

Schiff-염기인 모노히드라존 치환체와 $UO_2(VI)$, $Th(IV)$, $ZrO(IV)$ 및 $VO(IV)$ 의 동종이핵 착물에 대한 합성 및 특성

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Synthesis and Characterization of Homobinuclear Complexes of $UO_2(VI)$, $Th(IV)$, $ZrO(IV)$ and $VO(IV)$ with Schiff-Base Monohydrazone Derivatives

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요약. $[M_2(L)(NO_3)_n(H_2O)_2]$ [$n=2$ 의 경우, $M = UO_2^{2+}$, Th^{4+} , ZrO^{2+} ; 단, UO_2^{2+} 및 ZrO^{2+} 의 경우 $n = 2$; Th^{4+} 의 경우 $n = 6$], $[(VO)_2(L)(SO_4)(H_2O)]$, [$L = 1,15$ -di(*o*-hydroxyphenyl)-2,3,6,7,9,10,13,14-octaaza-4,5,11,12-tetraphenyl/tetramethyl-pentadeca-1,3,5,10,12,14-hexa-ene-8-thione (*optH₂/omtH₂*)] 형태의 일련의 동종이핵착물을 thiocarbohydrazide, benzilmonohydrazone/diacetylmonohydrazone 및 salicylaldehyd로부터 주형법에 의해 합성한 후, 원소분석, 열분석, 몰 전기전도도, 자기모멘트, UV, IR 및 1H NMR 실험으로부터 그 특성을 조사하였다. 이 결과로부터 UO_2^{2+} 및 ZrO^{2+} 이온은 육배위 그리고 Th^{4+} 이온은 팔배위의 반자기성 착물을 형성하는 반면, VO^{2+} 의 경우 위의 조성을 갖는 오배위의 상자기성 착물을 형성하는 것이 확인되었다.

주제어: Schiff 염기, 주형합성, 구조 및 열적 성질, IR 및 1H -NMR 스펙트럼

ABSTRACT. A series of homobinuclear complexes of the type $[M_2(L)(NO_3)_n(H_2O)_2]$, [where $M=UO_2^{2+}$, Th^{4+} , ZrO^{2+} , $n=2$ for UO_2^{2+} , ZrO^{2+} , $n=6$ for Th^{4+}] and $[(VO)_2(L)(SO_4)(H_2O)]$, $L=1,15$ -di(*o*-hydroxyphenyl)-2,3,6,7,9,10,13,14-octaaza-4,5,11,12-tetraphenyl/tetramethyl-pentadeca-1,3,5,10,12,14-hexa-ene-8-thione (*optH₂/omtH₂*) have been synthesized in template method from thiocarbohydrazide, benzilmonohydrazone/diacetylmonohydrazone, salicylaldehyde and characterized on the basis of elemental analysis, thermal analysis, molar conductivity, magnetic moment, UV, IR and 1H NMR studies. The results indicate that UO_2^{2+} and ZrO^{2+} ions are hexa-coordinated; Th^{4+} ion is octa-coordinated yielding diamagnetic complexes whereas the VO^{2+} ion is penta-coordinated yielding paramagnetic complexes of above composition.

Keywords: Schiff Base, Template Synthesis, Structure and Thermal Properties, IR and 1H -NMR Spectra

INTRODUCTION

In recent years, much attention has been given to the synthesis and characterization of multimetallic complexes in connection with their potential relevance to bioinorganic chemistry.¹ The polydentate and compartmental ligands can form such multimetallic clusters by binding two or more metal centres in close proximity. The homo-multimetallic molec-

ular complexes are of interest in areas like multimetallic enzymes, homogeneous catalysis and heterogeneous catalysis. Many enzymes in biological systems are homo-multimetallic that performs their biological functions by redox co-operativity.² A close proximity of the metal ions in multimetallic complexes considerably varies the properties of the system, which may be significantly different from the properties of the monometallic complexes.

