Vol. 4 (2000) Nos.1-4. **Journal of International Academy of Physical Sciences** pp.75-78

Synthesis, Structural and Biological Studies of Oxovanadium (IV) and Dioxouranium (VI) Chelates with Polymeric Schiff Bases (PSB)

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(Received September 10, 2000)

Oxovanadium (IV) and dioxouranium (VI) chelates involving the polymeric schiff base (PSB) ligands derived from 4, 4' dihydrory-3, 3'-dibenzoyl biphenyl and 1, 3-diaminopropane or o-phenylenediamine or 2, 3-buanedione dihydrazone have been synthesized. The structural characterisation of chelates were made on the basis of elemental analysis, magnetic moment, TGA, IR and electronic spectral data. The d. c. electrical conductivity antimicrobial studies of ligands and the chelates have also been carried out. The tetradentate nature of ligands is inferred from IR studies coordinating through azomethine nitrogens and phenolic oxygens. A square pyramidal and octahedral geometry have been tentatively proposed for all VO(IV) and UO_2(VI) chelates. Thermal activation energy has been determined by Broido method.

Schiff base is an important class of ligands in coordination chemistry and find extensive applications in different spheres[1, 3]. The survey of literature reveal that much work has been done on the synthesis and physico-chemical studies of schiff base complexes, but little attention has been paid to polychelates derived from polymeric schiff bases. This inspired us to study polymeric ligands derived from hydroxy ketone and diamines and their polychelates with VO(IV) and UO_2(VI) ions.

Experimental

All the chemicals used were of AR grade and used without further purification. 4, 4'-dihydroxy-3, 3'-dibenzoylbiphenyl (DDBB) and 3, 3'-butane dionedihydrazone were prepared by the reported methods[4,5].

Preparation of Ligands

Ligands were synthesised by the condensation of 4,4'-dihydroxy-3,3'dibenzoyl biphenyl (DDBB) with 1,3-diaminopropane, or o-phenylenediamine or 2,3'-butanedione dihydrazote respectively using DMF-ethanol (40 : 60 v/v) as solvent. The reaction mixtures were refluxed for 4-5-h. On cooling the reaction mixture, light yellow small crystals started separating out. The product was then filtered. It was washed with DMF, ethanol and methanol. The ligands were dried at room temperature. Purity of ligands was checked by tlc and m. ps.

Preparation of Polychelates

To the polymeric ligands (0.01 mol) dissolved in DMF (25 ml.), a suspension of metal ions (vanadyl sulphate and uranyl nitrate) in ethanol (0.01 mol) were added dropwise with constant stirring. On reflexing the mixture on an oil bath at 135° for 4-6 h, the solid polychelates were separated. More satisfactory results were obtained by slowly adding the ketone in dimethylformamide in stochiometric proportion to a well stirred solution in the metal complex of diamines. The reaction mixture was kept under reflex for 8 h to complete chelation. It was filtered and washed with hot DMF and ethanol and dried. They were purified by soxhlet extraction in ethanol and DMF to remove impurities and dried in an oven at 80°C.

Carbon, Hydrogen and Nitrogen analysis results were obtained from CDRI Lucknow. The metal content of the polychelates were estimated volumetrically and gravimetrically with a mixture of concentrated hydrochloric, nitric and sulphuric acid[6]. IR spectra were recorded on PERKIN-ELMER-577 spectrophotometer using KRr pelletes. The diffuse reflectance spectra were recorded on a PAS-2 and Backman DK-2A spectrophotometers using $BaSO_4$ and MgO as a calibrants. The magnetic succeptibility measurements were carried out at room temperature by the Gouy method using $Hg[Co(NCS)_4]$ as a calibrant. Thermal studies were recorded on a Perkin-Elmer TGS-2 thermobalance with heating rate 10° min^{-1} in air atmosphere. The d.c. electrical conductivity was measured by voltage drop method using microvoltmeter in pellet form. All the compounds were screened for their antimicrobial activity by the disc diffusion method.

Results and Discussion

All the polychelates are coloured, non hygroscopic and air stable solids. They are insoluble in water and common polar and nonpolar organic solvents and do not melt even upto 300°C. Elemental data (Table 1) revealed 1 : 1 metal ligand stoichiometry and all the polychelates have general formula $[ML]_n$.

The IR spectra of the ligands show a broad band in the region 2900-3000 cm^{-1} which may be due intramolecular hydrogen bonded-OH group[7]. This band disappears in complexes which indicates the replacement of hydrogen of phenolic group by metal ion[8]. A strong band at 1598-1610 cm^{-1} in the spectra of schiff bases is assigned to $\upsilon C = N$, which undergoes negative shift by 5-20 cm^{-1} in the polychelates, indicating coordination of both azomethine nitrogens of schiff bases[10]. The phenolic $\upsilon(C\text{-}O)$ mode of schiff bases (1268-1277 cm^{-1}) undergoes a positive shift by 15-25 cm^{-1} suggesting coordination of the phenolic C-O group[11]. Weak bands found at 510-600 cm^{-1} and 415-480 cm^{-1} are assigned to $\upsilon M\text{-}O$ and $\upsilon M\text{-}N$ vibrations respectively. In all chelates, bands observed at 939-1005 and 902-956 cm^{-1} suggest the presence of $V = 0$ group[10] and symmetrical stretching confirm the linear nature of the $O = U = O$ group[12].

