

Synthesis & characterization of dioxouranium(VI), oxovanadium(IV) and hydroxozirconium(IV) complexes of poly(imidazolyl)borate anion

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Received 8 June 1989; revised 16 January 1990;
accepted 19 February 1990

Several five-, six- or eight-coordinated complexes of dioxouranium(VI), oxovanadium(IV) and hydroxozirconium(IV) with dihydridobis(imidazolyl)borate (DIB), hydridotris(imidazolyl)borate (HIB) and tetrakis(imidazolyl)borate (TIB) have been prepared and characterized on the basis of analytical data, infrared and electronic spectra and magnetic susceptibility measurements. U–O bond length and force constant for dioxouranium complexes have also been calculated.

The coordination chemistry of poly(imidazolyl)borate ligand containing B–N bond has been the subject of many recent investigations¹⁻³. Although complexes of this ligand with a number of bivalent transition metal ions are reported, complexes with trivalent ions are very few and no complexes with quadrivalent metal ions are known. It was, therefore, of interest to study the complexes of dioxouranium(VI), oxovanadium(IV) and hydroxozirconium(IV) with the ligands dihydridobis(imidazolyl)borate (DIB), hydridotris(imidazolyl)borate (HIB) and tetrakis(imidazolyl)borate (TIB). The chemistry of oxozirconium(IV) and oxovanadium(IV) has added interest due to the controversy regarding the Zr=O bond and the increasing discoveries of biological importance involving vanadium and oxovanadium systems⁴⁻⁷. The linear dioxouranium(VI) ion is also known to give a number of high coordinated complexes with different ligands⁸.

Experimental

All the metal salts and potassium borohydride were BDH reagents. Imidazole was recrystallized from cyclohexane.

Preparation of the complexes

The ligands were prepared by the methods reported earlier¹⁻³. A hot methanol solution (0.01

M) of $\text{UO}_2(\text{NO}_3)_2$, ZrOCl_2 (30 ml) or VOSO_4 (in 30 ml ethanol) was added with stirring to the hot solution of the ligand (0.02 *M*) in aqueous DMF (30 ml). The contents were heated under reflux on a steam bath for 0.5 h. Solid products separated out on cooling. These were filtered, washed and dried at room temperature over anhydrous calcium chloride, yield 30-50%.

IR spectra ($4000\text{-}200\text{ cm}^{-1}$) of the complexes were recorded on a Perkin Elmer 621 spectrophotometer. Diffuse reflectance spectra were obtained with Carl-Zeiss VSU-2P spectrophotometer using MgO as the calibrant. Magnetic susceptibility measurements were made using a vibrating sample magnetometer model 155 at 21°C. Microanalyses were carried out using a Carlo Erba instrument. Metal analyses were carried out by standard methods⁹.

Results and discussion

The analytical data of the complexes (Table 1) indicate a 1:2 (metal:ligand) stoichiometry. The observed shifts in some of the ring vibrations ($1670\text{-}1310\text{ cm}^{-1}$) in the IR spectra of the complexes as compared to those of the free ligands suggest that the pyridyl nitrogen is a possible bonding site¹⁰. The appearance of a broad doublet at 2300 and 2400-2450 cm^{-1} in the spectra of DIB complexes and a singlet at 2300-2350 cm^{-1} in the spectra of HIB complexes indicates the presence of two and one hydrogen respectively attached to boron. TIB complexes are devoid of B–H band. In the complexes $\nu\text{B-N}$ occurs in the range 1370-1390 cm^{-1} , which indicates the possibility of pyrrolic nitrogen coordination. Coordination through nitrogen is further supported by the appearance of new bands at 520-550, 460-480 and 435-455 cm^{-1} in dioxouranium, oxovanadium and hydroxozirconium complexes, respectively which can be assigned to $\nu\text{M-N}$ mode.

The dioxouranium(VI) and hydroxozirconium(IV) complexes are diamagnetic. The magnetic moments of the oxovanadium complexes (1.61-1.66 BM) are consistent with the values reported for $3d^1$ complexes with orbital contribution to the magnetic moment completely quenched¹¹.

The appearance of $\nu_{\text{v=O}}$ mode at 940 cm^{-1} in $\text{VO}(\text{DIB})_2$ and at 920 and 915 cm^{-1} in $\text{VO}(\text{HIB})_2$ and $\text{VO}(\text{TIB})_2$ complexes indicates the presence of double bond in the VO^{2+} moiety arising from

