Pergamon

0277–5387(94)00246–0

Polyhedron Vol. 14, No. 2, pp. 219–222, 1995
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0277–5387/95 $9.50+0.00

INFLUENCE OF STERIC HINDRANCE ON THE FORMATION OF NINE-COORDINATE ADDUCTS OF TETRAKIS(THENOYLTRIFLUOROACETONATO)URANIUM(IV) IN BENZENE SOLUTION

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(*Received* 17 *May* 1994; *accepted* 6 *June* 1994)

Abstract—Equilibrium constants ($\log_{10}\beta_1$) for the formation of nine-coordinate adducts of tetrakis(thenoyltrifluoroacetonato)uranium(IV), [U(TTA)$_4$] have been determined for some imidazole and antipyrine derivatives in benzene solution in which [U(TTA)$_4$] itself is eight-coordinate. Comparing imidazoles with a 2-hydrogen and a 2-methyl substituent, the effect of steric hindrance reverses the order of stability expected from the pK_a values of the ligands. For 4-aminoantipyrine complexes coordination occurs through only the carbonyl function as found from ^{1}H NMR spectroscopy. Marked depression of $\log_{10}\beta_1$ is observed for the hindered bases. There is evidence to suggest that the unhindered five-membered imidazoles have greater stability in their nine-coordinate adducts than six-membered pyridines with comparable pK_a values. This could be a further demonstration of the separation of five- and six-membered heterocyclic bases through group specific factors.

We[1] and others[2] have shown previously that the equilibrium constant β_1 for the process below which describes the formation of a nine-coordinate adduct

$$U(TTA)_4 + S = U(TTA)_4S$$

can be conveniently determined by electronic spectroscopy in benzene solution (where S is a neutral donor ligand). The nine-coordinate adduct has a distinctly different spectrum from that of U(TTA)$_4$ in benzene solution whereas in a donor solvent such as acetone where U(TTA)$_4$ is nine-coordinate no useful changes in the electronic spectrum are observed.

We prefer the computer program SQUAD[3–5] for the calculation of β_1 since it requires no predetermined extinction coefficients which are refined at each analytical wavelength. The experimental values of the extinction coefficient of U(TTA)$_4$ are readily available in the absence of S so that there is a useful internal validation of the results.

Oxidation of uranium(IV) to uranium(VI) can be prevented[2] by the addition of a large excess of HTTA or minimized[1] by rapid manipulation of the experimental solutions.

We have also shown[1] that the induced paramagnetic shifts in the proton resonances of S caused by the presence of the $5f^2$ uranium(IV) can be used to find β_1 from the ^{1}H NMR spectra which provides an acceptable procedure for both acetone and benzene solutions.

All previous work[1,2,6–8] demonstrated that U(TTA)$_4$ and similar actinide(IV) diketonates and tropolonato complexes form nine-coordinate adducts with S and that there is no evidence for higher coordination numbers. The reluctance of these actinide species to expand the coordination number beyond nine even with a substrate as small as water[1,7,8] prompted us to explore the effect of steric hindrance in S for imidazoles and 2,3-dimethyl-1-phenyl-3-pyrazolin-5-one (antipyrine) derivatives.

The method involves the determination of β_1 values and then comparing these with the basicity of S expressed where possible as a pK_a value. For

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substrates with more than one potential donor atom the time-averaged chemical shifts in the ^{1}H NMR spectrum of S will be used to identify those atoms coordinated at the metal centre.

In an earlier report[1] the value of β_1 for 4-picoline was found to be about 40 times greater than that of 2-picoline although the bases have comparable pK_a values and there was a more marked effect for the stronger base, 2,4,6-collidene.

EXPERIMENTAL

Materials

The imidazoles and antipyrines were from Aldrich to the highest available quality and used without further purification. Benzene, d_6-benzene and U(TTA)$_4$ were as described previously.[1]

Spectrophotometric measurements

Electronic and ^{1}H NMR spectra were obtained as described[1] previously as was the degree of oxidation of U(TTA)$_4$ in the presence of the substrates S. The equilibrium constant, $\log_{10}\beta_1$, was calculated using the computer program SQUAD[3–5] in the wavelength range 445–500 nm with an interval of 5 nm. Uranium concentrations varied between 1.07×10^{-4} and 2.39×10^{-4} mol dm^{-3} with substrate concentrations between 2.51×10^{-6} and 4.22×10^{-1} mol dm^{-3} depending on the magnitude of $\log_{10}\beta_1$. The mean experimental values of the extinction coefficient (dm^3 mol^{-1} cm^{-1}) for U(TTA)$_4$ at 445 nm were 1514(40) and at 500 nm 655(32) compared with mean values calculated from SQUAD at 445 nm of 1514(42) and at 500 nm of 659(28). Values in parentheses throughout the paper refer to one standard deviation. The degree of complex formation varied between 1 and 90% and 5–7 solutions were used for each determination.

The pK_a *values of the imidazoles*

These were determined in water/ethanol solvent (40:5 v/v) at 20.0(0.5)°C by potentiometric titration using the computer program Miniquad[9,10] for data handling. The values (Table 1) were used for comparative purposes.

RESULTS AND DISCUSSION

Effects of steric hindrance

The values of $\log_{10}\beta_1$ (Table 1) demonstrate the fundamental importance of steric hindrance in determining the thermodynamic stability of the nine-coordinate adducts.

