Complexes of Tetravalent Plutonium, Uranium and Thorium with Acylpyrazolones

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Abstract

The tetravalent complexes of plutonium, uranium and thorium with acylpyrazolones such as 1-phenyl-3-methyl-4-benzoylpyrazol-5-one (PMBP), 1-phenyl-3-methyl-4-acetylpyrazol-5-one (PMAP) and 1-phenyl-3-methyl-4-trifluoroacetylpyrazol-5-one (PMTFP) have been synthesized and characterized as tetrakis-chelates. The PMR spectra indicate they exist as a mixture of stereoisomers and also reveal the presence of contact shift interactions in the case of paramagnetic uranium chelates. Sinha's parameter, calculated from the electronic spectra, indicate a small amount of covalent character in the case of uranium chelates.

Introduction

Among β-diketones, 4-acylpyrazolones have assumed significance as solvent extracting agents for actinides in view of their relatively lower cost [1] and their ability to extract metal ions from solutions of lower pH [2–4] as compared to the more common extractant, *viz.*, 2-thenoyltrifluoroacetone (TTA). The more common of these are the benzoyl substituted (PMBP), acetyl substituted (PMAP) and trifluoroacetyl substituted (PMTFP) pyrazolones. Extensive solvent extraction studies of metal ions with acylpyrazolones have been reported [5–7] but few attempts have been made to isolate and characterize the solid complexes involved therein. Okafor [8, 9] has carried out studies on solid chelates of trivalent lanthanides with benzoyl- and acetylpyrazolones. The possible use of these compounds in laser chemistry [10, 11] and as shift reagents in NMR spectroscopy [12–16] prompted us to investigate the complexes of some tetravalent actinides with acylpyrazolones. The present paper deals with the synthesis, characterization and spectral investigations of tetravalent plutonium, uranium and thorium complexes with PMBP, PMAP and PMTFP.

Experimental

All the chemicals used were of B.D.H./AR quality. PMBP was synthesized by Jensen's method [17] and recrystallized from chloroform to obtain yellow crystals of the enol form. *Anal.* Calc. for $C_{17}H_{14}O_2N_2$ (m.p.* 92 °C): C, 73.36; H, 5.02; N, 10.07. Found: (m.p. 91 °C) C, 73.10; H, 5.18, N, 9.77%. PMAP and PMTFP were also synthesized by the same procedure and recrystallized from n-hexane to obtain yellow and pinkish cream crystals, respectively. *Anal.* Calc. for PMAP: $C_{12}H_{12}O_2N_2$ (m.p. 67 °C): C, 66.65; H, 5.60; N, 12.96. Found: (m.p. 66–67 °C): C, 66.56; H, 5.62; N, 12.90%. *Anal.* Calc. for PMTFP: $C_{12}H_9O_2N_2F_3$ (m.p. 144 °C): C, 53.34; H, 3.36; N, 10.30. Found: (m.p. 144 °C): C, 52.87; H, 3.69; N, 10.33%.

Preparation of the Complexes

Uranium and plutonium complexes

Tetravalent uranium was prepared by passing uranyl nitrate solution in 0.5 M HCl through a Jones reductor column and a stock of plutonium solution was conditioned to the tetravalent state by the addition of sodium nitrite in 0.5 M nitric acid. The tetravalent metal ions in aqueous solution were extracted by vigorous shaking with a benzene solution containing 4 times the calculated amount of the acylpyrazolone. The benzene extract was washed twice with 0.5 M mineral acid, reduced to 0.5 ml, and the products were recrystallized twice from n-hexane.

Thorium complexes

The thorium complexes could not be prepared in the same way because of precipitation of the solid complex during solvent extraction. In this case, thorium in aqueous solution was mixed with 95% ethanol containing 4 times the requisite amount of the respective pyrazolone. Distilled water was added to this solution until a permanent turbidity was observed. This was cleared by warming, and the solution was cooled and allowed to evaporate at room temperature for crystallization. The solid thus obtained was recrystallized twice from n-hexane.

