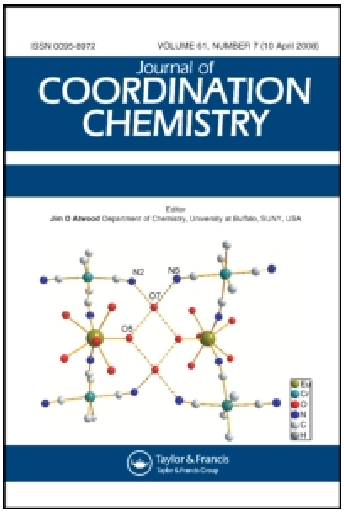

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Synthesis, spectroscopic and thermodynamic studies of new transition metal complexes with *N*,*N'*-bis(2-hydroxynaphthalin-1-carbaldehydene)-1,2-bis(*m*-aminophenoxy)ethane and their determination by spectrophotometric methods

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To cite this Article Temel, Hamdi , Ziyadanoğullari, Berrin , Aydin, Işil and Aydin, Firat(2005) 'Synthesis, spectroscopic and thermodynamic studies of new transition metal complexes with *N*,*N'*-bis(2-hydroxynaphthalin-1-carbaldehydene)-1,2-bis(*m*-aminophenoxy)ethane and their determination by spectrophotometric methods', Journal of Coordination Chemistry, 58: 14, 1177 — 1185

To link to this Article: DOI: 10.1080/00958970500078890

URL: http://dx.doi.org/10.1080/00958970500078890

Journal of Coordination Chemistry
Vol. 58, No. 14, 20 September 2005, 1177–1185

Taylor & Francis
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Synthesis, spectroscopic and thermodynamic studies of new transition metal complexes with *N*,*N*′-bis(2-hydroxynaphthalin-1-carbaldehydene)-1,2-bis(*m*-aminophenoxy)ethane and their determination by spectrophotometric methods

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(*Received 19 July 2004; revised 8 September 2004; in final form 9 February 2005*)

A novel tetradentate N_2O_2-type Schiff base, synthesized from 1,2-bis(*m*-aminophenoxy)ethane and 2-hydroxynaphthalin-1-carbaldehyde, forms stable complexes with transition metal ions such as Cu(II), VO(IV) and Zn(II) in DMF. Microanalytical data, elemental analysis, magnetic measurements, UV, visible and IR spectra as well as conductance measurements were used to confirm the structures. The stability constants of these complexes in 60% (v/v) DMF–water were determined at different ionic strengths (0.07, 0.13, 0.2 M) and at different temperatures (45, 50, 55, 60 ± 0.1°C) using a spectrophotometric method. From these constants, thermodynamic stability constants and thermodynamic parameters (ΔG^0, ΔH^0, ΔS^0) were calculated. The values of enthalpy change are negative for all systems. The acid dissociation constant of the ligand, investigated in 60% (v/v) DMF–water, has also been calculated at different temperatures.

Keywords: Schiff base; Cu(II), VO(IV) and Zn(II) complexes; Thermodynamic studies

1. Introduction

Transition metal complexes of tetradentate Schiff-base ligands find applications as models of certain metal enzymes and in catalysis and materials chemistry. Recently, the introduction of lateral polar hydroxyl groups was reported to enhance the molecular polarizability of liquid crystalline compounds as well as stabilizing them. A typical example is the effect of lateral hydroxyl groups on the mesomorphism of azobenzene derivatives. Schiff bases have found extensive applications in analytical

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ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970500078890

chemistry, used in the determination of some transition metals [1–12]. In the present article Cu(II), VO(IV) and Zn(II) complexes with a Schiff base derived from 1,2-bis(*m*-aminophenoxy)ethane and 2-hydroxynaphthalin-1-carbaldehyde are reported. These have been characterized by elemental analysis, magnetic measurements, UV, visible and IR spectra as well as conductance studies. As far as we know, this is the first report on this ligand. Thermodynamic studies of complexes of Schiff bases with some metal ions using potentiometric and spectrophotometric methods have been reported [13–17]. Thermodynamic stability constants and thermodynamic parameters of the complexes of this ligand with Cu(II) and Zn(II) were determined using a spectrophotometric method.

