Dinuclear UO$_2$(VI), Th(IV), ZrO(IV) and VO(IV) complexes based on some Schiff-base ligands: Synthesis and structural elucidation

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Abstract

A series of homo binuclear complexes of the type [M$_2$(L/L')(NO$_3$)$(\text{H}_2\text{O})_n$], [where M=UO$_2$$^{2+}$, Th$^{4+}$, ZrO$^{2+}$] and [(VO)$_2$(L/L')(SO$_4$)(H$_2$O)], L= 4, 17-di(o-hydroxyphenyl)-5,6,9,12,15,16-hexaaza-7,8,13,14-tetraphenyl heptadec-4, 6, 8, 12, 14, 16-hexene or L'= 10:11-benzo-4, 17-di(o-hydroxyphenyl)-5,6,9,12,15,16-hexaaza-7,8,13,14-tetraphenyl heptadec-4, 6, 8, 12, 14, 16-hexene, n=2 for UO$_2$$^{2+}$, ZrO$^{2+}$ n=6 for Th$^{4+}$, have been synthesized in template method from ethylenediamine/orthophenylene diamine, benzil monohydrazone and salicyldehyde and characterized on the basis of elemental analysis, thermal analysis, molar conductivity, magnetic moment, electronic, infrared, $^1$H-NMR studies. The results indicate that the VO(IV) ion is penta co-ordinated yielding paramagnetic complexes; UO$_2$(VI), ZrO(IV) ions are hexa co-ordinated where as Th(IV) ion is octa co-ordinated yielding diamagnetic complexes of above composition.

Keywords

Schiff Base, Binuclear complexes, Template Synthesis, Structure and Spectral Properties.

Academic Discipline And Sub-Disciplines

Chemistry, Coordination chemistry

SUBJECT CLASSIFICATION

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TYPE (METHOD/APPROACH)

Provide examples of relevant research types, methods, and approaches for this field: Experimental: synthesis and characterization

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INTRODUCTION

One major topic of interest is to develop homo-multimetallic complexes because they exhibit distinct reactivity pattern as compared to corresponding monometallic complexes. The magnetic interactions and coupling between the metal ions present in such complexes play key role in both natural and synthetic catalysts. As a result, the synthesis and characterization of homo bimetallic complexes continue to attract attention. Following all these observations and as a part of our continuing research on the coordination chemistry of multidentate ligands, we report here the synthesis and structural studies of some unknown homo binuclear macrocyclic complexes from the reaction of ethylenediamine/orthophenylene diamine, benzil monohydrazone and salicyldehyde in presence of UO$_2^{2+}$, ZrO$_2^{4+}$, Th$^{4+}$ and VO$^{2+}$ ions.

RESULTS AND DISCUSSION

The complexes were formulated from the analytical data and molar conductance data support the suggested formulae (Table 1). The complexes are highly coloured and insoluble in water and common organic solvents such as ethanol, methanol, acetone, CCl$_4$, CHCl$_3$, benzene and ether but moderately soluble in highly coordinating solvents such as DMF and DMSO. They are non-hygroscopic, highly stable under normal conditions and all of them decompose above 250°C. The molar conductance data in DMSO for the complexes indicate them to be non-electrolyte in nature. However, the conductivity value is higher than that expected for non-electrolytes probably due to partial solvolysis of the complexes in DMSO medium.

| Sl. no. | Compounds | Colour | Yield (%) | $\Lambda_m$ | Found(calc.)% |
|--------|-----------|--------|-----------|-------------|---------------|
|        |           |        |           | C | H | N | S | M |
| 1 | [(UO$_2$)$_2$(L)(NO$_3$)$_2$(H$_2$O)$_2$] | Canary yellow | 67 | 22.12 | 35.06 (35.10) | 2.62 (2.65) | 10.27 (10.30) | - | 31.60 (31.64) |
| 2 | [(UO$_2$)$_2$(L')(NO$_3$)$_2$(H$_2$O)$_2$] | Brownish yellow | 69 | 21.25 | 37.03 (37.06) | 2.65 (2.70) | 8.96 (9.00) | - | 30.60 (30.63) |
| 3 | [(Th)$_2$(L)(NO$_3$)$_2$(H$_2$O)$_2$] | Lemon yellow | 58 | 32.84 | 31.79 (31.84) | 2.27 (2.29) | 11.79 (11.82) | - | 27.93 (27.98) |
| 4 | [(Th)$_2$(L')(NO$_3$)$_2$(H$_2$O)$_2$] | Red oxide | 62 | 35.43 | 33.67 (33.72) | 2.42 (2.45) | 11.43 (11.47) | - | 27.12 (27.16) |
| 5 | [(ZrO)$_2$(L)(NO$_3$)$_2$(H$_2$O)$_2$] | Cream | 65 | 31.67 | 44.10 (44.14) | 3.49 (3.51) | 11.66 (11.70) | - | 15.18 (15.21) |
| 6 | [(ZrO)$_2$(L')(NO$_3$)$_2$(H$_2$O)$_2$] | Golden Brown | 64 | 33.85 | 46.18 (46.22) | 3.50 (3.53) | 11.19 (11.23) | - | 14.57 (14.60) |
| 7 | [(VO)$_2$(L)(SO$_4$)(H$_2$O)] | black | 63 | 16.35 | 50.62 (50.67) | 3.79 (3.83) | 8.02 (8.06) | 6.10 | 9.73 (9.78) |
| 8 | [(VO)$_2$(L')(SO$_4$)(H$_2$O)] | brown | 65 | 18.58 | 52.71 (52.74) | 3.81 (3.84) | 7.65 (7.69) | 5.83 (5.86) | 9.30 (9.34) |