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.³ The magnetic interactions and coupling between the metal ions present in such complexes play key role in both natural and synthetic catalysts.⁴ As a result, the synthesis and characterization of homo bimetallic complexes continue to attract attention.⁵

Interest in the study of Schiff base hydrazones and their complexes has been growing because of their wide importance as antimicrobial, anti-tuberculosis, anti-tumour and antiviral activities⁶⁻¹⁶ as well as models for biologically important species especially for the metal containing sites in metallo-proteins and -enzymes.^{17,18}

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 complexes²¹⁻²³ we report here the synthesis and characterization of hitherto unknown homo binuclear complexes with some Schiff base monohydrazone derivatives obtained from the reaction of thiocarbohydrazide, benzilmonohydrazone/diacetylmonohydrazone and salicylaldehyde 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.*²⁴

Preparation of benzilmonohydrazone/diacetylmonohydrazone

The analytical monohydrazones were synthesized according to literature method.²⁵ 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 salicylaldehyde.

Preparation of the complexes of the type $[M_2(L)(NO_3)_6(H_2O)_2]$, $M= UO_2^{2+}$, ZrO^{2+} , Th^{4+} and $[(VO)_2(L)(SO_4)]2H_2O$

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 salicylaldehyde (2 mmol in 10 ml EtOH), which is followed by the 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 $CaCl_2$.

There is possibility of the formation of the mixture consisting reactant complexes and product complexes. This possibility has been ruled out by carrying out fractional crystallization in DMSO solvent taking in to account their different in solubilities. The purity of the complexes was further checked by carrying out TLC on silica gel.

Analysis and Physical Measurements

The metal contents in the complexes were determined gravimetrically following standard proce-

dures.²⁶ A weighed quantity of the compound (0.2-0.3 g) was treated with a few drops of concentrated H₂SO₄ and 1 cc. of concentrated HNO₃. 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 U₃O₈, thoria (ThO₂), zirconia (ZrO₂) and V₂O₅. Sulphur was determined as BaSO₄.²⁶ Room temperature magnetic susceptibilities were measured by Gouy method²⁷ 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 Perkin-Elmer spectrophotometer. Thermogravimetric analysis was done by Netzsch-429 thermoanalyser. The ¹H-NMR spectra of the complexes were recorded in DMSO-d₆ 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, CCl₄, CHCl₃, 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 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,

Table 1. Analytical and physical data of the complexes

Sl. no.	Compounds	Colour	Yield (%)	M.P. (°C)	μ _{eff} (B.M)	Λ _m ^o	Found(calc.)%				
							C	H	N	S	M
1	[(UO ₂) ₂ (opt)(NO ₃) ₂ (H ₂ O) ₂]	Cream	58	>250	Dia	23.42	36.21 (36.23)	2.55 (2.53)	9.78 (9.83)	2.20 (2.24)	33.38 (33.42)
2	[(Th) ₂ (opt)(NO ₃) ₆ (H ₂ O) ₂]	Pale cream	52	>250	Dia	34.81	32.29 (32.25)	2.21 (2.25)	12.19 (12.25)	2.03 (2.00)	29.21 (29.25)
3	[(ZrO) ₂ (opt)(NO ₃) ₂ (H ₂ O) ₂]	New lemon tint	54	>250	Dia	22.66	47.04 (46.99)	3.23 (3.28)	12.79 (12.75)	2.85 (2.91)	16.53 (16.57)
4	[(VO) ₂ (opt)(SO ₄) ₂ (H ₂ O)]	Greenish black	55	>250	2.53	14.73	53.01 (53.08)	3.54 (3.50)	11.47 (11.52)	6.51 (6.58)	10.42 (10.49)
5	[(UO ₂) ₂ (omt)(NO ₃) ₂ (H ₂ O) ₂]	Pale cream	56	>250	Dia	22.38	23.51 (23.47)	2.35 (2.38)	11.93 (11.90)	2.68 (2.72)	40.50 (40.47)
6	[(Th) ₂ (omt)(NO ₃) ₆ (H ₂ O) ₂]	Citron	55	>250	Dia	32.77	20.35 (20.41)	2.01 (2.07)	14.46 (14.50)	2.33 (2.36)	34.55 (34.61)
7	[(ZrO) ₂ (omt)(NO ₃) ₂ (H ₂ O) ₂]	Daffodil	57	>250	Dia	24.18	32.43 (32.47)	3.25 (3.29)	16.51 (16.47)	3.71 (3.76)	21.38 (21.41)
8	[(VO) ₂ (omt)(SO ₄) ₂ (H ₂ O)]	Light chocolate	59	>250	2.47	12.25	38.17 (38.12)	3.53 (3.59)	15.43 (15.47)	8.80 (8.84)	14.02 (14.08)

