

Complexes of Oxovanadium(IV), Dioxouranium(VI) and Zirconium(IV) with Schiff Bases Derived from 2,2'-Diamino-Diphenyl-Disulphide

P.M. PRABHU* and B.H. MEHTA

Department of Chemistry

University of Bombay, Vidyanaagri, Bombay-400 098, India

Six complexes of vanadium, uranium and zirconium have been synthesised using Schiff bases derived from 5-nitro-salicylaldehyde, 2-hydroxy-1-naphthaldehyde and 2,2'-diamino-diphenyl-disulphide. The complexes are characterized by elemental analysis, magnetic measurements, UV/visible absorption spectra, infrared spectral, diffused reflectance spectra and conductance measurements. Thermogravimetric analysis played a supporting role to picture the geometrical structures of the complexes.

INTRODUCTION

A drastic development has taken place in the field of Schiff base ligands and their complexes with transition metals because of the flexible nature of structures of Schiff bases which depends upon the nature of aldehydes and amines^{1,2}. In the recent years a great deal of work has been reported on the synthesis and characterisation of complexes of oxovanadium(IV)³, dioxouranium (VI)⁴ and zirconium(IV)⁵.

However, little work appears to have been done on metal complexes of ligands having nitrogen-sulphur and nitrogen-oxygen-sulphur donor systems. The present investigation was undertaken since Schiff bases in particular derived from 2,2'-diamino-diphenyl-disulphide and aldehydes like 5-nitro-salicylaldehyde, 2-hydroxy-1-naphthaldehyde are not reported. The correlation between presence and location of different functional groups and chromophores with structural features and absorption properties of complexes has been studied in detail. A detailed systematic data related to the transition metal $UO_2(II)$, $VO(II)$, $Zr(IV)$ complexes with different substituted Schiff bases was obtained by using analytical techniques.

EXPERIMENTAL

2-Hydroxy-1-naphthaldehyde, 5-nitro-salicylaldehyde, and all the metal salts *viz.* vanadyl sulphate monohydrate, uranyl acetate and zirconium(IV) oxochloride of A.R. grade were used to prepare the Schiff bases and respective metal complexes. The amine *viz.* 2,2'-diamino-diphenyl-disulphide was prepared

according to the method suggested by Gialdi⁶. Schiff base ligands have been synthesised involving condensation reactions of the aldehydes and the amines in ethanolic solution in 1:2 molar ratio of amine and aldehyde.

Synthesis of the complexes: A mixture of aldehyde (2 M) and amine (1 M) in alcohol was added to the respective metal salt (1 M) in alcohol. This mixture was refluxed for 3–4 h on a hot water bath. The pH of the reaction mixture was recorded and subsequently adjusted to 6 using dilute ammonia solution with vigorous stirring. A good amount of solid complexes separated out which were filtered, washed with alcohol and hot water, and dried at 60°C.

RESULTS AND DISCUSSION

The Schiff bases and the respective metal complexes were analysed for the various physical parameters. The analytical data of these experiments are summarized in Table-1.

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF COMPLEXES

Ligand/ Complexes	% Analysis, Found (Calcd.)					Molar Conductance $\times 10^{-6}$ mhos. $\text{cm}^2 \text{mole}^{-1}$	μ_{eff} B.M.
	C	H	N	S	Metal		
L1	57.91 (57.14)	2.46 (3.30)	9.27 (10.26)	12.14 (11.72)	—	1.010	—
L2	71.51 (73.38)	3.13 (4.32)	4.45 (5.04)	13.00 (11.51)	—	1.056	—
VO-L1	46.06 (45.68)	3.18 (3.51)	7.11 (8.19)	10.23 (9.37)	6.79 (7.46)	8.225	1.69
VO-L2	71.51 (73.38)	3.13 (4.32)	4.45 (5.04)	11.41 (11.51)	7.07 (7.35)	6.461	1.89
UO ₂ L1	33.44 (32.57)	3.26 (3.34)	6.79 (5.85)	7.36 (6.68)	24.71 (24.84)	7.023	Dia
UO ₂ L2	46.19 (45.54)	4.43 (3.35)	2.72 (3.13)	7.88 (7.14)	26.74 (26.56)	5.819	Dia
Zr-L1	50.08 (49.21)	3.19 (2.52)	7.63 (8.83)	10.29 (10.90)	14.05 (14.19)	4.049	Dia
Zr-L2	64.08 (63.35)	4.38 (3.41)	2.71 (4.34)	10.03 (9.93)	14.31 (13.97)	6.981	Dia

