligands generally form discrete molecular complexes rather than more complex polymeric species.

Acknowledgment. We acknowledge support by the National Science Foundation, Grant No. CHE 80-10809 (M.J.H.), and the Office of Basic Energy Sciences, Department of Energy (N.A.).

Registry No. $UO_2(H(DBA))_2(CH_3OH)\cdot CH_3OH$, 81141-31-3; $[(C_2H_5)_3NH]_2[(UO_2)_3(DBA)_3O]$, 81141-33-5; $[(C_2H_5)_3NH]_2[(UO_2)_3(DPA)_3O]$, 81157-55-3; $UO_2(C_2H_3O_2)_2$, 541-09-3.

Supplementary Material Available: Tables containing anisotropic thermal parameters, isotropic thermal parameters, hydrogen positional parameters, hydrogen bond lengths, rms displacements, calculated and observed structure factors, nonessential bond distances and bond angles, and least-squares planes and atomic deviations (61 pages). Ordering information is given on any current masthead page.

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Heterobinuclear Complexes of Heavy Metals with 1,3,5-Triketonates and Their Diamine Schiff-Base Derivatives. Synthetic Strategies Based on Positional and Geometric Isomerism of Mononuclear Palladium(II) and UO_2^{2+} Complexes

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Received September 18, 1981

Several new mononuclear complexes of Pd(II) and UO_2^{2+} have been prepared with the binucleating ligands 1,3,5-triketones and their Schiff-base diamine derivatives. The mononuclear complexes have been used as precursors in the preparation of heterobinuclear complexes by means of two different strategies. One depends upon the site selectivity, i.e., positional isomerism, observed for certain metal ions in the Schiff-base ligands that contain two distinctly different coordination sites. The other, which can be applied to symmetric 1,3,5-triketones, depends upon geometric isomerism. In this case, the UO_2^{2+} ion binds two triketonates in a cis-type configuration due to the steric constraints of a fifth equatorial ligand. The cis complex may then be used to bind a second metal ion. Under similar conditions Pd(II) forms a trans-type complex in which it is not possible to add a second metal ion. This work describes the use of preferred isomerism to design specific heterobinuclear complexes containing heavy metal ions.

Introduction

Cooperative interactions between metal ions and their influence on reactivity are subjects of considerable current interest. In order to carefully assess the nature of the cooperativity and the reactivity, several workers have designed new ligand systems capable of binding more than one metal ion and used them to prepare polynuclear metal complexes of a discrete molecular nature. Clearly, among the type of things that one might consider in designing potentially useful polynuclear metal complexes are incorporation of metals that have a demonstrated catalytic capability in *mono*nuclear complexes, incorporation of metal ions in which reactive states can be photochemically generated, and/or incorporation of metal ions that may undergo multielectron-transfer reactivity. One or more of these considerations have led us to investigate the synthesis and characterization of polynuclear heavy-metal β-polyketonate complexes with special emphasis on heteropolynuclear complexes.

Very few complexes of β-polyketonates (with exception of the 1,3-diketonates) and their Schiff-base derivatives have been reported with other than first transition series metal ions. Several years ago Ueno and co-workers described a Pd^{2+} complex of 2,4,6-heptanetrionate.[1] Later there were a few reports of mononuclear UO_2^{2+} Schiff-base triketonates[2-4] and one example of a heterobinuclear Ni(II)–UO_2^{2+} complex.[4] In the previous paper, we report the structure of a mononuclear UO_2^{2+} complex containing symmetric 1,3,5-triketonate ligands and an unusual trinuclear UO_2^{2+} triketonate containing a tribridging planar oxide ion.[5] To our knowledge, these are the only reported heavy-metal complexes of the β-polyketonates and their Schiff-base derivatives in which the basic ligand is more complex than the 1,3-diketones.

In our initial work on heterobinuclear complexes we developed a strategy that depends upon (1) using binucleating ligands with two distinctively different coordination sites, (2) selectively binding one metal ion to one of the two sites and characterizing this mononuclear precursor, and (3) adding to the precursor complex a different metal ion that binds to the second site.[6] This procedure has the advantage that one can be reasonably certain of obtaining pure products in which the position of the metal ions is known. However, a high degree of site selectivity is important to ensure that the metal ions are not scrambled, giving rise to considerable quantities of other, undesired, binuclear products. This method which has

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