whose slope is equal to $K_{1A}$ and intercept equal to $K_{1A}K_{1B}$. A linear plot was indeed obtained, but the slope was negative. Thus, this model was concluded to be incorrect. It is interesting, however, to note that the intercept of this plot ($p(K_{1A}K_{1B}) = 16.05$) was identical with the value of $K_{1AB}$ given in Table I. The product $K_{1A}K_{1B}$ is mathematically equal to $K_{1AB}$.

That the two peptide protons are displaced simultaneously (eq 9) is further demonstrated by the constancy of the values of $K_{1AB}$ calculated from all points between $a = 2$ and $a = 4$ in the 1:1 titration curve and between $a = 1.5$ and $a = 3$ in the 1:2 titration curve. Peptide proton dissociation occurs at about the same pH in nickel(II) complexes of both DGEN and tetraglycine.[16]

As with $CuH_{-2}L$, $NiH_{-2}L$ does not react with hydroxide ion. This is in accord with the planar nature of this chelate. The observation from the 1:2 titration (Figure 3, curve 3) that only $NiH_{-2}L$ is formed from both $NiL^{2+}$ and $NiL_2^{2+}$ is also in accord with the square-planar nature of $NiH_{-2}L$.

**Spectra.** With the equilibrium constants given in Table I, the concentrations of the various species present in the spectral solutions may be calculated. With eq 15 the molar absorbances of all species may be obtained at all wavelengths.

$$A = l(\epsilon_{Ni^{2+}}[Ni^{2+}] + \epsilon_{NiL^{2+}}[NiL^{2+}] + \epsilon_{NiL_2^{2+}}[NiL_2^{2+}] + \epsilon_{NiH_{-2}L}[NiH_{-2}L]) \quad (15)$$

The band maxima so obtained are given in Table III. The first three entries for nickel(II) show the expected trend of decreasing wavelengths of band maxima with increasing coordination. But $NiH_{-2}L$ exhibits a reversal in this trend, which indicates that a different mode of electronic transition is occurring. This also suggests structural transition from the octahedral to the planar form. The $NiH_{-2}L$ exhibits absorption characteristics almost identical with those of $NiH_{-3}L^{2-}$ ($L^- =$ tetraglycinate). This is expected from the suggestions of Gould and Mason[26] as discussed above.

**Coordinate Bonding.** Definite evidence for the structural transition to the diamagnetic planar form ($NiH_{-2}L$) is further provided by the spectra in Figure 5. The fact that the paramagnetic Ni(II) bands of $NiL^{2+}$ in the 1:1 solution and of $NiL_2^{2+}$ in the 1:2 solution exhibit the highest intensities, and that the bands disappear completely for $NiH_{-2}L$, is evidence for octahedral-planar transition in going from the former to the latter. The square-planar, diamagnetic complex of nickel(II) with ethylenebisbiguanide[28] also gives only one band in the visible-near-infrared region (300–1600 mμ), the band maximum lying at 478 mμ. Usually only one band is observed in square-planar complexes of nickel(II) in solution.[29]

The nickel(II) complexes of amides[17] or peptides[15,16,30,31] in which the amide or peptide protons are displaced are yellow[15,16] or orange,[17] diamagnetic,[17,30,31] and planar,[15,16,31] and in many complexes the dissociation of the peptide protons is slow[15,16] and takes place simultaneously.[16,30,31]

The structures of $NiL^{2+}$ and $NiL_2^{2+}$ are not known, but are most certainly octahedral. The arrangement of coordinate bonds in the square-planar diamagnetic $NiH_{-2}L$ is probably similar to that of the analogous Cu(II) chelate, illustrated by III.

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(28) D. J. MacDonald, *Inorg. Chem.*, 6, 2269 (1967).

(29) W. Manch and W. C. Fernelius, *J. Chem. Educ.*, 38, 192 (1961).

(30) R. Mathur and R. B. Martin, *J. Phys. Chem.*, 69, 668 (1965).

(31) M. K. Kim and A. E. Martell, *J. Am. Chem. Soc.*, 91, 872 (1969).

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# Chelate Chemistry. VI. Solution Behavior of Tropolonates[1]

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**Abstract:** The solution behavior of six-, seven-, eight-, and ten-coordinate metal derivatives of the α, β, and γ isomers of isopropyltropolone has been investigated with respect to association, dissociation, ligand lability, and intra- and intermolecular exchange of polytopal[2] and stereoisomeric forms, and compared, where possible, with analogous derivatives of β-diketones. Qualitatively, the lability of the isopropyltropolonate ligand is comparable to that of the β-diketonates. The integrity of the previously postulated ten-coordinated pentakis(isopropyltropolono)thorium anion in solution has been confirmed. Eight-coordinate complexes derived from thorium are associated in solution, but those from uranium(IV), zirconium(IV), and hafnium(IV) are not. Ligand lability in the tetrakis metal complexes follows the order Th > U > Hf ∼ Zr > Ta. Attempts to definitively establish the presence of polytopal isomers or stereoisomers by low-temperature nmr studies of the seven-, eight-, and ten-coordinate complexes were unsuccessful. *cis-* and *trans*-stereoisomer interconversion for six-coordinate complexes was examined.

The facility with which the tropolone ion or derivatives thereof form high-coordinate complexes with a variety of metal ions was emphasized in earlier papers.[3–7] Specifically, seven-, eight-, nine-, and ten-

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(1) E. L. Muetterties and C. M. Wright, *J. Am. Chem. Soc.*, 86, 5132 (1964).

