stable than the tilted bond in 2-methylpyridine. This simple interpretation by Falk for the spatial mobility of the nonbonding orbitals in these two solvents, and, in fact, in any heterocyclic amine molecule, is yet to be substantiated by additional quantitative evidence.

IV. Summary

Studies of solvent effects on the electronic structure on the square-bonded Co^{2+} ion in the phthalocyanine molecule have been performed with several heterocyclic amine solvents and their substituted derivatives. The most notable feature of the e.s.r. spectra is the superhyperfine structure arising from the magnetic interaction between the Co^{2+} unpaired electron and out-of-plane nitrogen atoms of the solvating molecules. A qualitative comparison between the e.s.r. nitrogen-orbital bonding coefficient and the calculated charge density at the out-of-plane nitrogen atoms has shown agreement. Additional investigations with substituted pyridine solutions are under way to determine a relationship between the e.s.r. bonding coefficients, π-electron densities, and basicity of these molecules.

Acknowledgment. The author wishes to acknowledge the assistance of Drs. J. Goldmacher, W. K. Kahn, and S. E. Harrison in the various aspects of this work.

Chelate Chemistry. III.[1] Chelates of High Coordination Number

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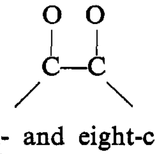
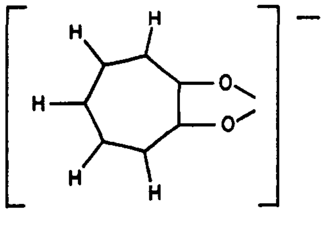
Synthesis, properties, and structural interpretations are presented for seven- and eight-coordinate structures based on the tropolone anion and the following elements: scandium, yttrium, titanium, zirconium, hafnium, thorium, vanadium, niobium, tantalum, rare earth metals, indium, tin, and lead. Oxygen atoms in the chelated tropolone anion apparently are three-coordinate in the tris chelates of some rare earth metals and yttrium but not in scandium, titanium, iron, and rhodium.

Introduction

In the first paper[2] of this series, an argument was presented that the tropolone anion, T, is ideally suited to the formation of structures of high coordination number by virtue of the planarity and compactness of the ligand and the rigidity of the



functionality. Seven- and eight-coordinate structures were described for the tropolone anion with indium, tin, and lead. A more detailed assay of high coordination structures based on tropolone is the subject of this paper.



T

Group III Tetrakis Chelates. The tristropolonates of scandium, yttrium, and the rare earth trivalent ions react with sodium tropolonate in polar media to form sodium salts of the respective metal tetrakistropolonate anions, Na$^+$MT$_4^-$. These salts are analogous to the earlier described[2] indium compound, Na$^+$InT$_4^-$.

There appears to be a real structural identity among all these tetrakistropolonates. Firstly, the infrared spectra of the crystalline salts are simple and strikingly similar. Secondly, and more definitively, the lattices are isomorphous by X-ray powder diffraction criterion. Because eight-coordination is a well-established phenomenon for rare earth ions such as europium, and because of the spectral and diffraction similarities of the solid lattices, we believe that these chelates are eight-coordinate in the solid state. Owing to the low solubility of the diamagnetic salts, no spectral information relevant to the solution state was obtained. However, the proton n.m.r. spectra of the paramagnetic salts displayed pseudo-contact shifts significantly different from the tris chelates. For example, (CD$_3$)$_2$SO solutions of Na$^+$PrT$_4^-$ showed broad proton resonances at -8.7 and -10 p.p.m. compared to -10, -11.7, and -13.3 p.p.m. for PrT$_3$ in (CD$_3$)$_2$SO. These large diamagnetic shifts for PrT$_4^-$ relative to PrT$_3$ suggest that there is no gross dissociation of PrT$_4^-$ in solution. There is, however, ligand exchange between tropolone and PrT$_4^-$ in (CD$_3$)$_2$SO solutions as judged by the averaging in the proton n.m.r. spectra of such mixtures.

An isomorphous group of acids, H$^+$RT$_4^-$, and an isomorphous group of ammonium salts, NH$_4^+$RT$_4^-$, were also prepared and characterized.

Attempts were made to extend this chemistry to other trivalent ions. We obtained no evidence of

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[1] Paper II: E. L. Muetterties and C. M. Wright, *J. Am. Chem. Soc.*, **87**, 21 (1965).

[2] E. L. Muetterties and C. M. Wright, *ibid.*, **86**, 5132 (1964).

reaction between sodium tropolonate and the tristropolonates of iron(III), gallium(III), and rhodium(III).

Group IV Chelates. Many metal salts react with tropolone to give tetrakis chelate derivatives. These include the tetrahalides of zirconium, hafnium, and thorium, the nitrate of cerium(IV), and the tetraacetate of lead. The tetrakis chelates, MT_4, of zirconium, hafnium, and thorium sublime at $\sim 300^\circ$ (0.01 μ), whereas those of cerium and lead decompose below these temperatures. The lead chelate is slowly converted to lead dioxide at 100°. Analyses of X-ray powder patterns indicate that ZrT_4 and HfT_4 are isomorphous, ThT_4 and CeT_4 are isomorphous, and PbT_4 is unique.

Since eight-coordinate chelates of Zr, Hf, Th, and Ce with β-diketones are well known,[3] there appears to be little basis to question the formulation of the analogous tropolone chelates as eight-coordinate structures, at least for the solid state. Moreover, the infrared spectra of the solids are simple and give no indication that tropolone ion or distinctly different tropolone ligands are present. The zirconium, hafnium, and thorium tropolone chelates sublime without significant degradation, and, on this basis, it seems reasonable that eight-coordination is sustained in the gaseous state for these molecules. The only data that bear on the solid-state structure of the lead compound are derived from the infrared spectrum which is similar to the spectra of ZrT_4, HfT_4, ThT_4, and CeT_4.

The proton n.m.r. spectra (60 Mc.) of ZrT_4, HfT_4, and ThT_4 in $(CD_3)_2SO$ are similar to that of T_4Ta^+. Discernible in these spectra are a distorted β proton triplet and an α proton doublet. The γ proton triplet is obscured by the α doublet. There does not appear to be any rapid exchange (n.m.r. criterion) between these tetrakis chelates and tropolone in $(CD_3)_2SO$ solutions; however, the similarity in the chemical shifts for the tropolone and chelate resonances precludes a rigorous characterization of exchange. The proton resonances of these chelates are to slightly higher (0.7 p.p.m.) fields than for T_4Ta^+; approximate values for $J_{H_\alpha H_\beta}$ and $J_{H_\beta H_\gamma}$ are ~ 10 and 9 c.p.s., respectively. Similar spectra were obtained for SnT_4 (*vide infra*) and PbT_4, except in the tin compound the α and β doublet and triplet are not well defined. The $\alpha\beta$ and $\beta\gamma$, HH coupling constants appear to be nearly identical, ~ 10 c.p.s. There is a relatively large $\alpha\beta$ chemical shift of 48 c.p.s. in CeT_4; the two HH coupling constants are ~ 10 c.p.s. There is no fast (n.m.r. time scale) exchange between CeT_4 and tropolone in $(CD_3)_2SO$ at 25°. A unique definition of eight-coordination in solution is not achieved with these n.m.r. data, but the spectral data are, nevertheless, strongly indicative of a complex in which all four ligands are equivalent.

A relatively common phenomenon in tropolone chelates is color. In many instances, we believe that this arises from a low-lying excited state in which there is electron transfer from the ligand to the metal atom. This is evident in the cerium(IV) and lead(IV) derivatives which are intensely colored. Ease of electron transfer in these derivatives undoubtedly contributes to their thermal instability as contrasted to the high stability of the nearly colorless tropolone chelates of the much more reduction-resistant, four-valent zirconium, hafnium, and thorium cations.

Tin tetrachloride reacts with the sodium salt of tropolone in aqueous media to give primarily T_3SnOH which appears analogous to the nonionic T_3SnCl and $T_3SnC_6H_5$ complexes described in paper I.[2] The hydroxy derivative is nonbasic and displays no ionization tendencies. Formulation of this compound as a hydroxy species rather than the oxide $T_3SnOSnT_3$ rests on the presence of an OH infrared stretching absorption and on elemental analyses. In alcoholic media, tin tetrachloride and sodium tropolonate yield a pale yellow compound of the composition SnT_4. This apparent eight-coordinate chelate has an infrared spectrum quite similar to those of lead, zirconium, hafnium, etc., and an X-ray powder pattern that has similarities to PbT_4. The yellow tetrakis chelate retains its integrity in recrystallizations from nonaqueous media but slowly degrades to T_3SnOH in aqueous media. Thermal stability of SnT_4 is fair. Above 250° *in vacuo*, SnT_4 decomposes with sublimation of a material that appears to be largely $T_3SnOSnT_3$.

In paper I,[2] it was reported that the chloride salts of the silicon and germanium chelate cations T_3Si^+ and T_3Ge^+ react with silver tropolonate to give tropolone salts which on dehydration become black. Analysis of

$$2H_2O + AgT + T_3Si^+Cl^- \longrightarrow AgCl + T_3Si^+T^- \cdot 2H_2O \text{ (orange)}$$

$$T_3Si^+T^- \cdot 2H_2O \xrightarrow[60^\circ]{\text{vacuum}} SiT_4 \text{ (black)}$$

the black derivatives precisely agrees with that for tetrakis chelates, *i.e.*, SiT_4 and GeT_4, but the infrared spectra of these derivatives suggest that more than one kind of tropolone ligand is present. This is confirmed by the proton n.m.r. spectra (chlorohydrocarbon solutions) which show multiplets in the region characteristic of the cation, T_3M^+, and of the tropolone anion, T^-. However, integration of the chelate and anion resonances consistently shows a ratio of chelate to anion of greater than 3:1 (the range is $\sim$5:1 to 3.5:1). These n.m.r. results raise the possibility of a solution equilibrium between the salt and a seven- or eight-coordinate structure. Attempts to appraise

$$T_3Si^+T^- \rightleftharpoons SiT_4$$

this hypothesis by varying the dielectric constant of the medium failed because of the reactivity of these anhydrous chelates towards most solvents; even with chloroform, there is slow reaction. Since these anhydrous chelates are essentially amorphous by X-ray criterion, a definitive structural investigation is beyond realization with present techniques. The only description that can be given is that SiT_4 and GeT_4 are largely in the form of salts or ion pairs, *i.e.*, $T_3Si^+T^-$ and $T_3Ge^+T^-$, in chloroform solution and in the solid state. Hydrolysis with NaOD established that none of the tropolone ligands is bound to the silicon atom through a carbon atom.

