2356 *Inorg. Chem.* **1982**, *21*, 2356-2359

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.

Contribution from the Chemistry Department,
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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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(2) Vigato, P. A.; Vidoli, M.; Costellato, U.; Grazioni, R.; Benetollo, F. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 595.

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(5) Lintvedt, R. L.; Heeg, M. J.; Ahmad, N.; Glick, M. D. *Inorg. Chem.*, preceding paper in this issue.

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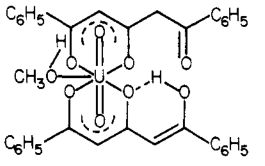
0020-1669/82/1321-2356$01.25/0

employed the diamine Schiff-base derivatives of 1,3,5-triketones as the ligands continues to be useful and is extended in this work to some heavy-metal heterobinuclear complexes.

Development of new synthetic approaches for heteropolynuclear complexes is necessary to extend the series to other unusual combinations of metal ions. In particular, it would be advantageous to be able to use symmetric binucleating ligands rather than the unsymmetric diamine Schiff-bases and not have to depend upon site selectivity for the formation of pure compounds since this restricts the metals that can be used. Another approach that can be taken depends upon a coordination selectivity in which the first metal ion would force the ligands into a configuration conducive to accepting a second metal ion. The UO_2^{2+} ion, because of its requirements for five equatorial donor atoms, is ideally suited to this approach. A representation of the basic structure of bis[1,5-diphenyl-1,3,5-pentanetrionato(1−)](methanol)dioxouranium(VI) in which the ligands are in an appropriate configuration is[5]



$[UO_2(H(DBA))_2(CH_3OH)]$

It is obvious that the necessity for the CH_3OH ligand forces the "cis" arrangement and makes it greatly preferred over the "trans". As a result, the ligands are positioned to bind a second metal ion. In principle, any mononuclear complex of this type in which the cis product is nonlabile or greatly thermodynamically and/or sterically favored could be used as a precursor to heterobinuclear complexes with symmetric ligands.

Experimental Section

Ligand Synthesis. The 1,3,5-triketones were synthesized by the method of Miles, Harris, and Hauser.[7] This method involves the condensation of a 1,3-diketone with an appropriate ester using NaH in refluxing THF. The ethylenediamine Schiff-base derivatives have been reported.[6]

Synthesis of Complexes.[8] **$Pd(H(BAA))_2en$ and $Pd(H(PAA))_2en\cdot{}^1/_2H_2O$.** Equimolar quantities of the ligand dissolved in hot acetone and $Pd(CH_3CO_2)_2$ dissolved in H_2O are mixed, and the resulting red solution is stirred for 30 min. Precipitation occurs shortly after mixing. This mixture is heated at reflux until the color changes from red to yellow, a period of about 1–1.5 h. The solution is filtered and the filtrate concentrated at room temperature. The resulting $Pd(H(BAA))_2en$ is light yellow and may be recrystallized from acetone. Anal. Calcd for $Pd(C_{26}H_{26}N_2O_4)$: C: 58.16; H, 4.85; N, 5.22. Found: C, 58.06; H, 5.10; N, 5.26. This compound melts at 187–189 °C and is soluble in acetone, benzene, and chloroform and sparingly soluble in methanol.

The resulting $Pd(H(PAA))_2en$ may be recrystallized from methanol, yielding orange-yellow cubic crystals, which melt at 135–140 °C. The compound is soluble in most organic solvents including acetone, methanol, acetonitrile, benzene, etc. Anal. Calcd for $Pd(C_{22}H_{35}N_2O_{4.5})$: C, 52.28; H, 6.93; N, 5.54; Pd, 21.07. Found: C, 51.90; H, 6.95; N, 5.52; Pd, 21.01.

By far, the major isomer formed in both cases is the one in which Pd(II) is bonded to two nitrogens and two oxygens (N_2O_2). However, during the recrystallization of $Pd(H(BAA))_2en$, deep yellow microcrystals, obviously different from the bulk of the product, form first on the walls of the beaker. These are physically removed, recrystallized twice from acetone, and found to melt at 225 °C. Anal. Calcd for $Pd(C_{26}H_{26}N_2O_4)$: C, 58.16; H, 4.85; N, 5.22; Pd, 19.84. Found: C, 58.14; H, 4.93; N, 5.25; Pd, 19.59. The infrared spectrum indicates that this product is the oxygen-bonded isomer (O_2O_2). There is no evidence for the formation of a similar isomer in the $Pd(H(PAA))_2en$ synthesis.