(2) E. L. Muetterties, *ibid.*, 91, 1636 (1969).

(3) E. L. Muetterties and C. M. Wright, *ibid.*, 87, 21 (1965).

(4) E. L. Muetterties and C. M. Wright, *ibid.*, 87, 4706 (1965).

(5) E. L. Muetterties, *ibid.*, 88, 305 (1966).

coordinate complexes based on metal ions as small as scandium and as large as thorium were proposed. Evidence for these structures was not definitive but inferential. Since that time X-ray crystal structures by Hoard and coworkers[8,9] have (1) confirmed the postulated[1,4] seven-coordination in tris(tropolono)tin chloride and tris(tropolono)tin hydroxide; (2) established nine-coordination in a hydrated form of the tetrakis(γ-isopropyltropolono)thorium(IV) complex; and (3) shown the ammonium salt of the tetrakis(tropolono)holmium anion[4] to have an eight-coordinate holmium atom with a distorted trigonal dodecahedral configuration (the idealized stereoisomeric form would have $D_{2d}$ symmetry). Professor Hoard is continuing these investigations to gain a more definitive characterization of the metal tropolonates in the crystalline state. The purpose of this study was to rigorously characterize the solution state of these metal chelates.

Following the conventions employed in earlier papers, T represents the tropolone anion and TJ the isopropyltropolone anion (thujaplicin).

**Ten Coordination.** The pentakisthorium derivative, $Na^+Th(\gamma\text{-}TJ)_5^-$, is not significantly dissociated, nor is there rapid (nmr time scale) ligand exchange in toluene at 23°. The proton nmr spectrum of $Na^+Th(\gamma\text{-}TJ)_5^-$ in perdeuteriotoluene is distinct from the spectra of $Th(\gamma\text{-}TJ)_4$ and free γ-isopropyltropolone (see Table I). Addition of γ-isopropyltropolone to a toluene solution of the pentakisthorium complex caused no significant perturbations of the characteristic nmr spectrum of the thorium anionic complex or of γ-isopropyltropolone, and the spectrum showed the correct concentration of each for a given mixture.

**Table I.** Comparison of the Nmr Spectra of $(\gamma\text{-}C_{10}H_{11}O_2)_4Th$ and $(\gamma\text{-}C_{10}H_{11}O_2)_5Th^-$ at 23°

| Compound | Solvent | $\sigma_\alpha - \sigma_\beta$, ppm[a] | $J_{\alpha,\beta}$ |
|---|---|---|---|
| $Na^+\gamma\text{-}TJ_5Th^-$ | $C_6D_5CD_3$ | 0.71 | 11 |
| $Na^+\gamma\text{-}TJ_5Th^-$ | $C_6D_5CD_3\text{–}CD_3OD$ | 0.37 | 11 |
| $\gamma\text{-}TJ_4Th$ | $C_6H_5CD_3$ | 0.39 | 11.5 |
| $\gamma\text{-}TJ_4Th$ | $C_6D_5CD_3\text{–}CD_3OD$ | 0.17 | 11.5 |
| γ-TJH | $C_6D_5CD_3$ | 0.40 | 12 |
| γ-TJH | $C_6D_5CD_3\text{–}CD_3OD$ | 0.21 | 12 |

[a] The α and β protons on the aromatic ring.

At elevated temperatures, exchange between free ligand and $Th(\gamma\text{-}TJ)_5^-$ is rapid with respect to the nmr time scale. The lifetime of $Na^+Th(\gamma\text{-}TJ)_5^-$ in the presence of free ligand in toluene at 40° is approximately $10^{-2}$ sec. Addition of methanol to the toluene solution of $Na^+Th(\gamma\text{-}TJ)_5^-$ and γ-isopropyltropolone at 23° enhances lability as evidenced by fast exchange (nmr time scale). This increased lability is fully consistent with results of earlier studies.[5]

Nmr studies of mixtures of the tetrakis(isopropyltropolono)uranium derivatives and the sodium salts of the isopropyltropolone ion gave no evidence of complexation in nonpolar media at 25°.[10]

**Eight Coordination. Lewis Acid Character.** Neutral tetrakis derivatives of tetravalent zirconium, hafnium, thorium, and uranium were prepared with the α and γ isomers of isopropyltropolone. Based on X-ray powder diffraction data, the zirconium and hafnium complexes of the α isomers are isomorphous, and the zirconium and hafnium complexes of the γ isomer are isomorphous; the thorium is unique. The uranium derivative based on the γ isomer does not appear to be isomorphous with the zirconium, hafnium, or thorium derivatives.

The tetrakis(tropolono)thorium derivatives readily complex with nucleophilic or basic molecules[5] including water to form nine-coordinate thorium complexes.[11] The complex, recrystallized from methanol, can be obtained solvent-free by sublimation or vacuum drying at elevated temperatures. This behavior is in marked contrast to the zirconium, hafnium, and uranium complexes which are obtained unsolvated. Differences in solution molecularity are discussed in the following section.

**Tetrakis Chelates. Molecularity in Solution.** The tetrakis(isopropyltropolono)zirconium, -hafnium, and -uranium complexes are monomeric in solution based on molecular weight studies. Solution proton nmr studies of these presumed eight-coordinate complexes showed no indication of ligand dissociation or fast (nmr time scale) ligand exchange between complexed and free ligand at room temperature. These data are consistent with the formulation of these complexes as eight coordinate.

