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Syntheses and Spectroscopic Studies on Dioxouranium(VI), Oxovanadium(IV) and Oxozirconium(IV) Complexes with Tetradentate Macrocyclic Ligands

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Abstract

The macrocyclic complexes of types $[UO_2(mac)(NO_3)_2]$, $[VO(mac)]SO_4$ and $[ZrO(mac)H_2O]Cl_2$ or $[Zr(OH)_2(mac)]Cl_2$ (where mac = macrocyclic ligands derived by condensation of benzil or diacetyl with diamines, carbohydrazide and thiocarbohydrazide) have been prepared by *in situ* method or by the reactions of metal salts with presynthesized ligands. The stoichiometry of the complexes has been proposed on the basis of elemental analyses, conductance and magnetic moment data. The coordination behaviour of the ligands has been determined with the help of spectroscopic (infrared and electronic) studies. Probable structures of the complexes are proposed.

Introduction

Although more than sixty oxocation species are known, the complexes of only a few, e.g., UO_2^{VI}, VO^{IV} and ZrO^{IV}, have been extensively investigated [1]. Some papers have appeared on the chemistry of their macrocyclic complexes [2–4], but complexes with tetraaza macrocyclic ligands have not been studied. Moreover, very few reports are available on the macrocyclic ligands involving mixed nitrogen, sulphur or oxygen donor atoms. The emphasis on these species is undoubtedly related to the existence of naturally occurring metal complexes such as metalloporphyrins, vitamin B_{12} and chlorophyll etc. [5–8]. These ligands are also of theoretical interest since they are capable of furnishing an environment of controlled geometry and ligand field strength [9–11]. The possibility of using them as models for intricate biological systems has prompted us to synthesize and characterize some macrocyclic ligands derived from reactions of diamines or hydrazides with carbonyl compounds [12–14].

In the present communication, we report the preparation and characterization of dioxouranium(VI), oxovanadium(IV) and oxozirconium(IV) complexes with macrocyclic ligands derived by the condensation of benzil or diacetyl with ethylenediamine, *o*- or *p*-phenylenediamine, carbohydrazide and thiocarbohydrazide.

Experimental

All the solvents and chemicals used were reagent grade B.D.H. products. Carbohydrazide and thiocarbohydrazide were prepared by the methods of Möhr *et al.* [15] and Bürns [16], respectively.

Preparation of Macrocyclic Ligands Derived by Condensation of Benzil or Diacetyl with Carbohydrazide or Thiocarbohydrazide

A solution of benzil or diacetyl (0.04 mol) in ethanol (25 ml) was added to a refluxing solution of carbohydrazide or thiocarbohydrazide (0.04 mol) in aqueous ethanol (30 ml) followed by addition of concentrated hydrochloric acid (1 ml). The reaction mixture was refluxed for 4–6 h, then the solution was kept overnight. A yellow mass separated out which was filtered and dried. The product was recrystallized in ethanol.

Benzil–carbohydrazide condensation product (mac^1)

Yield ~88%, melting point (m.p.) 108 °C (d). *Anal.* Found: C, 68.0; H, 4.4; N, 21.1. Calc. for $C_{30}H_{24}N_8O_2$: C, 68.1; H, 4.5; N, 21.2%.

Diacetyl–carbohydrazide condensation product (mac^2)

Yield ~80%, m.p. 175 °C (d). *Anal.* Found: C, 42.7; H, 5.5; N, 39.9. Calc. for $C_{10}H_{16}N_8O_2$: C, 42.8; H, 5.7; N, 40.0%.

Benzil–thiocarbohydrazide condensation product (mac^3)

Yield ~82%, m.p. 95 °C (d). *Anal.* Found: C, 64.1; H, 4.0; N, 19.9. Calc. for $C_{30}H_{24}N_8S_2$: C, 64.2; H, 4.2; N, 20.0%.

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Diacetyl–thiocarbohydrazide condensation product (mac^4)

Yield ~68%, m.p. 208 °C (d). *Anal.* Found: C, 38.2; H, 5.0; N, 35.8. Calc. for $C_{10}H_{16}N_8S_2$: C, 38.4; H, 5.1; N, 35.9%.