^oOhm⁻¹ cm² mole⁻¹

the spectra of the complexes were compared with spectra of the starting materials and other related compounds. The bands observed in the spectra of metal complexes at ~ 1520 , ~ 1315 , ~ 1090 and ~ 770 cm^{-1} are assigned to thioimide I, II, III and IV bands of TCH skeleton, respectively²⁹. 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 ~ 1625 and ~ 1070 cm^{-1} assignable to azomethine $\nu\text{C}=\text{N}$ and $\nu\text{N}-\text{N}$. The position of former band at comparatively lower frequency region than usual free $\nu\text{C}=\text{N}$ value (~ 1650 cm^{-1})^{30,32} and that of latter band at comparatively higher frequency region than that of free $\text{N}-\text{N}$ ³³ leads us to suggest that azomethine nitrogen atom has taken part in complexation as evidenced from the appearance of band in the region ~ 475 cm^{-1} due to $\nu(\text{M}-\text{N})$ ³⁴. The occurrence of $\text{N}-\text{N}$ band at higher frequency in the IR spectra of the complexes is due to reduction of the repulsion between the lone pairs of nitrogen atoms as a result of coordination via azomethine nitrogen atoms. The splitting of ($\nu\text{C}=\text{N}$) band is probably due to the presence of the methine group in different chemical environment. 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 $\nu(\text{C}-\text{O})$ phenolic at much higher frequencies (~ 1450 cm^{-1}) in the complexes^{35,36} due to partial double bond character. The coordination of the phenolic oxygen is further supported by the appearance of a non ligand band at $520-540$ cm^{-1} , due to $\nu(\text{M}-\text{O})$ ³⁷. One would therefore expect the absence of band due to $\nu\text{C}=\text{O}$ to suggest that Schiff base reaction has taken place. On scanning the spectra of metal complexes no bands due to $\nu\text{C}=\text{O}$ 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 $940-920$ cm^{-1} and the medium intensity band in the region $830-815$ cm^{-1} assignable to $\nu_{as}(\text{O}=\text{U}=\text{O})$ and $\nu_s(\text{O}=\text{U}=\text{O})$ mode respectively³⁸.

This observation indicates that the linearity of the $\text{O}=\text{U}=\text{O}$ group is maintained in the complexes.³⁹ The band at 1024 cm^{-1} is assigned to the ν_3 mode of the NO_3 group. The bands at 1480 and 1380 cm^{-1} are the two split bands ν_4 and ν_1 respectively, of the coordinated nitrate ion. The magnitude of $\Delta\nu = (\nu_4 - \nu_1) = 100$ cm^{-1} shows the unidentate coordination of the nitrate ion.⁴⁰ The zirconyl complexes exhibit one strong band in the region $890-870$ cm^{-1} which can be attributed to the $\nu(\text{Zr}=\text{O})$ as reported earlier³⁹ indicating the presence of $(\text{Zr}=\text{O})^{2-}$ moiety in these complexes. In the oxovanadium polychelates a strong bands at ~ 950 cm^{-1} are assigned to $\nu(\text{V}=\text{O})$ mode.⁴¹ However in vanadyl complexes, an additional series of four bands appeared at ~ 1160 , ~ 1115 , ~ 865 and ~ 650 cm^{-1} , indicating the coordination of sulphate group in unidentate manner through oxygen atom⁴². Besides, the bands observed at ~ 3430 cm^{-1} may be assigned to $\nu(\text{O}-\text{H})$ of coordinated or lattice water. The representative spectrum of $[(\text{Th})_2(\text{omt})(\text{NO}_3)_6(\text{H}_2\text{O})_2]$ complex is shown in Fig. 1.

Thermal analysis

The thermogram of the complexes exhibited the characteristics of co-ordinated water. The complexes remain almost unaffected up to $\sim 130^\circ\text{C}$. After this slight depression up to 200°C is observed. The weight loss at this temperature range is equivalent to one water molecule for $\text{VO}(\text{IV})$ and two water molecules for other complexes, indicating them to be coordinated water in conformity with our earlier observations for analytical and IR spec-

