Journal of the Korean Chemical Society
2011, *Vol. 55, No. 2*
Printed in the Republic of Korea
DOI 10.5012/jkcs.2011.55.2.317

단 신

폴리아자 거대고리 Schiff-염기의 동종이핵 UO_2(VI), Th(IV), ZrO(IV) 및 VO(IV) 착물의 합성 및 특성 규명

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(접수 2010. 3 19; 수정 2010. 10. 8; 게재확정 2010. 12. 14)

Synthesis and Characterization of Homo Binuclear Complexes of UO_2(VI), Th(IV), ZrO(IV) and VO(IV) with Polyaza Macrocyclic Schiff-Bases

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(Received March 19, 2010; Revised October 8, 2010; Accepted December 14, 2010)

주제어: Schiff-염기, 주형합성, 구조 및 열적성질, IR 및 H^1-NMR 스펙트럼

Keywords: Schiff base, Template synthesis, Structure and Thermal Properties, IR, H^1-NMR spectra

INTRODUCTION

The introduction of pendant arms into the macrocyclic framework can lead to important changes in the complexation capability of the ligands and can enhance the metal-ion selectivity and the stability of metal complexes depending on the coordination properties of the pendant arms. There is an emerging interest in the synthesis of macrocyclic complexes of transition and inner transition cations, because of their applications and interesting properties.[1,2] One reason for the interest in this field is that it offers exciting possibilities for creative minds to construct novel, supramolecular assemblies that are capable of performing highly specific molecular functions. The precise molecular recognition between macrocyclic ligands and their guests provides a good opportunity for studying key aspects of supramolecular chemistry, which are also significant in a variety of disciplines including chemistry, biology, physics, medicine and related science and technology.

The chemistry of macrocyclic complexes has attracted the interest of both inorganic and bioinorganic chemists in recent years.[3] The field of macrocyclic chemistry of metals is developing very rapidly because of its importance in the area of coordination chemistry.[4] Macrocyclic compounds and their derivatives are interesting ligand systems because they are good hosts for metal anions, neutral molecules and organic cation guests.[5] The metal ion and host-guest chemistry of macrocyclic compounds are very useful in fundamental studies (in phase transfer catalysis and biological studies).[6] Template condensation reactions lie at the heart of the macrocyclic chemistry.[7] Therefore template reactions have been widely used for synthesis of macrocyclic complexes.[8] The family of complexes with aza-macrocyclic ligands has remained a focus of scientific attention for many decades.[9] Schiff base polyazamacrocyclic complexes have under gone a phenomenal growth during the recent years because of the versatility offered by these complexes in the field of industries, catalysis and in biological systems[10-15] etc.

The homo-multimetallic complexes have the potential to mediate certain chemical reactions of industrial relevance either more efficiently than, or in a different manner to monometallic complexes. They exhibit distinct reactivity pattern as compared to corresponding monometallic complexes.[16] The magnetic interactions and coupling between the metal ions present in such complexes play key role in both natural and synthetic catalysts.[17] As a result, the synthesis and characterization of homo bimetallic complexes continue to attract attention.[18]

The monohydrazones of benzil and diacetyl may exist in trans position. In the presence of metal ion, they may attain a cis (vicinal) configuration. Complexes involving such hydrazones may be used as an intermediate to prepare homo/hetero binuclear complexes by template condensation with suitably oriented aldehyde or ketones[19,20] in the presence of homo/hetero metal ions. In continuation of our consistent efforts towards synthesis and characterization of such type of complexes[21-24] we report here the synthesis and characterization of hither to unknown homo binuclear complexes with some Schiff base monohydrazone derivatives obtained from the reaction of thiocarbohydrazide, benzilmonohydrazone/diacetylmonohydrazone and acetylacetone in presence of UO_2^{2+}, ZrO^{2+}, Th^{4+} and VO^{2+} ions.