Preparation of Complexes of UO_2(VI), VO(IV) and ZrO(IV) with Macrocyclic Ligands Derived by Condensation of Benzil or Diacetyl with Carbohydrazide or Thiocarbohydrazide

A general procedure was adopted as follows:

An ethanolic solution (20 ml) of uranylnitrate (0.02 mol) or a methanolic solution (20 ml) of vanadylsulphate (0.02 mol) or an aqueous solution (20 ml) of zirconylchloride (0.02 mol) was added to the refluxing solution (30 ml) of the appropriate ligand (0.02 mol) in ethanol. The reaction mixture was refluxed for 8–9 h, when the colour of the solution intensified. The solvent was removed *in vacuo* and the solid products were obtained. The complexes were thoroughly washed with dichloromethane and dried *in vacuo.*

In Situ Synthesis of Macrocyclic Complexes of UO_2(VI), VO(IV) and ZrO(IV) with Benzil or Diacetyl and Diamines

A general procedure was adopted as follows:

Benzil or diacetyl (0.02 mol) dissolved in ethanol (20 ml) was mixed with the appropriate diamine (0.02 mol) solution in ethanol (20 ml). To this, an ethanolic solution (20 ml) of uranylnitrate (0.01 mol) or a methanolic solution (20 ml) of vanadylsulphate (0.01 mol) or an aqueous solution (20 ml) of zirconylchloride (0.01 mol) was added and the reaction mixture was refluxed for 30 min. Then concentrated hydrochloric acid (1 ml) was added and the reaction mixture was again refluxed for 5 ~ 6 h, when the colour of the solution intensified. The solvent was removed *in vacuo* and solid products were obtained. The dioxouranium(VI) complexes were crystallized from methanol (10 ml). The oxovanadium(IV) complexes were thoroughly washed with methanol and ethanol mixture (10 ml, 1:1), whereas oxozirconium(IV) complexes were thoroughly washed with dichloromethane (10 ml) and dried *in vacuo.*

The colour, decomposition temperature, yield and analytical data of the complexes are given in Table I.

Analytical Procedures

Microanalysis for carbon, hydrogen and nitrogen were performed at the CDRI, Lucknow. Uranium and zirconium were estimated by standard gravimetric procedure as oxides [17]. Vanadium was

TABLE I. Physical and Analytical Data

Complex	Yield (%)	Colour	Decomposition temperature (°C)	Calc. (Found) (%)			
				C	H	N	M
$[UO_2(mac^1)(NO_3)_2]$	56	yellowish brown	80	39.0	2.6	15.2	25.8
				(38.9)	(2.5)	(15.0)	(25.8)
$[UO_2(mac^2)(NO_3)_2]$	48	red	86	17.8	2.4	20.8	35.3
				(17.7)	(2.3)	(20.7)	(35.2)
$[UO_2(mac^3)(NO_3)_2]$	52	brown	128	37.7	2.5	14.6	24.8
				(37.5)	(2.4)	(14.5)	(24.8)
$[UO_2(mac^4)(NO_3)_2]$	44	dark brown	142	16.9	2.3	19.8	33.7
				(16.7)	(2.1)	(19.8)	(33.6)
$[UO_2(mac^5)(NO_3)_2]$	46	reddish brown	125	44.5	3.2	9.7	27.6
				(44.3)	(3.1)	(9.6)	(27.5)
$[UO_2(mac^6)(NO_3)_2]$	42	light brown	98	50.1	2.9	8.7	24.8
				(50.0)	(2.8)	(8.7)	(24.8)
$[UO_2(mac^7)(NO_3)_2]$	45	brown	110	50.1	2.9	8.7	24.8
				(49.9)	(2.7)	(8.6)	(24.6)
$[UO_2(mac^8)(NO_3)_2]$	42	brown	136	23.4	3.2	13.6	38.7
				(23.2)	(3.1)	(13.5)	(38.6)
$[UO_2(mac^9)(NO_3)_2]$	48	brown	122	33.8	2.8	11.8	33.5
				(33.6)	(2.7)	(11.6)	(33.4)
$[UO_2(mac^{10})(NO_3)_2]$	40	brown	115	33.8	2.8	11.8	33.5
				(33.7)	(2.6)	(11.6)	(33.5)
$[VO(mac^1)]SO_4$	62	brown	128	52.1	3.5	16.2	7.4
				(52.0)	(3.4)	(16.1)	(7.3)
$[VO(mac^2)]SO_4$	50	brown	120	27.0	3.6	25.3	11.5
				(26.9)	(3.5)	(25.2)	(11.5)
$[VO(mac^3)]SO_4$	58	dark brown	156	49.8	3.3	15.5	7.0
				(49.7)	(3.2)	(15.5)	(6.8)