The analogous thorium complexes are associated under anhydrous conditions in nonpolar media. The molecular weight under rigorously dry conditions indicated that the average molecular weight in benzene (cryoscopic) was slightly greater than that of a trimer,[12] and the α-isopropyltropolono derivative was on the average slightly less than a dimer. These results contrast sharply with those found for the tetrakis derivatives of zirconium and hafnium. A further relevant observation is the distinctive tendency of the thorium derivatives to separate from nonpolar solvents as gummy semisolids; there may be a distribution of oligomers in solution. We have proton nmr evidence (*vide infra*) of association in the thorium derivatives, but the data available do not permit any structural formulation of the association mechanism. Molecular models show that there could be a compact clustering and stacking of the tetrakis derivatives in either the square-antiprismatic or trigonal-dodecahedral form. Utilizing Stewart–Briegleib models, we found it very difficult to generate associated species by using one or more tropolone ligands as bridging groups with two- or three-coordinate oxygen atoms. Despite this difficulty with model representation, we tend to favor an association model with tricoordinate oxygen atoms,[4,6,13] because thorium

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(6) E. L. Muetterties, H. Roesky, and C. M. Wright, *J. Am. Chem. Soc.*, **88**, 4856 (1966).

(7) E. L. Muetterties, *J. Pure Appl. Chem.*, **10**, 53 (1965).

(8) Paper presented by J. L. Hoard before the Division of Inorganic Chemistry, 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1967.

(9) J. L. Hoard, personal communication, Sept 5, 1968.

(10) Attempts to isolate crystalline salts of the pentakis(isopropyltropolono)uranium derivatives were unsuccessful in contrast to the earlier isolation of the lithium pentakistropolonouranium.[5]

(11) As established by Professor Hoard and Mrs. Huber from single-crystal X-ray studies, $(\gamma\text{-}TJ)_4Th$ recrystallizes from methanol as a hydrate with thorium coordinated to two oxygen atoms from each of the four γ-isopropyltropolone anions and one oxygen atom *from a water molecule*.[8]

(12) It was reported[5] that the derivative of the γ isomer is monomeric in chloroform and in benzene. We obtained essentially identical results when these measurements were repeated without taking extensive precautions to prevent ingress of moisture.

in the tropolone system seems to behave as a coordinately unsaturated species with only eight ligand atoms.

**Tetrakis Chelates. Ligand Exchange.** The eight-coordinate tantalum[4] cations $T_4Ta^+$ and $(\gamma\text{-TJ})_4Ta^+$ are the most stable eight-coordinate tropolone complexes investigated with respect to *inter*molecular ligand exchange for mixtures of the chelate cation and free ligand in tetrachloroethane. There was no nmr evidence of exchange in tetrachloroethane at temperatures up to 146°, the boiling point of the solvent. This was true even for the tantalum derivative of the sterically hindered α-isopropyltropolone ion. The exchange rate in these systems must be something less than $10^2$/sec at 150°. Earlier studies[4] indicated no *nmr evidence* of ligand exchange between tropolone and $T_4Ta^+$ in water, alcohol, and acetonitrile up to the boiling point of the solution, but ligand exchange does occur. Exchange between $T_4Ta^+$ and $O^{18}$-labeled tropolone was essentially complete within 0.5 hr in an aqueous solution at a pH of about 2.[4] The exchange was slower in nonaqueous media under comparable conditions: 71% complete in ethanol and 45% complete in acetonitrile in 0.5 hr.

Proton nmr studies of mixtures of the tetrakis(isopropyltropolono)metal species and free ligand have demonstrated that ligand exchange will occur at elevated temperatures. Estimation of the rate of intermolecular ligand exchange from the transition collapse region of the nmr spectra yields the following approximate rates for these complexes in tetrachloroethane: $Zr(\gamma\text{-TJ})_4$ and $Hf(\gamma\text{-TJ})_4$, 50/sec at 140°; and α, β, and γ isomeric derivatives of $U(TJ)_4$, a *maximum* rate of $10^3$/sec at 110°. The rates for the zirconium and hafnium complexes may be compared with 80/sec at 70°, or an extrapolated value of $\sim 10^3$ at 140°, for tetrakis(trifluoroacetylacetonato)zirconium and -hafnium[14] in benzene. We believe that the differences in rates are beyond experimental error and suggest that the isopropyltropolone derivatives of zirconium and hafnium are less labile with respect to intermolecular ligand exchange than are the analogous β-diketone derivatives.

Consistent with our formulations of the tropolonothorium complexes as coordinately unsaturated with a coordination number of eight, we found the tetrakis(isopropyltropolono)thorium(IV) derivatives to be most labile with respect to ligand exchange. The rate of intermolecular ligand exchange between the γ-isopropyltropolono derivative and free γ-isopropyltropolone in toluene is about $10^2$/sec at 0°. Comparable rates of exchange in the zirconium and hafnium systems are not achieved until temperatures well above 100° are reached. The high lability in the thorium system could be ascribed to the lower charge density for this large ion; however, this is probably a minor factor.

**Stereochemistry.** The possibility of polytopal[2] isomerism as well as stereoisomerism is quite extensive for seven-, eight-, and nine-coordinate complexes. Possibilities will not be enumerated here since there are discussions of this subject in the literature.[15,16] We have searched for evidence of such isomers in seven-, eight-, and ten-coordinate complexes by examining the low-temperature nmr spectra of isopropyltropolone derivatives of various metals. We found that the α-, β-, and γ-isopropyl derivatives of presumed eight-coordinate zirconium and hafnium, and also seven-coordinate tin, showed no change in their characteristic nmr spectra down to temperatures of about −50° at 220 Mc/sec and about −85 to −100° at 100 Mc/sec. In some instances there was evidence of broadening in the lower temperature regions, but this could be ascribed to effects upon relaxation time emanating from viscosity changes or solution ordering. The six-coordinate tris(α-isopropyltropolono) complexes show the expected *cis–trans* isomers in solution.