Titanium tetrachloride and tropolone react in nonaqueous media to give primarily T_2TiCl_2 which is nonionic and very similar to T_2SnCl_2 which was described in paper I.[2] Extensive attempts were made to

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(3) *Cf.* (a) J. L. Hoard and J. V. Silverton, *Inorg. Chem.*, **2**, 235 (1963); (b) J. V. Silverton and J. L. Hoard, *ibid.*, **2**, 243 (1963).

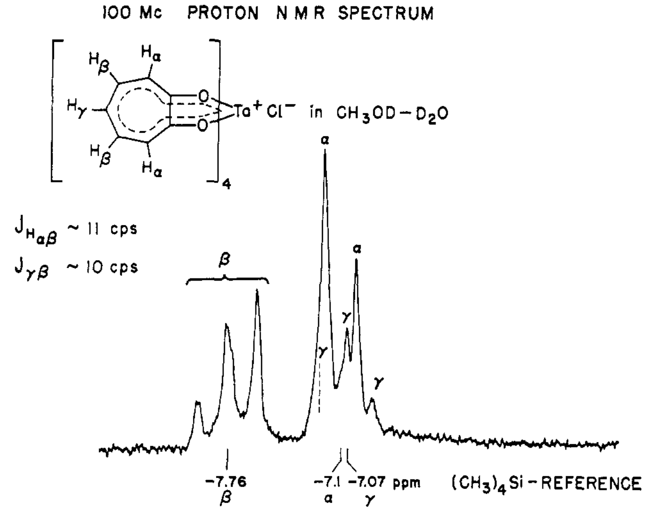

Figure 1. The 100-Mc. proton n.m.r. spectrum of $(C_7H_5O_2)_4Ta^+Cl^-$ in CH_3OD-D_2O.

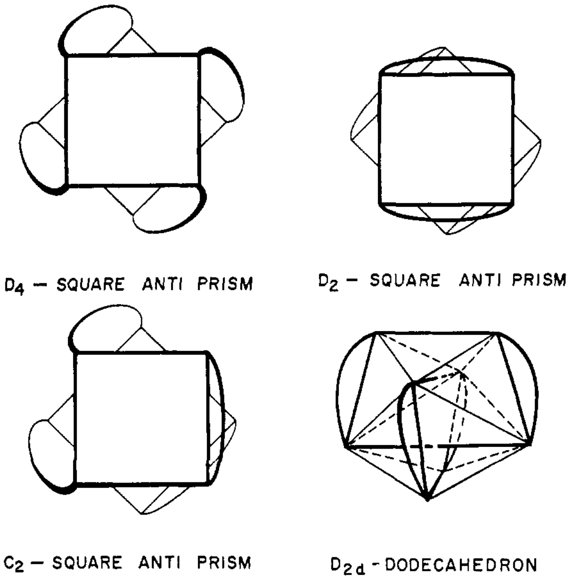

Figure 2. Possible structures for an eight-coordinate metal chelate. The curved lines represent a symmetrical bidentate ligand.

prepare a cationic chelate of the type T_3Ti^+ comparable to the cation obtained with acetylacetone,[4] $Ti(AcAc)_3{}^+$, but these efforts were unsuccessful. A bright red compound of the composition T_3TiCl was obtained from a high-temperature reaction of $TiCl_4$ (or T_2TiCl_2) and tropolone, but this compound behaves like a discrete molecular species analogous to the tin compound T_3SnCl reported earlier. The infrared spectra of T_3SnCl and T_3TiCl are very similar, but there is no correspondence between their X-ray powder patterns. Unlike T_3SnCl, the titanium chelate is rapidly hydrolyzed in aqueous media. Reaction of tropolone and $TiCl_4$ in dimethyl sulfoxide media followed by a low-temperature hydrolysis yielded a compound, soluble in chlorohydrocarbons; the formula $T_3TiOTiT_3$ was indicated by analysis. Our studies with titanium(IV) suggest a tendency for this tetravalent ion to form seven-coordinate chelates with tropolone. Synthesis efforts to prepare eight-coordinate species were unsuccessful.

Group V Chelates. Niobium and tantalum pentachlorides react with acidic aqueous solutions of tropolone to give the tetrakistropolono cations T_4Nb^+ and T_4Ta^+, respectively. Yields are nearly quantitative. These cations form insoluble salts with large symmetrical anions such as PF_6^-, I^-, $B_{12}Cl_{12}{}^{2-}$, and ClO_4^-. Solutions of the salts in water–alcohol media are faintly yellow. The color of the crystalline salts varies from very pale yellow for PF_6^- to yellow for the chloride to orange for the iodide. The sequence of color relative to the reducing properties of the anions suggests that there is some electron transfer from the anion to the cation. A comparable phenomenon for the salts of T_2B^+, T_3Si^+, T_3Ge^+, and T_3P^{2+} was reported in paper I.[2]

The tantalum and niobium chelates are not solvated in solution.[5] The electronic spectra of $T_4Ta^+Cl^-$ and of $T_4Ta^+PF_6^-$ are nearly the same in water and in methanol. Beer's law is obeyed for these solutions. There are significant changes in the spectra in dimethyl sulfoxide and acetonitrile solutions (Table IV). However, this does not reflect solvate formation but probably strong ion-pair formation. Addition of 1 to 2 equiv. of dimethyl sulfoxide or other strong donor molecules to an aqueous solution of T_4Ta^+ does not alter the aqueous spectrum. Recrystallization of $T_4Ta^+PF_6^-$ from dimethyl sulfoxide and from media containing dimethyl sulfoxide yields the hexafluorophosphate unsolvated by sulfoxide. The proton n.m.r. spectrum of T_4Ta^+ is unaltered in going from a water (D_2O) to a dimethyl sulfoxide solution except for a slight change in the absolute chemical shifts.

The proton n.m.r. spectra of T_4Nb^+ and T_4Ta^+ are very similar and are comparable to other heavy metal tropolonates in that at 60 Mc. the aromatic CH multiplet is spread over a relatively large range of ~60 c.p.s. compared to the spread of only 20–30 c.p.s. for T_3Si^+. At 100 Mc., the chemical shifts of the α, β, and γ ring protons in T_4Ta^+ are sufficiently large to discern the β triplet and the overlapping α doublet and γ triplet (Figure 1). These data suggest[6] eight-coordination for T_4Ta^+ in solution, but they provide no insight to its stereochemistry. Strict environmental equivalence of the two α protons and of the two β protons can be achieved in the D_4 square antiprismatic model (Figure 2). Such an isomer has never been observed, in the solid state, for any eight-coordinate structure based on four equivalent bidentate ligands although this does not exclude it from consideration. The only geometries detected in X-ray studies are the D_2 square antiprism and the D_{2d} dodecahedron (Figure 2). The tantalum chelate may not have D_4 symmetry, and the n.m.r. spectroscopic equivalence of α (and of β) protons may simply reflect a very small chemical

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(4) M. L. Reynolds, *J. Inorg. Nucl. Chem.*, **26**, 667 (1964).

(5) If T_4Ta^+ or T_4Nb^+ were hydrated in aqueous media, there should be no attack of the tropolone ligand by OH^-. The fast step would be conversion of $T_4TaOH_2{}^+$ to T_4TaOH. The latter, devoid of formal positive charge, should undergo no hydrolysis through ligand attack. In fact, T_4Ta^+ undergoes significant ligand attack by OH^- in aqueous media. See paper II[1] and the section on "Stability of T_4Nb^+ and T_4Ta^+" in this paper for a more detailed discussion of hydrolysis mechanism.

(6) Consistently, the proton n.m.r. spectra of the analogous tantalum cation derived from γ-isopropyltropolone shows a simple AB pattern ($J_{\alpha\beta}$ = 11 c.p.s.) for the α and β ring protons and doublet–septuplet resonances for the isopropyl group.

shift between nonequivalent α (and β) protons, a not unexpected situation. Equivalence might also arise from an averaging process based on vibrationally excited states of the structure. In fact, a distinction between any of the idealized eight-coordinate geometries is realistic[7] only if the time scale of the description is relatively short because vibrational excitation should suffice to interconvert these very similar conformations (see Figure 3 for comparison of the D_2 and D_{2d} models).

Antimony pentachloride and the sodium salt of tropolone react in strongly acidic media to give a red solution from which a crystalline $B_{12}Cl_{12}^{2-}$ salt can be isolated. The analyses of the salt suggest that the cation is T_4Sb^+, and the infrared spectrum of the salt is similar to that of $(T_4Ta^+)_2B_{12}Cl_{12}^{2-}$. However, the cation is unstable and does not undergo clean metathetical reactions in aqueous media. Proton n.m.r. spectra of the salt in aqueous media show the presence of tropolone in addition to chelated tropolone ion, indicating that hydrolysis is significant. Basic hydrolysis of the antimony chelate in H_2O^{18} yields tropolone unenriched in O^{18}. This behavior is analogous to that of $T_2As(OH)_2^+$, another chelate cation that has little integrity in solution.[2] In total, the data do not define T_4Sb^+, and the existence of this cation has, therefore, not been established. Molybdenum pentachloride in concentrated hydrochloric acid yields no cationic species; the sole product is T_2MoOCl.

Vanadium oxychloride and tropolone yield a deep blue octahedral chelate, T_2ClVO (VO absorption at 970 cm.$^{-1}$). Reaction of the oxychlorochelate with sodium tropolonate yields T_3VO which displays a strong infrared band at 950 cm.$^{-1}$ that we ascribe to the vanadyl absorption. This species appears then to be seven-coordinate.[8] The oxyniobium chelate, T_3NbO, prepared by hydrolysis of T_4Nb^+, is relatively insoluble and so there are no spectroscopic or moleculer weight data to characterize the solution structure. This chelate could be analogous to T_3VO or it could be eight-coordinate through NbONb bonding as in solid Cl_3NbO. Since the infrared spectrum of T_3NbO has little resemblance to that of T_3VO, and since T_3NbO has low solubility, it may be associated in the solid state.

