

Base adducts of dioxobis(acetoacetanilidato)uranium(VI)

P SREEMAN and N THANKARAJAN*

Department of Chemistry, University of Calicut, Calicut 673 635, India

MS received 1 May 1980; revised 27 October 1980

Abstract. Uranyl complexes of the type $[\text{UO}_2\text{L}_2\text{B}]$, where L is the enolate of acetoacetanilide, and B a monodentate base like pyridine, picoline, aniline or N-substituted aniline, have been synthesised and characterised by analysis, conductance and magnetic measurements, thermal, IR and NMR spectral studies. The order of thermal stability and features of IR spectra of the series have been explained. Pentagonal bipyramidal structure has been assigned for the complexes based on the NMR spectral evidence.

Keywords. Base adducts; uranyl complexes; acetoacetanilide; thermogravimetry; infrared spectra; nuclear magnetic resonance.

1. Introduction

Uranyl β -ketoenolates are known to form adducts with acetophenone, water (Comyns *et al* 1958; Sacconi *et al* 1958; Wendlandt *et al* 1960), ammonia, pyridine and aliphatic amines (Hager 1927; Sacconi and Giannoni 1954; Nakamoto *et al* 1961; Sacconi and Paoletti 1961; Szöke 1959, 1965; Haigh and Thornton 1971). Base adducts of acetoacetanilide chelate of uranyl are reported in this paper.

2. Experimental

Adducts of dioxobis(acetoacetanilidato)uranium(VI) with pyridine, picolines, aniline and N-alkylanilines were prepared by following the common procedure. Uranyl acetate (1 g, 0.0025 mol) in warm water (20 cm³) was added dropwise to a stirred solution of acetoacetanilide (0.88 g, 0.005 mol) in ethanol (25 cm³) containing the base (2 cm³). The product was filtered after stirring for 1 hr, and the residue washed with ethanol and recrystallised from acetone.

Analytical data and other details of the complexes are presented in table 1. Instruments used are Perkin-Elmer 137 infrared spectrometer, Varian A 60 D

* To whom all correspondence should be made.

Table 1. Analytical data and other details of the base adducts of dioxobis(acetoacetanilidato)uranium(VI)

B in [UO ₂ (acacN) ₂ B]	Yield (%)	m.p. (° C)	Conduc- tance (in ohm ⁻¹ cm ² mole ⁻¹)	Analytical data ^a			
				U (%)	C (%)	H (%)	N (%)
Pyridine	62·5 ^b	220–222 ^d	20	33·21 (33·95)	42·95 (42·80)	3·85 (3·57)	5·39 (5·99)
2-Methylpyridine	55·5 ^b	90 ^d	22	33·90 (33·29)	44·40 (43·64)	3·99 (3·78)	5·21 (5·87)
3-Methylpyridine	72·5 ^b	226 ^d	15	33·75 (33·29)	44·20 (43·64)	3·95 (3·78)	6·20 (5·87)
4-Methylpyridine	96·2 ^b	226–228 ^d	10	32·73 (33·29)	42·75 (43·64)	3·98 (3·78)	5·21 (5·87)
Aniline	59·8 ^c	95 ^d	12	32·65 (33·29)	42·83 (43·64)	3·95 (3·78)	4·97 (5·87)
N-Methylaniline	56·9 ^c	226 ^d	13	32·05 (32·65)	43·68 (44·44)	4·45 (3·98)	5·01 (5·76)
N-Ethylaniline	49·7 ^c	235–237 ^d	23	33·20 (32·07)	44·50 (45·22)	4·72 (4·17)	5·25 (5·65)
N,N-Dimethylaniline	75·5 ^c	157 ^d	21	32·50 (32·07)	44·88 (45·22)	4·27 (4·17)	5·15 (5·65)

a = Calculated percentages in brackets; *b* = reddish-brown; *c* = orange-red; *d* = decomposes.

NMR spectrometer, Stanton thermobalance (heating rate 5° C min⁻¹), Toshniwal conductivity bridge and a Gouy type magnetic balance. Unless otherwise stated the infrared spectral data are of mulls in 'Nujol', the bands having been calibrated using the nearest polystyrene band. Microanalyses were carried out at the Central Drug Research Institute, Lucknow. Uranium was determined as U₃O₈.

3. Results and discussion

3.1. Characterisation of the complexes

All the complexes are diamagnetic and non-conducting and their analytical data fit well for [UO₂L₂B] where L is the enolate of acetoacetanilide and B the base employed.