The α-, β-, and γ-tetrakis(isopropyltropolono) derivatives of uranium in chloroform–dichloromethane solution showed a sequential broadening on lowering of temperature and eventual disappearance of the resonances associated with the aromatic protons in the α, β, and γ positions. This broadening occurred over the range −40 to −90°. The effect is field dependent and independent of viscosity.[17]

No significant changes were observed in the low-temperature spectra with the γ- and β-isopropyltropolono derivatives of niobium and tantalum in the eight-coordinate form, *i.e.*, $M(TJ)_4^+$. In contrast the spectra of the eight-coordinate tantalum and niobium cations derived from the α-isopropyltropolone ion underwent a transition in which aromatic and aliphatic proton resonances broadened in dichloromethane–chloroform solution. The isopropyl methyl doublet at −1.2 ppm from TMS broadened and essentially disappeared; then at about −80°, two broad peaks appeared at −0.8 and −1.6 ppm. The intensities of these two broad peaks appeared to be roughly equivalent. Structural interpretation is not possible; the data cannot be taken as evidence for either different polytopal[2] or stereoisomeric forms.

Solution nmr studies of the tetrakis(α-isopropyltropolono)thorium complex showed, depending upon solvent and temperature, as many as three or four methyl group environments, over a range of 0.4 ppm, in perdeuteriotoluene at −50°, and the aromatic resonances were significantly broadened and quite complex. Because the solution molecular weight studies established association in these species and because analogous nonequivalences were not observed in the zirconium and hafnium species, the nonequivalence of methyl groups may reflect association phenomena. Similar results were found for tris(α-isopropyltropolono)niobium oxide, which is also associated in nonpolar media.

Since, in general, the higher coordinate complexes based on the tropolone ion and its derivatives appear to be somewhat more labile than the six-coordinate complexes (*vide infra*), one could ascribe the failure to detect polytopal isomers or stereoisomers to bond rupture processes analogous to those formulated in the *cis–*

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[13] Precedent for such oxygen atom sharing is found in the nickel and cobalt bisacetylacetonates which are trimeric and tetrameric, respectively: (a) G. F. Bullen, R. Mason, and P. Pauling, *Nature*, **189**, 291 (1961); *Inorg. Chem.*, **4**, 456 (1965); (b) F. A. Cotton and R. C. Elder, *J. Am. Chem. Soc.*, **86**, 2294 (1964).

[14] A. C. Adams and E. M. Larsen, *Inorg. Chem.*, **5**, 814 (1966).

[15] J. L. Hoard and J. V. Silverton, *ibid.*, **2**, 235 (1963).

[16] E. L. Muetterties and C. M. Wright, *Quart. Rev.* (London), **21**, 109 (1967), and references therein.

[17] Probably this broadening, which is similar for all three isomers, is a result of chemical shift averaging between different conformers assuming that $\Delta\nu_\alpha > \Delta\nu_\beta > \Delta\nu_\gamma$. However, the alternative of a change in correlation time inducing nuclear relaxation cannot be discounted since the dependence of the relaxation time would be a function of the distance of the proton from the metal atom, which would fit the observed order of $\alpha > \beta > \gamma$.

*trans* isomerization in six-coordinate complexes. However, an intramolecular rearrangement could be occurring at a rate comparable to bond rupture. Certainly the ease of intramolecular or polytopal[2,15] rearrangements in the higher coordinate complexes will be greater than for the six-coordinate octahedral species.

**Six Coordination. Stereoisomerism.** Employing the $\alpha$- and $\beta$-isopropyltropolone ions, six-coordinate complexes of silicon and germanium of the type $M(TJ)_3^+$ and of aluminum and gallium of the type $M(TJ)_3$ were prepared. Proton nmr evidence for the presence of *cis* and *trans* isomers, expected with these ligands, was found only for the $\alpha$ isomer. Similar results were obtained using $\alpha$- and $\beta$-methyltropolone ion as a ligand in the silicon system. For the aluminum and germanium systems the equilibrium mixtures contained 22 ± 2% *cis* as compared to a theoretical value of 25% assuming statistical distribution.

The proton nmr spectra of the *cis* and *trans* isomers of the aluminum, silicon, and germanium derivatives of $\alpha$-isopropyltropolone are similar. The temperature-dependent 220-Mc/sec spectra for the aluminum derivative in tetrachloroethane are presented in Figure 1. Spectral reproduction is limited to the region characteristic of the methyl groups associated with the isopropyl group since the regions characteristic of the aliphatic CH proton and the aromatic CH protons are too complicated for interpretation. Assignments for the equilibrium mixture at $-40°$ are two methyl doublets for the *cis* isomer at $-1.09$ and $-1.2$ ppm, and for the *trans* isomer three doublets of equal intensity at $-0.88$, $-0.91$, and $-0.94$ ppm and a doublet of intensity equal to that of the total of the three other doublets at $-1.2$ ppm. Coincidence of peaks associated with the *cis* and *trans* isomers at $-1.2$ ppm was confirmed by proton nmr spectra of partially separated fractions of $(\alpha\text{-TJ})_3Si^+$.

The most notable feature of the temperature-dependent spectra for the aluminum system is that the methyl environments in the *cis* form and in the *trans* form are equilibrated before *cis–trans* equilibration is fast on the nmr scale, *i.e.*, racemization appears to be faster than *cis–trans* isomerization.