EXPERIMENTAL

Materials

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

Preparation of thiocarbohydrazide

Thiocarbohydrazide was synthesized according to literature method of Audrieth *et al.*.[25]

Preparation of benzilmonohydrazone/diacetylmonohydrazone

The analytical monohydrazones were synthesized according to literature method.[26] As the isolation of Schiff base ligand proved futile, all the metal complexes were synthesized (in an identical method) in situ by taking different amount of metal salts, thiocarbohydrazide, benzilmonohydrazone/diacetylmonohydrazone and acetylacetone.

Preparation of the complexes

All complexes were prepared according to the following procedure. An ethanolic solution of hydrated UO_2(VI)/Th(IV)/ZrO(IV) nitrates/vanadyl sulphate (1 mmol in 10 mL) was added to a hot ethanolic solution of the mixture of thiocarbohydrazide (1 mmol in 10 mL), benzilmonohydrazone/diacetylmonohydrazone (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 above complexes were treated with acetylacetone (2 mmol in 10 mL EtOH) and thiocarbohydrazide (1 mmol in 10 mL) followed by the addition of corresponding metal salt (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. The progress of the reaction was signaled by colour change of the resulting mixture. These were filtered off, washed several times with ethanol followed by ether and finally dried over anhydrous $CaCl_2$.

Analysis and Physical Measurements

The metal contents in the complexes were determined gravimetrically following standard procedures.[27] A weighed quantity of the compound (0.2-0.3 g) was treated with a few drops of concentrated H_2SO_4 and 1 cc. of concentrated HNO_3. It was heated till all the organic matter decomposed and sulphur trioxide fumes came out. The same process was repeated two to three times to decompose the substance completely. Then it was dissolved in water and the resulting solution was used for analysis of metal ions. Uranium, thorium, zirconium and vanadium were precipitated as ammonium diuranate, thorium oxalate, zirconium mandelate and ammonium vanadate followed by subsequent ignition to their respective oxides as U_3O_8, thoria (ThO_2), zirconia (ZrO_2) and V_2O_5. Sulphur was determined as $BaSO_4$. Room temperature magnetic susceptibilities were measured by Gouy method using Hg[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 microanalyser. 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 PerkinElmer* spectrophotometer. Thermogravimetric analysis was done by Netzch-429 thermoanalyser. The ^{1}H-NMR spectra of the complexes were recorded in DMSO-d_6 medium on JEOL GSX-400 model equipment.

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 highly stable under normal conditions and all of them decompose above 250 °C. The molar conductance data values in DMSO for

***Table* 1.** Analytical and physical data of the complexes

Sl. no.	Compounds	Colour	Yield (%)	Λ_m [a]	Found(calc.)%				
					C	H	N	S	M
1	$[(UO_2)_2(L)(NO_3)_4]$ $3H_2O$	Steel grey	64	19.31	30.05 (30.11)	2.85 (2.88)	14.09 (14.05)	3.95 (4.01)	29.81 (29.86)
2	$[(Th)_2(L)(NO_3)_8]$ $3H_2O$	Canary yellow	62	35.75	27.03 (27.12)	2.54 (2.60)	15.75 (15.82)	3.57 (3.61)	26.38 (26.44)
3	$[(ZrO)_2(L)(NO_3)_4]$ $2H_2O$	Pale Cream	56	21.53	38.35 (38.40)	3.48 (3.52)	17.87 (17.92)	5.09 (5.12)	14.51 (14.56)
4	$[(VO)_2(L)(SO_4)_2]$ $2H_2O$	Black	64	13.23	43.01 (43.08)	3.91 (3.95)	15.04 (15.08)	11.53 (11.49)	9.11 (9.15)
5	$[(UO_2)_2(L')(NO_3)_4]$ $3H_2O$	Light brown	63	17.67	17.77 (17.83)	2.79 (2.82)	16.58 (16.64)	4.71 (4.75)	35.31 (35.36)
6	$[(Th)_2(L')(NO_3)_8]$ $3H_2O$	Straw yellow	62	32.68	15.69 (15.76)	2.45 (2.49)	18.34 (18.39)	4.17 (4.20)	30.69 (30.74)
7	$[(ZrO)_2(L')(NO_3)_4]$ $2H_2O$	Cream	58	18.21	23.91 (23.95)	3.54 (3.59)	22.29 (23.35)	6.34 (6.38)	18.11 (18.16)
8	$[(VO)_2(L')(SO_4)_2]$ $2H_2O$	Greenish black	63	11.75	27.65 (27.71)	4.12 (4.15)	19.35 (19.40)	14.82 (14.78)	11.71 (11.77)