IR spectra

As the Schiff base ligands could not be isolated, the spectra of the complexes were compared with spectra of the starting materials and other related compounds. The IR spectra of the complexes show strong bands appearing at 1615 and ~1060 cm$^{-1}$ assignable to azomethine vC=N and vN-N. The position of former band at comparatively lower frequency region than usual free vC=N value$^{16}$ and that of later band at comparatively higher frequency region than that of free N-N$^{16}$ leads us to suggest that azomethine nitrogen atom has taken part in complexation as evidenced from the appearance of band in the region ~470 cm$^{-1}$ due to v(M-N)$^{15}$. The occurrence of N-N band at higher frequency in the IR spectra of the complex is due to reduction of the repulsion between the lone pair of nitrogen atoms as a result of coordination via azomethine nitrogen atoms. A sharp band due to the phenolic (O-H) of salicylaldehyde is absent in the complexes indicating the coordination of the phenolic oxygen after deprotonation to the metal ion, which is further supported by the appearance of a band due to v C-O (phenolic) at much higher frequencies (~1450 cm$^{-1}$) in the complexes due to partial
double bond character. The coordination of phenolic oxygen is further supported by the appearance of a non ligand band at 520-540 cm\(^{-1}\) due to ν M-O\(^1\)15.

The uranyl complexes exhibit a strong band at ~935-920 cm\(^{-1}\) and the medium intensity band at ~840-825 cm\(^{-1}\) assignable to ν\(_{as}\)(O=U=O) and ν\(_{s}\)(O=U=O) mode respectively\(^16\). The co-ordination of nitrate ions in unidentate manner has been indicated by the appearance of additional band at the region ~1480 cm\(^{-1}\) and ~1380 cm\(^{-1}\) corresponding to the ν\(_4\) and ν\(_1\) modes of the vibration respectively, of coordinating nitrate ion under C\(_{2v}\) symmetry\(^17\). The magnitude of Δν = (ν\(_4\) - ν\(_1\)) = 100 cm\(^{-1}\) shows the unidentate coordination of the nitrate ion. The zirconyl complexes exhibit one strong band in the region ~950 cm\(^{-1}\) which can be attributed to the ν(Zr=O) as reported earlier indicating the presence of (Zr=O)\(^{2+}\) moiety in these complexes. In the oxovanadium polychelates strong bands at ~955 cm\(^{-1}\) are assigned to ν(V=O) modes. However, these bands are absent in the complexes of Th(IV). However in vanadyl complexes, an additional series of four bands appeared at ~1160, ~1125, ~860 & ~635 cm\(^{-1}\) indicating the coordination of sulphate group in unidentate manner through oxygen atom\(^18\); the symmetry being lowered from T\(_D\) to C\(_{3v}\) upon coordination. Besides the bands observed at ~3460 cm\(^{-1}\) may be assigned to ν(O-H) of coordinated or lattice water.