The electronic spectra of the VO(IV) chelates exhibits a bands in the range of 11737-11834, 17240-17361 and 25906-26000 cm^{-1} which are assigned to ${}^2B_{2g} \rightarrow {}^2B_{1g}$, ${}^2B_{2g} \rightarrow {}^2B_{1g}$ and ${}^2B_{2g} \rightarrow {}^1A_{1g}$ transitions respectively for square pyrymidal structure[12]. The UO_2(VI) chelates are found to be diamagnetic as expected. The electronic spectra of uranyl chelates show bands at 21750, 25200 and 37000 cm^{-1}. The lower energy bands appear to originative from uranyl moity and are essentially vibronic in nature[13]. The UO_2(VI) chelates show a well defined band at 21505 cm^{-1}. These chelates have octahedral geometry.

The main feature of the TGA curves are the two steps decomposition. The VO(IV) and UO_2(VI) polychelates, the first step begins at $T > 150°$. This suggests the absence of

Table 1

Analytical, Thermal and Electrical conductivity data of polychelates

Compound	C % found (calcd.)	H % found (calcd.)	N % found (calcd.)	M % found (calcd.)	Decomposition Temp. (0°C)	Thermal Activative energy Kjmol^{-1}	Electrical Cond. ohm^{-1} cm^{-1}	Activation energy Ea (eV)
DDBBBD	73.90 (74.07)	4.13 (4.93)	14.90 (14.40)	- -	- -	- -	- -	- -
$[VO(DDBBBD)]_n$	64.01 (65.11)	4.22 (4.34)	12.31 (12.66)	9.40 (9.79)	260 -	25.30 -	5.039×10^{-8} -	0.2719 -
$[UO_2(DDBBBD)]_n$	46.65 (47.68)	3.10 (3.44)	9.11 (9.38)	38.32 (39.31)	201 -	30.11 -	5.177×10^{-10} -	0.8345 -
[DDBBDP)]	77.12 (78.06)	4.92 (5.38)	8.82 (9.41)	- -	200 -	34.30 -	- -	- -
$[VO(DDBBDP)]_n$	68.20 (67.85)	4.30 (4.67)	8.12 (8.18)	9.20 (9.91)	260 -	50.51 -	1.65×10^{-8} -	0.449 -
$[UO_2(DDBBDP)]_n$	45.11 (46.09)	3.22 (3.37)	5.70 (5.96)	30.10 (31.31)	180 -	42.39 -	5.7×10^{-10} -	0.3264 -
$[DDBBPD)]_n$	82.02 (82.40)	4.11 (4.72)	5.92 (6.0)	- -	270 -	38.20 -	- -	- -
$[VO(DDBBPD)]_n$	71.77 (72.66)	4.52 (4.62)	5.70 (5.95)	9.30 (9.54)	320 -	55.57 -	4.8×10^{-10} -	0.7948 -
$[UO_2(DDBBPD)]_n$	51.98 (52.24)	3.05 (3.14)	3.71 (3.80)	31.01 (32.24)	287 -	22.33 -	1.25×10^{-8} -	0.518 -

any type of water molecules in chelates. The organic moity decomposes further with increasing temperature. Although decomposed fragments of the ligands could not be approximated owing to continuous weight loss, the complete decomposition of the ligands occur at ~ 650° in all polychelates. The thermal activation energy was calculated by employing the Broido method[14] and values are summarised in Table 1. The slightly higher values of activation energy suggest the higher stability but some other physical and chemical factors causes a change or deviation in this trend.

The d.c. electrical conductivity of polychelates was measured in pellet from in the temperature range 300-520 K. The electrical conductivity (σ) varies exponentially with absolute temperature according to relation[18] $\sigma = \sigma_{0\,\exp}(-Ea/KT)$. The values of electrical conductivity (σ) and activation energy are listed in Table 1. In all cases, the conductivity increased with increasing temperature indicating that these chelates lie in the range of semiconductors[16]. It has been observed that, there are two distinct regions. The lower temperature range is the region of extrinsic semiconductors where the conduction is due to excitation of carriers from linear localised levels to the conduction band. At the higher temperature range the intrinsic region is reached where carriers are thermally activated from the valence band to the conduction band[17]. The small activation energy observed may be attributed to the interaction between the electrons of the cation and the π orbits of the ligands. The interaction will localise the π electronic charge on the ligand molecule.

All the ligands and polychelates were screened for their antimicrobial activity by disc diffusion method[18] against E-coli staphylococcus. Klebsiella and Bacillus 19. The results indicates that the ligands are active towards E-coli and Bacillus 19, while S, aurens and Klebsiella shows a poor inhibitory effect. S. typhi is highly inhibited by VO(V) chelates. Klebsiella is moderate[17] inhibited by UO_2(VI) polychelates. However S. aurens and Bacillu 19 shows lesser activity against VO(IV) and UO_2(VI) polychelates.

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