(continued)

TABLE I. *(continued)*

Complex	Yield (%)	Colour	Decomposition temperature (°C)	Calc. (Found) (%)			
				C	H	N	M
$[VO(mac^4)]SO_4$	46	dark brown	138	25.3 (25.2)	3.4 (3.3)	23.6 (23.5)	10.7 (10.6)
$[VO(mac^5)]SO_4$	52	brown	192	60.8 (60.6)	4.4 (4.3)	8.8 (8.5)	8.0 (8.0)
$[VO(mac^6)]SO_4$	50	brown	178	66.0 (65.8)	3.8 (3.7)	7.7 (7.6)	7.0 (6.9)
$[VO(mac^7)]SO_4$	54	brown	168	66.0 (65.9)	3.8 (3.6)	7.7 (7.7)	7.0 (6.9)
$[VO(mac^8)]SO_4$	56	dark brown	172	37.6 (37.5)	5.2 (5.1)	14.6 (14.5)	13.3 (13.1)
$[VO(mac^9)]SO_4$	48	brown	150	50.1 (50.0)	4.2 (4.1)	11.7 (11.7)	10.6 (10.5)
$[VO(mac^{10})]SO_4$	52	brown	156	50.1 (49.9)	4.2 (4.0)	11.7 (11.6)	10.6 (10.5)
$[ZrO(mac^1)H_2O]Cl_2$	76	yellowish brown	135	49.7 (49.6)	3.6 (3.5)	15.5 (15.4)	12.7 (12.5)
$[ZrO(mac^2)H_2O]Cl_2$	68	orange	148	25.2 (25.1)	3.8 (3.7)	23.5 (23.4)	19.2 (19.0)
$[ZrO(mac^3)H_2O]Cl_2$	72	dark brown	130	47.6 (47.5)	3.4 (3.4)	14.8 (14.8)	12.0 (12.0)
$[ZrO(mac^4)H_2O]Cl_2$	60	dark brown	140	23.6 (23.5)	3.5 (3.4)	22.0 (22.0)	17.9 (17.8)
$[ZrO(mac^5)H_2O]Cl_2$	76	reddish brown	165	57.8 (57.6)	4.5 (4.4)	8.4 (8.3)	13.7 (13.5)
$[ZrO(mac^6)H_2O]Cl_2$	68	light brown	185	63.1 (63.0)	3.9 (3.8)	7.4 (7.3)	11.9 (11.9)
$[ZrO(mac^7)H_2O]Cl_2$	72	brown	160	61.1 (63.0)	3.9 (3.7)	7.4 (7.2)	11.9 (11.8)
$[ZrO(mac^8)H_2O]Cl_2$	64	reddish brown	195	34.6 (34.5)	5.3 (5.1)	13.4 (13.2)	21.9 (21.8)
$[ZrO(mac^9)H_2O]Cl_2$	78	brown	180	46.8 (46.6)	4.3 (4.3)	10.9 (10.8)	17.8 (17.7)
$[ZrO(mac^{10})H_2O]Cl_2$	70	brown	188	46.8 (46.5)	4.3 (4.2)	10.9 (10.9)	17.8 (17.6)

mac^1 = macrocyclic ligand derived by condensation of benzil and carbohydrazide, mac^2 = macrocyclic ligand derived by condensation of diacetyl and carbohydrazide, mac^3 = macrocyclic ligand derived by condensation of benzil and thiocarbohydrazide, mac^4 = macrocyclic ligand derived by condensation of diacetyl and thiocarbohydrazide, mac^5 = macrocyclic ligand derived by condensation of benzil and ethylenediamine, mac^6 = macrocyclic ligand derived by condensation of benzil and *o*-phenylenediamine, mac^7 = macrocyclic ligand derived by condensation of benzil and *p*-phenylenediamine, mac^8 = macrocyclic ligand derived by condensation of diacetyl and ethylenediamine, mac^9 = macrocyclic ligand derived by condensation of diacetyl and *o*-phenylenediamine, mac^{10} = macrocyclic ligand derived by condensation of diacetyl and *p*-phenylenediamine.

estimated gravimetrically as its vanadate [17] after decomposing the complex with concentrated nitric acid.

