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Oxovanadium(IV) and Dioxouranium(VI) Complexes with Thiocarbohydrazones

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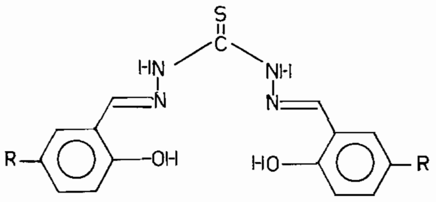
Oxovanadium(IV) and dioxouranium(VI) complexes with thiocarbohydrazones have been prepared in an ethanolic medium and characterised by elemental analysis and molecular weight determination. They have 1:1 stoichiometry. The IR observations suggest that the ligands have coordinated through azomethine nitrogen atoms and reacted through hydroxy groups. The ν(M–N) and ν(M–O) vibrations have been assigned. The PMR spectral information supports the IR inference. The oxovanadium(IV) complexes show magnetic moments in the range of 1.74–1.94 B.M. The electronic spectra have been interpreted in the light of the BG model. Various NSH parameters have been calculated. The ESR spectra also render support for the spectral information. On the basis of this information it is suggested that oxovanadium(IV) complexes exhibit coordination number five and dioxouranium coordination number six.

Introduction

The Schiff base complexes of oxovanadium(IV) and dioxouranium(VI) are well documented in the literature [1–4]. However, the information on oxovanadium(IV) and dioxouranium(VI) complexes with hydrazones, semicarbazones, and thiosemicarbazones is scanty [5–10]. The paucity of literature in this sphere has encouraged us to undertake a systematic study of the complexes of thiocarbohydrazones.

In this paper we choose to focus upon our efforts towards the synthesis and characterisation of oxovanadium(IV) and dioxouranium(VI) complexes with the thiocarbohydrazones shown below.



	R
I	H
II	CH_3
III	OCH_3
IV	Cl

Experimental

Materials and Method

All the chemicals used for preparing the ligands were of reagent grade. Vanadyl sulphate monohydrate and uranyl acetate dihydrate were B.D.H. reagents. The substituted salicylaldehydes were prepared according to Duff's method [11]. Thiocarbohydrazide was synthesised by the known method [12]. The ligands were prepared according to a method reported elsewhere [13].

Preparation of Oxovanadium(IV) Complexes

To an ethanolic solution of 0.01 mol of thiocarbohydrazone was added 0.01 mol of vanadyl sulphate in the minimum amount of water followed by 2 g of sodium acetate. The reaction mixture was refluxed for about 3 hrs and precipitation of the complex was initiated by adding water drop by drop to the reaction mixture. The complex was filtered, washed with water containing a little alcohol and dried under vacuum over fused calcium chloride.

Preparation of dioxouranium(VI) Complexes

Uranyl acetate (0.01 mol) was refluxed with 0.01 mol of thiocarbohydrazone in ethanolic medium for about 3 hrs. The reaction mixture was evaporated somewhat and precipitation of the complex was initiated by adding water containing ammonia drop by drop. The precipitated complex was filtered and washed thoroughly with water containing a little alcohol. The complex was then dried under vacuum over fused calcium chloride.

Elemental Analysis

Vanadium and uranium in the complexes were determined respectively by volumetry and gravimetry [14, 15]. Nitrogen was determined by Dumas' method and sulfur was estimated gravimetrically as the sulphate after oxidizing with fuming nitric acid.

Physical Measurements

The magnetic susceptibility of the complexes at room temperature was measured on a Gouy balance using $Hg[Co(SCN)_4]$ as calibrant. The

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TABLE I. Molecular Weight and Analytical Data of Oxovanadium(IV) and Dioxouranium(VI) Complexes.

Complex No.	Ligand No.	Empirical Formula of the Complex	Molecular Weight		Analytical Data					
			Calcd.	Found	%M	%N	%S	%M	%N	%S
					Calcd.			Found		
1	I	$(C_{15}H_{12}N_4O_2S)VO$	378.9	375.0	13.44	14.78	8.44	13.60	14.50	8.25
2	II	$(C_{17}H_{16}N_4O_2S)VO$	406.9	399.0	12.52	13.76	7.86	12.81	13.78	7.75
3	III	$(C_{17}H_{16}N_4O_4S)VO$	438.9	413.0	11.61	12.76	7.29	11.26	12.87	7.36
4	IV	$(C_{15}H_{10}N_4O_2SCl_2)VO$	447.9	410.0	11.37	12.50	7.14	11.15	12.41	7.27
5	I	$(C_{15}H_{12}N_4O_2S)UO_2$	582.0	625.0	40.89	9.62	5.50	41.00	9.52	5.36
6	II	$(C_{17}H_{16}N_4O_2S)UO_2$	610.0	593.0	39.02	9.18	5.25	38.90	9.39	5.15
7	III	$(C_{17}H_{16}N_4O_4S)UO_2$	642.0	648.0	37.07	8.72	4.98	36.82	8.90	4.85
8	IV	$(C_{15}H_{10}N_4O_2SCl_2)UO_2$	651.0	632.0	36.56	8.60	4.92	36.40	8.66	5.00