$Ni(H(BAA))_2en$. The synthesis and characterization of this compound in which Ni(II) is bound to two nitrogen and two oxygen donor atoms have been reported.[6]

$UO_2(H(BAA))_2en\cdot H_2O\cdot 0.5C_3H_6O$ and $UO_2(H(PAA))_2en\cdot C_3H_6O$. Five millimoles of the ligand ($H_2(PAA)_2en$, 1.96 g; or $H_2(BAA)_2en$, 2.16 g) is dissolved in 300 mL of boiling acetone. A solution of $UO_2(CH_3CO_2)_2$ (2.12 g, 5 mmol) in 30–40 mL of water is added to the ligand solution. Then 1.1 g (10.5 mmol) of triethylamine is added, upon which the solution turns intensely red. The reaction mixture is refluxed for 6 h and filtered while hot, and the filtrate is left to evaporate at room temperature. After 24–36 h maroon, needlelike crystals form. Filtration, washing with acetone, and air-drying give the compound in about 80% yield. The product $UO_2(H(PAA))_2en\cdot C_3H_6O$ is soluble in CH_3OH, $(CH_3)_2CO$, CH_3CN, and $CHCl_3$. It decomposes at 222–225 °C. Anal. Calcd for $UO_2(C_{22}H_{34}N_2O_4)\cdot C_3H_6O$: C, 41.78; H, 5.57; N, 3.90; U, 33.14; O, 15.60. Found: C, 41.46; H, 5.59; N, 3.87; U, 33.64; O (by difference), 15.44. The maroon crystals of $UO_2(H(BAA))_2en\cdot H_2O\cdot 0.5C_3H_6O$ melt at 235 °C and are soluble in $(CH_3)_2CO$, CH_3CN, and $CHCl_3$ but almost completely insoluble in CH_3OH. Anal. Calcd for $UO_2(C_{26}H_{26}O_4N_2)(H_2O)\cdot 0.5C_3H_6O$: C, 44.18; H, 4.15; N, 3.75; U, 31.86; O, 16.06. Found: C, 44.12; H, 4.27; N, 3.93; U, 31.74; O, 15.94 (by difference). This product may be crystallized from acetone to yield blue-black needlelike crystals, which turn maroon at 175 °C and melt at 235 °C. Analysis of this product indicates the composition $UO_2(H(BAA))_2en\cdot H_2O$. Anal. Calcd for $UO_2(C_{26}H_{26}O_4N_2)(H_2O)$: C, 43.45; H, 3.89; N, 3.89. Found: C, 43.74; H, 4.18; N, 3.92.

$PdUO_2(BAA)_2en\cdot H_2O$ and $PdUO_2(PAA)_2en\cdot 2H_2O$. These compounds are prepared by dissolving 5×10^{-4} mol of $Pd(H(BAA))_2en$ or $Pd(H(PAA))_2en$ in boiling methanol and slowly adding an equimolar amount of dioxouranium(VI) acetate dissolved in methanol. The solution is refluxed for 3 h, during which a shiny brown precipitate forms. The precipitate is collected, dried, and recrystallized from acetone. For $PdUO_2(BAA)_2en$ a dark green powder is obtained, which melts at 305 °C. Anal. Calcd for $PdUO_2(C_{26}H_{24}N_2O_4)(H_2O)$: C, 37.93; H, 3.16; N, 3.40; U, 28.93; Pd, 12.94. Found: C, 38.47; H, 3.31; N, 3.39; U, 29.16; Pd, 12.92. Recrystallization of $PdUO_2(PAA)_2en\cdot 2H_2O$ from acetone is accomplished by reducing the volume of the solution to half and placing the resulting solution in the refrigerator for several days, after which blue-black cubic crystals form that melt at 295–298 °C. Anal. Calcd for $PdUO_2(C_{22}H_{32}N_2O_4)(H_2O)_2$: C, 32.98; H, 4.50; N, 3.50; U, 29.73; Pd, 13.29. Found: C, 32.83; H, 4.59; N, 3.38; U, 29.51; Pd, 12.92.