[a] Ohm^{-1} cm^2 $mole^{-1}$

the complexes indicate them to be non-electrolyte in nature. However, the conductivity value is higher than as expected for non-electrolytes probably due to partial solvolysis of the complexes in DMSO medium.[28]

IR spectra

As the Schiff base ligands could not be isolated, the spectra of the complexes (*Table* 2) were compared with spectra of the starting materials and other related compounds. The bands observed in the spectra of metal complexes at ~1525, ~1315, ~1100, ~765 cm^{-1} are assigned to thioimide I, II, III, IV bands respectively of TCH skeleton.[29] All the above bands appear nearly the same position as found in the free TCH implying non co-ordination of thioimide sulphur or nitrogen atom to the metal ion. The IR spectra of the complexes show strong bands appearing at 1630 and ~1060 cm^{-1} assignable to azomethine νC=N and νN-N. The position of former band at comparatively lower frequency region than usual free νC=N value (~1650 cm^{-1})[30-32] and that of later band at comparatively higher frequency region than that of free N-N leads us to suggest that azomethine nitrogen atom has taken part in complexation as evidenced from the appearance of band in the region ~480 cm^{-1} due to ν(M-N). The occurrence of N-N band at higher frequency in the IR spectra of the complexes is due to reduction of the repulsion between the lone pair of nitrogen atoms as a result of coordination via azomethain nitrogen atoms. The splitting of (νC=N) band is probably due to the presence of the methaine group in different chemical environment. One would therefore expect the absence of band due to ν C=O to suggest that Schiff base reaction has taken place. On scanning the spectra of metal complexes no bands due to ν C=O at ~1700 cm^{-1} is observed. This clearly suggests that Schiff base reaction has taken place.

The uranyl complexes exhibit a strong band in the region 940-910 cm^{-1} and the medium intensity band in the region 830-810 cm^{-1} assignable to ν_{as} (O=U=O) and ν_s (O=U=O) mode respectively.[33] This observation indicates that the linearity of the O=U=O group is maintained in the complexes.[34] The band at 1020 cm^{-1} is assigned to the n_2 mode of the NO_3 group. The bands at 1475 and 1375 cm^{-1} are the two split bands ν_4 and ν_1 respectively, of the coordinated

***Table* 2.** IR spectral data of the complexes

Complex								Band assignment
1	2	3	4	5	6	7	8	
3425	3425	3430	3430	3425	3425	3428	3428	ν_{OH+NH} (Combined)
1626	1628	1630	1629	1632	1630	1634	1635	$\nu_{C=N}$ (Coordinated)
477	475	480	480	475	478	484	482	ν_{M-N}
1057	1060	1055	1058	1058	1062	1065	1058	ν_{N-N}
763	765	765	762	765	768	762	760	$\nu_{C=S}$
1095	1090	1098	1095	1100	1102	1096	1098	ν_{C-S}
1370	1372	1375	-	1375	1373	1376	-	ν_1
1470	1472	1475		1475	1473	1476		ν_4 for NO_3^-
938	-	-	-	915	-	-	-	νas (O=U=O)
824	-	-	-	818	-	-	-	νs (O=U=O)
-	-	885	-	-	-	878	-	ν (Zr=O)
-	-	-	945	-	-	-	950	ν (V=O)