Within each of the two pairs of imidazoles an increase in the basicity (pK_a) gives rise to a decrease in $\log_{10}\beta_1$ when the 2-methyl group was introduced i.e. comparing compound **1** with **2** and compound **3** with **4**. When comparing bases of similar steric requirement, e.g. the unhindered compounds **1** with

Table 1. Effect of steric hindrance on the complexation(1:1) of some organic bases with U(TTA)$_4$ in benzene solution at 20 °C

Compound	$\mathrm{Log}_{10}\beta_1$	pK_a	% Oxidation min^{-1}
1. 1-methylimidazole	3.89(0.01)	6.7[a]	0.004
2. 1,2-dimethylimidazole	3.08(0.01)	7.6[a]	0.07
3. 1-benzylimidazole	3.48(0.04)	6.3[a]	0.004
4. 1-benzyl-2-methylimidazole	2.80(0.01)	7.1[a]	0.26
5. antipyrine[b]	3.95(0.01)	12.30[c]	0.003
6. 4-aminoantipyrine	3.03(0.01)		0.003
7. 4-dimethylaminoantipyrine	1.53(0.01)	11.38[c]	0.025
8. 4-picoline[d]	2.44(0.01)	6.03[e]	0.03
9. 2-picoline[d]	0.83(0.01)	5.95[e]	0.10
10. 2,4,6-picoline[d]	0.94(0.01)	7.43[e]	0.15
11. 3,4-lutidene[d]	2.31(0.02)	6.46[e]	0.08
12. 3,5-lutidene[d]	2.37(0.01)	7.43[e]	0.15

[a] This work (water/ethanol).

[b] 2,3-Dimethyl-1-phenyl-3-pyrazolin-5-one.

[c] Determined in butanone, ref. 11.

[d] Ref. 1.

[e] Determined in water, ref. 12.

3 and the 2-methyl compounds **2** with **4**, the expected changes are observed with the ligand of higher pK_a giving rise to the higher value of $\log_{10}\beta_1$.

There has been some work[11] on the basicity of the antipyrines (compounds **5**–**7**). It would appear that antipyrine is protonated at the carbonyl function but at the amino nitrogen atom for the 4-dimethyl derivative. This makes it difficult to compare the compounds. However, the effect of steric hindrance is very marked in the formation of the adduct even though the position of the hindering group is more distant from the site of coordination compared with the imidazoles and pyridine derivatives. Thus the 4-dimethylamino derivative has a formation constant two orders of magnitude smaller than that of antipyrine. It would be of interest to compare $\log_{10}\beta_1$ for these ligands with their effectiveness in the synergic extraction of the metal ion to a non-aqueous solvent from water.

Values previously reported[1] are given in Table 1 (compounds **8**–**12**) for the sake of comparison.

^{1}H *NMR spectroscopy of the antipyrine derivatives*

The induced paramagnetic shifts showed that the amino nitrogen atom is not coordinated in the adducts and that the ligands are monodentate complexing through the carbonyl oxygen atom. For example, the bound chemical shift (ppm) for the methyl protons of the dimethylamino group in 4-dimethylaminoantipyrine was 4.6 compared with a value of 34 for the 2-H atom in 4-picoline and 13 for the 2-H atom in 4-toluidine. The results indicate that for the paramagnetic f^2 uranium(IV) ion, where broadening of the ^{1}H resonances on coordination is not usually a problem, the induced shifts are generally useful in determining the site(s) of coordination.

The $\log_{10}\beta_1$ values determined in d_6-benzene by the ^{1}H NMR method were: antipyrine 3.50(0.10), 4-aminoantipyrine 3.25(0.09), and 4-dimethylaminopyrine 1.56(0.02) which are in reasonably good agreement with those from electronic spectroscopy (Table 1) given that the values are probably less reliable using the NMR method.

Influence of uranium(IV) oxidation

In all cases there was an acceptably low rate of oxidation of uranium(IV) (Table 1) given that the electronic spectroscopy was complete within 30 min of solution preparation. The reliability of the $\log_{10}\beta_1$ values is reflected in the small calculated standard deviations (Table 1) and the good agreement between the calculated and experimental values of the extinction coefficients of $U(TTA)_4$ at the analytical wavelengths (see Experimental).

Group specific factors

The unhindered five-membered heterocycles gave higher values of $\log_{10}\beta_1$ than the six-membered heterocycles in the pyridine series with similar pK_a values. Thus 1-methylimidazole (compound **1**) and 1-benzylimidazole (compound **3**) have $\log_{10}\beta_1$ values an order of magnitude greater than those for 3,4- and 3,5-lutidenes (compounds **11** and **12**) which have similar pK_a values (Table 1). Pratt and co-workers[13–17] have found emphatic evidence for group specific factors through the use of free energy relationships which link pK_a and $\log_{10}\beta_1$ in extensive studies of iron and cobalt complexes. Thus clear differences were found between the five-membered imidazoles, the six-membered pyridines, and alkyl amines. The greater stability of the imidazole complexes is likely to have profound effects in bioinorganic chemistry.

The smooth conversion of the eight-coordinate $U(TTA)_4$ to the nine-coordinate adducts affords a further system in which group specific factors might be investigated. Uranium(IV) is a hard acid in comparison with cobalt and iron so that it would be interesting to test the generality of the effect. The addition of a single ligand simplifies the analysis such that substrate specific properties are readily identified.

Acknowledgement—We thank the Syrian Atomic Energy Commission for granting study leave to M.O.

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