Adducts derived from the tertiary bases show infrared band for N–H stretching of the acetoacetanilide moiety at 3250 cm⁻¹, which is about 50 cm⁻¹ higher than that of acetoacetanilide. This upward shift provides evidence for the abstention of nitrogen atom from coordinating to the metal, since that would have caused

only a depression of $\nu_{\text{N-H}}$ (Nakamoto 1977). The acetyl and amide carbonyl stretching frequencies of acetoacetanilide at 1727 and 1661 cm^{-1} respectively (Belford *et al* 1956; Sen and Umopathy 1968) are shifted to 1580 and 1600 cm^{-1} . These shifts provide strong evidence for chelation of acetoacetanilide moiety as β -amidoenolate to the central atom.

An acetoacetanilide complex of uranyl, $[\text{UO}_2\text{L}_2(\text{LH})]$, containing an extra molecule of acetoacetanilide, LH, was reported (Sen and Thankarajan 1968). The coordination site, occupied by LH in this complex, appears occupied by the base in the adducts prepared.

Band shifts indicating coordination of the bases are observed in the IR spectra of all the adducts. Thus, instead of the two N-H stretching bands at 3481 and 3395 cm^{-1} shown by aniline (Masson 1958), the aniline adduct shows only a single band at 3320 cm^{-1} , which seems superimposed on the N-H stretching band of coordinated acetoacetanilide. The twisting vibration of N-H at 1054 cm^{-1} (Evans 1960) is shifted to 1055 cm^{-1} , pointing further to the coordinated nature of aniline. As reported in the cases of complexes of N,N-dimethylaniline and N-methylaniline (Braunholtz *et al* 1958), a medium intensity band each in the C-H stretching region (2795 and 2807 cm^{-1}) disappeared in the spectra (KBr pellets) of adducts of these bases. As expected, in the adducts of N-methylaniline and N-ethylaniline, $\delta_{\text{N-H}}$ at 1510 cm^{-1} and $\nu_{\text{C-N}}$ at 1260 cm^{-1} (Hazdi and Skrbliak 1957) are shifted to 1530 and 1295 cm^{-1} respectively.

Thermal studies, while lending further evidence to the coordination of the bases, afford a comparison of their thermal stabilities. Adducts of pyridine, β -picoline and γ -picoline decompose in one step in the temperature range 180–460° C. The percentage weight loss corresponds to two molecules of acetoacetanilide and one molecule of the corresponding base. That the bases are removed only with the chelating ligands indicates that the bases are bonded strongly. In the case of adducts of aniline and α -picoline, the base first splits off in the temperature range 170–480° C. For the adduct of aniline this is expected since aniline, being the least basic among the series, may form only a weak coordinate bond. The unexpected early expulsion of α -picoline (one of the most basic among the series) must, therefore, be due to steric reasons. That steric factor is important is evident from the observed failure of quinoline to form a similar adduct. The increase in yield (table 1) from α - through β - to γ -picoline adducts can also be explained on steric grounds.

NMR spectral data provide further clue to the structure of the complexes. The spectra (in DMSO- d_6) show that the two acetoacetanilide moieties are equivalent in the complexes studied. On the basis of this evidence a pentagonal bipyramidal structure, in which the four oxygen atoms of the chelating ligands and the nitrogen atom of the base form a plane normal to the O=U=O axis, is proposed (figure 1). This geometry has been established in the case of dioxobis(acetylacetonato)aquouranium(VI) (Fasson *et al* 1964), and $\text{K}_3[\text{UO}_2\text{F}_5]$ (Zachariason 1954). The spectrum of dioxobis(acetoacetanilidato)pyridineuranium(VI) revealed five signals: singlet at 2.2 δ (CH_3); singlet at 4.5 δ (α -CH); multiplet centred at 6.3 δ (pyridine ring protons); multiplet centred at 7.3 δ (phenyl protons of acetoacetanilide moieties); and broad singlet at 9.3 δ (NH). Dioxobis(acetoacetanilidato)anilineuranium(VI) showed absorptions at 1.3 δ (singlet of CH_3), 2.2 δ (broad singlet of NH_2), 4.4 δ (singlet of α -CH), 6.3 δ (multiplet of phenyl

Table 2. Infrared spectral data of adducts of dioxobis(acetoacetamidato) uranium(VI) with bases, and $\nu_{\text{C=O}}$ values of the bases.