nitrate ion. The magnitude of $\Delta\nu = (\nu_4 - \nu_1) = 100$ cm^{-1} shows the unidentate coordination of the nitrate ion.[35] The zirconyl complexes exhibit one strong band in the region 890-875 cm^{-1} which can be attributed to the ν(Zr=O) as reported earlier[34] indicating the presence of $(Zr=O)^{2+}$ moiety in these complexes. In the oxovanadium polychelates a strong bands at ~950 cm^{-1} are assigned to ν(V=O) mode.[36] However, in vanadyl complexes, an additional series of four bands appeared at 1155, 1115, 855, 665 cm^{-1} indicating the coordination of sulphate group in unidentate manner through oxygen atom.[37] Besides, the bands observed at ~3430 cm^{-1} may be assigned to ν(O-H) of coordinated or lattice water. However all the complexes loss water when heated to ~50 °C indicating the presence of lattice water molecules which has been conformed by thermal analysis.

Thermal analysis

All these complexes follow the same pattern of thermal decomposition. The complexes remain almost unaffected upto ~50 °C. After this a slight depression upto ~110 °C is observed. The weight loss at this temperature range is equivalent to two for the complexes (3), (4), (7) and (8) and three for the complexes (1), (2), (5) and (6) water molecules in the complexes indicating them to be lattice water[38] in conformity with our earlier observations from analytical and IR spectral investigations. Once the lattice water was eliminated, the anhydrous complexes remain stable upto ~355 °C and thereafter the complexes show gradual degradation presumably due to decomposition of organic constituents of the complex molecules. The decomposition continues upto ~600 °C 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* 3. The thermal stability of the complexes decreases in the order:

(L) complexes: Th(IV) > VO(IV) > ZrO(IV) > UO_2(VI)

(L') complexes: Th(IV) > VO(IV) > UO_2(VI) > ZrO(IV)

Electronic spectra

The electronic spectra of the UO_2(VI) complexes are quite similar. The complexes display mainly one weak band at ~460 nm and a highly intense band in the range 270-290 nm, which may be due to $^1\Sigma_g^+ \rightarrow {}^3\Pi_u$ transitions and charge transfer transitions respectively.[39] The first one of the transition is typical of the O=U=O symmetric stretching frequency of the first excited state.[40] It may be noted that the band occurring at 370 nm is due to uranyl moiety because of apical oxygen f^0(U) transition[41] is being merged with the ligand band due to $n \rightarrow \pi^*$ transition as evident from broadness and intensity. The electronic spectra of ZrO(IV) complexes 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 ~12280, ~18490 and ~25740 cm^{-1} corresponds to transitions, $d_{xy}(b_2) \rightarrow d_{xz}d_{yz}(e)$, $d_{xy}(b_2)d_{x^2-y^2}(b_1)$ and $d_{xy}(b_2) \rightarrow d_{z^2}(a_1)$ respectively, indicating the complexes to be in distorted octahedral environment under C_{4V} symmetry.[42]

Magnetic moment

All the complexes except VO(IV), are diamagnetic consistent with their d^0 and f^0 electronic configuration. The magnetic moment values for the oxovanadium(IV) complexes (4) and (8) lie in the range 2.60-2.70 BM. These values are less than spin-only value required for two unpaired electrons indicating spin-spin coupling in the solid state between unpaired electrons belonging to different VO(IV) ions in the same structural unit.[43]

^{1}H NMR spectra

The ^{1}H NMR spectra of the diamagnetic complexes are recorded in DMSO-d_6 medium. The complexes do not show any signal attributable to amino protons, suggesting

***Table* 3.** Important features of thermo gravimetric analysis (TGA)

Complexes	Total wt. for TG (mg)	Temp. range of Water loss (°C)	% of water loss		Temp. range of decomposition (°C)	% of residue		Composition of the residue
			Found	Calc.		Found	Calc.	
1	102	70-110	3.34	3.39	365-590	35.16	35.21	U_3O_8
2	105	60-105	3.01	3.05	395-610	29.99	30.05	ThO_2
3	103	60-100	2.83	2.88	370-595	19.64	19.68	ZrO_2
4	106	50-90	3.20	3.23	385-600	16.29	16.34	V_2O_5
5	108	70-105	3.95	4.01	360-570	41.63	41.70	U_3O_8
6	104	55-105	3.51	3.55	390-600	34.91	34.95	ThO_2
7	107	55-100	3.56	3.59	355-575	24.49	24.55	ZrO_2
8	109	50-95	4.12	4.16	375-580	20.96	21.01	V_2O_5