The molar conductance of the present ligands and complexes was measured in nitrobenzene solvent. The extreme low value ($\sim \times 10^{-6}$ mhos. $\text{cm}^2 \text{mole}^{-1}$) suggests non-electrolytic nature of these samples.

The isothermal heating experiments of the samples indicate that these complexes are crystalline in nature. Oxovanadium(IV) and dioxouranium(VI) com-

plexes suggest major loss during heating at about 110°C. This indicates the presence of water of crystallisation. However such loss was not indicated by zirconium(IV) complexes indicating their anhydrous nature. On further heating to higher temperature, the appearance and colour of the complexes are changed indicating probable decomposition of the complexes.

The magnetic susceptibility measurements indicate that the complexes of oxovanadium(IV) are paramagnetic in the range 1.69 to 1.89 B.M. at room temperature while the complexes of dioxouranium(VI) and zirconium(IV) obtained from the present Schiff base ligands are diamagnetic in nature.

The VO(II) bond can be regarded as multiple with ' π ' component arising from electron density $O(p\pi) \rightarrow V(d\pi)$. It is quite possible that such pentacoordinate complexes can take up sixth ligand quite rapidly to become octahedral, especially with the ligand containing donor atoms like nitrogen⁷. Three spin allowed transitions are expected for oxovanadium(IV) complexes as suggested by Syamal and Kale⁸ at around 13.00 kK, 16.00 kK and 18.00 kK which were assigned as $d_{xy} \rightarrow d_{xz}$, d_{yz} ; $d_{xy} \rightarrow d_{x^2-y^2}$ and $d_{xy} \rightarrow d_z^2$. In the electronic absorption spectra of the present oxovanadium(IV) complexes three bands at around 12.05 kK, 15.38 kK and 17.86 kK which can be assigned to the above d-d transitions, while the band appearing at around 25.58 kK is assigned to metal ligand charge transfer transitions.

The electronic absorption spectra of actinide elements are generally similar since majority of transitions takes place at inner f-f orbitals. However, some characteristic absorption peaks are isolated for dioxouranium(VI) complexes and it was found that position of such bands differs from that of corresponding ligands. Based on the literature survey⁹, the bands appearing at 24.03 kK and 25.34 kK in the solution spectra of the present dioxouranium(VI) complexes can be assigned to charge transfer transition.

The electronic absorption bands in the UV and visible region for zirconium complexes of the present ligands were characterised by few absorption bands in the region 24.09 kK to 25.60 kK which were assigned to the charged transfer transitions.

In the infrared spectrum of the samples the characteristic bands due to $\nu(C=N)$ with strong intensity were found in the region 1622–1616 cm^{-1} for the Schiff base ligands, whereas these bands were shifted to lower frequencies in the spectra of the complexes in the region 1620–1614 cm^{-1} respectively.

The infrared spectra of monomeric vanadyl complexes usually display a strong band in the region 1000–950 cm^{-1} due to $V=O$ group while polymeric oxovanadyl(IV) complexes containing the $V-O-V-O$ bridges display $\nu(V=O)$ at much lower frequencies¹⁰⁻¹² usually in the range 900–850 cm^{-1} . The infrared spectra of present vanadyl complex contain strong peak at around 979 cm^{-1} , which may be assigned to stretching mode of non-bridging $V=O$ group. In the spectrum of the present oxovanadium(IV) complexes two bands located at around 640 cm^{-1} and 545 cm^{-1} can be assigned to $\nu(V-N)$ and $\nu(V-O)$ respectively.