electronic spectra of the complexes in DMF were taken with an ELICO-24-spectrophotometer in the 350–900 nm region. The IR spectra of the ligands and their complexes in nujol mull were recorded on a Perkin-Elmer IR-297 spectrophotometer in the 4000–600 cm^{-1} region. The far IR spectra were obtained with a Polytec FIR-30 in the 600–100 cm^{-1} region. The PMR spectra of the ligands and their dioxouranium(VI) complexes in DMSO were recorded on a Varian V-60 spectrometer using TMS as an internal reference. The ESR spectra of oxovanadium(IV) complexes in powder form were recorded on a Varian X-band ESR spectrometer at 77 K using DPPH as reference. Molecular weights of the complexes were determined in nitrobenzene by the cryoscopic method.

Results and Discussion

Oxovanadium(IV) complexes are brownish green in colour whereas dioxouranium(VI) complexes are orange yellow in colour. They are all soluble in nitrobenzene, DMF, DMSO and pyridine. The results of the elemental analysis (Table I) agree well with 1:1 stoichiometry, *viz.* VOL and UO_2L, where L represents a doubly deprotonated ligand. The molecular weight determination in nitrobenzene suggests that these complexes are monomeric and do not undergo any dissociation.

Infrared Spectra

The important infrared frequencies which characterise the complexes are discussed in the text below:

1. All the complexes exhibit a broad band of medium intensity around 3300 cm^{-1} attributable to the ν(NH) vibration.

2. A broad weak band with fine structure in the region 2675–2630 cm^{-1} assignable to the H-bonded OH disappears in these complexes. The high intensity band due to the phenolic C–O appearing around 1280 cm^{-1} appears as a medium to high intensity band in the region 1330–1300 cm^{-1} in these complexes suggesting that the H-atoms of the OH groups have been replaced by the metal ions [16].

3. The phenolic C–O occurring around 1510 cm^{-1} in the ligands can be used as a sensitive probe to estimate the monodentate and bridging bidentate nature of oxygen atoms [17–19]. In these thiocarbohydrazones we observe a medium intensity band around 1520 cm^{-1} and this is located in the 1540–1530 cm^{-1} region in the complexes. A shift of the order of 10–15 cm^{-1} in all these complexes rules out the bridging probability.

4. The medium intensity band in the region 1630–1610 cm^{-1} due to ν(C=N) of the ligands is observed at 1610–1600 cm^{-1} in the complexes indicating that the C=N groups of the ligands have coordinated to the metal ion through nitrogen.

5. The band due to the ν(C=S) [20–22] in the region 750–740 cm^{-1} is unaffected in the complexes.

6. A narrow band of medium intensity appearing around 980 cm^{-1} has been attributed to the ν(V=O) in view of the previous assignments [23].

7. The high intensity bands located in the region 900–880 cm^{-1} for dioxouranium(VI) have been attributed to the ν_3(asym) of the O=U=O group by analogy with the previous assignments [24–26].

8. All the oxovanadium(IV) complexes contain medium to high intensity bands in the regions 530–510 cm^{-1} and 435–320 cm^{-1}. The dioxouranium(VI) complexes show such bands in the 520–510 and 410–350 cm^{-1} regions. These have been regarded as due to the ν(M–N) vibrations [27–29].

9. Considering the previous assignments [30–32] we have assigned the bands in the regions 455–

TABLE II. Magnetic and Electronic Spectral Data (in cm^{-1}) of Oxovanadium(IV) Complexes.

Complex No.	μ_{eff} B.M.'	ν_1	ν_2	ν_3	*Dq*	*Ds*	*Dt*	*DQ*	*DS*	*DT*	*DT/DQ*
1	1.73	12500	15380	23810	1538	−2990	706	42415	20930	9566	0.226
2	1.79	12820	15380	23260	1538	−2957	789	41355	20699	10690	0.258
3	1.76	12820	16130	23310	1613	−2857	849	42454	19999	11503	0.271
4	1.93	12660	15630	22730	1563	−2822	838	41223	19754	11354	0.276

TABLE III. ESR Parameters (in G) for Oxovanadium(IV) Complexes.

Complex No.	g_a	$g_\parallel$	$g_\perp$	A_a	$A_\parallel$	$A_\perp$	λ (cm^{-1})
1	1.956	1.925	1.972	86.32	156.3	51.33	166.1
2	1.957	1.927	1.973	82.76	155.6	46.34	168.8

445, 375–360 and 310–300 cm^{-1} for oxovanadium(IV) complexes and those found in the 450–430 cm^{-1} and 320–300 cm^{-1} region for dioxouranium(VI) complexes to the ν(M–O) vibrations.

These observations focus upon the tetradentate behaviour of the ligands (I–IV).

Magnetic Data

The magnetic moments obtained for these complexes are listed in Table II.