**Six-Coordination Isomerization Mechanism.** The exchange mechanism evident in the temperature-dependent nmr spectra of the gallium and aluminum derivatives must be intramolecular in nature since the exchange between the tris complex and free ligand is a much more highly activated (see below) process. These observations and conclusions are identical with those reported by Fay and Piper[18] and Linck and Sievers[19] for analogous complexes based on 1,3-diketones. Fay and Piper further concluded that the mechanism of stereochemical rearrangement in all cases probably involves rupture of one chelate bond to give a five-coordinate intermediate. In principle, the $(\alpha\text{-TJ})_3M$ system provides an opportunity to distinguish between a dissociative process and an intramolecular rearrangement or twist[20–22] because of the distinctive isomer features (*cis* and *trans*) and the nonequivalent isopropyl methyl group environments in each isomer. The nonequivalent methyl environments are intrinsic; there is long-range asymmetry,[23] *i.e.*, a chiral center in the complex. Unfortunately, the rate differences for *cis–trans* isomerism and the loss of $CH_3$ nonequivalence in the *cis* and the *trans* forms are too similar for substantive statements concerning the isomerization mechanism. More meaningful analysis may be derived from $(\alpha\text{-TJ})_3M$ where significant pseudocontact shifts may obtain.

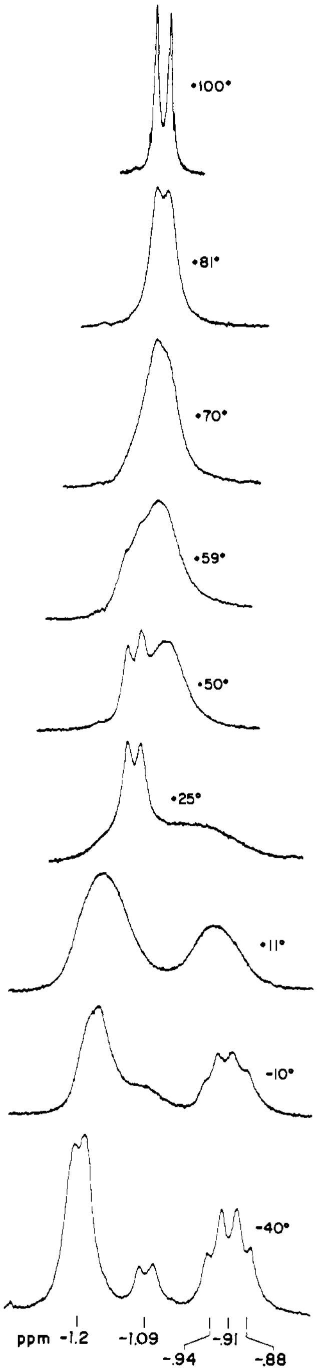

Figure 1. Proton spectra at 220 Mc/sec of the methyl region of the tris($\alpha$-isopropyltropolono)aluminum in tetrachloroethane as a function of temperature.

**Six Coordination. Comparison of Inter- and Intramolecular Exchange Rates.** Rates were estimated for these intramolecular exchange reactions in the six-coor-

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(18) R. C. Fay and T. S. Piper, *Inorg. Chem.*, 3, 348 (1964).

(19) R. G. Linck and R. E. Sievers, paper presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1964.

(20) J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, 8, 165 (1958).

(21) P. Rây and N. K. Dutt, *J. Indian Chem. Soc.*, 20, 81 (1943).

(22) C. S. Springer, Jr., and R. E. Sievers, *Inorg. Chem.*, 6, 852 (1967).

(23) The corresponding tris($\beta$-isopropyltropolono)complexes do not show nonequivalence of methyl groups.

**Table II**

| | New complexes | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Calculated, % | | | Found, % | | | | |
| Compound[a] | C | H | Metal | C | H | Metal | Mp, °C | Solvent of recrystallization |
| $(\alpha\text{-}C_{10}H_{11}O_2)_3SnCl$ | 56.0 | 5.16 | | 55.4 | 5.47 | | 222–225 dec | |
| $(\alpha\text{-}C_{10}H_{11}O_2)_4TaCl \cdot 3H_2O$ | 52.0 | 5.45 | 19.6 | 51.2 | 5.45 | 19.6 | 288–289 | Water–methanol |
| $NaTh(\alpha\text{-}C_{10}H_{11}O_2)_5$[b] | 56.1 | 5.17 | 21.7 | 56.1 | 5.19 | 22.9 | 350–355 dec | Tetrahydrofuran |
| $(\alpha\text{-}C_{10}H_{11}O_2)_4NbCl \cdot 2H_2O$ | 58.8 | 5.92 | 4.3 (Cl) | 58.9 | 5.71 | 4.9 (Cl) | 232–238 dec | Methanolic HCl |
| $(\alpha\text{-}C_{10}H_{11}O_2)_3NbO$ | 60.2 | 5.55 | 0 (Cl) | 59.8 | 6.19 | 0.0 (Cl) | 168–188 dec | Water–methanol |
| $(\alpha\text{-}C_{10}H_{11}O_2)_3GePF_6$ | 51.0 | 4.70 | | 51.2 | 4.85 | | 180–188 dec | Water–methanol |
| $(\alpha\text{-}C_{10}H_{11}O_2)_3SiPF_6$ | 54.4 | 5.01 | 4.67 (P) | 54.3 | 5.07 | 4.40 (P) | 198–201 | Water–methanol |
| $(\gamma\text{-}C_{10}H_{11}O_2)_3SiPF_6$ | 54.4 | 5.01 | | 54.6 | 5.17 | | | Water–methanol |
| $(\alpha\text{-}C_8H_7O_2)_3SiPF_6$ | 49.8 | 3.69 | | 49.7 | 3.90 | | Slowly dec ~328 | Water–ethanol |
| $(\gamma\text{-}C_{10}H_{11}O_2)_4Zr$ | 64.6 | 5.96 | | 64.0 | 5.94 | | 374 dec | Ethanol–chloroform |
| $(\gamma\text{-}C_{10}H_{11}O_2)_4Hf$ | 57.8 | 5.33 | | 57.9 | 5.41 | | 376 dec | Ethanol–chloroform |
| $(\alpha\text{-}C_{10}H_{11}O_2)_2Hg$ | 45.5 | 4.20 | | 46.1 | 4.04 | | 107–108 | Sublimed 110° (0.001 mm) |