The infrared spectrum of the dioxouranium(VI) complexes shows an intense band in the region 937 cm^{-1} which is attributable to the $\nu_{\text{asym}}(\text{UO}_2)$ mode whereas

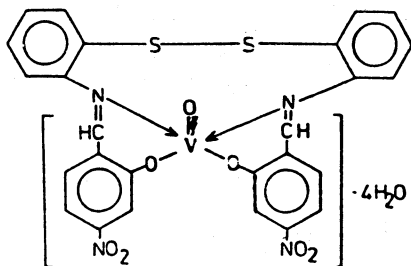
the $\nu_{\text{sym}}(\text{UO}_2)$ mode in these complexes appears in the range $800\text{--}780\text{ cm}^{-1}$. Infrared spectrum of the present dioxouranium(VI) complexes shows bands pointed at around 580 cm^{-1} and 460 cm^{-1} which are assigned to $\nu(\text{U—N})$ and $\nu(\text{U—O})$ vibrations respectively.

Based on the literature survey^{13, 14} the bands appearing in the range $580\text{--}576\text{ cm}^{-1}$ and $440\text{--}426\text{ cm}^{-1}$ in the spectrum of the zirconium(IV) complexes can be assigned to $\nu(\text{Zr—N})$ and $\nu(\text{Zr—O})$ respectively.

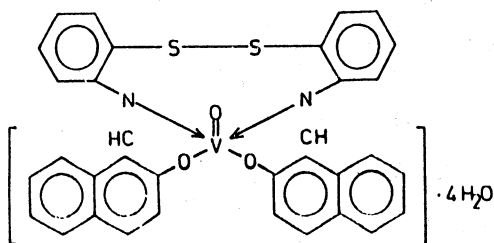
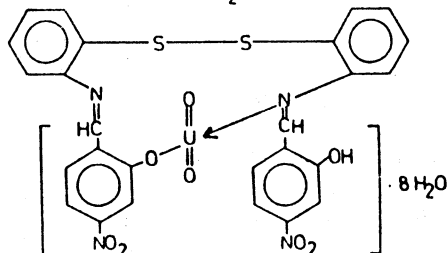
Similarly, all other major stretching vibrations like $\nu(\text{C=O})$, $\nu_{\text{sym}}(\text{NO}_2)$ and $\nu_{\text{asym}}(\text{NO}_2)$ and $\delta(\text{OH})$ bands appeared at the positions reported in literature. Some of these vibrations show shifts from their positions in the ligands which is also in accordance with the reported work. The absorption band pointed at 466 cm^{-1} in all the complexes is assigned to the $\nu(\text{S—S})$ stretching vibrations.

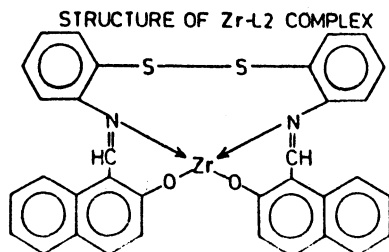
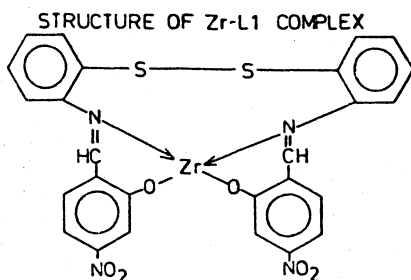
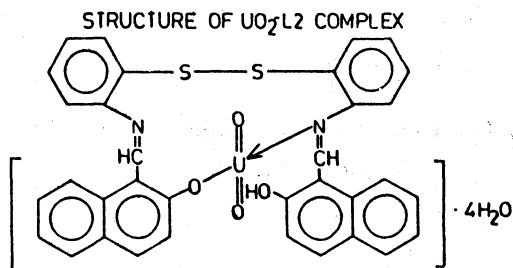
Conclusively, at par with the literature reported in the past and various scientific footings all the six complexes of vanadyl, dioxouranium and zirconium possess an octahedral geometry and their structures can be assigned as follows:

STRUCTURE OF VO-L1 COMPLEX



STRUCTURE OF VO-L2 COMPLEX

STRUCTURE OF UO₂L1 COMPLEX



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