**Thermal analysis**

All these complexes follow the same pattern of thermal decomposition. The complexes remain almost unaffected upto ~1400°C. After this a slight depression upto ~2000°C is observed. The weight loss at this temperature range is equivalent to one water molecule for the complexes (7) and (8), two water molecules for other complexes indicating them to be coordinated water in conformity with our earlier observations from analytical and IR spectral investigations. Simultaneous elimination of coordinated water suggests them to be in the same chemical environment\(^19\). The anhydrous complexes remain stable upto ~355°C then the complexes show rapid degradation presumably due to decomposition of organic constituents of the complex molecules as indicated by the steep fall in the percentage weight loss. The decomposition continues upto ~700°C and reaches to a stable product in each complex as indicated by the consistency in weight in the plateau of the thermogram. The decomposition temperature varies for different complexes as shown in Table 2. The representative thermogram of [(ZrO)\(_2\)(L)(NO\(_3\))\(_2\)(H\(_2\)O)\(_2\)] complex is shown in Fig. 1. The thermal stability of the complexes decreases in the order:

(L) complexes: UO\(_2\)(VI) > Th(IV) > ZrO(IV) > VO(IV)

(L') complexes: UO\(_2\)(VI) > ZrO(IV) > Th(IV) > VO(IV)

![Fig. 1. Thermogram of [(ZrO)\(_2\)(L)(NO\(_3\))\(_2\)(H\(_2\)O)\(_2\)]](image-url)
Table 2. Important features of thermo gravimetric analysis (TGA)

| Sl. no. | Total wt. for TG(mg) | Temp. range of water loss (°C) | % of water loss (%) | Decomposition temperature (°C) | % weight of residue (%) | Composition of the residue |
|--------|----------------------|--------------------------------|---------------------|-------------------------------|--------------------------|----------------------------|
| 1      | 108                  | 140-185                        | 3.61 (3.64)         | 385-715                       | 36.84 (36.87)            | U₂O₈                      |
| 2      | 105                  | 140-190                        | 3.50 (3.52)         | 380-690                       | 35.65 (35.69)            | U₂O₈                      |
| 3      | 102                  | 135-200                        | 3.45 (3.49)         | 365-680                       | 31.81 (31.84)            | ThO₂                      |
| 4      | 97                   | 140-195                        | 1.32 (3.37)         | 360-680                       | 30.86 (30.91)            | ThO₂                      |
| 5      | 98                   | 130-185                        | 3.14 (3.16)         | 355-675                       | 20.52 (20.56)            | ZrO₂                      |
| 6      | 101                  | 135-180                        | 3.00 (3.03)         | 370-690                       | 19.70 (19.74)            | ZrO₂                      |
| 7      | 84                   | 135-185                        | 3.61 (3.65)         | 360-670                       | 17.41 (17.46)            | V₂O₅                      |
| 8      | 86                   | 130-180                        | 3.40 (3.43)         | 350-665                       | 16.62 (16.66)            | V₂O₅                      |

**Electronic spectra**

The electronic spectra of the UO₂(VI) complexes are quite similar. The complexes display mainly one weak band at ~455 nm and a highly intense band at ~275-290 nm, which may be due to $\Sigma_g^\pm \rightarrow \Pi_u^+$ transitions and charge transfer transitions respectively. It may be noted that the band occurring at 365 nm is due to uranyl moiety because of apical oxygen →f(U) transition is being merged with the ligand band due to n→Π* transition as evident from broadness and intensity. The electronic spectra of Th(IV) and ZrO(IV) exhibit only one extra highly intensive band in the region 350-375 nm which may be due to charge transfer band besides the ligand bands. However the electronic spectra could not provide structural details of these complexes. The electronic spectra of VO(IV) complexes show three bands at ~12430, ~18470 and ~25880 cm⁻¹ corresponds to transitions, $d_{xy} (b_2) \rightarrow d_{xz} (e)$, $d_{xy} (b_2) \rightarrow d_x^2 y^2 (b_1)$ and $d_{xy} (b_2) \rightarrow d_z^2 (a_1)$ respectively, indicating the complexes to be in distorted octahedral environment under C₄ᵥ symmetry.

**¹H NMR spectra**

The ¹H NMR spectra of the diamagnetic complexes are recorded in DMSO-d₆ medium. The complexes do not show any signal attributable to amino protons, suggesting that the proposed skeleton has been formed by the condensation reactions, which is also conformed from the IR spectra of the complexes. The disappearance of the signal due to the phenolic OH protons (which is normally observed at δ ~13.07 ppm) and the downfield signal (δ ~8.32 ppm) to the azomethine protons as compared to free –CH=N (δ ~8.55 ppm) in the corresponding complexes, indicate the coordination of the phenolic oxygen (through deprotonation) and azomethine nitrogen to the metal ion. On the other hand the complexes show a complex broad multiplet in the region δ 6.53-8.06 ppm corresponding to eight aromatic protons of two oxophenyl groups and twenty aromatic protons of C₆H₅-C=N groups. For all the complexes, the signals due to (–NH–N=; 2H) protons appear at δ 5.98-6.12 ppm. In the complexes (1), (3), (5) and (7) a signal is observed at δ 3.75 ppm due to 4 protons (NCH₂CH₂N)²⁺. Besides, an additional peak at δ ~3.5 ppm is observed in all the complexes indicating the presence of coordinated water.