Physical Measurements

The details of physical measurements are the same as described earlier [18].

Results and Discussion

The macrocyclic complexes of dioxouranium(VI), oxovanadium(IV) and oxozirconium(IV) were synthesized by refluxing the ligand with uranylnitrate or vanadylsulphate or zirconylchloride in ethanol. The reactions appear to proceed according to the following equations

$$UO_2(NO_3)_2\cdot 6H_2O + mac \xrightarrow{\text{ethanol}} [UO_2(mac)(NO_3)_2]$$

$$VOSO_4 + mac \xrightarrow{\text{ethanol}} [VO(mac)]SO_4$$

$$ZrOCl_2\cdot 8H_2O + mac \xrightarrow{\text{ethanol}} [ZrO(mac)H_2O]Cl_2$$

or

$$[Zr(OH)_2(mac)]Cl_2$$

where mac = macrocyclic ligands derived from condensation of benzil or diacetyl with carbohydrazide or thiocarbohydrazide

The *in situ* process of synthesis was used for the preparation of macrocyclic complexes of the same metal cations with benzil or diacetyl and diamines. The reactions appear to proceed according to the following equations

$$\mathrm{UO_2(NO_3)_2\cdot 6H_2O} + \underset{\substack{\text{or}\\ \text{diacetyl}}}{\text{benzil}} + \text{diamines} \xrightarrow[\text{HCl}]{\text{ethanol}} [\mathrm{UO_2(mac)(NO_3)_2}]$$

$$\mathrm{VOSO_4} + \underset{\substack{\text{or}\\ \text{diacetyl}}}{\text{benzil}} + \text{diamines} \xrightarrow[\text{HCl}]{\text{ethanol}} [\mathrm{VO(mac)}]\mathrm{SO_4}$$

$$\mathrm{ZrOCl_2\cdot 8H_2O} + \underset{\substack{\text{or}\\ \text{diacetyl}}}{\text{benzil}} + \text{diamines} \xrightarrow[\text{HCl}]{\text{ethanol}}$$

$$[\mathrm{ZrO(mac)(H_2O)}]\mathrm{Cl_2} \text{ or } [\mathrm{Zr(OH)_2(mac)}]\mathrm{Cl_2}$$

where mac = tetraaza macrocyclic ligands derived from condensation of benzil or diacetyl with different diamines.

The elemental analyses (Table I) of complexes show 1:1 metal to ligand stoichiometry. The dioxouranium(VI) and oxozirconium(IV) complexes are soluble in methanol, ethanol, dimethylformamide and dimethylsulphoxide, whereas oxovanadium(IV) complexes are only soluble in dimethylformamide and dimethylsulphoxide. The conductance measurements for oxovanadium(IV) complexes in dimethylformamide and oxozirconium(IV) complexes in methanol show an electrolytic nature. Dioxouranium(VI) complexes are nonelectrolytes in methanol.

Magnetic Moments and Electronic Spectra

The dioxouranium(VI) complexes are diamagnetic in nature. The electronic spectra of various uranyl complexes have been studied, to reveal that ligation has a relatively minor influence and the electronic spectra of such complexes are mainly dependent upon the triatomic UO_2 moiety [7, 19, 20]. The two bands occurring at *ca.* 22 400 and 25 300 cm^{-1} appear to be vibrational in nature. The electronic bands in the region 36 000–38 000 cm^{-1} are assigned [21] to $\pi \rightarrow \pi^*$ transitions of the azomethine ($\gt$C=N linkages, which are also observed in the ligands.