2. Experimental

All chemicals, including the metal salts $Cu(OAc)_2 \cdot H_2O$, $Zn(OAc)_2 \cdot H_2O$ and $VOSO_4 \cdot 2H_2O$ and the solvents, were from Merck and were used without purification. Conductivities of 10^{-3} M solution of the complexes were measured in DMF at 25°C using a hand-held conductivity meter LF 330. Electronic spectra of the complexes were recorded in DMF solutions using a Shimatzu Model 160 UV–visible spectrophotometer. IR spectra were recorded in KBr pellets with a Midac 1700 instrument. Magnetic moments were determined on a Sherwood Scientific MK1 magnetic moment balance at room temperature (23°C) using $Hg[Co(SCN)_2]$ as calibrant: diamagnetic corrections were calculated from Pascal's constants [18]. Elemental analyses were conducted on a Carlo Erba instrument. A Nell 890 model pH-ion meter with a combined glass–calomel electrode was used. A buffer solution of sodium acetate–acetic acid (pH 4) was prepared. Sodium nitrate solution (1 M) was prepared using acetate buffer and ligand solution of 0.001 M was prepared in DMF.

2.1. *Synthesis of ligand [N,N′-bis(2-hydroxynaphthalin-1-carbaldehydene)-1,2-bis(m-aminophenoxy)ethane]*

A solution of 2-hydroxynaphthalin-1-carbaldehyde (20.00 mmol, 2.72 g) in 50 mL absolute ethanol was added dropwise over 2 h to a stirred solution of 1,2-bis(*m*-aminophenoxy)ethane (10.00 mmol, 2.44 g) in 50 mL warm absolute ethanol. A solid separated out on cooling; the solution was kept in a refrigerator for better crystallization. It was then filtered, washed with ethanol, ether and subsequently dried over anhydrous $CaCl_2$ in a desiccator. This ligand is insoluble in all common organic solvents, including acetone, alcohol and benzene, and is soluble in polar organic solvents such as DMF and DMSO. The yellow imines were purified by recrystallization from DMF, m.p. 262°C; yield 4.68 g (85%).

2.2. *Spectral characterization of the ligand*

Characteristic IR bands ($KBr\,cm^{-1}$): 3045(arom, C–H), 2922 (aliph, C–H), 1618 (–C=N), 1250 (phen, C–O). Characteristic UV–vis spectra (λ_{max}): 268, 320, 385, 439, 460 nm.

2.3. *Synthesis of Cu(II) and Zn(II) complexes*

A solution of metal acetate in DMF (20 mmol) was mixed with the Schiff-base ligand in DMF (20 mmol, 0.96 g) in a 1 : 1 molar ratio. The contents were refluxed in 100 mL of DMF on an oil bath for 2–3 h. The refluxed solution was then poured into ice-cold water and a colored solid separated out. The product was isolated by filtration, washed with ether, recrystallized from dimethylsulfoxide and dimethylformamide and dried over anhydrous $CaCl_2$ in vacuum at room temperature. The yield was 55–60% for all complexes with respect to the ligand. They decompose at 287–291°C and are almost insoluble in common organic solvents such as ethanol, methanol, benzene, acetone, nitrobenzene, dichloromethane and chloroform. However, they are slightly to fairly soluble in polar organic solvents (DMSO and DMF).

2.4. *Synthesis of the VOL(IV) complex*

The salt $VOSO_4 \cdot 2H_2O$ (20 mmol) was dissolved in hot methanol (50 mL) and a mixture of NEt_3 (40 mmol) and the ligand (20 mmol, 0.96 g) in DMF (50 mL) was added with stirring over about 10 min. The mixture was kept hot (60–64°C) and stirred for about 2–3 h. The solid that separated out over 24 h was filtered, washed with diethylether, hot water and ethyl alcohol. The resulting solid was recrystallized in 50 mL DMSO/ 50 mL DMF and dried over anhydrous $CaCl_2$ in vacuum at room temperature. The yield was 55%. The complex decomposes at 275°C and is almost insoluble in water but partially soluble in polar organic solvents (DMSO and DMF).