$NiUO_2(BAA)_2en\cdot H_2O$. This compound is prepared by dissolving $Ni(H(BAA))_2en$ in boiling methanol and slowly adding to it an equimolar amount of dioxouranium(VI) acetate dissolved in methanol. The solution is refluxed for 3 h, after which the red product is filtered, dried, and recrystallized from acetone. The product does not melt below 330 °C. Anal. Calcd for $NiUO_2(C_{26}H_{24}N_2O_4)(H_2O)$: C, 40.26; H, 3.35; N, 3.61; U, 30.71; Ni, 7.61. Found: C, 40.68; H, 3.82; N, 3.50; U, 31.40; Ni, 7.40.

$UO_2(H(DBA))_2(CH_3OH)\cdot CH_3OH$. The synthesis, analysis, and X-ray structure determination of this compounds are reported in the previous paper.[5]

$Pd(H(DBA))_2$. H_2DBA (1.33 g, 5 mmol) is dissolved in 250 mL of acetone with stirring and heating. After complete dissolution, the solution is cooled to room temperature and added to a solution of 0.56 g of $Pd(CH_3CO_2)_2$ in 50 mL of 1:1 acetone–water. The resulting solution is stirred for 1 h, during which a yellow precipitate forms. The resulting mixture is refluxed for 2 h. After cooling of the mixture to room temperature, the product is removed by filtration, washed with acetone, and air-dried. The yellow powder has a melting point of 225 °C and may be recrystallized from $CHCl_3$. Anal. Calcd for $Pd(C_{17}H_{13}O_3)_2$: C, 64.11; H, 4.08; Pd, 16.72. Found: C, 64.18; H, 4.09; Pd, 16.63.

$Pd(H(DPA))_2$. H_2DPA (1.13 g, 5 mmol) is dissolved in 200 mL of acetone, and a solution ofo $Pd(CH_3CO_2)_2$ (0.56 g, 2.5 mmol) in

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(7) Miles, M. L.; Harris, T. M.; Hauser, C. R. *J. Org. Chem.* **1965**, *30*, 1007.

(8) Abbreviations for the ligands follow the trivial nomenclature in which H_2BAA is benzoylacetylacetone (1-phenyl-1,3,5-hexanetrione), H_2PAA is pivaloylacetylacetone (2,2-dimethyl-3,5,7-octanetrione), H_2DBA is dibenzoylacetone (1,5-diphenyl-1,3,5-pentanetrione), and H_2DPA is dipivaloylacetone (2,2,8,8-tetramethyl-3,5,7-nonanetrione). $(H_2BAA)_2en$ and $(H_2PAA)_2en$ are the ethylenediamine Schiff-base derivatives of H_2BAA and H_2PAA, respectively (see ref 6). The hydrogens in each case designate the enolizable protons. When appropriate, the metal ion donor atoms in the Schiff-base derivatives are noted by N_2O_2 or O_2O_2 meaning two imino nitrogens and two enolate oxygens or four enolate oxygens, respectively.

50 mL of 1:1 acetone–water is added to it. The resulting red solution is stirred for 2 h at room temperature, during which it changes to yellow. The solution is refluxed for 1.5 h. If a slight turbidity occurs, additional acetone is added until the solution is clear. The yellow solution is cooled to room temperature and left for slow evaporation upon which orange crystals are formed. The crystals melt at 160 °C into a red oil. Anal. Calcd for $Pd(C_{13}H_{21}O_3)_2$: C, 56.07; H, 7.55; Pd, 19.12. Found: C, 56.02; H, 7.50; Pd, 18.94.