***Table* 4.** Fungi toxicity of ZrO(IV) and VO(IV) complexes against the fungal pathogens

complexes	Aspergillus niger					Aspergillus flavus				
	100	200	400	800	1000	100	200	400	800	1000
$[(ZrO)_2(L)(NO_3)_4]\ 2H_2O$	12.3	16.4	22.5	33.2	53.1	11.2	15.4	23.3	29.1	53.2
$[(ZrO)_2(L')(NO_3)_4]\ 2H_2O$	17.1	22.6	28.3	47.3	62.2	16.4	21.8	30.3	46.2	66.3
$[(VO)_2(L)(SO_4)_2]\ 2H_2O$	13.4	17.6	23.6	41.4	54.2	13.3	18.1	26.5	34.2	56.4
$[(VO)_2(L')(SO_4)_2]\ 2H_2O$	19.5	26.3	34.1	62.3	77.5	18.7	26.5	37.1	67.5	76.4

that the proposed skeleton has been formed by the condensation reactions. The complexes (1), (2) and (3) show a broad multiplet at δ 6.73-7.25 ppm corresponding to aromatic (C_6H_5-C=N; 20H) protons[44] of four phenyl groups and a twin peak at δ ~2.40, δ ~2.60 ppm corresponding to imine methyl (CH_3-C=N; 12H) protons.[45] A singlet is also observed in the region δ 2.18-2.26 ppm, which may be assigned to methylene (C-CH_2-C; 4H) protons for these complexes. The complexes (5), (6) and (7) show a signal, appear in several groups in the region δ 2.25-2.70 ppm corresponding to imine methyl (CH_3-C=N; 24H) and methylene (C-CH_2-C; 4H) protons.[44] Besides, the signals due to (-NH-N=; 2H) protons appear at δ 6.05-6.17 ppm for all the complexes.

Based on the foregoing observations the following tentative structures have been proposed for the present complexes.

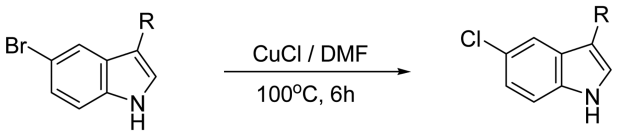
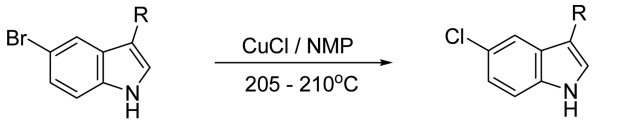


***Fig.* 1**



1a R=H
1b R=CN
1c R=CHO
1d R=COOH

2a R=H
2b R=CN
2c R=CHO
2d R=COOH

***Fig.* 2**

M = UO_2(VI), ZrO(IV) and Th(IV)
X = NO_3^- for Th(IV)
X = 0 for UO_2(VI) and ZrO(IV)
Y = NO_3^-
Z = SO_4^{2-}
R = C_6H_5, CH_3

Fungicidal Screening

The antifungal activity of ZrO(IV) and VO(IV) complexes have been studied by potato dextrose agar diffusion method in DMSO solvent against A. niger and A. flavus. The complexes showed good antifungal activity (*Table* 4) against the species. This may be explained on the basis that their structures mainly possess C=N bonds. Moreover, coordination reduces the polarity[42,46] of the metal ion mainly because of the partial sharing of its positive charge within the chelate ring formed during coordination. This process increases the lipophilic nature of the central metal atom, which favors its permeation more efficiently through the lipid layer of the micro-organism[47-49] thus destroying them more aggressively.

Acknowledgement. The authors gratefully acknowledge the services rendered by Director, Regional Sophisticated Instrumentation Center, I.I.T., Madras, for recording the spectra.

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