2.5. *Spectral characterization of complexes*

Characteristic IR bands for the Cu(II) complex (KBr cm^{-1}): 3046 (arom, C–H), 2922 (aliph, C–H), 1610 (–C=N), 1245 (phen, C–O), 560 (M–N) and 420 (M–O). Characteristic IR bands for VO(IV) (KBr cm^{-1}): 3042 (arom, C–H), 2921 (aliph, C–H), 1622 (–C=N), 1250 (phen, C–O), 964 (V=O) 673 (M–N) and 448 (M–O). Characteristic IR bands for Zn(II) (KBr cm^{-1}): 3041 (arom, C–H), 2924 (aliph, C–H), 1628 (–C=N), 1253 (phen, C–O), 505 (M–N) and 430 (M–O). Characteristic UV–vis spectra for Cu(II) (λ_{max}): 261, 351 nm. Characteristic UV–vis spectra for Zn(II) (λ_{max}): 260, 310, 349 nm. Characteristic UV–vis spectra for VO(IV) (λ_{max}): 268, 302, 331 nm.

2.6. *Determination of* pK_a *values*

The spectrophotometric method of Stenström and Goldsmith [19] modified by Banks and Carlson [20] was used to determine dissociation constant, K_a, values. The method was devised for determining the dissociation constant of weak monobasic acids from spectrophotometric data. An experimentally demonstrated isobestic point would fulfill this requirement.

The experimental procedure to be followed involves determination of the absorption spectra of the unionized molecule, the ion and a mixture of ionic and nonionic forms having a pH near the pK_a values. The pH of the solution containing this mixture, together with absorbance measurements of the three solutions, is used to calculate K_a from data taken at several wavelengths.

The dissociation constant, K_a, is given by

$$K_a = \frac{A - A^\circ}{A' - A}[\mathrm{H}^+]$$

where A is the absorbance of a mixture of absorbing species, A° the absorbance of the unionized molecules, A' the absorbance of the ionized molecules and $[\mathrm{H}^+]$ the molar concentration of hydrogen ions in solution containing a mixture of two absorbing species [19, 20].

2.7. *Determination of stability constants of the complexes*

To a 10 mL standard flask were added 5.8–5.2 mL of DMF, 0.1–0.3 mL of 0.001 M stock metal solution, 2 mL of 1 M sodium nitrate solution and an appropriate volume of distilled water such that when the ligand solution was finally added, the total volume was 10.0 mL. Five mixtures of differing metal concentrations were prepared. The mixtures were warmed for 10 min at $25 \pm 0.1^\circ$C in a thermostated bath. Keeping the ligand/metal mole ratio about 2, the reaction was initiated by adding ligand solution that was kept in the same bath to each mixture [ionic strength $(I) = 0.20$]. The changes in absorbance at maximum wavelength were recorded against a similar solution containing no metal ion. At 0.20 ionic strength, experiments were performed for the determinations of the molar absorption coefficients and stability constants at 30, 35, $40 \pm 0.1^\circ$C by preparing the mixtures afresh. The experiments were also performed at ionic strengths of 0.13 and 0.07 at each of these temperatures.

3. Results and discussion

The new Schiff-base *N*,*N*′-bis(2-hydroxynaphthalin-1-carbaldehydene)-1,2-bis(*m*-aminophenoxy)ethane (H_2L) was synthesized by condensation of 1,2-bis(*m*-aminophenoxy)ethane [21] and 2-hydroxynaphthalin-1-carbaldehyde. The preparation of the Schiff base is described by the scheme shown in figure 1.

Microanalytical, molar conductance and magnetic susceptibility data for the ligand and its complexes are given in table 1. The stoichiometries of the ligand and its complexes were confirmed by their elemental analyses. The molar conductances measured in DMF of 10^{-3} M solutions of these complexes fall in the range 3.0–4.0 $\mathrm{ohm^{-1}\,cm^2\,mol^{-1}}$, indicating their nonelectrolytic behavior [1–6].