Table 1 – Analytical data of the complexes

Complex*	Colour (% yield)	Found (Calc.), %			
		C	H	N	M
UO ₂ (DIB) ₂	Dark yellow (35)	25.81 (25.53)	3.10 (2.84)	19.30 (19.86)	42.70 (42.20)
UO ₂ (HIB) ₂	Dirty yellow (40)	31.40 (31.03)	2.99 (2.87)	24.00 (24.14)	34.65 (34.20)
UO ₂ (TIB) ₂	Light yellow (50)	34.52 (34.78)	2.99 (2.90)	27.46 (27.05)	28.50 (28.74)
VO(DIB) ₂	Grey (45)	40.45 (39.89)	4.40 (4.43)	31.40 (31.02)	14.55 (14.13)
VO(HIB) ₂	Dark Grey (40)	43.30 (43.81)	4.40 (4.06)	33.69 (34.08)	10.90 (10.34)
VO(TIB) ₂	Dark Grey (45)	46.78 (46.08)	3.90 (3.84)	35.70 (35.84)	8.67 (8.16)
Zr(OH) ₂ (DIB) ₂	Colourless (35)	34.76 (34.37)	3.90 (3.82)	26.50 (26.73)	21.90 (21.72)
Zr(OH) ₂ (HIB) ₂	Colourless (40)	31.80 (31.63)	3.17 (2.93)	24.40 (24.60)	17.00 (16.52)
Zr(OH) ₂ (TIB) ₂	Colourless (50)	42.60 (42.17)	3.80 (3.51)	33.10 (32.80)	13.79 (13.32)

*DIB = (C₆H₈N₄B), HIB = (C₉H₁₀N₆B) and TIB = (C₁₂H₁₂N₈B).

Table 2 – Calculated U – O bond length and force constant

Complex	\bar{R}_{U-O} (Å)	Force constant (mdynes/Å)
UO ₂ (DIB) ₂	1.68	9.49
UO ₂ (HIB) ₂	1.66	10.70
UO ₂ (TIB) ₂	1.66	10.70

a combination of σ bond and π component due to electron flow $O(p\pi) \rightarrow V(d\pi)$ ¹⁷. The decrease by 20 and 25 cm⁻¹ in the V=O frequency in HIB and TIB complexes may probably be due to the increase in electron density on vanadium thereby reducing its acceptor property towards oxygen and hence lowering the V–O multiple bond character. This may be taken as an indication of the increase in coordination number from five in DIB to six in HIB and TIB complexes.

The IR spectra of the dioxouranium complexes exhibit absorption bands in the region 970-1010 cm⁻¹ assignable to non-degenerate asymmetric

stretching vibration (ν_3). The appearance of a strong band assignable to the symmetric stretching mode ν_1 between 855 and 870 cm⁻¹ implies the non-linear nature of the O–U–O group. The doubly degenerate O–U–O (ν_2) is obtained as a band of medium intensity in 280-310 cm⁻¹ range.

The electronic spectrum of VO(DIB)₂ exhibits bands at 12200, 16250 and 23480 cm⁻¹. These band positions are consistent with those reported for other five-coordinated oxovanadium(IV) complexes with square pyramidal geometry¹²⁻¹⁴. These bands can be assigned to the transitions¹⁵ ${}^2E \leftarrow {}^2B_2$, ${}^2B_1 \leftarrow {}^2B_2$ and ${}^2A_1 \leftarrow {}^2B_2$. The second transition directly corresponds to 10 Dq. The spectra of VO(HIB)₂ and VO(TIB)₂ display two bands in the regions 17000-17200 and 24250-24750 cm⁻¹ and a shoulder at 13330-13650 cm⁻¹ which are assigned to the transitions ${}^2B_1 \leftarrow {}^2B_2$, ${}^2A_1 \leftarrow {}^2B_2$ and ${}^2E \leftarrow {}^2B_2$, respectively on the basis of octahedral geometry¹⁶.

The reflectance spectra of the UO₂ complexes show some weak bands at 20480-20600, 21310-

21500 and 22100-22400 cm^{-1} . The band at 21310-21500 cm^{-1} is assigned to $^1\Sigma_g^+ \leftarrow ^3\pi_u^5$ transition¹⁸ which is lower than that reported for UO_2^{2+} ion¹⁹ and is indicative of the covalent nature of the metal-ligand bond. The remaining two bands may be due to the vibration of the UO_2^{2+} group²⁰.

The asymmetry of the complexes has been used to calculate the U-O bond lengths ($R_{\text{U-O}}$) according to the equation²¹, $R_{\text{U-O}} = 81.2 \nu^{-2/3} + 0.85$, and substituting these values in the Jones equation²², $E_{\text{U-O}} = 1.08 f^{-1/3} + 1.17$, the force constant f has been calculated; the values are listed in Table 2. The U-O bond distances do not have a constant value and are in the required range (~ 1.6 - 2.0 Å)²³. High force constant values for the U-O bond indicate a bond order greater than two.

The expected $\nu_{\text{Zr=O}}$ vibration in the region 850-950 cm^{-1} is not observed in the IR spectra of the zirconyl complexes, which rules out the existence of the Zr=O unit in these complexes. The observation is in agreement with the results of the X-ray study²³ that $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, is devoid of Zr=O bond and has the structure $[\text{Zr}_4(\text{OH})_8(\text{H}_2\text{O})_{16}]\text{Cl}_8$. The IR bands at 840 and 1130-1140 cm^{-1} may probably be due to Zr-OH stretching vibration and Zr-O-H bending vibration²⁴. These observations together with the results of elemental analysis favour the formulation of the complexes as $\text{Zr}(\text{OH})_2\text{L}_2$.

Acknowledgement

We thank Prof. S M Osman for providing research facilities. Two of us (TAK and SRAZ) are thankful to the UGC, New Delhi, and CSIR, New Delhi, respectively, for financial support.

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