Based on the foregoing observations the following tentative structures have been proposed for the present complexes.
Fig. 2. Complexes with L ligand

Fig. 3. Complexes with L’ ligand

M = UO$_2$(VI), ZrO(IV) and Th(IV)
Y = NO$_3^-$ for Th(IV)
Y = 0 for UO$_2$(VI) and ZrO(IV)
X = NO$_3^-$

Fig. 4. [(VO)$_2$(L)(SO$_4$)(H$_2$O)]
Materials and methods

All the chemicals used of AR grade. The solvents were purified before use by standard procedures.

Preparation of benzilmonohydrazone

The analytical monohydrazones were synthesized according to literature method \(^\text{25}\). As the isolation of Schiff base ligand proved futile, all the metal complexes were synthesized (in an identical method) \textit{in situ} by taking different amount of metal salts, ethylene diamine/orthophenylene diamine, benzilmonohydrazone and salicyldehnyde.

Preparation of the complexes of the type \([\text{M}_2(\text{L})(\text{NO}_3)_n(\text{H}_2\text{O})_2]\), \(\text{M}=\text{UO}_{2}^{2+}, \text{ZrO}^{2+}, \text{Th}^{4+}\) and \([(\text{VO})_2(\text{L})(\text{SO}_4)(\text{H}_2\text{O})]\)

An ethanolic solution of hydrated \(\text{UO}_2(\text{VI})/\text{Th(IV)/ZrO(IV)}\) nitrates/vanadyl sulphate (1 mmol in 10 mL) was added to a hot ethanolic solution of the mixture of ethylene diamine (1 mmol in 10 mL) and benzil monohydrazone (2 mmol in 20 mL). The resulting mixture was refluxed on a water bath for 2-3 hours during which a coloured complex was precipitated out in each case. The ethanolic suspension of the complexes was treated with salicyldehnyde (2 mmol in 20 mL), which is followed by the corresponding metal salts (1 mmol in 10 mL EtOH). The mixture was again refluxed for 3-4 hours on a water bath during which the metal complexes of different colour than the precursor complexes were obtained (\textit{Table-1}).

The progress of the reaction was signaled by colour change of the resulting solution. These were filtered off, washed several times with ethanol followed by ether and finally dried in vacuo over anhydrous \(\text{CaCl}_2\) (fused).

Preparation of the complexes of the type \([\text{M}_2(\text{L})(\text{NO}_3)_n(\text{H}_2\text{O})_2]\), \(\text{M}=\text{UO}_{2}^{2+}, \text{ZrO}^{2+}, \text{Th}^{4+}\) and \([(\text{VO})_2(\text{L})(\text{SO}_4)(\text{H}_2\text{O})]\)

Same procedure was adopted for preparation of \([\text{M}_2(\text{L})(\text{NO}_3)_n(\text{H}_2\text{O})_2]\) and \([(\text{VO})_2(\text{L})(\text{SO}_4)(\text{H}_2\text{O})]\) by taking orthophenylene diamine instead of ethylene diamine.

Analysis and Physical Measurements

The metal contents in the complexes were determined gravimetrically following standard procedures \(^\text{26}\). Sulphur was determined as \(\text{BaSO}_4\). Room temperature magnetic susceptibilities were measured by Gouy method using \(\text{Hg}[\text{Co(NCS)}_4]\) as the calibrant. The molar conductance measurements were carried out at room temperature with a Toshniwal conductivity Bridge (Model CL-01-06, cell constant 0.5 cm\(^{-1}\)) using 1 × 10\(^{-3}\) M solution of the complexes in DMSO. Carbon, hydrogen and nitrogen contents of the complexes were determined by using a MLW-CHN microanalysrer. FTIR spectra in KBr pellets were recorded on a Varian FTIR spectrophotometer, Australia. The electronic spectra of the complexes in DMSO were recorded on a Perkin Elmer spectrophotometer. Thermogravimetric analysis was done by Netzch-429 thermoanlyser. The \(^1\text{H-NMR}\) spectra of the complexes were recorded in DMSO-\(d_6\) medium on Jeol GSX-400 model equipment.

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