The magnetic moments of the oxovanadium(IV) macrocyclic complexes lie in the range 1.71–1.80 BM at room temperature. These values are well within the range reported for vanadyl(IV) complexes with one unpaired electron [22]. Vanadyl complexes exhibit three bands in the regions 11 000–12 500, 15 200–16 000 and 21 200–23 000 cm^{-1}. These spectra resemble those of other five-coordinate oxovanadium(IV) complexes [23–26]. Several schemes have been advanced to interpret the electronic spectra of oxovanadium(IV) [27] complexes. These schemes predict a three band spectrum for five-coordinate complexes possessing the effective C_{4v} symmetry of a square pyramid. Recently, Wasson *et al.* [28] have reported an energy level scheme: $d_{xy} < d_{yz} < d_{xz} < d_{x^2-y^2} < d_{z^2}$ to interpret the electronic spectra of distorted five-coordinate square pyramidal oxovanadium(IV) complexes. This scheme is similar to that proposed by Ballhausen and Gray [29], except for the splitting of d_{xz} and d_{yz} levels. Accordingly, the bands observed for the present complexes can be assigned to $d_{xy} \rightarrow d_{yz}$, $d_{xy} \rightarrow d_{xz}$ and $d_{xy} \rightarrow d_{x^2-y^2}$ transitions. In addition to these bands, one more band is observed at *ca.* 36 500 cm^{-1}, which is assigned to $\pi \rightarrow \pi^*$ transitions of the azomethine linkages ($\gt$C=N).

The oxozirconium(IV) macrocyclic complexes are diamagnetic. The two bands are observed at *ca.* 22 800 and 35 600 cm^{-1} in oxozirconium(IV) complexes. The first band is due to charge transfer in origin, whereas the second band may be attributed to the $\pi \rightarrow \pi^*$ transitions of the azomethine ($\gt$C=N) groups.

Infrared Spectra

(i) Complexes with macrocyclic ligands derived by condensation of benzil or diacetyl with carbohydrazide or thiocarbohydrazide

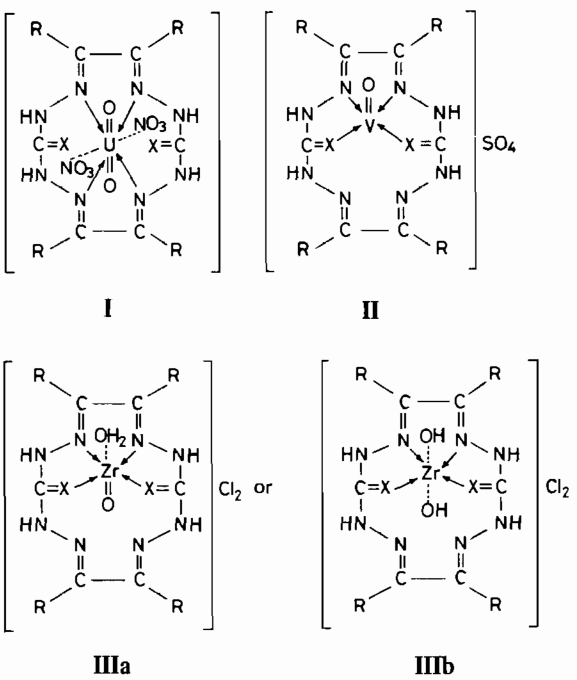
The macrocyclic ligands derived by condensation of carbohydrazide with benzil or diacetyl show bands at *ca.* 1675, 1500, 1260 and 660 cm^{-1}, which may be assigned [30, 31] to amide-I, amide-II, amide-III and amide-IV vibrations, respectively. The macrocyclic ligands derived by condensation of thiocarbohydrazide with benzil or diacetyl show bands at *ca.* 1560, 1215, 1080 and 765 cm^{-1}, which are assigned [32, 33] to thioamide-I, -II, -III and -IV vibrations respectively. In the oxovanadium(IV) and oxozirconium(IV) complexes all these bands (except amide-I and thioamide-I) show upward shifts (~60 cm^{-1}) whereas amide-I and thioamide-I show a downward shift (~30 cm^{-1}). These changes in amide group vibrations indicate that amide oxygen (ketonic) and thioamide sulphur atoms coordinate to the metal atom [31]. This has further been confirmed by the appearance of new bands at *ca.* 445 and 385 cm^{-1} assigned [34] to ν(M–O) and ν(M–S). However, in dioxouranium(VI) complexes, amide or thioamide group vibrations appear at the same position indicating noncoordination of the oxygen or sulphur atom to uranium. The noncoordination of the sulphur atom to the uranyl ion may be explained on the basis of hard acid soft base concept. Since the uranyl ion is a 'hard' Lewis acid the formation of coordinate bonds of the type $>S \rightarrow UO_2$ with the typical 'soft' sulphur atom is not to be expected.