$UO_2Pd(DBA)_2(H_2O)_{1.5}$. Two solutions, one containing $UO_2(H(DBA))_2(CH_3OH)\cdot CH_3OH$ (0.43 g, 0.5 mmol) in 500 mL of methanol and the other $Pd(CH_3CO_2)_2$ (0.11 g, 0.5 mmol) in 150 mL of methanol, are mixed at room temperature. The resulting solution is stirred at room temperature for 8 h and then left undisturbed for 36 h at room temperature. The precipitated product is separated and air-dried. The reddish brown powder decomposes at 243 °C. Anal. Calcd for $UO_2Pd(C_{17}H_{12}O_3)_2(H_2O)_{1.5}$: C, 43.82; H, ;2.90; U, 25.56; Pd, 11.43. Found: C, 43.86; H, 3.15; U, 25.54; Pd, 11.57.

$UO_2Co(DBA)_2(H_2O)_3$. $UO_2(H(DBA))_2(CH_3OH)\cdot CH_3OH$ (0.43 g, 0.5 mmol) is dissolved in 700 mL of methanol, and this solution is stirred under N_2 at room temperature. A second solution containing $Co(CH_3CO_2)_2(H_2O)_4$ (0.25 g, 0.5 mmol) in methanol is added dropwise to the first at room temperature. The resulting solution turns dark red. Stirring is continued under N_2 for 8 h, after which the solvent is removed under reduced pressure. The dark red reaction mass is washed with 20 mL of ethanol and diethyl ether and dried in a vacuum desiccator. The red product decomposes at 315–318 °C. Anal. Calcd for $UO_2Co(C_{17}H_{12}O_3)_2(H_2O)_3$: C, 44.79; H, 3.29; Co, 6.14; U, 26.13. Found: C, 45.11; H, 3.39; Co, 5.87; U, 26.16.

$UO_2Ni(DBA)_2(H_2O)_3\cdot 2H_2O$. $UO_2(H(DBA))_2(CH_3OH)\cdot CH_3OH$ (0.86 g, 1 mmol) is dissolved in about 1.2 L of methanol. A methanol solution containing 1.0 mmol of $Ni(CH_3CO_2)_2(H_2O)_4$ is added dropwise to the original solution with stirring. The dark red solution is stirred for 4 h and concentrated at room temperature to about 150 mL. Continued slow evaporation of the solvent yields small, almost black crystals. This product is recrystallized twice from a small volume of methanol. The dark product changes to a light red above 200 °C but does not change further up to 325 °C. Anal. Calcd for $UO_2Ni(C_{17}H_{12}O_3)_2(H_2O)_3\cdot 2H_2O$: C, 43.10; H, 3.59; Ni, 6.20. Found: C, 43.20; H, 3.44; Ni, 5.91.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 283B spectrophotometer using KBr pellets and calibrated with polystyrene. The solution electronic spectra were recorded on a Cary Model 17B spectrophotometer in methanol and/or acetonitrile. Melting points were taken in capillary tubes with a Thomas-Hoover Unimelt and are uncalibrated. Magnetic measurements were done on solid samples by using standard Faraday balance techniques with $Hg[Co(SCN)_4]$ as the standard. The values were corrected for diamagnetism by using Pascal's constants.

Results and Discussion

The compounds reported containing the ethylenediamine Schiff-base derivatives illustrate the site selectivity that can be achieved with different metal ions. In our previous papers[6] the fact that Ni(II) is coordinated exclusively to N_2O_2 donors in the mononuclear complex of $(H(BAA))_2en^{2-}$ was used to develop a series of heterobinuclear complexes of first transition series complexes. A similar specificity can be seen in the mononuclear Pd^{2+} complexes of $(H(BAA))_2en^{2-}$ and $(H(PAA))_2en^{2-}$. In the case of $Pd(HBAA)_2en$, both isomers can be isolated with the $Pd(H(BAA))_2en$, N_2O_2 isomer in much greater abundance than the $Pd(H(BAA))_2en$, O_2O_2 isomer. The two are easily distinguished by their IR spectra since the N_2O_2 isomer contains a strong, sharp unchelated carbonyl bond at about 1690 cm^{-1}, whereas in the O_2O_2 isomer the highest energy band in this spectral region is a strong absorption at 1640 cm^{-1}. The only isomer of the comparable $(H_2PAA)_2en$ compound isolated is $Pd(H(PAA))_2en$, N_2O_2, which has a strong, sharp unchelated carbonyl absorption at 1710 cm^{-1}. No trace of the other isomer could be detected. There are also significant differences in the electronic absorption spectra of the different isomers (Table I). The difference in the isomeric distribution suggests that electronic and/or steric effects are significant in the control of selectivity and that it is not trivially determined by nitrogen- vs. oxygen-donating ability for a given metal ion. This observation is further supported by work we have done with the mononuclear Cu(II) complexes of $(H_2BAA)_2en$[9] and $(H_2PAA)_2en$.[10] For $Cu(H_2BAA)_2en$, only the O_2O_2 isomer has been isolated under a variety of synthetic conditions. However, the room temperature reaction of $Cu(CH_3CO_2)_2\cdot H_2O$ with $(H_2PAA)_2en$ yields only the N_2O_2 isomer. Thus, in the case of Cu(II) it would appear that the determining factor in the isomer formation is the electronic effect of the phenyl vs. the *tert*-butyl groups.