The reactions of the transition metal salts with the Schiff base are indicated by the following equations.

$$\mathrm{H_2L + Cu(OAc)_2 \cdot H_2O \rightarrow CuL + 2AcOH + H_2O}$$

$$\mathrm{H_2L + Zn(OAc)_2 \cdot 2H_2O \rightarrow ZnL + 2AcOH + 2H_2O}$$

$$\mathrm{H_2L + VOSO_4 \cdot 2H_2O \rightarrow [VO(IV)L] + H_2SO_4 + 2H_2O}$$

The metal/ligand mole ratio was found to be 1 : 1 using Job's method (figures 2 and 3). The observed magnetic moment of the Cu(II) complex is 1.62 BM, suggesting square-planar geometry. The VO(IV) complex has a magnetic moment of 1.74 BM, suggesting square-pyramidal geometry. The Zn(II) complex is diamagnetic as expected,

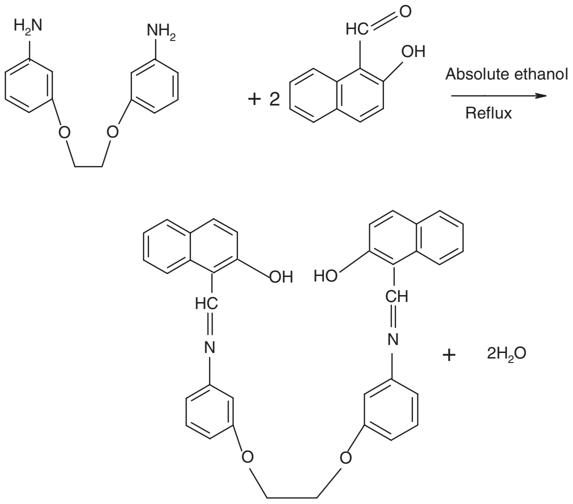

Figure 1. Scheme for the preparation of the ligand (H_2L): *N*,*N*′-bis(2-hydroxynaphthalin-1-carbaldehydene)-1,2-bis(*m*-aminophenoxy)ethane.

Table 1. The colors, formulas, formula weight, yields, melting points and elemental analyses of the ligand and the complexes.

Compound	FW ($g\,mol^{-1}$)	m.p. (°C)	yield (%)	Elemental analysis calculated (found), % C	H	N	μ_{eff} (BM)	Λ[a]
Ligand (H_2L) (yellow) $C_{36}H_{28}N_2O_4$	552.00	260.0	60.0	78.26 (78.49)	5.07 (5.31)	5.07 (5.25)	–	–
CuL (brown) $C_{36}H_{26}N_2O_4Cu$	613.5	290.0	55.0	70.42 (70.60)	4.24 (4.37)	4.56 (4.65)	1.62	4.0
[VO(IV)L] (dark yellow) $C_{36}H_{26}N_2O_5V$	616.9	275.0	55.0	70.02 (70.30)	4.21 (4.25)	4.54 (4.20)	1.74	2.4
ZnL (light yellow) $C_{36}H_{26}N_2O_4Zn$	615.4	288.0	52.0	70.20 (69.90)	4.22 (4.21)	4.55 (4.61)	Diamagnetic	3.0

[a] $Ohm^{-1}\,mol^{-1}\,cm^2$ (measured in 10^{-3} M solution in DMF).

consistent with any geometry. The complexes are fine powders and we could not prepare single crystals.

Values for the maximum absorption wavelength, λ_{max}, molar absorption coefficient, ε, at various ionic strengths (I/mol dm^3) and optimum pH for these complexes are given in table 2. No appreciable change in the pK_a value of the ligand was observed at different ionic strengths; however, the value was found to decrease with increasing temperature (table 3). M, L and ML represent, respectively, the metal, the ligand and the complex.

$$M + L \rightarrow ML$$

If the L/M ratio is very large, the equilibrium shifts completely to the right, and we can write