The ligands show a weak band at *ca.* 1640 cm^{-1}, which can be assigned [35] to the $\nu(>C{=}N)$ vibration of azomethine linkage. The appearance of a weak $\nu(>C{=}N)$ band is in accordance with the observations of several other workers [31, 35]. In dioxouranium(VI) complexes this band appears at *ca.* 1610 cm^{-1} suggesting [35] the coordination of nitrogen atoms of azomethine groups to the uranium. However, in oxovanadium(IV) and oxozirconium(IV) complexes, the $\nu(C{=}N)$ band splits into two bands. One band appears at *ca.* 1640 cm^{-1} while the other appears at *ca.* 1615 cm^{-1}. The band occurring at *ca.* 1615 cm^{-1} is assigned to the coordinated $>C{=}N$ group while the band at *ca.* 1640 cm^{-1} is assigned to the noncoordinated $>C{=}N$ group of the tetradentate ligand [36, 37]. It appears that only two azomethine ($>C{=}N$) groups are coordinated to vanadium or zirconium (Scheme 1: **II**, **IIIa** or **IIIb**). The new bands occurring at *ca.* 370, 305 and 410 cm^{-1} may be assigned [38] to $\nu(U{-}N)$, $\nu(V{-}N)$ and $\nu(Zr{-}N)$ respectively. A number of bands also arise due to the phenyl ring and different alkyl groups, but definite assignments of these bands are not possible due to the complexity of the spectrum.

In dioxouranium(VI) complexes new bands at *ca.* 860, 210 and 930 cm^{-1} are observed. These are assigned [39] to symmetric stretching (ν_1), bending (ν_2) and asymmetric stretching (ν_3) vibrations of the UO_2 moiety confirming the presence of UO_2 group. The bands occurring in the regions 1450–1480, 1230–1250 and 745–760 cm^{-1} are due to the monodentatively coordinated nitrate group of C_{2v} symmetry [40].

In vanadyl complexes new bands appear at *ca.* 975 cm^{-1}, which are assigned to the $\nu(V{=}O)$ vibration [27]. The presence of an ionic sulphate group has been confirmed by the appearance of three bands at *ca.* 1135 (ν_3), 960 (ν_1) and 605 (ν_4) cm^{-1}. The absence of a ν_2 band and nonsplitting of the ν_3 band indicate that *Td* symmetry is still held [30].

Zirconyl complexes show bands at *ca.* 3480 cm^{-1}, which are assigned [40] to the $\nu(OH)$ vibration of the coordinated water molecule. Further a weak band at *ca.* 825 cm^{-1} is assigned to the $\nu(Zr{=}O)$ vibration [38]. However there is no reliable evidence for the existence of the (Zr=O) moiety in zirconyl complexes. The structure determination of '$ZrOCl_2 \cdot 8H_2O$' by Clearfield and Vaughan [41] was a great step forward, since it showed that this salt contained $[Zr(OH)_2]^{2+}$ or $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ ions in aqueous solution. With this view, the zirconyl complexes can either be assigned the structure **IIIa** or **IIIb**. Thus on the basis of above studies, the tentative structures shown in Scheme 1 may be proposed for dioxouranium(VI), oxovanadium(IV) and oxozirconium(IV) complexes.