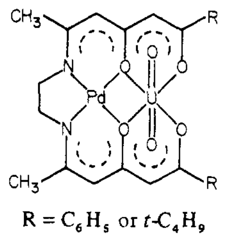
Table I. UV Absorption Spectra of the Mononuclear Palladium(II) Diamine Schiff-Base Derivatives of the 1,3,5-Triketones in Acetonitrile

$Pd(H(BAA))_2en$, N_2O_2[a]		$Pd(H(BAA))_2en$, O_2O_2[a]		$Pd(H(PAA))_2en$, N_2O_2	
λ_{max}, cm^{-1}	$10^{-3}\epsilon$, M^{-1} cm^{-1}	λ_{max}, cm^{-1}	$10^{-4}\epsilon$, M^{-1} cm^{-1}	λ_{max}, cm^{-1}	$10^{-3}\epsilon$, M^{-1} cm^{-1}
22 220 sh					
23 700 sh		23 260 sh		24 690 sh	
29 400	1.07	26 110	1.68	28 740	5.48
		30 300 sh			
36 900	1.05	35 700 sh		37 590	4.37
41 670	3.16	41 670	1.6		

[a] N_2O_2 indicates the metal is bound to two nitrogens and two oxygens and O_2O_2 indicates the metal is bound to four oxygens.

The situation for UO_2^{2+} coordination to the Schiff-base derivatives is quite different. Here the predominate factor is the preferred seven-coordinate pentagonal-bipyramidal geometry of the U atom, which requires an additional donor atom, usually from a solvent molecule. As a result, the only isomer of the UO_2^{2+} complex ever observed is the O_2O_2 one in which UO_2^{2+} is in the more external position with a solvent molecule coordinated between the two coordinated outermost enolate oxygens. Presumably, the steric requirements of the seventh ligand together with the apparent preference of UO_2^{2+} for oxygen donor atoms act to make UO_2^{2+} totally selective for the O_2O_2 site. This selectivity is supported by the fact that neither $UO_2(H(BAA))_2en$ nor $UO_2(H(PAA))_2en$ have any trace of an IR band above about 1610 cm^{-1} and therefore contain no free carbonyl. In addition crystal structure determinations of $UO_2(H(BAA))_2en$[11] and the analogous methyl-substituted complex[2,3] confirm that the U atom is at the O_2O_2 position. The UV absorption spectra are quite simple in that they contain one relatively symmetric, intense bond in the 25 000–30 000-cm^{-1} region. For $UO_2(H(PAA))_2en$ the maximum is at 28 900 cm^{-1} with an extinction coefficient of 4.52×10^4 M^{-1} cm^{-1} and for $UO_2(H(BAA))_2en$ the maximum is 25 900 cm^{-1} with an extinction coefficient of 4.55×10^4 M^{-1} cm^{-1}.

The site selectivities of Pd(II) and Ni(II) for the N_2O_2 position and of UO_2^{2+} for the O_2O_2 position in $(H_2BAA)_2en$ and $(H_2PAA)_2en$ leave little question that heterobinuclear complexes should be readily formed, with only one positional isomer whose generalized structure is



R = C_6H_5 or *t*-C_4H_9

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(9) Lintvedt, R. L.; Glick, M. D.; Tomlonovic, B. K.; Gavel, D. P.; Kuszaj, J. M. *Inorg. Chem.* **1976**, *15*, 1633.