[a] $C_8H_7O_2$ = methyltropolone ion; $C_{10}H_{11}O_2$ = isopropyltropolone ion. [b] The X-ray powder pattern of this complex shows no similarities to the powder pattern of $Th(\alpha\text{-}TJ)_4$ or $Na^+(\alpha\text{-}TJ)^-$.

dinate complexes from the collapse regions in the nmr spectra. The approximate rate of *cis–trans* isomerization in gallium is 66/sec at −30°. For the aluminum system, equilibration of *cis* environments occurs at a rate of about $10^2$/sec at 18° and of *trans* environments at $3 \times 10^2$/sec at 50°, and the rate of *cis–trans* isomerization is about $10^2$/sec at 80°. For germanium, equilibration of *cis* environments occurs at a rate of 90/sec at 75° and of *trans* environments of 182/sec at 100°; *cis–trans* isomerization did not occur up to 140° where reaction with the solvent occurs. No equilibration was observed in the nmr spectra of the silicon complex up to 140° where reaction with solvent occurs.

The rates of *cis–trans* isomerization in the aluminum and gallium complexes may be compared with those found by Fay and Piper[18] for the analogous trifluoroacetylacetonate complexes. Approximate isomerization rate constants reported[18] for aluminum and gallium are 34/sec at 103° and 38/sec at 61.5°, respectively. Quantitatively, the isopropyltropolono derivatives of the six-coordinate system appear to be somewhat more labile than the trifluoroacetylacetonates.

Attempts to detect *inter*molecular exchange of ligands between the six-coordinate complexes and free ligand were unsuccessful by the nmr techniques. For the nmr time scale, no ligand exchange was observed for the gallium, aluminum, germanium, and silicon systems up to 146°, the boiling point of the solvent. Thus, the six-coordinate tropolone complexes are definitely less labile than the eight-coordinate complexes with the exception of $(TJ)_4Ta^+$. This again follows the pattern of the metal complexes based on 1,3-diketones.[14,18,19]

## Experimental Section

**Reagents and Procedure.** Reagent grade metal salts were used without further purification. In most syntheses, the appropriate chloride was used. The exceptions were thorium(IV) nitrate and uranium(IV) acetate. α-Methyltropolone was prepared by the method of Takase.[24] Separation of the isopropyltropolone isomers is described below. Many of the complexes reported here (Table II) were synthesized analogously to the other tropolono complexes described in preceding papers.[1,3–6]

X-Ray powder data were obtained on a 114.6-mm Debye-Sherrer camera with Cu Kα radiation and a nickel filter.

Proton nmr spectra were obtained on the Varian Associates Model HA 100 with a Varian V4343 temperature unit controller and HR 220 spectrometer with a variable-temperature unit. Temperatures on the 220-Mc spectra were determined by measuring the separation in the methanol peaks in the range +26 to −50°.

Solutions used to study exchange between free ligand and complexed ligand contained 1 equiv of free ligand/equiv of complexed ligand.

**Separation of α-, β-, and γ-Monosubstituted Isopropyltropolones.** A crude oil containing the three isopropyltropolone isomers was purchased from the Crown Zellerbach Corp., Camas, Wash. The mixture was distilled at 1 mm, and cuts were taken from 80 to 120°. Seed crystals of γ-isopropyltropolone were added to the cuts which distilled at 107–120°. The colorless crystals of γ-isopropyltropolone were separated from the mother liquor and recrystallized from petroleum ether (bp 30–60°), mp 78° lit.[25] 78.5–82°). A similar procedure was followed with the cuts which distilled at 80–100° to give α-isopropyltropolone, mp 32–33°. Small amounts of β-isopropyltropolone were obtained from cuts boiling at 100–107°, mp 50–51°. In a typical separation 232 g of the crude oil gave 40 g of the γ isomer, 8 g of the α isomer, and 1.5 g of the β isomer.

Individual yields of the isomers varied greatly with the lot number of the crude oil.

**$(\alpha\text{-}C_{10}H_{11}O_2)_3Al$ and $(\alpha\text{-}C_{10}H_{11}O_2)_3Ga$.** Aluminum trichloride (0.088 g, 0.66 mmole) slurried in 2 ml of methanol was added to α-isopropyltropolone (0.33 g, 2 mmoles) in 7 ml of chloroform. Concentrated ammonium hydroxide was added to neutralize the solution (pH 6–7 by litmus paper). The solution was filtered and the filtrate evaporated to dryness under reduced pressure. The yellow solid was recrystallized from methanol and vacuum dried 8 hr at room temperature, yield 100%, mp 220–221° dec.