Characterization of the Complexes

Carbon and hydrogen were determined by microanalysis using the empty tube combustion procedure

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*m.p., melting point.

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TABLE I. Analytical Data of $M(L)_4$ Complexes[a]

M	L	Colour	Melting point (°C)	C(%)	H(%)	N(%)	M(%)
Pu	PMBP	red	240(d)	60.6 (60.4)	4.2 (4.2)	8.3 (8.3)	17.9 (17.7)
Pu	PMAP	red	235.4	52.4 (52.4)	4.1 (4.0)	9.9 (10.2)	22.0 (21.7)
Pu	PMTFP	tan	300(d)	43.5 (43.4)	2.8 (2.4)	8.5 (8.4)	18.7 (18.0)
U	PMBP	yellow	231.6	61.0 (60.4)	4.2 (4.2)	8.4 (8.3)	17.2 (17.6)
U	PMAP	buff	249.5	52.8 (52.4)	4.0 (4.0)	10.2 (10.2)	21.4 (21.7)
U	PMTFP	yellow	300(d)	43.6 (43.4)	2.6 (2.4)	8.4 (8.4)	18.3 (17.9)
Th	PMBP	yellow	226.3	60.2 (60.7)	4.0 (4.2)	8.8 (8.4)	17.1 (17.3)
Th	PMAP	buff	237.1	52.7 (52.7)	4.6 (4.0)	10.2 (10.3)	20.8 (21.2)
Th	PMTFP	yellow	128	43.3 (43.6)	2.7 (2.4)	8.5 (8.5)	17.2 (17.6)

[a] Figures in parentheses indicate calculated values. d = decomposes.

of Belcher and Spooner [18]. Nitrogen was determined by the Dumas method assembled in a glove box. The metal contents were determined from the weights of the corresponding oxides left behind after the combustion procedure for the determination of carbon and hydrogen. In the case of PMTFP complexes, however, the metal contents were determined by alpha scintillation counting for plutonium, cerimetric titration for uranium, and EDTA titration for thorium. The analytical data are summarized in Table I.

IR spectra were measured in Nujol mulls between CsI discs using a Perkin-Elmer-577 grating spectrophotometer in the range 4000–200 cm^{-1} for the uranium and thorium complexes and in the range 4000–600 cm^{-1} for the plutonium complexes, using a Perkin-Elmer-237 spectrophotometer adapted for glove box operation. PMR spectra of the uranium and thorium chelates were measured with a Fourier Transform Varian FT-80A spectrometer using saturated solutions in $CDCl_3$ and TMS as internal standard.

Results and Discussion

Infrared Spectra

A few characteristic bands observed in the infrared spectra of these chelates have been assigned empirically following Okafor's assignment for the corresponding rare earth tris-chelates of PMAP and PMBP [8, 9]. The asymmetric stretching frequency of the carbonyl group is slightly lowered on complexation (1640–1610 cm^{-1}). The spectra also indicate very strong bands due to CH in-plane deformation of the monosubstituted phenyl ring (1090, 1030 cm^{-1}), as well as intense peaks due to the ν(CH) of the acyl grouping (725–840 cm^{-1}). Bands at 400–500 cm^{-1}, which are absent in the free ligands, have been identified as the M–O stretching frequency. In addition, strong peaks which are ascribable to the pyrazole ring stretching vibration are observed in the free ligands and the complexes. These IR spectral bands give conclusive proof of the bonding of carbonyl oxygen and the enolic oxygen of the acylpyrazolone to the metal.

PMR Spectra

The PMR spectra of the methyl and phenyl protons of tetravalent thorium and uranium chelates with PMBP and PMAP show very sharp lines, which are explained by short relaxation times characteristic of actinide ions. However, the PMR signals observed for the thorium and uranium chelates of PMTFP are somewhat broad, as are the signals of the free ligand.