(10) Mack, J. L. Ph.D. Thesis, Wayne State University, 1978.

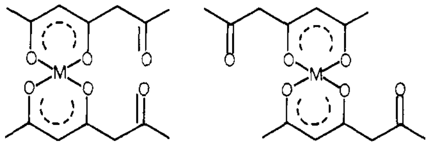
(11) Unpublished results from our laboratory.

Table II. Molecular Magnetic Moments of Some Uranyl Complexes of 1,5-Diphenyl-1,3,5-pentanetrione

compd	magnetic moment/ molecule (μ_{eff}), μ_B	
	295 K	77 K
$UO_2(H(DBA))_2(CH_3OH)\cdot CH_3OH$	0.69	0.55
$UO_2Co(DBA)_2(H_2O)_3$	4.96	4.55
$UO_2Ni(DBA)_2(H_2O)_3\cdot 2H_2O$	3.44	3.27

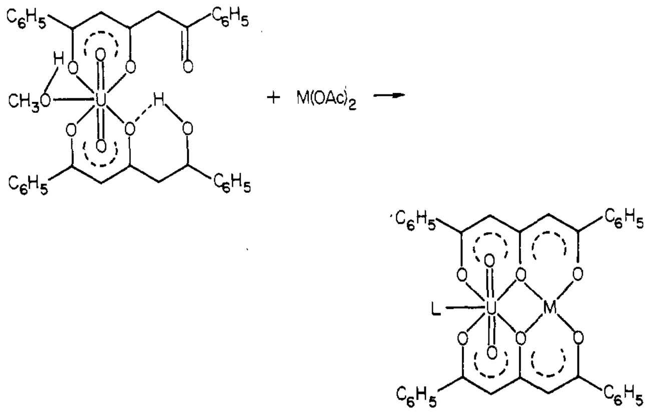
The IR spectra in both cases show a strong band at about 1600 cm^{-1}, which is the highest frequency absorption in this region, and a strong U=O stretch at very near 900 cm^{-1}.

An approach significantly different from the preparation of similar heterobinuclear complexes that may be employed depends upon geometric isomerism rather than positional isomerism. In this case a symmetric 1,3,5-triketone ligand can be used. This method depends upon producing a cis-type isomer of a mononuclear bis[1,3,5-triketonate(1−)] complex. In this configuration, it is capable of binding a second metal ion while clearly an inert trans isomer is not capable of forming a molecular, binuclear complex.



cis isomer trans isomer

In the previous paper[5] we reported the preparation and single-crystal X-ray structure determination of *cis*-bis(1,5-diphenyl-1,3,5-pentanetrionato)(methanol)dioxouranium(VI). In this case the necessity of the seventh ligand, methanol, forces the triketonates into the cis configuration. The subsequent reaction of this compound with a second divalent metal ion yields a neutral heterobinuclear complex:



In the case where M = Ni(II) or Co(II) there are ligands occupying the fifth and sixth coordination positions in the usual manner. Perhaps the strongest experimental evidence for this comes from magnetic moments of these complexes (Table II), which show rather typical values associated with octahedial coordination.

The precursor, mononuclear UO_2^{2+} complex is easily identified by spectral means since its IR spectrum contains a strong, sharp unchelated carbonyl band at 1680 cm^{-1} while none of the resulting heterobinuclear complexes have bands above 1600 cm^{-1} in the carbonyl region. They all contain a strong U=O stretch in the 880–910-cm^{-1} region. The UV absorption spectrum of $UO_2(H(DBA))_2(CH_3OH)$ is quite complex presumably due to the fact that the uncomplexed parts of the ligands are in keto and enol forms.[5] Upon complexation with the second metal ion the spectrum is considerably simplified. This information is given in Table III.