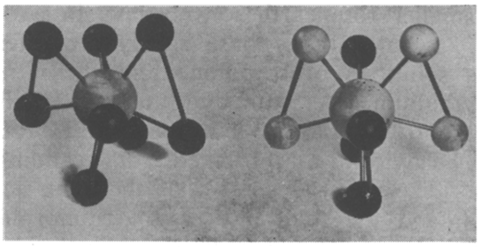

Figure 3. Perspective of the D_2 square antiprismatic (left) and D_{2d} dodecahedral structures of T_4Ta^+. The symmetrical tropolono ligand is represented by two small spheres connected by a stick.

Rare Earth Tristropolonates. In rare earth chelates, the metal ions are rarely satisfied with coordination numbers less than seven. This behavior is well documented in two recent studies of β-diketone chelates of the rare earths.[9] Separation of the rare earth trisacetylacetonates from solution always occurs with retention of solvent to give a solid-state aggregate in which the coordination number for the metal ion exceeds six. Attempts to desolvate these lattices have generally been rewarded only with degradation. The solvated trisacetylacetonates are soluble in a variety of solvents and give every appearance of discrete molecular entities. Excess acetylacetonate ion readily converts the tris to tetrakis chelates, $M(AcAc)_4^-$. Similarly, strong bidentate bases such as *o*-phenanthroline convert the solvated tris chelates to tetrakis chelates, *e.g.*, $M(AcAc)_3 \cdot$*o*-phenanthroline. These general characteristics provide a background discordant with the behavior we find for some of the rare earth tropolonates.

Lanthanum ion and the larger rare earth ions, Ce^{3+} through Ho^{3+}, react with tropolone to give the respective tristropolonates. The crystals are free of solvent and are insoluble in common solvents. The intractability of these tropolonates is significant since all other previously reported tristropolonates, FeT_3, AlT_3, and InT_3, are soluble in such media as ethanol and chloroform. Strongly basic solvents like dimethyl sulfoxide do dissolve these rare earth tristropolonates but only at elevated temperatures and then at a low rate. Such solutions may contain discrete, solvated tristropolonates, but concentration or addition of water or alcohol yields the tris chelate lattice again, free of solvent. Neutral bidentate donor molecules do not complex the tristropolonate of europium.

We believe that the characteristics of the intractable rare earth tristropolonates, within the purview of rare earth acetylacetonate chemistry, is explicable only with the assumption that the tropolonate lattices are not based on discrete six-coordinate chelates. We suggest that there is a sharing of some of the chelate oxygen atoms between metal atoms (three-coordinate oxygen atoms) so that the coordination of these metal atoms exceeds six. There is precedent for such behavior in β-diketone chelate chemistry. The nickel and cobalt bisacetylacetonates[10] are trimeric and tetrameric, respectively, through oxygen atom sharing of polyhedra. Interestingly, the infrared spectra of the rare earth tristropolonates are unique in the 1600–1500-cm.$^{-1}$ region. There is a weak, sharp band at $\sim$1590 cm.$^{-1}$ that is not present in FeT_3, CrT_3, AlT_3, GaT_3, etc. We do not attempt to assign this weak band other than to ascribe it primarily to a carbon atom movement which we believe to be characteristic of "polymeric" metal tropolonates. This weak band is also found in the intractable[11] cobalt and nickel bistropolonates but not in the tractable and monomeric beryllium and copper bistropolonates.

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[7] (a) E. L. Muetterties, *Inorg. Chem.*, **4**, 769 (1965); E. L. Muetterties, *J. Pure Appl. Chem.*, **10**, 53 (1965). (b) Isolation of a *crystalline d* or *l* configuration of an eight-coordinate D_2 structure is in principle possible; however, the optical characterization must be restricted to experiments on the solid since racemization should proceed almost instantaneously on dissolution of the crystals.

[8] A probable model for seven-coordination here is the C_{2v} distorted trigonal prism (NbF_7^{2-}–TaF_7^{2-} structure). Alternatives include the pentagonal bipyramid ($UO_2F_5^{3-}$) and a C_3 model from the La_2O_3 structure.

[9] L. R. Melby, N. J. Rose, E. Abramson, and J. C. Caris, *J. Am. Chem. Soc.*, **86**, 5117 (1964); H. Bauer, J. Blanc, and D. L. Ross, *ibid.*, **86**, 5125 (1964).

[10] G. F. Bullen, R. Mason, and P. Pauling, *Nature*, **189**, 291 (1961); *Inorg. Chem.*, **4**, 456 (1965); F. A. Cotton and R. C. Elder, *J. Am. Chem. Soc.*, **86**, 2294 (1964).

[11] The cobalt and nickel compounds sublime at 310° (0.1 μ) compared to the copper and beryllium chelates, which sublime at 240° (0.1 μ) and 100° (0.1 μ), respectively.

The smaller rare earth ions behave in a different fashion. A crystalline phase slowly separates from aqueous solutions of tropolone and the nitrates of erbium, thulium, ytterbium, and lutetium. This phase is not the tristropolonate but the acid $H^+RT_4^-$. A similar behavior was observed for scandium and yttrium. The infrared spectra of these six acids are identical, and the solid lattices are isomorphous by X-ray powder diffraction criterion. The acid derivatives of erbium, thulium, ytterbium, and lutetium decompose at ~170° under vacuum with loss of tropolone and formation of the tristropolonates. These tristropolonates have a distinctly different lattice from those of the larger rare earth ions as judged by X-ray powder data, infrared spectra, and their greater tractability (they dissolve rapidly in dimethyl sulfoxide to give rather concentrated solutions). The tristropolonate of ytterbium was heated to 250° with no evidence of a thermal transition to the LaT_3 polymeric lattice. We have no data that bear definitively on the aggregation in this second type of lattice although there is a very weak, barely resolved infrared band at 1590 cm.$^{-1}$ suggestive of polymerization (*vide infra*). In any case, the lattice energy of the Er–Lu group tropolonates appears to be significantly lower than in the La–Ho group. This is evident in (1) the rapid dissolution in dimethyl sulfoxide, (2) facile reaction with $NH_4^+T^-$ to give $NH_4^+RT_4^-$ (EuT_3 and GdT_3 do not react with NH_4T), and (3) reaction with *o*-phenanthroline to give an eight-coordinate neutral complex.

A monohydrate of tristropolonatoerbium was obtained from a water–methanol mixture of erbium nitrate and tropolone. This solvate decomposes above 100° to give a tristropolonate lattice isomorphous with those of thulium, ytterbium, and lutetium.

There is evidence of polymorphism in the tristropolonates of thulium and lutetium. When these are prepared by pyrolysis of $NH_4^+TmT_4^-$ and $NH_4^+LuT_4^-$ at 170–200°, the solids, poorly crystalline by X-ray criterion, appear to be isomorphous with the "soluble" form of YT_3 described below.

Trivalent yttrium ion is comparable in size to dysprosium. If metal ion size rather than the f^x configuration is the critical factor in determining the stable lattice of this group of tristropolonates (empty d shell), then yttrium tristropolonate should be, and it is, isomorphous with the polymeric LaT_3 lattice. However, a poorly crystalline metastable phase also forms along with the polymeric phase in the aqueous preparation of this tristropolonate. This "soluble" phase undergoes a solid transition at ~180° to the polymeric phase.

Trivalent scandium ion is significantly smaller than any of the rare earth ions. The tristropolonate of this metal ion is soluble in chloroform and is isomorphous with FeT_3. Scandium is, however, capable of achieving eight-coordination as found in the ScT_4^- anion (*vide supra*).

The various lattice types based on X-ray powder data are listed in Table I. Groups F and G have similar diffraction patterns and are probably isomorphous. Groups A and B also display some similarities in their diffraction patterns but their infrared spectra are distinctly different. Within the lanthanide group, the stable tristropolonate lattice appears to be determined solely by the size of the metal ion. Size of the metal ion also gives rise to some variation of properties within an isomorphous group, *e.g.*, the most stable polymeric lattice is formed by the largest ion, lanthanum(III). The tristropolonate of lanthanum when formed from solution is colloidal and evinces no solubilization phenomena in contact with water–ethanol–acetonitrile mixture for 1 week. Moreover, this chelate is not reactive towards sodium tropolonate as are the other rare earth tristropolonates. However, lithium tropolonate does convert the lanthanum chelate to a solid phase approximating $LiLaT_4$. Cerium(III) tropolonate is more tractable and maximum solubility is found for HoT_3 and YT_3 among the chelates isomorphous with LaT_3.

Table I. Tristropolonate Lattices

Group	Compound	d^xf^x	M^{3+}, ionic radius, Å.	Lattice
A	YT_3, LaT_3	d^0, f^0	0.9, 1.06	Polymeric
	CeT_3–HoT_3	d^0, f^{1-10}	1.03–0.894	
B	ErT_3–LuT_3	f^{11-14}	0.88–0.84	Intermediate
C	YT_3, TmT_3, LuT_3	d^0, f^{12}, f^{14}	0.9–0.84	Soluble
D	$ErT_3 \cdot H_2O$	f^{11}	0.88	Soluble
E	ScT_3, FeT_3	d^0, d^5	0.68, 0.64	Molecular
	InT_3, TlT_3	d^{10}	0.81, 0.95	
F	AlT_3, GaT_8	d^0, d^{10}	0.50, 0.62	Molecular
G	CrT_3, RhT_3	d^3, d^6	0.69, 0.69	Molecular

Table II. Proton N.m.r. Data for Rare Earth Tristropolonates in $(CD_3)_2SO^a$

Compound	f^x	Ligand resonances,^{b} p.p.m.^{c}	$(CH_3)_2$-SO	H_2O
$YT_3{}^d$	f^0	$\beta = -7.1, \alpha = -6.6$	−2.3	−3.3
$LaT_3{}^d$	f^0	$\beta = -7.2, \alpha = -6.7$	−2.5	−3.3
CeT_3	f^1	−9.2 (2), −8.1 (1)	−2.2	−3.0
PrT_3	f^2	−10 (1), −11.7 (2), −13.3 (2)	−1.8	−2.2
NdT_3	f^3	−10.7 (2), −10.3 (2), −8.3 (1)	−2.0	−3.0
SmT_3	f^5	−40, −19, −17	−2.3	−3.0
EuT_3	f^6	−6.5, −4.3, −2.7	−1.8	−2.7
$GdT_3{}^e$	f^7	+3.3	...	...
TbT_3	f^8	−24 (3), −23 (2)	+5.3	+5.6
$DyT_3{}^e$	f^9	−58, −23, −20	+26	+29
HoT_3	f^{10}	−28(2), −7.8 (2), −6 (1)	+16	...
$ErT_3{}^e$	f^{11}	+25, +26, +31	+20	+18
TmT_3	f^{12}	+4.0	+6.3	...
YbT_3	f^{13}	+6.1, +15	+1.3	+1.1
$LuT_3{}^f$	f^{14}	$\beta = -7.15, \alpha = -6.8$		

[a] The deuterated solvent contained small, varying amounts of $(CH_3)_2SO$ and H_2O. [b] Relative intensities in parentheses. [c] Tetramethylsilane reference. [d] $J_{\alpha\beta}$ and $J_{\beta\gamma}$ = 10–11 c.p.s. [e] Saturates very readily. [f] $J_{\alpha\beta}$ and $J_{\beta\gamma} \cong 10$ c.p.s.