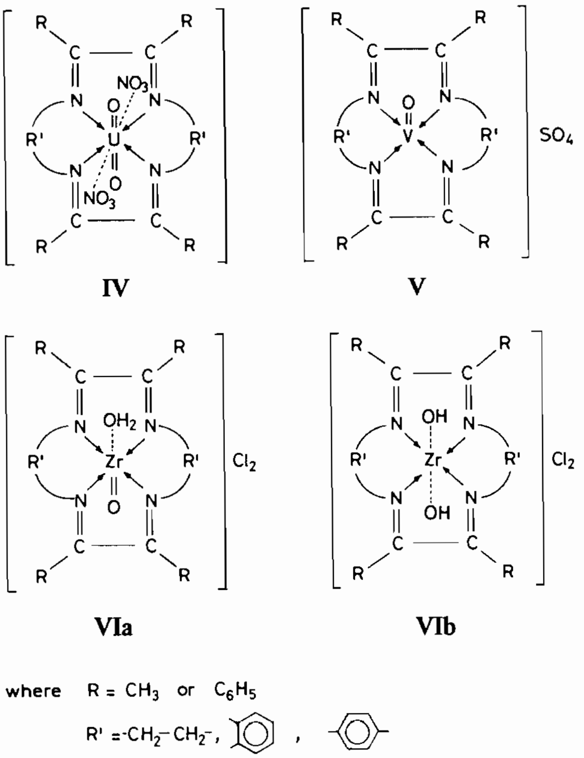
where R = CH_3 or C_6H_5
X = O or S

Scheme 1.

(ii) Complexes with macrocyclic ligands derived by condensation of benzil or diacetyl with diamines

These complexes exhibit $>C{=}N$ absorption around 1625–1610 cm^{-1}, which normally appears at 1660–1650 cm^{-1} in free ligands [42–44]. The lowering of this band in the complexes indicates the coordination of nitrogen atoms of the azomethine groups to the metals [42–44]. The presence of bands at *ca.* 375, 300 and 415 cm^{-1} may be assigned [34] to $\nu(U{-}N)$, $\nu(V{-}N)$ and $\nu(Zr{-}N)$ respectively. The appearance of the $>C{=}N$ band and the absence of the $>C{=}O$ band around 1700 cm^{-1} is conclusive evidence for condensation of the amine with the ketone [43]. A large number of bands also arise due to the phenyl ring and different alkyl groups, but definite assignments of these bands are not possible due to the complexity of the spectrum arising out of the overlap of these absorptions.

The infrared spectra show the same pattern of bands for the nitrate group or UO_2 moiety in dioxouranium(VI) complexes, for the ionic sulphate group and V=O moiety in oxovanadium(IV) complexes and for the coordinated water molecule and Zr=O moiety in oxozirconium(IV) complexes as described in part (i). Thus, the structures shown in Scheme 2 have been proposed for dioxouranium(VI), oxovanadium(IV) and oxozirconium(IV) complexes.



Scheme 2.