$$C_M = [ML]$$

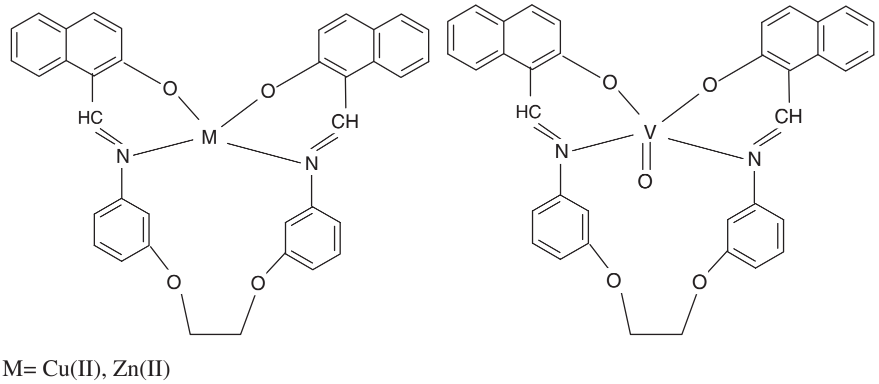

Figure 2. Suggested structure of the tetrahedral Zn(II), square-planar Cu(II) and square-pyramidal VO(IV)L complexes of the ligand H_2L.

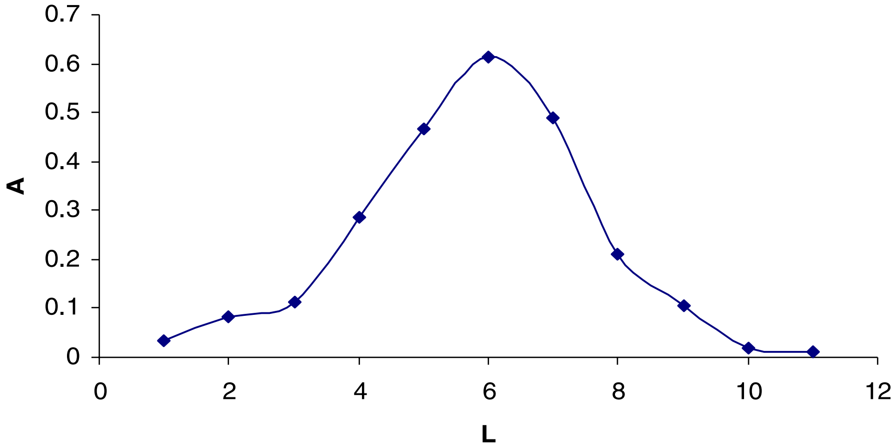

Figure 3. The metal and ligand ratio (1 : 1) with Job's method.

Table 2. Spectrophotometric characteristics of the complexes.

Complex	λ_{max} (nm)	ε ($dm^3\,mol^{-1}\,cm^{-1}$) $I = 0.20$	$I = 0.13$	$I = 0.07$	Optimum pH
CuL	261.5	$(3.53 \times 10^5) \pm 50$	$(2.66 \times 10^5) \pm 52$	$(1.25 \times 10^5) \pm 48$	4.0
ZnL	349	$(4.20 \times 10^5) \pm 72$	$(3.12 \times 10^5) \pm 54$	$(1.30 \times 10^5) \pm 30$	4.0

Table 3. pK_a values of the ligand at different temperatures.

	45°C	50°C	55°C	60°C
H_2L	11.51	11.44	11.25	11.08

Table 4. Stability constants ($\ln K$) at different temperatures and ionic strengths (I, mol dm^{-3}), and the thermodynamic parameters.

		$\ln K$						
System	Temp. (°C)	$I=0.20$	$I=0.13$	$I=0.07$	$\ln K^0$	$-\Delta G^0$ (kJ mol^{-1})	$+\Delta H^0$ (kJ mol^{-1})	$+\Delta S^0$ (J mol^{-1} K^{-1})
CuL	45	37.48 ± 0.02	37.44 ± 0.02	37.10 ± 0.04	36.96	98	−1.74	−0.98
	50	36.92 ± 0.03	36.91 ± 0.05	36.85 ± 0.02	36.82	99		
	55	36.23 ± 0.04	36.21 ± 0.04	36.15 ± 0.05	36.12	99		
	60	35.34 ± 0.04	35.19 ± 0.02	35.06 ± 0.06	34.91	97		
ZnL	45	37.42 ± 0.08	37.37 ± 0.06	37.34 ± 0.03	36.92	98	−1.81	−1.23
	50	36.85 ± 0.04	36.82 ± 0.03	36.76 ± 0.05	36.72	99		
	55	36.08 ± 0.07	36.00 ± 0.07	35.86 ± 0.05	35.76	98		
	60	35.15 ± 0.04	35.12 ± 0.05	34.94 ± 0.04	34.86	97		

where C_M is the analytical concentration of the metal. Using measured absorbances of the mixtures, the molar absorption coefficients are determined from Beer's law. Because the measured absorbances pertain only to the ML complex [22], the following equation can be written for the stability constant of the complex.