Proton n.m.r. data for the metal tristropolonates in $(CD_3)_2SO$ are presented in Table II. The paramagnetic rare earth species yielded broad resonances; there were relatively large pseudo-contact shifts, particularly in DyT_3. Comment on the chemical shifts is reserved until the questions of solvation phenomenon and geometry are resolved. The very large diamagnetic shifts for H_2O and $(CH_3)_2SO$ protons in the solutions of the tristropolonates of the smaller ions, Tb through Yb, suggest that solvation is significant in this series. There are relatively small paramagnetic solvent shifts in the cerium to europium series; these tristropolonates may still be appreciably associated in solution.

The tristropolonates of europium and terbium do not visibly fluoresce with excitation at 3660 and 2537 Å.

Stability of T_4Nb^+ and T_4Ta^+ in Solution. The hydrolytic stabilities of T_4Nb^+ and T_4Ta^+ differ rather significantly. The niobium cation is stable only in strongly acidic media. With increasing pH or increasing temperature, the niobium chelate undergoes partial hydrolysis to T_3NbO which separates from solution. This reaction is reversed by addition of concentrated hydrochloric acid. In basic solution, the niobium cation is rapidly and completely hydrolyzed; initial hydroxide attack is on the ligand not the metal atom (see paper II[1]).

$$H_2O + T_4Nb^+ \xrightarrow[\text{or pH} > 3]{\sim 60^\circ} T_3NbO + TH + H^+$$

In contrast to T_4Nb^+, the tantalum chelate cation is resistant to hydrolysis provided the pH is not appreciably above 7. The 60-Mc. proton spectrum of T_4Ta^+ is nearly constant over the temperature range of 20 to 140° for acidic aqueous solution and over the pH range of 1 to 7. However, because of the low sensitivity of n.m.r. measurements, these data do not exclude the possibility of minor hydrolysis (5% or less). Attempts to evaluate hydrolytic stability in acidic media through ultraviolet studies provided no definitive data because of the relatively low extinction coefficient of tropolone and the similarity in the position of the main absorption maxima of tropolone and of T_4Ta^+.

Like all other tropolone chelates, the tantalum derivative is completely degraded by aqueous base. In paper II,[1] it was shown from tracer studies that initial hydroxide ion attack does take place at the ligand, *i.e.*, the C–O carbon atom, but is not the major or predominating mechanism. Furthermore, the enrichment of tropolone in O^{18} in the $O^{18}H^-$ hydrolysis varied for the various T_4Ta^+ salts. Since then we have reconfirmed these findings and have examined other anions. Summarily, the tracer hydrolysis results are as follows.

Salt	% O^{18} enrichment
$T_4Ta^+Cl^-$	3
$T_4Ta^+ClO_4^-$	5
$T_4Ta^+PF_6^-$	6
$(T_4Ta^+)_2B_{12}Cl_{12}^{2-}$	10.5

The enrichment figures are to be compared with a 25% theoretical value if initial attack at a ligand position is the sole hydrolysis mechanism. In the earlier paper,[1] it was suggested that the variation in observed enrichment with associated anion reflected the varying degrees of ion pairing. If this thesis is correct, there should be a dependence of enrichment on the dielectric constant of the hydrolysis medium. We have found such a correlation. The % O^{18} enrichment in the tropolone from $T_4Ta^+Cl^-$ hydrolysis is ~0, 3, and 11.6 from water–methanol solutions with water mole percentages of 20, 53, and 100, respectively. These data support but do not define ion-pair formation as an inhibiting factor[12] in ligand attack of T_4Ta^+ by hydroxide ion *in concentrated solutions.*

In many eight-coordinate metal chelates, the ligands are highly labile. For example, Adams and Larsen[13] established by n.m.r. that there is rapid ligand exchange between tetrakis β-diketone complexes of zirconium(IV). In contrast, we found no evidence from n.m.r. spectra of ligand exchange between tropolone and T_4Ta^+ in water, alcohol, and acetonitrile media at temperatures up to 140°. The lifetime of the ligands in T_4Ta^+ under these conditions is at least the order of magnitude of 1 msec. However, the ligands in T_4Ta^+ are labile. Ligand exchange between T_4Ta^+ and tropolone (O^{18} labeled) is essentially complete (94%) within 0.5 hr. in aqueous solution at a pH of ~2. The exchange may occur by a reversible hydrolysis process or ligand dissociation. If reversible hydrolysis were the origin of the ligand exchange, it might be expected that ligand attack by OH^- or OH_2 would still be operative as is the case for T_3Si^+ (paper II[1]). This would require O^{18} exchange between the tropolone in T_4Ta^+ and H_2O^{18}, but no exchange was observed in 48 hr. However, the experiment is nondefinitive with respect to ligand-exchange mechanism because, in acidic media, hydrolysis *by the ligand attack mechanism* could be severely depressed. More substantive observations on ligand-exchange mechanisms are described in the following paragraph.

Fast ligand exchange between T_4Ta^+ and labeled tropolone was also observed in nonaqueous media. Exchange is about 71% complete in ethanol and 45% in acetonitrile within 0.5 hr. for much less concentrated solutions than those employed for the aqueous exchange. Experimental conditions here preclude a hydrolysis mechanism. The similarity of exchange rates with those in water suggest a common mechanism may be operative. A dissociative process[14] is not too appealing in the light of these experiments. If a highly polar intermediate or transition state implicit in a dissociative process were involved, then rates should have been drastically lowered in the nonaqueous media. A mechanism consistent with fast ligand exchange in these various solvents and with the tendency of T_4Ta^+ salts to ion pair in concentrated solution is

$$^{18}TH \overset{\text{solvent}}{\rightleftharpoons} H\cdot\text{solvent}^+ + {}^{18}T^-$$

$$^{18}T^- + T_4Ta^+ \rightleftharpoons [T_4Ta^{18}T] \rightleftharpoons T_3{}^{18}TTa^+ + T^-$$

Detailed kinetic data are required before a distinction can be made among the various possible mechanisms.

General Comments. With the main group elements, the tropolone ion yields chelates in which the central atom apparently attains coordination numbers of seven and eight at the fourth period, *i.e.*, indium and tin (d^{10} configuration). For the subgroup elements, a tendency toward eight- or seven-coordination appears earlier, at the third period as with scandium, ScT_4^-, and titanium, TiT_3Cl (d^0 configuration). In the fourth and fifth periods of subgroup III, the tristropolonates

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[12] Crudely, it may be considered that ion-pair formation reduces the *formal* charge of the cation; and, as established earlier,[1] *formal* charge is the critical factor in hydroxide ion attack at a ligand position.

[13] A. C. Adams and E. M. Larsen, *J. Am. Chem. Soc.*, **85**, 3508 (1963).

[14] The proton n.m.r. spectrum of a solution of T_4Ta^+ and $(i\text{-}C_3H_7\text{-}C_7H_4O_2)Ta^+$ did not change over a time period of 1 week beginning 15 sec. after mixing solutions of the two chelate cations. This suggests that no ligand dissociation followed by exchange took place, but the experiment is not definitive because there may be no significant change in chemical shifts for a mixed chelate cation. Efforts to characterize a mixed chelate were unsuccessful.

do not appear to be discrete, and the solid-state properties seem explicable only on the basis of a polymeric lattice with seven- or eight-coordinate metal atoms (Y, La, and some of the rare earths). This is in distinct contrast to the molecular tristropolonates of rhodium, indium, and thallium. Thus, the results with tropolone ligand clearly display the trend,[15] found with other ligands, that high coordination structures are more readily achieved with central atoms of electronic configuration of d^0 than with those of d^{10}.

The scandium chelate, ScT_4^-, appears to have the lightest eight-coordinate atom reported to date for a molecular entity. Its neighbor, titanium, has been reported to yield an eight-coordinate complex with a bisarsine ligand.[16]

Experimental Section

Preparation of $NaYT_4$ and $NaScT_4$. A slurry of YT_3 (0.001 mole) and NaT (0.0011 mole) in 50 ml. of acetonitrile, 50 ml. of water, and 30 ml. of methanol was heated to reflux for 15 hr. The slurry was filtered while hot, and the solid was washed with a hot mixture of methanol and water, m.p. >400°. *Anal.* Calcd. for $NaY(O_2C_7H_5)_4$: Na, 3.84; Y, 14.9; C, 56.4; H, 3.36. Found: Na, 3.60; Y, 14.9; C, 56.4; H, 3.53.

The scandium and rare earth tetrakistropolonates were prepared in a similar fashion and vacuum dried at 100–150°. None of these compounds melted below 400°. The analytical data are summarized in Table III.

