of an intermediate complex having a maximum at 410 nm ($[H^+] = 2\ M$, ϵ_{max} 38). This complex reacts further by a bimolecular reaction or decomposes back to the original species. In the case of V^{2+}(aq) the formation of the complex in the first stage of the reaction is completed within the time of mixing. Fast complex formation is also observed with Eu^{2+}(aq).

In the reaction between picolinic acid and Eu^{2+}(aq) direct formation of Eu^{3+}(aq) and free aldehyde is not observed. In a solution, for example, containing initially 0.3 *M* Eu^{2+}(aq) and 0.7 *M* picolinic acid at pH $\simeq 1$, a yellow-gray complex (or complexes) is formed which is stable over a period of many days. It is believed that in this complex europium is in the +2 state, since it can be readily oxidized by air or by Fe(III). With SO_2 the Eu(II)-picolinic acid solution does not form a precipitate. If europium together with some organic material is first precipitated with soda, the SO_2 and 2,4-dinitrophenylhydrazine tests on the filtrate are positive. The yield, however, is small and irreproducible, as indicated by titrating with $KMnO_4$. It seems that aldehyde is formed only during the neutralization procedure.

A complex is also formed upon mixing a Cr^{2+}(aq) with a picolinic acid solution, *e.g.*, an acid solution 0.5 *M* in Cr^{2+} with an acid solution 1.8 *M* in picolinic acid. This complex is deeply colored (red-brown), stable, and inert. Extraction with ether or chloroform gave no indication of a free organic product and chromium could not be precipitated with alkali. The complex was destroyed only by adding sodium pyrophosphate and boiling under reflux for several hours, but under these vigorous conditions the organic product underwent further reactions. Thus, ether extraction gave a product having a proton nmr spectrum consistent with what would be expected for *o*-hydroxymethylpyridine.[6] The boiled solution also contained other unidentified organic products.

The complex between V(III) and the product of the reaction between vanadous and picolinic acid is labile. It can be readily dissociated by acidifying the solution. Precipitation with SO_2 of picolinaldehyde can be achieved after removing vanadium with alkali, provided that picolinic acid is in excess. Even in acid solution, without removing the metal ion, the SO_2 test for the aldehyde is positive. At lower picolinic acid concentrations the organic product coprecipitates with V(III), if the solution is made alkaline. In the pH range between 1 and 3 the oxidation of V^{2+}(aq) by picolinic acid is second order in V^{2+}, having a maximum rate at pH $\simeq 2$. At this pH, with a solution containing initially $1.5 \times 10^{-2}\ M\ V^{2+}$ and 0.19 *M* picolinic acid the pseudo-second-order rate constant has the value 2.5 $mol^{-1}\ min^{-1}$.

Under the conditions of our experiments nicotinic acid does not seem to be reduced by any of the three ions. Europous and chromous do not even seem to form complexes, while the complexes formed by vanadous are very unstable. Heating a mixture of Cr^{2+}(aq) with excess nicotinic acid at 80° for several hours leads to oxidation of Cr(II), but without apparent intermediate formation of a colored complex. Moreover, the organic product obtained in small yield, after removing chromium with alkali, does not give the characteristic reactions of the aldehyde group; it reduces I_2 and $KMnO_4$ but not methylene blue; with SO_2 it does not give a precipitate.

Our previous results[5] indicated that the first step in the two-electron reduction of isonicotinic acid by chromous ion involves an ion-radical intermediate rather than an organic free radical. Nevertheless, the spin densities of the radical anions, in the absence of the perturbing influence of the metal ion, obtained by esr spectroscopy and by theoretical calculations[7] have some relevance to the present work. They provide some basis for correlating the behavior of the three pyridinecarboxylic acids, since at the positions occupied by the carboxylic group isonicotinic and picolinic acids have higher spin densities than nicotinic acid. Correspondingly, isonicotinic and picolinic acids interact with the three ions strongly, whereas nicotinic acid does not. The interaction with isonicotinic acid leads to the formation of the aldehyde. Formation of aldehyde from picolinic acid and Eu^{2+}(aq) or V^{2+}(aq) is observed at low hydrogen ion concentrations, indicating an accelerating influence of chelation. Aldehyde formation from picolinic acid and chromous ion was not observed, presumably because of the substitution-inert character of the complex formed in the first step.

It must be recalled in this context, that Norris and Nordmeyer[8] found that free isonicotinamide catalyzes the reaction between Eu^{2+}(aq) and isonicotinamide-, pyridine-, and nicotinamidepentaamminecobalt(III) complexes, whereas the corresponding amide of nicotinic acid did not have any catalytic effect. It seems, therefore, that the study of the mechanism of the reduction of free ligands by metal ions is not only interesting for its own sake and for synthetic reasons but it can also help to gain a better understanding of the electron transfer process, when the ligand is bound to a metal ion center. Moreover, it can provide criteria for recognizing the cases in which the transfer of the electron proceeds by a radical-intermediate mechanism.

Acknowledgments. The authors wish to thank Mrs. S. Philippakopoulou for laboratory assistance.