The PMR spectrum of neat PMAP gives only a single sharp line at 2.43 ppm, which is indicative of the equivalence of the two methyl protons. In complexes of PMAP with thorium and uranium also,

TABLE II. PMR Spectra of $M(L)_4$ Chelates in $CDCl_3$ at 60 MHz (ppm)

M	L	Methyl	Phenyl	Complexation shift		Contact shift	
				CH_3	C_6H_5	CH_3	C_6H_5
	PMBP	2.03	7.28–7.80				
Th	PMBP	1.52, 165	6.98–7.80	0.38	0.30		
U	PMBP	1.85, 2.35	3.25–5.50	−0.32	4.03	−0.70	3.73
	PMAP	2.43	7.33–7.82				
Th	PMAP	2.25	7.12–7.91	0.18	0.21		
U	PMAP	3.50	3.87–5.42	−1.07	3.46	−1.25	3.25
	PMTFP	2.47	7.27–7.50				
Th	PMTFP	2.25	7.13–7.28	0.22	0.14		
U	PMTFP	3.00	4.31–7.21	−0.53	2.96	−0.75	2.82

TABLE III. Electronic Spectra of $M(L)_4$ Complexes

Substance	Maxima (nm)					
	1	2	3	4	5	6
PMBP	314.5	362.0				
$Th(PMBP)_4$	272.0	363.5	415.0			
$U(PMBP)_4$	314.0	363.5	444.5	515.0	557.0	659.0
PMAP	313.0	329.0				
$Th(PMAP)_4$	270.5	352.5	429.0			
$U(PMAP)_4$	314.0	363.5	420.5	512.5	553.5	657.5
PMTFP	313.5	360.5				
$Th(PMTFP)_4$	301.5	364.5	404.0			
$U(PMTFP)_4$	314.0	364.5	450.5	515.0	555.0	659.0
Th(IV)aq						
U(IV)aq			429.5	495.0	549.5	648.5

only one methyl signal is observed, although in the former case the signal is somewhat broad. This is also true in the case of PMTFP complexes, where only a single methyl peak of the pyrazolone ring is observed both in the ligand and in the complexes. In PMBP systems, however, whereas the free ligand shows a single sharp line due to the methyl of the pyrazole ring, both the thorium and uranium chelates show two methyl peaks of equal intensity. This indicates the existence of the PMBP chelates as a mixture of two stereoisomers. It is quite probable that all these metal complexes may exist as a mixture of two stereoisomers with the possibility of quick interconversion from one form to another. The existence of such stereoisomers has been observed in the case of dipivoylmethane complexes of tetravalent actinides [19].

Table II shows the chemical shift data of the PMR spectra of the thorium and uranium complexes. The methyl peaks are shifted downfield for the paramagnetic uranium chelates, whereas they are shifted upfield for the diamagnetic thorium chelates. On the other hand, the phenyl protons of the paramagnetic uranium chelates show extensive upward shifts, while the shift of the diamagnetic thorium complexes are much the same as those of the methyl peaks. The isotropic contact shift for the methyl and phenyl protons between the paramagnetic uranium chelate and the diamagnetic thorium chelate with each ligand has been calculated from the shift values. A comparison of these shift values enables us to separate the isotropic component of the shifts. This indicates partial covalent bonding involving 5f orbitals in the case of U(IV) chelates.

Electronic Spectra

The electronic spectra of the ligands and their chelates have been measured using a Beckmann DU-7 spectrophotometer and the characteristic peaks are listed in Table III. Although the ligands were found to be soluble in alcohol, all the spectra were measured in dimethylformamide in which the ligands and the complexes could be dissolved. The spectra of the neat ligands exhibit only two peaks which can reasonably be assigned to $\pi^* \leftarrow \pi$ transitions. These bands do not appear to suffer any significant shift in the uranium complexes, although a hypsochromic shift is observed for the 314 nm peak of the thorium complexes. Peaks 4, 5 and 6 of the uranium chelates listed in Table III show bathochromic shifts as compared to the peaks of U(IV) in aqueous HCl. A measure of covalency has been deduced from the shifts of peaks 5 and 6 based on Sinha's parameter [20], which was found to range from 1–1.6%, indicating a small amount of covalent character in conformity with the PMR data.

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