Table III. Analytical Data for the Sodium Salts of Tetrakistropolonometallates

	Calcd., %			Found, %		
	C	H	M	C	H	M
$NaScT_4$[a]	60.9	3.63	Sc 8.15	60.9	3.71	Sc 8.14
$NaCeT_4$[a]	51.9	3.12	Ce 21.7	52.0	3.22	Ce 20.1
$NaPrT_4$	51.8	3.11	Pr 21.7	51.7	3.03	Pr 22.2
$NaNdT_4$	51.6	3.10	Nd 22.2	51.5	2.90	Nd 22.3
$NaSmT_4$	51.2	3.07	Sm 22.9	51.3	3.09	Sm 23.1
$NaEuT_4$[a]	51.0	3.06	Eu 23.0	51.6	3.02	Eu 23.6
$NaGdT_4$	50.6	3.04	Gd 23.6	50.4	3.03	Gd 23.8
$NaTbT_4$	50.4	3.02	Tb 23.9	50.9	2.98	Tb 23.9
$NaDyT_4$	50.3	3.01	Dy 24.3	50.4	3.02	Dy 24.1
$NaHoT_4$	50.0	3.00	Ho 24.5	50.1	3.02	Ho 24.8
$NaErT_4$	49.9	2.99	Er 24.8	49.9	2.95	Er 24.6
$NaTmT_4$	49.7	2.98	Tm 25.1	50.3	3.51	Tm 25.2
$NaYbT_4$	49.4	2.96	Yb 25.4	49.5	2.95	Yb 25.6
$NaLuT_4$	49.3	2.95	Lu 25.7	49.7	3.16	Lu 25.7

[a] Sodium calculated and found for $NaScT_4$: 4.16 and 3.90; for $NaEuT_4$: 3.49 and 3.19; for $NaCeT_4$: 3.55 and 3.55.

Synthesis of $LiLaT_4$ and $LiCeT_4$. The tristropolonate of lanthanum (1 g., 0.002 mole) was added to a solution of lithium tropolonate (0.64 g., 0.005 mole) in 75 ml. of water, 75 ml. of ethanol, and 75 ml. of acetonitrile. The slurry was heated to 70° for 2 days, then filtered, and the solid was thoroughly washed. The infrared spectrum of the solid had some similarities to that of the starting tristropolonate. *Anal.* Calcd. for $LiLa(O_2C_7H_5)_4$: Li, 1.09; La, 22.1; C, 53.4; H, 3.19. Found: Li, 0.77; La, 23.8; C, 52.7; H, 3.41. Under similar conditions there was no reaction between the tristropolonate of lanthanum and sodium tropolonate within a period of 1 week at 80°.

The lithium salt of the tetrakistropolonocerium anion was prepared in an analogous fashion. *Anal.* Calcd. for $LiCe(O_2C_7O_5)_4$: Li, 1.10; Ce, 22.1; C, 53.2; H, 3.17. Found: Li, 1.02; Ce, 24.3; C, 53.4; H, 3.24. The infrared spectrum of this salt was strikingly similar to that of $Ce(O_2C_7H_5)_4$.

Preparation of $H^+RT_4^-$. Aqueous solutions of the nitrates of scandium, yttrium, thulium, and ytterbium and lutetium (0.005 mole) were mixed with ethanolic tropolone (0.02 mole). The solutions were warmed to about 40°, whereupon solids separated. These solids were collected, washed with ethanol and water, and vacuum dried at 70°. *Anal.* Calcd. for $HSc(O_2C_7H_5)_4$: Sc, 8.50; C, 63.4; H, 3.96. Found: Sc, 7.77; C, 62.6; H, 4.02. Calcd. for $HY(O_2C_7H_5)_4$: Y, 15.5; C, 58.5; H, 3.67. Found: Y, 15.2; C, 58.5; H, 3.78. Calcd. for $HTm(O_2C_7H_5)_4$: Tm, 25.9; C, 51.4; H, 3.22. Found: Tm, 26.1; C, 51.1; H, 3.26. Calcd. for $HYb(O_2C_7H_5)_4$: Yb, 26.3; C, 51.0; H, 3.29. Found: Yb, 26.4; C, 51.4; H, 3.27. Calcd. for $HLu(O_2C_7H_5)_4$: Lu, 26.5; C, 50.8; H, 3.20. Found: Lu, 25.9; C, 50.5; H, 3.29. All these complexes are isomorphous by X-ray powder diffraction criterion. These derivatives are not very soluble in aqueous media. Saturated water–acetonitrile solutions have a pH between 4 and 5. The thulium, ytterbium, and lutetium derivatives are stable to 150° *in vacuo*. Above this temperature they lose tropolone to yield the tristropolonates.

Under similar conditions, the lanthanum through holmium group yield the polymeric tristropolonates.

Synthesis of $NH_4^+RT_4^-$. Tropolone (0.04 mole) was dissolved in 50 ml. of ethanol and 100 ml. of water, and about 10 ml. of concentrated ammonium hydroxide was added. The slurry was warmed until all of the solids dissolved and then a solution of a rare earth nitrate (0.01 mole) in 100 ml. of water was added to the basic tropolone solution. Solids separated immediately on the mixing of the two solutions. The slurry was heated to 70° for a period of 2 hr. The solid was collected, washed with water and ethanol, and then vacuum dried at 70°. *Anal.* Calcd. for $NH_4Tm(O_2C_7H_5)_4$: C, 50.1; H, 3.60. Found: C, 49.4; H, 3.61. Calcd. for $NH_4Lu(O_2C_7H_5)_4$: C, 49.6; H, 3.54. Found: C, 49.1; H, 3.80. Calcd. for $NH_4Eu(O_2C_7H_5)_4$: N, 2.14; Eu, 23.2; C, 51.4; H, 3.70. Found: N, 1.70; Eu, 24.3; C, 50.8; H, 3.78. Lanthanum nitrate under these conditions gave only the tristropolonate, LaT_3.

The tristropolonates of several rare earths were heated to 70° in contact with a solution of ammonium tropolonate in a water–methanol mixture. In a period of 2 hr., the tristropolonates of ytterbium, holmium, and dysprosium reacted to give the ammonium salt of the respective tetrakis chelate anions. Under the same conditions, tristropolonates of europium, gadolinium, and terbium were unreactive. *Anal.* Calcd. for $NH_4Yb(O_2C_7H_5)_4$: N, 2.08; Yb, 25.6; C, 49.7; H, 3.56. Found: N, 2.00; Yb, 25.4; C, 48.7; H, 3.57. Calcd. for $NH_4Ho(O_2C_7H_5)_4$: N, 2.10; Ho, 24.7; C, 50.4; H, 3.61. Found: N, 2.06; Ho,

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(15) R. J. H. Clark, D. L. Keppert, and R. S. Nyholm, *Nature*, **199**, 559 (1963).

(16) R. J. H. Clark, J. Lewis, R. S. Nyholm, P. Pauling, and G. B. Robertson, *ibid.*, **192**, 222 (1961).

24.6; C, 49.6; H, 3.61. Calcd. for $NH_4Dy(O_2C_7H_5)_4$: N, 2.11; Dy, 24.6; C, 50.5; H, 3.62. Found: N, 1.70; Dy, 24.6; C, 49.5; H, 3.75. All these RT_4^- salts are isomorphous by X-ray powder diffraction. The ammonium salts are stable *in vacuo* to about 150°. Above this temperature, ammonium tropolonate volatilizes to leave a residue of the tristropolonate.

Preparation of ZrT_4. A slurry of zirconium tetrachloride (0.01 mole) in 150 ml. of chloroform was added to a solution of tropolone (0.045 mole) in 75 ml. of chloroform. Most of the zirconium tetrachloride went into solution. About 100 ml. of chloroform was added to the reaction mixture which was then filtered. The filtrate was refluxed for 15 min. and then about 40% of the solvent was removed under reduced pressure to give a slurry. The slurry was filtered to give a tan solid, which was recrystallized from hot chloroform. *Anal.* Calcd. for $Zr(O_2C_7H_5)_4 \cdot 1.5CHCl_3$: Zr, 12.2; C, 46.2. Found: Zr, 12.6; C, 45.8. The solvated complex was suspended in refluxing methanol for 1 hr., recovered by filtration, and then vacuum dried at 150° for 4 hr. *Anal.* Calcd. for $Zr(O_2C_7H_5)_4$: Zr, 15.9; C, 58.3; H, 3.50. Found: Zr, 15.8; C, 58.3; H, 3.59.

Preparation of ThT_4 and HfT_4. A slurry of thorium tetrachloride (0.01 mole) in 100 ml. of chloroform was added to a solution of tropolone (0.04 mole) in 100 ml. of chloroform. The reaction mixture was stirred for 10 min. and 200 ml. of acetonitrile was added. Then the reaction mixture was heated at strong reflux to remove chloroform and about 30 ml. of methanol and 30 ml. of acetonitrile were added. The mixture was filtered while hot. Only a small amount of solid (0.68 g.) was removed in the filtration step. The filtrate was concentrated to give a tan solid (2.06 g.) which was recrystallized from chloroform and vacuum dried at 150° for 3 hr., m.p. >400°. *Anal.* Calcd. for $Th(O_2C_7H_5)_4$: Th, 32.4; C, 46.9; H, 2.82. Found: Th, 32.3; C, 47.2; H, 2.94.

A slurry of hafnium tetrachloride (0.01 mole) in 300 ml. of chloroform was added to a solution of tropolone (0.042 mole) in 300 ml. of chloroform. Essentially everything went into solution. About 30 ml. of methanol was added, and the solution was heated to reflux and filtered hot. The filtrate was partially evaporated under reduced pressure and filtered to give a tan solid (5.27 g.) which was recrystallized from hot chloroform and vacuum dried at 150°, m.p. >400°. *Anal.* Calcd. for $Hf(O_2C_7H_5)_4$: Hf, 26.9; C, 50.7; H, 3.04. Found: Hf, 27.0; C, 50.9; H, 3.15.

Preparation of CeT_4. A solution of $(NH_4)_2Ce(SO_4)_4 \cdot 2H_2O$ (0.01 mole) in a minimum of $\sim$5% H_2SO_4 was added to a solution of 0.04 mole of tropolone in a mixture of 60 ml. of methanol, 80 ml. of water, and 1 ml. of concentrated sulfuric acid. A copious brick red precipitate appeared immediately. The reaction mixture was stirred for 15 min. and then filtered. The solid was recrystallized from dichloromethane and then vacuum dried at 40°. The product was a black crystalline material that did not melt below 400°. *Anal.* Calcd. for $Ce(O_2C_7H_5)_4$: Ce, 22.4; C, 53.9; H, 3.23. Found: Ce, 22.3; C, 53.9; H, 3.34.