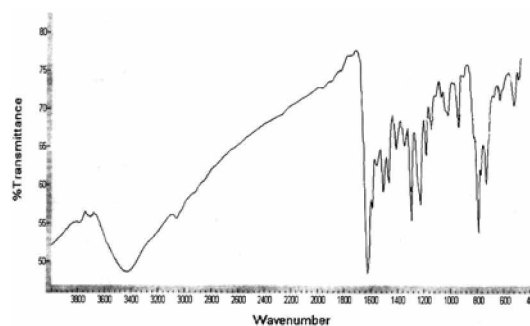
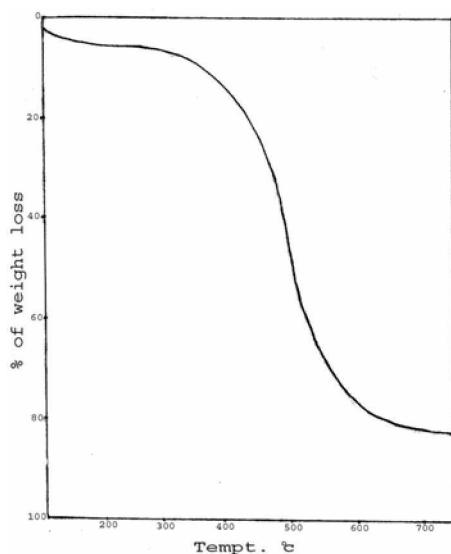


Fig. 1. IR spectra of $[(\text{Th})_2(\text{omt})(\text{NO}_3)_6(\text{H}_2\text{O})_2]$.

Table 2. 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)	% wt of residue Found (Calc.)	Composition of the residue
			Found	Calc.			
1	97	130-180	2.48	2.53	370-680	39.37(39.42)	U ₃ O ₈
2	102	140-190	2.21	2.25	355-675	32.94(33.00)	ThO ₂
3	93	135-190	3.24	3.28	380-675	22.36(22.40)	ZrO ₂
4	96	140-180	1.82	1.85	365-680	18.65(18.72)	V ₂ O ₅
5	94	140-200	3.01	3.06	385-665	47.68(47.73)	U ₃ O ₈
6	95	135-200	2.62	2.66	360-660	38.99(39.05)	ThO ₂
7	91	130-180	4.19	4.23	375-670	28.90(28.94)	ZrO ₂
8	87	140-185	2.42	2.48	370-670	25.07(25.13)	V ₂ O ₅

tral investigations. Simultaneous elimination of coordinated water suggests them to be in the same chemical environment.¹³ The anhydrous complexes remain stable up to ~350°C and there after the complexes shows 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 up to ~700°C in each complex as indicated by the consistency in weight in the plateau of the thermo gram. The decomposition temperature varies for different complexes as shown in Table 2. The thermal stability of such complexes is found to be in the following order. The representative thermogram of [(VO)₂(opt)(SO₄) H₂O] complex is

Fig. 2. Thermogram of [(VO)₂(opt)(SO₄) H₂O].

shown in Fig. 2.

(opt) Complexes: ZrO(IV) > UO₂(VI) > VO(IV) > Th(IV)

(omt) Complexes: UO₂(VI) > ZrO(IV) > VO(IV) > Th(IV)

Electronic spectra

The electronic spectra of complexes in DMSO are quite similar. The UO₂(VI) complexes display mainly one weak band at ~450 nm and a highly intense band in the range 280-290 nm, which may be due to ¹Σ_g⁻ → π_u³ transitions and charge transfer transitions respectively.⁴⁴ The first one of the transition is typical of the O=U=O symmetric stretching frequency of the first excited state.⁴⁵ It may be noted that the band occurring at 365 nm is due to uranyl moiety because of apical oxygen → f⁰(U) transition⁴⁶ is being merged with the ligand band due to n → π* transition as evident from broadness and intensity. The electronic spectra of ZrO(IV) complexes exhibit only one extra highly intensive band in the region 350-380 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 ~12320, ~18470 and ~25885 cm⁻¹ corresponds to transitions, d_{xy}(b₂) → d_{xz}d_{yz}(e), d_{xy}(b₂) → d_{x²-y²}(b₁) and d_{xy}(b₂) → d_{z²}(a₁) respectively, indicating the complexes to be in distorted octahedral environment under C_{4v} symmetry.⁴⁷ It is to be noted that though both the VO(IV) ions are in different chemical environment (N₄ and N₂O₂) no spectacular change is noticed in

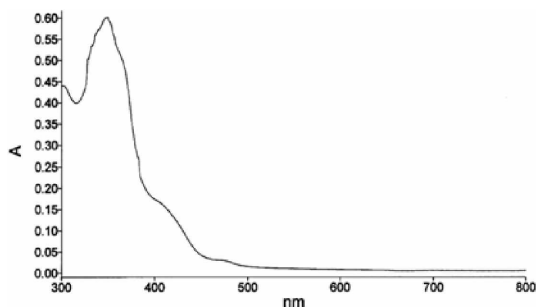


Fig. 3. Electronic spectra of [(ZrO)(opt)(NO₃)₂(H₂O)₂].

their electronic spectra. The representative spectrum of the [(ZrO)₂(opt)(NO₃)₂(H₂O)₂] complex is shown in Fig. 3.