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Received January 17, 1973

Structure of Tetracyclopentadienyluranium(IV)[1]

Sir:

When Fischer and Hristidu[2] first synthesized tetracyclopentadienyluranium(IV), $(C_5H_5)_4U$, they reported

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[6] The presence of *o*-hydroxymethylpyridine could be attributed to the easiness with which picolinaldehyde undergoes a Cannizzaro reaction.

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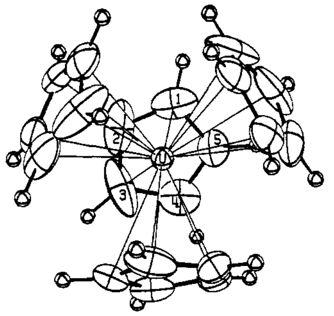

Figure 1. The tetrahedral tetracyclopentadienyluranium molecule.

that the molecule has a zero dipole moment and proposed a highly symmetric structure with four centrally bonded cyclopentadienyl rings surrounding the uranium atom tetrahedrally. Later a controversy arose over the cause of the chemical shift observed by von Ammon, *et al.*,[3] in the proton magnetic resonance spectrum of this paramagnetic compound. Their assertion that the shift was attributable to the Fermi contact mechanism was questioned, and data on several other U(IV) compounds were presented[4] to show that the magnetic dipolar (or pseudocontact) shift was also important. In reply, the original observers pointed out[5] that if the molecule is tetrahedral, it will have an almost isotropic spectroscopic splitting factor, *g*, and hence no dipolar shift. Although such a structure is quite credible, no determination had been made. Moreover, there was room for some doubt because (1) in $(C_5H_5)_4Zr$ three rings are pentahapto and one is monohapto bonded to the Zr(IV) atom,[6] (2) in $(C_5H_5)_4Ti$ two rings are pentahapto and two are monohapto bonded to the Ti(IV) atom,[7] and (3) in the structures of $(C_5H_5)_3UCl$[8] and $(C_6H_5CH_2(C_5H_4))_3UCl$[9] the bonds to U from C and from Cl are obviously of two different kinds. We have now completed a structure determination of $(C_5H_5)_4U$ by single-crystal X-ray diffraction, and the molecule is indeed tetrahedral as is shown in Figure 1.

A deep red crystal of $(C_5H_5)_4U$ was sealed in a glass capillary in an Ar atmosphere, and data were collected with a computer-controlled Picker X-ray diffractometer. Unit-cell data were obtained and intensity measurements for 700 independent reflections were made with Mo Kα radiation. The lattice is body-centered tetragonal, and the unit cell with a = 8.635 (2) and c = 10.542 (3) Å contains two molecules. The diffraction pattern, carefully checked by use of the diffractometer, has no systematic absences other than those of a body-centered lattice; a space group choice of $I\bar{4}2m$ was made from among the seven possibilities by consideration of the packing limitations. The structure was deduced in part from a Patterson map, but examination of a difference Fourier map revealed the presence of disorder. The U atom is at the origin, a point having D_{2d} symmetry in the crystal, but a single molecule with a U atom at its center has only S_4 symmetry. The higher crystallographic symmetry results from disorder in which a molecule and its mirror image obtained by reflection in the (110) plane are equally and randomly distributed throughout the crystal lattice.

The C atom coordinates and anisotropic thermal parameters of U and C atoms were adjusted by the method of least squares; after the final cycle, H atoms were included in the plane of the C_5 rings at radial distances of 1 Å and given isotropic B values of 5 Å^2. In describing the structure the space group $I\bar{4}$ was used, and the asymmetric unit contained one C_5 ring with each atomic site occupied by half an atom. To complete the structure and have it conform to $I\bar{4}2m$ symmetry, a second ring of half atoms was included and constrained to be mirror symmetric with the first. The final agreement index, $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, reached 0.0208 and the standard deviation of an observation of unit weight was 1.006.

The four C_5H_5 rings surrounding each U atom are identical by crystallographic symmetry, and the angle from the centroid of any one ring to U to the centroid of another ring is tetrahedral within ±0.6°. The C–C distances are all equal within experimental error and average to 1.386 (10) Å; the same is true for the U–C distances which average 2.807 (25) Å. The five C atoms of each ring are within about 0.05 Å of the best least-squares determined plane, and the perpendicular distance from the plane to the U atom is 2.55 Å. From the orientation of the 50% probability thermal ellipsoids shown in Figure 1, it is seen that the rings are preferentially oscillating about their fivefold axes. The rms amplitudes of vibration along the major axes range from 0.28 to 0.47 Å and average about 0.37 Å. This motion is typical for organometallic structures of this nature.

It is of interest to compare tetracyclopentadienyluranium(IV) with the molecular sandwich compound bis(cyclooctatetraenyl)uranium(IV), which is also called uranocene. The stability of uranocene to H_2O was given by Streitwieser and Müller-Westerhoff[10] as chemical evidence for covalency in this compound, and they proposed the use of molecular orbitals similar to those of ferrocene but expanded to include E_{2u} ring orbitals and f orbitals of the U(IV). Further studies[11–13] have to a certain extent substantiated this proposed involvement of f orbitals in the bonding.