Preparation of SnT_4. A solution of 1 ml. of tin tetrachloride in 100 ml. of methanol was added to a slurry of sodium tropolonate (8 g., 55.6 mmoles) in 100 ml. of methanol. Then, 200 ml. of acetonitrile was added, and the reaction mixture was refluxed for 2 days. The slurry was filtered while hot, and the solid was recrystallized from hot acetonitrile, m.p. 354–356°. *Anal.* Calcd. for $Sn(O_2C_7H_5)_4$: C, 55.8; H, 3.32; Cl, 0.00; Na, 0.00. Found: C, 54.6; H, 3.53; Cl, 0.00; Na, 0.00. An attempt was made to sublime this compound at 280° (0.01 μ). The sublimate appeared to be a mixture of compounds. It melted partially at 307–308° and then completely at 345°. *Anal.* Calcd. for $[(C_7H_5O_2)_3Sn]_2O$: C, 51.5. Found: C, 51.5.

Preparation of T_3SnOH. A slurry of sodium tropolonate (5.76 g., 0.04 mole) in 400 ml. of acetonitrile was added to a solution of tin tetrachloride (2.60 g., 0.01 mole) in about 150 ml. of acetonitrile. The slurry was stirred, heated to reflux, and then water was added until nearly all the solids were in solution. The reaction mixture was filtered, and a concentrated solution of sodium iodide was added. The solution was then partially concentrated by evaporation at reduced pressure. The slurry was filtered and the solid was recrystallized from hot 95% ethanol, m.p. 365–366°. *Anal.* Calcd. for $(C_7H_5O_2)_3SnOH$: C, 50.6; H, 3.21; Sn, 23.8; Cl, 0.00. Found: C, 50.5; H, 3.32; Sn, 23.2; Cl, 0.00.

Preparation of $T_4Nb^+Cl^-$. A solution of niobium pentachloride (0.01 mole) in a mixture of 200 ml. of dichloromethane and 30 ml. of ether was added to a solution of tropolone (0.04 mole) in 200 ml. of dichloromethane to give an orange solution from which solid slowly separated. The solvent was evaporated under reduced pressure, and then 400 ml. of acetonitrile was added to the residue. This was heated until solution was complete. On cooling, bright orange crystals (4.5 g.) separated. The solid was recrystallized from hot acetonitrile and vacuum dried at 120° for 3 hr., m.p. 302–305°. *Anal.* Calcd. for $(C_7H_5O_2)_4Nb^+Cl^-$: Nb, 15.2; C, 54.9; H, 3.29; Cl, 5.80. Found: Nb, 15.2; C, 54.5; H, 3.78; Cl, 6.66. A sample of $T_4Nb^+Cl^-$ was dissolved in acetonitrile–water mixture and quickly filtered. A concentrated aqueous solution of ammonium hexafluorophosphate was added to give a precipitate. The infrared spectrum of the precipitate contained all of the absorption bands found in $T_4Ta^+PF_6^-$ and in addition had absorptions which were identified as those arising from T_3NbO. In a second experiment the $T_4Nb^+Cl^-$ was dissolved in an acetonitrile–water–methanol mixture to give an orange solution. This solution slowly became cloudy and turned yellow, and a large amount of yellow solid ultimately separated. The infrared spectrum of the solid was identical with that of authentic T_3NbO.

Chemistry of $T_4Nb^+Cl^-$. A sample of $T_4Nb^+Cl^-$ was dissolved in a minimum of water and then warmed gently on a steam bath. Yellow solids immediately began to precipitate. These were collected and identified as T_3NbO by comparison of the infrared spectrum with that of an authentic sample. This oxy derivative was then slurried in water, and tropolone and concentrated hydrochloric acid were added. On warming an orange solution was obtained, and on concentration this gave orange crystals of $T_4Nb^+Cl^-$ which was identified by its infrared spectrum and conversion to the hexafluorophosphate salt.

Preparation of $T_4Ta^+Cl^-$. A solution of tantalum pentachloride (0.04 mole) in 40 ml. of concentrated hydrochloric acid and 40 ml. of methanol was added to a solution of tropolone (0.20 mole) in 20 ml. of concentrated hydrochloric acid and 320 ml. of methanol. A yellow precipitate formed during the addition. The slurry was heated to reflux for about 15 min. until a clear yellow solution was obtained. This solution on cooling yielded 27 g. of yellow crystalline $T_4Ta^+Cl^-$ (yield 96.3%). The compound was recrystallized from a hot water–methanol mixture and vacuum dried, m.p. 326.5–328°. *Anal.* Calcd. for $(C_7H_5O_2)_4Ta^+Cl^-$: C, 48.0; H, 2.85; Ta, 25.8; Cl, 5.06. Found: C, 47.2; H, 3.19; Ta, 25.7; Cl, 5.15. The chloride is hygroscopic.

Other salts of T_4Ta^+ were prepared by metathesis in water–methanol solutions. These salts were recrystallized from water–methanol or water–methanol–acetonitrile mixtures and vacuum dried. *Anal.* Calcd. for $[(C_7H_5O_2)_4Ta^+]_2B_{10}H_{10}{}^{2-}$: C, 46.4; H, 3.46; Ta, 25.0; B, 7.48. Found: C, 46.4; H, 3.89; Ta, 24.9; B, 7.57; m.p. >400°. Calcd. for $(C_7H_5O_2)_4Ta^+PF_6^-$: C, 41.5; H, 2.48; Ta, 22.3; F, 14.1. Found: C, 41.5; H, 2.85; Ta, 23.2; F, 13.6; m.p. 268–286° dec. Calcd. for $(C_7H_5O_2)_4Ta^+I^-$: C, 42.4; H, 2.53; Ta, 22.8; I, 16.0. Found: C, 42.4; H, 2.67; Ta, 22.7; I, 15.0; m.p. 365–375° dec. Ultraviolet data are given in Table IV.

Table IV. Ultraviolet Absorption for T_4Ta^+ Salts

λ_{max}, Å.	ϵ_{T_4TaCl}	$\epsilon_{T_4TaPF_6}$
	Water	
3580	21,600	21,100
3190	35,800	39,300
2410	101,000	109,000
	Methanol	
3580	18,800	20,300
3250	42,700	48,200
2380	95,100	105,000
	Acetonitrile	
4000	15,000	17,300
3490	55,400	63,200
2370	109,000	128,000
	Dimethyl Sulfoxide	
4050	17,700	13,800
3570	63,400	54,300

Synthesis of $(C_{10}H_{11}O_2)_4Ta^+$ *Salts*. A solution of γ-isopropyltropolone (6.56 g., 0.04 mole) in a warm (approximately 50°) 50:50 mixture of ethanol and methanol was added to a solution of tantalum pentachloride (3.58 g., 0.01 mole) in 12 ml. of concentrated hydrochloric acid and 10 ml. of methanol. Water was then added to the yellow reaction solution to the point of incipient precipitation. The solution was then partially concentrated by evaporation to give a yellow slurry. The solid was collected by filtration and recrystallized from a water–methanol mixture and then vacuum dried at 90°, m.p. 245° dec. *Anal.* Calcd. for $(C_{10}H_{11}O_2)_4Ta^+Cl^-$: C, 55.2; H, 5.10; Ta, 20.8; Cl, 4.08. Found: C, 55.0; H, 5.17; Ta, 20.4; Cl, 4.59. Other salts were made by metatheses in aqueous methanol and were recrystallized from hot water–methanol–acetonitrile mixtures. *Anal.* Calcd. for $(C_{10}H_{11}O_2)_4Ta^+PF_6^-$: C, 49.1; H, 4.57; F, 11.7. Found: C, 49.2; H, 4.89; F, 11.5, m.p. 258–264°. Calcd. for $[(C_{10}H_{11}O_2)_4Ta^+]_2B_{12}Cl_{12}{}^{2-}$: C, 43.3; H, 4.00; Cl, 19.2. Found: C, 44.0; H, 4.64; Cl, 18.2, m.p. 350° dec.

Reaction of Antimony Pentachloride and Tropolone in Aqueous Media. A solution of 1 ml. of antimony pentachloride in 3 ml. of concentrated hydrochloric acid was added to a solution of 0.005 mole of tropolone in 70 ml. of methanol to give a yellow-orange solution. Then solid sodium tropolonate was added directly to the solution until a very deep red solution was obtained. This was filtered, and to the filtrate was added a concentrated aqueous solution of $(H_3O)_2B_{12}Cl_{12}\cdot 2H_2O$ to give an orange precipitate. The precipitate was recrystallized from a hot water–acetonitrile mixture. The recrystallized product had an infrared spectrum essentially identical with that of $(T_4Ta^+)_2B_{12}Cl_{12}{}^{2-}$. *Anal.* Calcd. for $[(C_7H_5O_2)_4Sb^+]_2B_{12}Cl_{12}{}^{2-}$: C, 38.0; H, 2.27; Sb, 13.8; Cl, 24.1; B, 7.38. Found: C, 33–36; H, 2.4–2.7; Sb, 12–17; Cl (ionic), 0; Cl (total), 24.0–24.5; B, 7.8–8.1. The range in the analytical values represent data obtained from eight different samples.

Preparation of T_3NbO. Niobium pentachloride (0.01 mole) was dissolved in 10 ml. of concentrated hydrochloric acid and 10 ml. of methanol. This was added to a solution of tropolone (0.05 mole) in 5 ml. of concentrated hydrochloric acid and 80 ml. of methanol. Approximately 50 ml. of water was added and the reaction mixture was heated, whereupon solids began to separate. The reaction mixture was held at reflux for 15 min. and then cooled. The solid was collected by filtration (4.53 g.) and recrystallized from a hot acetonitrile–water mixture to give an orange-yellow solid that became tan colored after vacuum drying, m.p. 368–371.5° dec. *Anal.* Calcd. for $(C_7H_5O_2)_3NbO$: C, 53.5; H, 3.18; Nb, 19.7. Found: C, 53.6; H, 3.47; Nb, 19.6; Cl, 0.41.