*Anal.* Calcd for $(C_{10}H_{11}O_2)_3Al$: C, 69.7; H, 6.43. Found (α): C, 69.1; H, 6.49.

The synthesis of $(\gamma\text{-}C_{10}H_{11}O_2)_3Al$ is analogous, mp 328–389° dec.

*Anal.* Calcd for $(C_{10}H_{11}O_2)_3Al \cdot 0.2CHCl_3$: C, 67.2; H, 6.15; Cl, 3.94; mol wt, 540. Found: C, 67.6; H, 6.12; Cl, 3.89; mol wt, 509 (vapor pressure osmometry in $CHCl_3$). Nmr ($CDCl_3$, TMS external reference, +30°): −1.22 (d), −2.88 (septet), −7.42 (aromatics) ppm; $J_{CH_3-CH} = 7$ Hz.

Gallium tribromide (1.24 g, 0.004 mole) in 15 ml of ethanol was added to a solution of α-isopropyltropolone (1.99 g, 0.012 mole) in 12 ml of ethanol. Water was then added to incipient precipitation. After a short time, a gummy precipitate appeared and ethanol was added to give a clear solution. The slurry was warmed to mild reflux and filtered. Water was added to incipient precipitation. The reaction mixture was slowly cooled with stirring to give crystals, which were collected by filtration (1.86 g). The solid was recrystallized from ethanol–water and vacuum dried at 100° for 2 hr, mp 215–216°.

*Anal.* Calcd for $(C_{10}H_{11}O_2)_3Ga$: C, 64.4; H, 5.94. Found: C, 64.4; H, 5.98. Nmr ($CDCl_3$, TMS internal reference +30°): −1.11 (d), −3.88 (septet), −7.02 (t), −7.32 (t), −7.52 (d), −7.54 (d) ppm; $J_{CH_3-CH} = 6.5$ Hz, $J_{CH-CH_{aromatic}} = 10$ Hz.

**$(\alpha\text{-}C_{10}H_{11}O_2)_4Zr$ and $(\alpha\text{-}C_{10}H_{11}O_2)_4Hf$.** Zirconium tetrachloride (0.89 g, 3.8 mmoles) was added to a solution of α-isopropyltropolone (2.5 g, 0.015 mole) in 75 ml of chloroform. Essentially all the

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(24) K. Takase, *Bull. Chem. Soc. Japan*, 37, 1460 (1964).

(25) P. L. Pauson, *Chem. Rev.*, 55, 9 (1955), and references therein.

solid material dissolved to give a pale yellow solution which was warmed on a steam bath for 2 hr during which the volume of the solution was reduced to one-fourth the original volume. The hot solution was filtered and cooled in ice to give yellow crystals. The yield was 1.0 g, 35%. An additional 1.8 g of slightly impure product was obtained from evaporation of the filtrate to dryness. The product was recrystallized from chloroform and vacuum dried 8 hr at room temperature.

*Anal.* Calcd for $(\alpha\text{-}C_{10}H_{11}O_2)_4Zr$: C, 64.6; H, 5.96; Zr, 12.3; mol wt, 744 (monomer). Found: C, 64.0; H, 5.95; Zr, 12.1; mol wt, 752 (vapor pressure osmometry in chloroform). Nmr ($CDCl_3$, TMS internal reference, +30°): −1.14 (d), −3.64 (septet), −6.84 (t), −7.22 (d), −7.25 (t), −7.40 (d) ppm; $J_{CH_3-CH}$ = 6.5 Hz, $J_{CH-CH_{aromatics}}$ = 10 Hz.

$(\alpha\text{-}C_{10}H_{11}O_2)_4Hf$ was synthesized analogously, mp 292–299° dec.

*Anal.* Calcd for $(C_{10}H_{11}O_2)_4Hf$: C, 57.8, H, 5.33; Hf, 21.5; mol wt, 831 (monomer). Found: C, 57.1; H, 5.38; Hf, 21.5; mol wt, 804 (vapor pressure osmometry in chloroform).

X-Ray powder data show $(\alpha\text{-}C_{10}H_{11}O_2)_4Zr$ and $(\alpha\text{-}C_{10}H_{11}O_2)_4Hf$ are isomorphous. The nmr spectra in $CDCl_3$ are identical.

**$(\alpha\text{-}C_{10}H_{11}O_2)_4Th$.** A solution of α-isopropyltropolone (6.8 g, 0.041 mole) in 20 ml of methanol was added to a solution of thorium(IV) nitrate tetrahydrate (5.52 g, 0.01 mole) in 100 ml of water and 50 ml of methanol. A pale yellow solid separated. The slurry was stirred for 30 min and then placed on a steam bath for 15 min, during which the solid became somewhat gummy. After cooling, the solid phase was isolated by filtration (6.80 g) and recrystallized from 98:2 methanol–water. The solid was vacuum dried at 80°, mp 249.5–250° dec.

*Anal.* Calcd for $(C_{10}H_{11}O_2)_4Th$: C, 54.3; H, 5.01; Th, 26.2; mol wt, 885 (monomer). Found: C, 54.1; H, 5.04; Th, 26.5.

A molecular weight determination on a vacuum-dried and sealed sample with moisture carefully excluded gave 1511 (cryoscopic, dry benzene). The same sample was run cryoscopically in benzene containing 230 ppm of water as determined by Karl Fischer titration; the molecular weight was 757.

**$(\gamma\text{-}C_{10}H_{11}O_2)_4Th$.** The compound was synthesized by the previously reported method,[5] dried at 100° (0.001 mm) for 4 hr, and sealed in ampoules, mp 350°.