B in [UO ₂ (acacN) ₂ B]	$\nu_{\text{C=O}}$ (acetyl) cm ⁻¹	$\nu_{\text{U=O}}$ cm ⁻¹	Bands in the region 650–400 cm ⁻¹ which have contribution from $\nu_{\text{U=O}}$ and $\nu_{\text{U-N}}$ (cm ⁻¹)				
2-Methylpyridine	1585 (s)	895 (vs)	609 (w)	598 (w)	515 (w)	508 (m)	410 (m)
3-Methylpyridine	1583 (s)	898 (vs)	642 (m)	607 (m)	512 (m)	503 (w)	405 (m)
4-Methylpyridine	1586 (s)	894 (vs)		610 (m)	514 (m)	504 (m)	405 (m)
Pyridine	1581 (s)	903 (vs)	627 (m)	605 (m)	512 (m)	510 (m)	425 (w)
N,N-Dimethylaniline	1578 (s)	905 (vs)					
N-Ethylaniline	1577 (s)	908 (vs)					
N-Methylaniline	1574 (s)	913 (vs)					
Aniline	1572 (s)	915 (vs)					

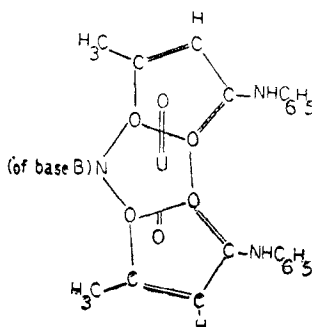


Figure 1. Structure of $[\text{UO}_2(\text{acacN})_2\text{B}]$.

protons of aniline), 7.1δ (multiplet of phenyl protons of acetoacetanilide moieties) and 9.7δ (broad singlet of NH). Integrated intensities agreed with the number of different kinds of hydrogen(s) present. The CH_3 and $\alpha\text{-CH}$ signals are relatively at higher fields, probably due to the increased electron density available around the metal ion due to coordination of the base.

3.2. Effect of donor strength of base on other metal-ligand bonds

The uranyl vibrational band at about 910 cm^{-1} (Nakamoto *et al* 1961) registers a depression with increased basicity of B (Smith 1968). Along with this, is observed (table 2) an increase in frequency of the acetyl carbonyl vibration, which implies that the corresponding metal-oxygen bond is also weakened. Bands between 400 and 650 cm^{-1} , though known to have a contribution from $\nu_{\text{U-O}}$ (Nakamoto 1961), did not show any clear trend in their shifts, probably because they are not pure.

Acknowledgements

PS thanks the Council of Scientific and Industrial Research, New Delhi, for a Fellowship. The authors thank Professor S S Moosath, Department of Chemistry, University of Calicut, for encouragement.

References

- Belford R L, Martell A E and Calvin M 1956 *J. Inorg. Nucl. Chem.* **2** 11
 Braunholtz J T, Mann F G, Ebsworth E A S and Sheppard N 1958 *J. Chem. Soc.* p. 2780
 Comyns A E, Gatehouse B M and Wait E 1958 *J. Chem. Soc.* p. 4655
 Evans J C 1960 *Spectrochim. Acta* **16** 128
 Fasson E, Bombieri G and Panattoni C 1964 *Nature (London)* **202** 1325
 Hager K 1927 *Z. Anorg. Allg. Chem.* **162** 82
 Haigh J M and Thornton D A 1971 *J. Inorg. Nucl. Chem.* **33** 1787
 Hazdi D and Skrbliak N 1957 *J. Chem. Soc.* p. 843.
 Masson S F 1958 *J. Chem. Soc.* p. 3619
 Nakamoto K 1977 *Infrared and Raman spectra of inorganic and coordination compounds* (New York: John Wiley) 3rd ed. p. 197
 Nakamoto K, Morimoto Y and Martell A E 1961 *J. Am. Chem. Soc.* **83** 4533
 Sacconi L, Carroti G and Paoletti P 1958 *J. Inorg. Nucl. Chem.* **8** 93

- Sacconi L, Carroti G and Paoletti P 1958 *J. Chem. Soc.* p. 4257
Sacconi L and Giannoni G 1954 *J. Chem. Soc.* p. 2368
Sacconi L and Paoletti P 1961 *J. Chem. Soc.* p. 4250
Sen D N and Umapathy P 1968 *Indian J. Chem.* **6** 516
Sen D N and Thankarajan N 1968 *Indian J. Chem.* **6** 278
Smith J W 1968 *The chemistry of functional groups : The chemistry of amino group* (ed.) Saul Patai (New York: Interscience) pp. 182, 188
Szöke J 1959 *Acta Phys. Chem. Szeged.* **5** 51
Szöke J 1965 *Proc. Symp. Coord. Chem.* (Tihany, Hungary) p. 835
Wendlandt W W, Bear J L and Horton G R 1960 *J. Phys. Chem.* **64** 1289
Zachariason 1954 *Acta Crystallogr.* **7** 783