Although the stability of $(C_5H_5)_4U$ to hydrolysis is not as great as that of uranocene, it does not react instantaneously as do the ionic tricyclopentadienides.[14] In its hydrolytic behavior it is close to that of tricyclopentadienyluranium(IV) chloride and triindenyluranium(IV) chloride which evidence some covalent character in their U–C bonding. This covalency is deduced from the failure of $(C_5H_5)_3UCl$ to react with maleic

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anhydride or to react with $FeCl_2$ to form ferrocene[15] and from various spectroscopic data[16] on $(C_9H_7)_3UCl$. Other, indirect, evidence for covalency in $(C_5H_5)_4U$ is the Mössbauer study[17] of $(C_5H_5)_4Np$, a compound isostructural with $(C_5H_5)_4U$. The isomer shift found for Np indicated covalency in the Np–C bonds, but less than that found[11] for $(C_8H_8)_2Np$. Thus, while the eight-membered-ring sandwich configuration of $(C_8H_8)_2U$[18] appears particularly favorable for use of 5f orbitals in the bonding, chemical evidence for covalency in U(IV) compounds with other configurations, such as the one shown here, suggests that they too may have some participation of these orbitals in the organometallic bonding.

Acknowledgment. I thank P. G. Laubereau and B. Kanellakopulos who each supplied crystals and J. L. Atwood who collaborated in the early part of this work.

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Received March 3, 1973

Strategies for the Study of Structure Using Lanthanide Reagents

Sir:

Utilization of lanthanide complexes in solution structural studies has focused on the predicted $\langle(3\cos^2\theta - 1)r^{-3}\rangle$ dependence of the assumed dipolar or pseudocontact interaction.[1-9] Here θ is the angle between a real or time-averaged axis of symmetry and the metal nucleus vector, and r is the length of this vector. Although the dipolar mechanism appears to dominate the observed shifts in the majority of cases, recent evidence for sizable contact contributions in proton[10] as well as carbon-13[11,12] isotropic shifts introduces a disquieting degree of ambiguity in a solution structure deduced solely from the observed relative isotropic shifts.

Solution structures deduced from shift studies could, in principle, be severely tested by requiring a simultaneous fit to the relative line widths induced by the lanthanide ion, which in favorable cases can be shown to depend solely on relative values of $\langle r^{-6}\rangle$. The potentiality of this $\langle r^{-6}\rangle$ dependence of the line widths due to a "relaxation" reagent has been ignored generally. In isolated instances,[8,13] induced line widths with and without concomitant isotropic shifts have been employed. In the former case, the broadening rapidly leads to overlap[8] of the closely spaced unshifted resonances precluding an accurate determination of the line widths. In the latter case, the use of lanthanides[8,13] which possess sizable magnetic anisotropy results in line widths which have a more complex dependence[14] on r, θ, and the magnetic anisotropy than even the dipolar shift. We demonstrate here how the simultaneous use of a "shift" reagent (maximum shift with minimal broadening) and a "relaxation" reagent (severe broadening with negligible shift) can overcome both the resolution and interpretation problems of earlier studies and thereby provide a complementary, if not superior, method for effecting structural analyses.

The long electron spin relaxation time and highly isotropic magnetic moment of Gd^{3+} makes it the ideal lanthanide "relaxation reagent" with the desired $\langle r^{-6}\rangle$ line width dependence.[15] The magnetic isotropy of the $Gd(fod)_3$ complex is confirmed by noting that addition of only $Gd(fod)_3$ to the substrate causes broadening without observable shifts. The general procedure proposed is that of inducing large shifts between resonances by the addition of a shift reagent, *i.e.*, $Eu(fod)_3$, and then adding Gd(fod) to broaden the lines. This method readily allows the determination of a broadening of several hundred hertz, which would be impossible without the expanded chemical shift scale induced by the shift reagent. The line widths due solely to the relaxation reagent are obtained by correcting the observed line widths for minor paramagnetic relaxation due to the shift reagent and for broadening due to incompletely collapsed spin–spin multiplet structure in both the presence and absence of the relaxation reagent. Rapid relaxation of spins close to the metal may eliminate some multiplet structure;[16,17] residual multiplet structure may always be eliminated by using a second rf oscillator to effect instrumental decoupling.

Complicating factors, such as nonspecific relaxation in the second coordination sphere and the presence of multiple correlation times in substrates with internal motions, must be considered. The former effect, which is not very important in dilute solution, can be estimated by using a model noninteracting substrate (*i.e.*, benzene for pyridine). Multiple correlation times are not likely to arise in nonviscous media, and their presence can generally be established[18] experimentally.

The main advantage of analyzing relaxation data over shift data is that the $\langle r^{-6}\rangle$ interpretation of the relative line widths for Gd rests on firmer theoretical ground[15] than the $\langle(3\cos^2\theta - 1)r^{-3}\rangle$ interpretation of the shifts for Eu or Pr. Furthermore, the line width

(1) Selected recent articles are given below.[2-9] The abbreviations dpm for dipivaloylmethanate and fod for 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedionate are used.

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