Magnetic moment

All the complexes except VO(IV), are diamagnetic consistent with their d⁰ and f⁰ electronic configuration. The magnetic moment values for the oxovanadium(IV) complexes (4) and (8) lie in the range 2.47-2.54 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.⁴⁸

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) due to the azomethine protons as compared to free -C=N (δ = 8.55 ppm) in the corresponding complexes, indicate the co-ordination of the phenolic oxygen (through deprotonation) and azomethine nitrogen to the metal ion.⁴⁹ The same result was confirmed by the IR spectra. On the other hand the complexes (5), (6) and (7) show a complex broad multiplet in the region δ 6.51-7.63 ppm and a twin peak at δ 2.45, 2.72 ppm, corre-

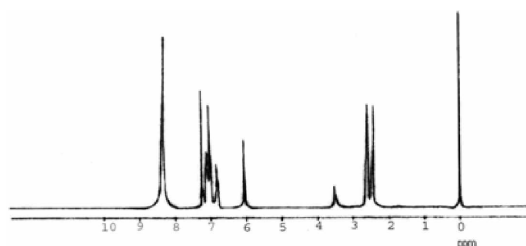


Fig. 4. ¹H NMR spectra of [(UO₂)₂(omt)(NO₃)₂(H₂O)₂].

sponding to eight aromatic protons of two oxophenyl groups and imine methyl (CH₃-C=N; 12H) protons⁵⁰ respectively. But in case of complexes (1), (2) and (3) it is difficult to distinguish the eight aromatic protons of two oxophenyl groups and twenty aromatic protons of C₆H₅-C=N groups, as only one signal (multiplet) observed in the region δ 6.53-8.06 ppm. For all the complexes, the signals due to (-NH-N=; 2H) protons appear at δ 5.98-6.12 ppm. Besides, an additional peak at δ ~3.6 ppm is observed in all the complexes indicating the presence of coordinated water.⁵¹ The representative spectrum of the [(UO₂)₂(omt)(NO₃)₂(H₂O)₂] complex is shown in Fig. 4.

Based on the foregoing observations the following tentative structures have been proposed for the present complexes (Figs. 5 and 6).

M = M' = UO₂(VI), ZrO(IV) and Th(IV)

X = NO₃ for Th(IV)

X = O for UO₂(VI) and ZrO(IV)

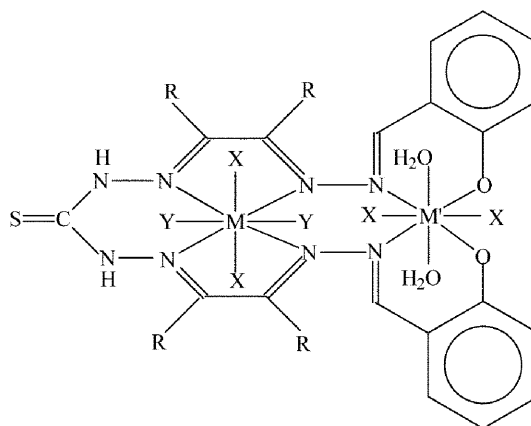


Fig. 5.

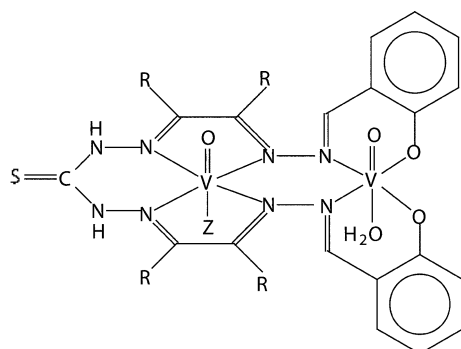
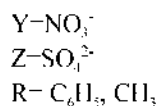


Fig. 6.



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