Preparation of T_2VOCl. To a solution of tropolone (4.88 g., 0.04 mole) in 200 ml. of toluene was added $VOCl_3$ (1.73 g., 0.01 mole). Then, 100 ml. of acetonitrile was added, and the reaction mixture was heated to 80° for 15 min. The hot reaction mixture was filtered to give a deep blue solid which was recrystallized from dichloromethane. *Anal.* Calcd. for $(C_7H_5O_2)_2VOCl$: C, 48.8; H, 2.90; V, 14.8. Found: C, 49.0; H, 3.01; V, 15.1.

Preparation of T_3VO. A slurry of T_2ClVO (0.01 mole, 3.44 g.) in 320 ml. of acetonitrile containing tropolone (0.01 mole, 1.22 g.) and sodium tropolonate (0.01 mole, 1.44 g.) was heated to reflux for 2 hr. and filtered while hot. The filtrate was evaporated, and the solid was dissolved in a chloroform–acetonitrile–methanol mixture. The solution was concentrated and then filtered. The solid was recrystallized from hot chloroform and vacuum dried, m.p. 342–345°. *Anal.* Calcd. for $(C_7H_5O_2)_3VO$: C, 58.7; H, 3.53; V, 11.8. Found: C, 57.5; H, 2.99; V, 11.9. This compound was contaminated with either T_2ClVO or chloroform because it contained about 1% chlorine.

Preparation of T_2MoOCl. Molybdenum pentachloride (5 g., 0.0183 mole) was dissolved in 30 ml. of concentrated hydrochloric acid. Tropolone was added to this solution until addition no longer yielded a brown precipitate. The reaction slurry was filtered; the solid was collected, washed, recrystallized from acetonitrile, and vacuum dried, m.p. 365–367° dec. *Anal.* Calcd. for $(C_7H_5O_2)_2MoOCl$: C, 43.2; H, 2.57; Mo, 24.6; Cl, 9.10. Found: C, 43.5; H, 2.77; Mo, 25.0; Cl, 8.07.

Preparation of CeT_3 and TbT_3. A solution of cerous nitrate (0.01 mole) in 100 ml. of 95% ethanol was added to a solution of tropolone (3.9 g., 0.032 mole) in 150 ml. of ethanol to give a clear solution. The solution was warmed to about 50°. After about 5 min., solid began to separate. The heating was continued for another 25 min. and then the slurry was filtered. The light orange solid was washed with ethanol and vacuum dried at 150°. *Anal.* Calcd. for $Ce(O_2C_7H_5)_3$: Ce, 27.8; C, 50.1; H, 2.98. Found: Ce, 27.7; C, 49.7; H, 2.82.

A similar procedure was followed with the other rare earth nitrates, except those of erbium through lutetium. The latter were prepared by vacuum pyrolysis of the ammonium salts of the respective tetrakistropolonate anions at 200°. The tristropolonates of holmium, erbium, thulium, ytterbium, and lutetium melt and decompose at about 390–395°. The other tristropolonates do not melt below 400°. The analytical data are summarized in Table V. Data for EuT_3 and LaT_3 are presented in paper I of this series.

Table V. Analytical Data for the Rare Earth Tristropolonates

	Calcd., %		Found, %	
	C	H	C	H
PrT_3	50.0	3.00	50.2	2.77
NdT_3	49.7	2.98	50.2	2.87
SmT_3	49.2	2.96	49.6	2.93
GdT_3	48.5	2.91	49.1	2.88
TbT_3	48.3	2.87	48.1	2.61
DyT_4	48.1	2.88	48.3	2.84
HoT_3	47.8	2.86	47.9	2.78
EtT_3	47.6	2.85	48.3	2.80
TmT_3	47.3	2.84	47.6	3.00
LuT_3	46.9	2.81	46.3	2.95
YbT_3	47.1	2.82	47.2	2.79

Synthesis of $ErT_3 \cdot H_2O$ and $H^+ErT_4^-$. Erbium nitrate hexahydrate (1 g., 0.0022 mole) was dissolved in 30 ml. of water and 10 ml. of methanol. To this was added a solution of tropolone (1 g., 0.0082 mole) in 5 ml. of methanol. A crystalline solid slowly separated from solution. The solid was collected and vacuum dried at 70°. *Anal.* Calcd. for $Er(O_2C_7H_5)_3 \cdot H_2O$: Er, 30.5; C, 46.0; H, 3.13. Found: Er, 30.4; C, 45.9; H, 3.24. The hydrate was vacuum dried at 150° for 2 hr. to give the anhydrous tristropolonate lattice.

When the methanol content of the nitrate solution was reduced to 5 ml., the crystalline phase that separated from solution was $H^+ErT_4^-$. *Anal.* Calcd. for $H^+Er(O_2C_7H_5)_4^-$: C, 51.6; H, 3.24. Found: C, 51.7; H, 3.40.

Preparation of the Phenanthroline Complex of TmT_3. A slurry of tristropolonate of thulium (0.532 g., 0.001 mole) in a solution of 1,10-phenanthroline (0.02 g., 0.0011 mole) in 250 ml. of a 50:50 mixture of ethanol and acetonitrile was heated to 70° for 6 hr. The slurry was filtered; the solid was washed with acetonitrile and ethanol and vacuum dried at 100°, m.p. 375–380° dec. *Anal.* Calcd. for $Tm(O_2C_7H_5)_3 \cdot C_{12}H_8N_2$: Tm, 23.8; C, 55.6; H, 3.25; N, 3.94. Found: Tm, 23.7; C, 55.2; H, 3.36; N, 3.92.

Under the same conditions the tristropolonate of europium underwent no reaction in a period of 2 days.

Preparation of YT_3. A solution of yttrium chloride hexahydrate (2.0 g., 0.0066 mole) in 70 ml. of methanol and 30 ml. of water was added to tropolone (5.6 g., 0.046 mole) in about 50 ml. of ethanol. The solution was warmed on a steam bath for 1 hr. during which time a solid separated. The yellow solid was collected, and an attempt was made to recrystallize it from a hot mixture of acetonitrile, ethanol, and chloroform. The insoluble fraction from the recrystallization attempt had an infrared spectrum identical with those of the other rare earth tristropolonates. The yellow solid, vacuum dried at 80°, melted with decomposition at 275–277°. *Anal.* Calcd. for $Y(O_2C_7H_5)_3$: Y, 19.6; C, 55.7; H, 3.32. Found: Y, 19.5; C, 56.2; H, 3.30. The pale yellow solution obtained from the recrystallization attempt was concentrated and a yellow solid was obtained and vacuum dried at 80°, m.p. 276–278° dec. The infrared spectrum of this solid was similar to but not identical with that of the insoluble fraction. *Anal.* Found: Y, 19.2; C, 55.7; H, 3.28. An X-ray powder pattern of this material showed that the sample was poorly crystalline. On thermal treatment *in vacuo* there was no change in the infrared spectrum until the temperature exceeded 160°. After 12 hr. at 196°, the solid had an infrared spectrum identical with that of the insoluble tristropolonate described above.

Preparation of ScT_3. Scandium nitrate hexahydrate (1.36 g., 0.004 mole) was dissolved in 60 ml. of water and added to a solution of tropolone (0.015 mole) in methanol to give a yellow solution. On standing yellow crystals of $H^+ScT_4^-$ slowly separated. After 2 hr., the slurry was filtered. The solid was dissolved in a hot methanol–chloroform mixture. On concentration of the solution, a solid separated. This was collected and vacuum dried at 80°, m.p. 365–375°. *Anal.* Calcd. for $Sc(O_2C_7H_5)_3$: Sc, 11.1; C, 61.7; H, 3.68. Found: Sc, 10.5; C, 60.6; H, 3.98.

Preparation of RhT_3. Tropolone (4 g., 0.0328 mole) was added to a solution of sodium acetate trihydrate (3 g., 0.022 mole) and Rh(III) chloride trihydrate (1.32 g., 0.0049 mole) in 100 ml. of water. The reaction slurry was warmed on a steam bath for 2 hr. and then filtered while hot. The orange solid was recrystallized from hot chloroform and then vacuum dried at 80° for 3 hr., m.p. 372–375° dec. *Anal.* Calcd. for $Rh(O_2C_7H_5)_3$: C, 54.1; H, 3.24. Found: C, 53.9; H, 3.14. The proton n.m.r. spectrum of this compound in deuteriochloroform indicated the presence of a small amount of chloroform. The X-ray powder pattern of this compound showed it to be isomorphous with InT_3.

Preparation of TiT_3. All the operations described below were effected in a nitrogen atmosphere.

Titanium trichloride (2.6 g., 0.016 mole) was dissolved in 100 ml. of methanol and 100 ml. of water which contained 15 ml. of concentrated hydrochloric acid. To this solution was added 7 g. of tropolone. A green precipitate appeared immediately. The slurry was stirred for 0.5 hr. and then was pressure filtered. The green solid was washed several times with a water–methanol mixture which contained hydrochloric acid; then the solid was vacuum dried, m.p. 315–320° dec. *Anal.* Calcd. for $Ti(O_2C_7H_5)_3$: Ti, 11.6; C, 61.3; H, 3.65. Found: Ti, 11.4; C, 61.5; H, 3.88. This chelate rapidly oxidized upon exposure to air. The infrared spectrum was somewhat similar to that of GaT_3.

Preparation of T_2TiCl_2. A solution of $TiCl_4$ (4 g., 20 mmoles) in 60 ml. of chloroform was added to a solution of tropolone (11 g., 90 mmoles) in 200 ml. of chloroform. During the addition an orange-red coloration developed, and later an orange-red precipitate appeared. The reaction mixture was heated on a steam bath for about 0.5 hr. To the reaction mixture was added 60 ml. of acetonitrile and 200 ml. of chloroform. The reaction mixture was held at strong reflux for 1 hr. and filtered. The orange solid obtained was recrystallized from hot chloroform to give yellow crystals which were vacuum dried, m.p. 256° dec. *Anal.* Calcd. for $(C_7H_5O_2)_2TiCl_2$: C, 46.8; H, 2.78; Ti, 13.3; Cl, 19.5. Found: C, 45.6; H, 2.99; Ti, 11.7; Cl, 19.3.