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References

1 G. A. Melson 'Coordination Chemistry of Macrocyclic Compounds', Plenum, New York, 1979.
2 U. Casellato, M. Vidali and P. A. Vigato, *Inorg. Nucl. Chem. Lett.*, *10*, 437 (1974).
3 V. W. Day, T. J. Marks and W. A. Wachter, *J. Am. Chem. Soc.*, *97*, 4519 (1975).
4 H. D. S. Yadav, S. K. Sengupta and S. C. Tripathi, *Synth. React. Inorg. Met.-Org. Chem.*, *14*, 993 (1984); *Acta Chim.*, *119*, 333 (1985); *Bull. Soc. Chim. Fr.*, *6*, 1180 (1985).
5 N. F. Curtis, *Coord. Chem. Rev.*, *3*, 3 (1968).
6 L. F. Lindoy and D. H. Busch, in W. L. Jolly (ed.), *Prep. Inorg. React.*, *6*, 1 (1971).
7 B. E. Douglas, *Inorg. Synth.*, *18, 1 (1978).*
8 M. G. B. Drew, J. D. Cabral, M. F. Cabral, E. S. Esho and S. M. Nelson, *J. Chem. Soc., Chem. Commun.*, 1033 (1979).
9 J. H. Wang, *Acc. Chem. Res.*, *1*, 90 (1970).
10 S. Chandra and K. K. Sharma, *Transition Met. Chem.*, *8*, 1 (1983).
11 W. U. Malik, R. Bembi and R. Singh, *Transition Met. Chem.*, *8*, 62 (1983).
12 V. B. Rana, D. P. Singh, P. Singh and M. P. Teotia, *Transition Met. Chem.*, *6*, 36 (1981).
13 V. B. Rana and M. P. Teotia, *Indian J. Chem.*, *19A*, 267 (1980).
14 V. B. Rana, D. P. Singh and M. P. Teotia, *Transition Met. Chem.*, *6*, 189 (1981).
15 E. B. Möhr, J. J. Brezinski and L. F. Audrieth, *Inorg. Synth.*, *Vol. IV*, 32 (1953).
16 G. R. Bürns, *Inorg. Chem.*, *7*, 277 (1968).
17 A. I. Vogel, 'A Text Book of Quantitative Inorganic Analysis', 4th edn., Longmans Green, London, 1978.
18 O. P. Pandey, S. K. Sengupta and S. C. Tripathi, *Inorg. Chim. Acta*, *90*, 91 (1984).
19 C. G. Willard and L. G. Vanquickenborn, *J. Chem. Phys.*, *54*, 4178 (1971).
20 S. P. McGlynn and J. K. Smith, *J. Mol. Spectrosc.*, *6*, 164 (1961).
21 P. C. H. Mitchell and J. A. Valero, *Inorg. Chim. Acta*, *71*, 179 (1983).
22 B. N. Figgis, 'Introduction to Ligand Fields', Wiley, New York, 1966, p. 266.
23 A. K. Srivastava, R. K. Agarwal, M. Srivastava, V. Kapur, S. Sharma and P. C. Jain, *Transition Met. Chem.*, *7*, 41 (1982).
24 S. Yamada and Y. Kuge, *Bull. Chem. Soc. Jpn.*, *42*, 152 (1969).
25 L. Sacconi and U. Campigli, *Inorg. Chem.*, *5*, 606 (1966).
26 C. N. Sathyanarayana and C. C. Patel, *Indian J. Chem.*, *3*, 486 (1965).
27 J. Selbin, *Chem. Rev.*, *65*, 153 (1965); *Coord. Chem. Rev.*, *1*, 293 (1966).
28 H. J. Stocklosa, J. R. Wasson and M. J. McCormick, *Inorg. Chem.*, *13*, 592 (1964).
29 C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, *1*, 111 (1962).
30 M. Nonoyama, S. Tomita and K. Yamasaki, *Inorg. Chim. Acta*, *12*, 33 (1975).
31 S. K. Sengupta, S. K. Sahni and R. N. Kapoor, *J. Coord. Chem.*, *12*, 113 (1982).
32 S. K. Sahni and V. B. Rana, *Indian J. Chem.*, *15A*, 890 (1977).
33 S. K. Sengupta, S. K. Sahni and R. N. Kapoor, *Acta Chim. Acad. Sci. Hung.*, *104*, 89 (1980).
34 D. M. Adams, 'Metal-Ligand and Related Vibrations', Arnold, London, 1967.
35 S. K. Sahni, *Transition Met. Chem.*, *4*, 73 (1979).
36 O. P. Pandey, S. K. Sengupta and S. C. Tripathi, *Transition Met. Chem.*, *8*, 362 (1983).
37 S. Satapathy and B. Sahoo, *J. Inorg. Nucl. Chem.*, *32*, 2223 (1970).
38 J. R. Ferraro, 'Low Frequency Vibrations of Inorganic and Coordination Compounds', Plenum, New York, 1971.
39 V. Kumari, S. K. Sahni, S. Kher and R. N. Kapoor, *Transition Met. Chem.*, *5*, 85 (1980).
40 K. Nakamoto, 'Infrared Spectra of Inorganic and Coordination Compounds', Wiley Interscience, New York, 1970.
41 A. Clearfield and P. A. Vaughan, *Acta Crystallogr.*, *9*, 555 (1956).
42 V. B. Rana, P. Singh, D. P. Singh and M. P. Teotia, *Transition Met. Chem.*, *7*, 174 (1982).
43 S. Chandra and K. K. Sharma, *Transition Met. Chem.*, *8*, 1 (1983).
44 W. U. Malik, R. Bembi and R. Singh, *Inorg. Chim. Acta*, *68*, 223 (1983).