Table III. UV Absorption Spectra of Some Uranyl Complexes of 1,3,5-Pentanetrione

compd	λ_{max}, cm^{-1}	ϵ, M^{-1} cm^{-1}
$UO_2(H(DBA))_2(CH_3OH)^a$	22470 sh	
	24690	3.40×10^4
	25970 sh	
	31750	2.01×10^4
	35970 sh	
	40000	2.77×10^4
$UO_2Pd(DBA)_2(H_2O)^a$	23590	5.19×10^4
	37040	3.67×10^4
	44440	3.64×10^4
$UO_2Ni(DBA)_2(H_2O)_3{}^b$	24690	4.62×10^3
	39060	3.06×10^3
$UO_2Co(DBA)_2(H_2O)_3{}^a$	24450	4.91×10^3
	39680	3.20×10^3

[a] Spectra obtained in acetonitrile. [b] Spectrum obtained in methanol.

Clearly, one precaution that must be taken in attempting to prepare heterobinuclear complexes with symmetric ligands is to design the synthesis so that homobinuclear products are not formed. In the present case, the best assurance that this does not happen comes from the fact that repeated attempts to prepare the binuclear UO_2^{2+} triketonates have failed. This is not surprising since the incorporation of two seven-coordinate U atoms would not be expected to be easy. It is interesting to note that under somewhat more stringent conditions (addition of $(C_2H_5)_3N$ as a base) a trinuclear, trigonal oxide-bridged UO_2^{2+} anionic triketonate is formed. The structure of one example is reported in a previous paper.[5] The ease with which this trinuclear molecular anion is isolated argues further that the formation of a "simple" binuclear UO_2^{2+} triketonate is not at all likely and that one need not be concerned with its presence as an impurity in the heterobinuclear complexes. This being the case, one can be certain, on the basis of elemental analysis, magnetic properties, and spectral results, that the heterobinuclear complexes are reasonably pure.

The mononuclear bis(1,3,5-triketonato)palladium(II) complexes behave entirely differently from the analogous UO_2^{2+} complexes. If the UO_2^{2+} and Pd(II) complexes of $H(DBA)^-$ both have the cis configuration, then reaction of either of them with the acetate of the other metal will give the same product. As seen above, $UO_2Pd(DBA)_2(H_2O)$ is readily formed by reacting $UO_2(H(DBA))_2(CH_3OH)$ and $Pd(CH_3CO_2)_2$. However, even on extended reaction times there is no reaction between $Pd(H(DBA))_2$ and $UO_2(CH_3CO_2)_2$. Neither will it react with other metal acetates to form binuclear species. The same is also true of $Pd(H(DPA))_2$. The IR spectra of both $Pd(H(DBA))_2$ and $Pd(H(DPA))_2$ show strong bands in the 1680–1710-cm^{-1} region due to unchelated carbonyls, and their elemental analyses are excellent, leaving no doubt as to their mononuclear nature. All of these observations are consistent with assigning the trans configuration to the mononuclear Pd(II) complexes.

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Registry No. $Pd(H(BAA))_2en$, (N_2O_2) isomer, 81141-77-7; $Pd(H(PAA))_2en$, 81141-78-8; $Pd(H(BAA))_2en$, (O_2O_2) isomer, 81141-79-9; $UO_2(H(BAA))_2en\cdot H_2O$, 81141-46-0; $UO_2(H(PAA))_2en\cdot C_3H_3O$, 81141-47-1; $PdUO_2(BAA)_2en\cdot H_2O$, 81157-60-0; $PdUO_2(PAA)_2en\cdot H_2O$, 81141-45-9; $NiUO_2(BAA)_2en\cdot H_2O$, 81141-44-8; $Pd(H(DBA))_2$, 81141-80-2; $Pd(H(DPA))_2$, 81141-81-3; $UO_2Pd(DBA)_2(H_2O)$, 81141-50-6; $UO_2Co(DBA)_2(H_2O)_3$, 81141-49-3; $UO_2Ni(DBA)_2(H_2O)_3$, 81141-48-2; $Ni(H(BAA))_2en$, 55998-67-9; $UO_2(H(DBA))_2(CH_3OH)$, 81141-30-2; $Pd(CH_3CO_2)_2$, 33571-36-7; $UO_2(CH_3CO_2)_2$, 541-09-3; $Co(CH_3CO_2)_2(H_2O)_4$, 19621-58-0; $Ni(CH_3CO_2)_2(H_2O)_4$, 21263-98-9.