*Anal.* Calcd for $(C_{10}H_{11}O_2)_4Th$: mol wt, 885. Found: mol wt, 2808 (1.34 wt % cryoscopic benzene under anhydrous conditions). Previously reported values[5] for determinations with exposure to the atmosphere are: 886 ($CHCl_3$, vapor pressure osmometry) and 843 (cryoscopic $C_6H_6$).

**Isopropyltropolone Complexes of Uranium.** In a typical synthesis an isomer of isopropyltropolone (6.56 g, 0.04 mole) was dissolved in 125 ml of acetonitrile in a nitrogen atmosphere, and uranium(IV) acetate (4.74 g, 0.01 mole) was added. The mixture was heated at reflux for 2 hr, during which the uranium acetate dissolved and the solution turned dark red. The reaction mixture was cooled in ice and filtered in a nitrogen atmosphere. The red solid was recrystallized from toluene–acetonitrile: $\alpha\text{-}T_4U$, mp 263–264° dec, sublimes 265° (0.001 mm); nmr ($CDCl_3$, TMS internal reference) +1.48 (t), +2.56 (septet), −5.97 (d), −14.06 (d), −13.22 (t), −9.78 (t) ±0.05 ppm; $\beta\text{-}T_4U$, mp 254–255° dec, sublimes 289° (0.001 mm); nmr (40% $CDCl_3$–60% $CD_2Cl_2$, TMS internal reference) −1.83 (d), −3.34 (septet), −4.91 (s), −7.73 (d), −14.15 (t), −9.79 (d) ppm; $\gamma\text{-}T_4U$, mp 360–362° dec, sublimes 345° (0.001 mm); nmr (40% $CDCl_3$–60% $CD_2Cl_2$, TMS internal reference) −2.99 (d), −5.58 (septet), −6.20 (d), −13.85 (d) ppm. Sublimation temperatures given are the heating bath temperatures.

*Anal.* Calcd for $(C_{10}H_{11}O_2)_4U$: C, 53.9; H, 4.97; mol wt, 891. Found for $\alpha\text{-}T_4U$: C, 54.0; H, 5.00; mol wt, 749 (cryoscopic in $C_6H_6$). $\beta\text{-}T_4U$: C, 54.0; H, 5.15; mol wt, 721 (cryoscopic in $C_6H_6$). $\gamma\text{-}T_4U$: C, 54.3; H, 5.23; mol wt, 852 (cryoscopic in $C_6H_6$). The discrepancy in the found molecular weight *vs.* theory is attributed to air oxidation.

The solution magnetic susceptibilities of the uranium(IV) complexes were measured by the nmr method.[26] The magnetic moment in chloroform was 2.80 BM at 302°K for $\alpha\text{-}T_4U$, $\beta\text{-}T_4U$, and $\gamma\text{-}T_4U$.[27] The solid-state magnetic susceptibility of $\gamma\text{-}T_4U$ was studied at 8 kOe from 77 to 296°K and from 2 to 8 kOe. The effective moment, $\mu_{eff}$, is 2.89 BM at 295°K and 2.36 BM at 77°K, and within experimental error the data fit the Curie–Weiss relation above 160°K.

The proton nmr spectra of these uranium species consisted of very sharp resonances associated with the aromatic and aliphatic protons which were shifted significantly from the positions characteristic of diamagnetic species. This shift may either be due to a dipolar or a Fermi contact interaction or both.[28]

Solutions of the isopropyltropolonouranium(IV) complexes oxidize on exposure to air to give the orange uranyl complexes $H(C_{10}H_{11}O_2)_3UO_2$: mp $(H\text{-}\alpha\text{-}T_3UO_2)$ 217–218°; mp $(H\text{-}\gamma\text{-}T_3UO_2)$ 250°; ir (Nujol) 900 $cm^{-1}$ O–U–O.

*Anal.* Calcd for $H(C_{10}H_{11}O_2)_3UO_2$: C, 47.4; H, 4.50. Found for $H\text{-}\alpha\text{-}T_3UO_2$: C, 47.6; H, 4.59. $H\text{-}\gamma\text{-}T_3UO_2$: C, 47.3; H, 4.58.

**Acknowledgments.** We are indebted to Dr. J. F. Weiher for the solid-state magnetic susceptibility studies, Mr. Albert F. Biddle for the X-ray powder studies, Dr. J. P. Jesson for many helpful discussions on the nmr studies, and Dr. T. Fukunaga for preparing the α-methyltropolone.

(26) (a) D. F. Evans, *J. Chem. Soc.*, 2003 (1959). (b) The reference solution was contained in a capillary inserted in the nuclear magnetic resonance tube containing the uranium(IV) complex and reference tetramethylsilane in chloroform.

(27) The "spin-only" moment for $U^{4+}$ gaseous ion was calculated to be 2.83 BM: C. A. Hutchison, Jr., and N. Elliott, *J. Chem. Phys.*, **16,** 920 (1948).

(28) For the Fermi contact interaction, the delocalization mechanism of spin into the ligand π system could involve donation either from the top-filled π-bonding orbital from the ligand to the metal or from the metal into the lowest antibonding π orbital of the ligand. If the metal orbital is energetically close to the top-filled π-ligand orbital, the first mechanism would dominate. If it is close to the bottom empty π-ligand orbital, the second mechanism would apply. Definitive analysis of these shifts would require single-crystal electron spin resonance or single-crystal susceptibility determinations coupled with a crystal structure determination.