$$K = \frac{\mathrm{ML}}{[\mathrm{M}][\mathrm{L}]} = \frac{[\mathrm{ML}]}{[C_\mathrm{M} - \mathrm{ML}][C_\mathrm{L} - \mathrm{ML}]}\left[\frac{K_\mathrm{a} + [\mathrm{H}^+]}{K_\mathrm{a}}\right]$$

$$K = \frac{A/\varepsilon}{(C_\mathrm{M} - A/\varepsilon)(C_\mathrm{L} - A/\varepsilon)}\left[\frac{K_\mathrm{a} + [\mathrm{H}^+]}{K_\mathrm{a}}\right]$$

In this equation, if A/ε is substituted for [ML], the equation becomes where A is the measured absorbance and ε the molar absorption coefficient. K is calculated from this equation [23]. For each temperature, the average values of $\ln K$ were plotted against ionic strength for each metal–ligand system, and the curves were extrapolated to zero ionic strength to give the thermodynamic stability constant, $\ln K^0$. For each metal–ligand system, values of $\ln K^0$ were plotted against $1/T$. A straight line was obtained, showing that ΔH^0 and ΔS^0 are essentially independent of temperature over the temperature range considered. The slope of the line is $-\Delta H^0/R$, and the intercept at $1/T=0$ is $\Delta S^0/R$. The values of ΔH^0 and ΔS^0 may be calculated, respectively, from the slope and intercept of the plot. Using the equation $\Delta G^0 = -RT \ln K^0$, the values of ΔG^0 for each complex were calculated [24, 25]. It was found that the average values of the stability constants ($\ln K$) of the metal complexes are proportional to the ionic strength and inversely proportional to the temperature (table 4). In this study, the calculated thermodynamic stability constants, $\ln K^0$, ΔG^0 and ΔS^0, are in agreement with the structures (table 4). The complex formation constants were found to be similar to each other because these two ions have similar electron configuration and their ion radii are close to each other. The experimental results support this. The negative values for ΔH^0 indicated the exothermic nature and values for ΔG^0 indicated spontaneous formation of the complexes.

3.1. *IR spectra*

Tentative assignments of the important bands of the Schiff base under investigation and its complexes are recorded in table 5. The important features of the Schiff base and its

Table 5. Some IR frequencies (in cm^{-1}) of the Schiff base and its complexes.

Ligand (H_2L)	CuL	VO(IV)	ZnL	Assignment
–	3440	3430	–	H_2O
3443w	–	–	–	Phenolic –OH (O–H $\cdots$ O)
1618s	1603	1615	1623s	Central C=N stretching
1250	1245	1250	1248	Phenolic C–O stretching
–	520w	525w	514w	ν(M–N)
–	455w	460w	459w	ν(M–O)
–	–	964	–	V=O stretching

complexes may be summarized as follows. The ligand exhibits a weak absorption of ν(O–H) near 3450 cm^{-1} due to hydrogen bonds associated with (O–H $\cdots$ O–H). The disappearance of this band in all the complexes suggests the coordination of phenolic oxygen after deprotonation [26–29]. The band at 1253 cm^{-1} in the IR spectrum of the ligand is ascribed to the phenolic C–O stretching vibration according to the assignment made by Kovacic [30] for salicylideneanilines. This band is found in the region 1245–1250 cm^{-1} in the IR spectra of the complexes. These changes suggest that the *o*-OH group of this Schiff-base moiety has taken part in complex formation. The solid-state IR spectra of the complexes compared with those of the ligand indicate that the C=N band at 1618 cm^{-1} is shifted to lower values for Cu(II) and VO(IV) and higher for Zn(II) [1–6]. Conclusive evidence of bonding is also shown by the observation that new bands in the spectra of the metal complexes appear at 455–460 and 514–525 cm^{-1}; these are assigned to (M–O) and (M–N) stretching vibrations and are not observed in the spectra of the ligand [19–22]. In addition, the vanadyl complex displays a band at 964 cm^{-1} assignable to V=O modes [31].

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