The μ_{eff} values obtained for oxovanadium(IV) complexes fall in the range 1.74–1.94 B.M. These are in the vicinity of spin only value for oxovanadium(IV) complexes when the orbital contribution is quenched [1]. The results preclude the existence of exchange interactions in the complexes. All the dioxouranium(VI) complexes are diamagnetic.

Electronic Spectra

The electronic spectra of oxovanadium(IV) complexes in DMF show bands in the following regions; 12820–12500, 16130–15380 and 23810–22730 cm^{-1}. Quite diverse models have been proposed to interpret the electronic spectra of oxovanadium(IV) complexes [33–39].

The electronic spectra of these complexes have been interpreted using the Ballhausen and Gray (BG) model and the assignments have been made accordingly (Table II). As the difference between ν_1 and ν_2 is less than 4000 cm^{-1}, Wasson's model cannot be used. The electronic spectra of these complexes are all alike indicating that they have similar configurations. The spectra of these complexes are comparable with well studied oxovanadium(IV) complexes of coordination number five.

The parameters *Dq* and *Dt* have been used to calculate the degree of distortion of the complexes by applying the Normalized Spherical Hormonic (NSH) Hamiltonian theory advanced by Lever *et al.* [40, 41]. The parameters of the NSH Hamiltonian theory have been fully used to relate them to those of the classical Hamiltonian theory. The parameters of two Hamiltonians are related as follows [40].

$$DT = \frac{7\sqrt{(15)}Dt}{2}$$

$$DQ = (6\sqrt{21})Dq - \frac{7\sqrt{21}}{2}Dt$$

$$DS = -7Ds$$

The theory takes into account an off diagonal contribution to *Dt*. *DQ* is a measure of the average ligand field experienced by the metal ion, unlike classical Dq which is a measure of inplane ligand field. *DT/DQ* gives the degree of tetragonal distortion.

The values of Ds and Dt reflect the σ and π donating abilities of the ligands. The *DT/DQ* values fall in the range of 0.226–0.276. These values are lower than the value postulated for square-planar complexes (*i.e.* 0.4226); a limiting case of tetragonally distorted molecules. It may, therefore, be concluded that the complexes are moderately distorted and the metal atom lies slightly above the molecular plane. The reason for this distortion may be due to the non-equivalence of donor atoms.

ESR Spectra

The ESR spectra of these oxovanadium(IV) complexes exhibit 8-line spectra (^{51}V, I = 7/2).

The 'g' and 'A' values calculated are listed in Table III. They are in good agreement with the values reported for well characterised complexes [42].

The ESR and electronic spectra can be correlated using the expressions given by Assour *et al.* [43]

$$g_{\perp} = g_e \left[1 - \frac{\lambda_{\perp} \gamma^2}{E(^2B_2 \rightarrow {}^2E)} \right]$$

and

$$g_{\parallel} = g_e \left[1 - \frac{4\lambda_{\parallel} \alpha^2}{E(^2B_2 \rightarrow {}^2B_1)} \right]$$

where $g_e = 2.0023$

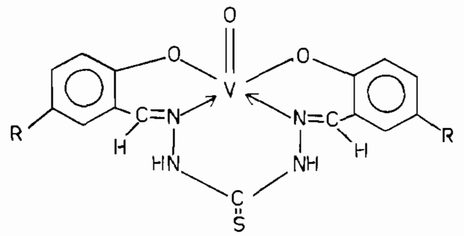
α and γ are assumed to be unity for weakly covalent bonding in the complexes. Using ESR-g values (Table III) and the band maxima ν_1 and ν_2 observed for these complexes (Table II), the spin-orbit coupling coefficient (λ) can be calculated. The average λ values obtained for these complexes (Table III) are in good agreement with the reported values [44, 45].

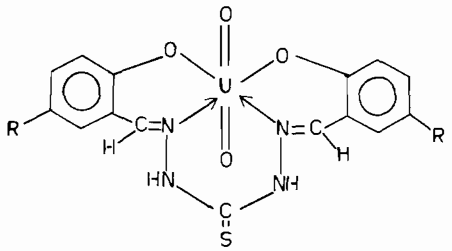
PMR Spectra

Two ligands (I and II) and their dioxouranium(VI) complexes have been chosen for the study. The PMR spectra of these ligands consist of signals due to azomethine (8.3 ppm), *o*-hydroxy (12.3 ppm), amino (7.5 ppm) and phenyl (6.72–7.20 ppm) protons. These observations suggest that these ligands exist in the phenolimine form [46].

In the dioxouranium(VI) complexes, the signal due to the azomethine proton appears at 8.6 ppm. This downfield shift is due to the deshielding caused by the coordination of azomethine nitrogen to the metal ion. The hydroxy proton signal disappears in these complexes suggesting that the reaction has proceeded *via* deprotonation. These results provide support for the infrared inferences.

The analytical data, molecular weight determination, magnetic data and other spectral observations lead us to propose the following structures having coordination numbers of five and six for these oxovanadium(IV) and dioxouranium(VI) complexes respectively.





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