Preparation of T_3TiCl. A mixture of tropolone (10 g., 82.0 mmoles) and T_2TiCl_2 (1.5 g., 41.8 mmoles) was heated to 160° for 1 hr. in a nitrogen atmosphere to give a red solution. Benzene was added to the reaction mixture, and the resultant slurry was filtered to give an orange-red solid. This solid was treated with warm dichloromethane to give insoluble yellow solids and a red filtrate. The filtrate was evaporated to give a red solid which was recrystallized from chloroform and then vacuum dried, m.p. 260–275° dec. *Anal.* Calcd. for $(C_7H_5O_2)_3TiCl$: C, 56.5; H, 3.36; Ti, 10.7; Cl, 7.95. Found: C, 56.1; H, 3.51; Ti, 10.6; Cl, 7.74.

Preparation of $T_3TiOTiT_3$. Titanium tetrachloride (1.9 g., 0.01 mole) was added to a melt of tropolone (25 g., 0.2 mole) at 80°. The mixture was held at 80° for about 10 min. On cooling, 60 ml. of dimethyl sulfoxide was added, and the reaction mixture was heated to 130° for 10 min. The hot reaction mixture was filtered into 200 ml. of water, which had been cooled to near 0°, whereupon an orange solid precipitated. This solid was collected and dissolved in dichloromethane to give a red solution. This solution on slow concentration yielded an orange solid, m.p. 330–335° dec. *Anal.* Calcd. for $[(C_7H_5O_2)_3Ti]_2O$: C, 60.2; H, 3.58; Ti, 11.4. Found: C, 60.3; H, 3.81; Ti, 11.0.

Hydrolysis of $T_4Ta^+Cl^-$. *20 Mole % Water.* A sample of $T_4Ta^+Cl^-$ (0.1000 g.) was added to a solution of NaOH (0.165 g.) in water (0.3038 g.) containing 11.5 atom % O^{18} and 2.7 ml. of methanol. The mixture was stirred 7 min. then neutralized with concentrated sulfuric acid to pH 7. The tropolone was extracted with benzene. After the benzene layer was evaporated to dryness, the tropolone was sublimed from the residue. The mass spectral analysis of the tropolone showed 0.03% increase in O^{18} (see paper II[1] for details of mass spectral assay of O^{18} in tropolone).

53 Mole % Water. The procedure was the same as above. The hydrolysis solution contained 0.205 g. of NaOH, 1.1047 g. of water (10.95 atom % O^{18}), and 1 ml. of methanol. The mass spectral analysis showed a 0.28% increase in O^{18}.

100 Mole % Water. An identical procedure was used with T_4TaCl (0.05 g.) in a solution of NaOH (0.0964 g.) and 1.6860 g. of water (10.6 atom % O^{18}). Mass spectral analyses showed a 1.20% increase in O^{18}.

Investigation of Ligand Exchange in $T_4Ta^+Cl^-$. A solution of $T_4Ta^+Cl^-$ (0.1000 g., 0.143 mmole), enriched tropolone (0.0970 g., 0.794 mmole) containing 18.2% $C_7H_5O^{16}O^{18}H$, natural tropolone (0.0067 g., 0.055 mmole), 1 ml. of water, and 1 ml. of methanol was stirred 30 min. Then a saturated aqueous solution of ammonium hexafluorophosphate was added. A yellow precipitate ($T_4Ta^+PF_6^-$) formed which was isolated by filtration, washed with 5–10-ml. portions of ether, recrystallized from a 66% methanol–34% water (v./v.) solution and dried at 80° for 6 hr. The infrared spectrum did not have any absorption characteristic of tropolone. The $T_4Ta^+PF_6^-$ was hydrolyzed in a basic water (H_2O^{16})–methanol solution (0.1455 g. of NaOH, 1 ml. of H_2O, 1 ml. of CH_3OH) as in the procedure described earlier. The mass spectral analysis showed a 9.79% increase in m/e 124 which is 94.3% of the theoretical 10.38% required for complete exchange.

A solution of enriched tropolone (0.0566 g., 0.465 mmole) containing 18.2% $C_7H_5O^{16}O^{18}H$, natural tropolone (0.0574 g., 0.570 mmole), T_4TaCl (0.103 g., 0.148 mmole), and 23 ml. of ethanol, dried over sodium ethoxide, was stirred 30 min. The solvent was then removed under reduced pressure and the sample was vacuum dried. The chloride salt was washed with 5–10-ml. portions of ether. After drying, the sample was dissolved in a minimum amount of water, and a saturated aqueous solution of ammonium hexafluorophosphate was added. The $T_4Ta^+PF_6^-$ salt which separated, was isolated by filtration, washed with ether, and recrystallized from 66% CH_3OH–34% H_2O mixture. After drying at 80° for 6 hr. the hydrolysis was carried out as previously described. The per cent increase in O^{18}-enriched tropolone was 5.51% which was 71% of theory.

A similar exchange experiment was run in 110 ml. of dry acetonitrile. The observed enrichment was 45% of theory.

Equilibration of $T_4Ta^+Cl^-$ *in* H_2O^{18}. A solution of $T_4Ta^+Cl^-$ (0.1000 g.) in 1 ml. of water (10.5 atom % O^{18}) and 1 ml. of methanol was stirred 48 hr. An aqueous solution of ammonium hexafluorophosphate was added and $T_4Ta^+PF_6^-$ separated. After vacuum drying, the chelate was hydrolyzed as above. The tropolone showed no enrichment by mass spectral analyses.

Hydrolyses of T_4Si *in NaOD.* The NaOD was prepared by adding sodium (0.3 g.) to 11 ml. of D_2O. This was then added to T_4Si (1.0 g.). The yellow-brown solution was stirred for 9 min., then concentrated under reduced pressure to about 3 ml. The yellow solid was isolated by filtration and vacuum dried for 12 hr. Then it was dissolved in 25 ml. of water and the solution was stirred for 0.5 hr. The solution was neutralized to pH 6 with 1 *N* sulfuric acid. Benzene (20 ml.) was added and the mixture was stirred for 15 min. The benzene layer was separated and evaporated to dryness under reduced pressure. Tropolone sublimed from the residue at 30° (0.1 μ).

Mass spectral analyses showed no increase in the deuterium content of tropolone over that of the natural abundance. The infrared spectrum run as a potassium chloride pellet (1 mg./300 mg. of KCl) on the Perkin-Elmer 21 infrared spectrophotometer showed no C–D absorption.

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Olefin Coordination Compounds of Rhodium.
II. The Mechanism of Ethylene Dimerization

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A four-step cyclic mechanism is proposed for the rhodium chloride catalyzed dimerization of ethylene to linear butenes: (a) protonation of a bis(ethylene)rhodium(I) complex to an ethylrhodium(III) compound; (b) the rate-determining rearrangement of this compound to a butylrhodium(III) complex; (c) collapse of the latter to butene and rhodium(I); and (d) coordination of ethylene to provide the initial bis(ethylene)rhodium(I) complex.

Introduction

Discovery of ferrocene and of Ziegler–Natta polymerization catalysts have aroused widespread interest in organometallic chemistry. Subsequent theoretical and synthetic developments have encouraged a prevalent opinion that it will be possible to detail the mechanisms of many syntheses that involve hydrocarbon, hydride, or carbonyl coordination compounds of transition metals as intermediates. This paper reports a study of such a reaction, namely, the rhodium chloride catalyzed dimerization of ethylene to linear butenes. Because of the tractability of the intermediates in polar media at easily accessible temperatures and pressures, it has been possible to isolate most of the steps that constitute a proposed mechanism. This mechanism includes and further elucidates some characteristic reactions of coordination chemistry: (1) the reversible oxidation of rhodium(I) by a protonic acid to give a rhodium(III) hydride; (2) an insertion of coordinated olefin between an alkyl group and the metal ion to which it is attached, a reaction which may be the chain-growth step of Ziegler polymerization; (3) the labilization of hydrogen in rhodium(III) alkyl and olefin complexes; and (4) the critical importance of appropriate auxiliary ligands to the catalytic effectiveness of rhodium.

The rhodium-catalyzed dimerization of ethylene has been described by Alderson, Jenner, and Lindsey.[1] It is run conveniently at 40°, in alcohol with 0.1 mole % “rhodium trichloride trihydrate,”[2] based upon ethylene, and with ethylene supplied at one to several hundred atmospheres. Although a mixture of linear butenes is obtained, the initial product is probably 1-butene. There is very little higher hydrocarbon; the yield of butenes is greater than 99% based upon consumed ethylene.[3]

Discussion

The proposed reaction cycle for the synthesis of 1-butene is summarized in Figure 1. It is supported by a variety of interlocking physical and chemical evidence relating to the intermediates and to the individual reactions. A brief over-all description will be given followed by a detailed discussion of the individual steps.

A bis(ethylene) complex of monovalent rhodium (A) is rapidly converted by reaction with HCl into an ethylrhodium(III) compound (B). B rearranges by a slow, rate-determining chain-growth reaction, giving a *n*-butylrhodium(III) complex (D). D decomposes rapidly through loss of HCl to give a 1-butene complex of monovalent rhodium (E). Coordinated 1-butene and solvent in E are rapidly displaced by ethylene reforming the initial rhodium(I) complex A. At high ethylene pressures and in ethanol solutions above about 0.1 *M* in HCl, most of the rhodium in the reaction system is in the form of the ethylrhodium complex B waiting to go through the rate-determining insertion or chain-growth step (eq. 4, Figure 1), but at ethylene pressures near 1 atm., B dissociates extensively, rapidly, and reversibly to ethylene and the ethylrhodium(III) complex C.

The rates of the steps may be classified by noting the temperatures at which they can be studied. Reaction

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(1) T. Alderson, E. L. Jenner, and R. V. Lindsey, Jr., *J. Am. Chem. Soc.*, in press; T. Alderson, U. S. Patent 3,013,066 (1961).

(2) “Rhodium trichloride trihydrate” is a noncrystalline, water-soluble solid with approximate composition $RhCl_{3.3}(H_2O)_{2.3}$. Material used in this work was purchased from Engelhard Industries.

(3) Ethylene is also dimerized cleanly with a cobalt–aluminum catalyst (G. Hata, *Chem. Ind.* (London), 223 (1965)), but large amounts of ethylene are converted to higher olefins by a $CH_3TiCl_3{\cdot}CH_3AlCl_2$ catalyst (H. Bestian, *et al.*, *Angew. Chem. Intern Ed. Engl.*, **2**, 32 (1963)).