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Preparation, Spectroscopic Characterisation and Thermal Analyses Studies of the Cu(II), Pd(II) and Vo(IV) Complexes of Some Schiff Base Ligands

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PREPARATION, SPECTROSCOPIC CHARACTERISATION AND THERMAL ANALYSES STUDIES OF THE Cu(II), Pd(II) AND VO(IV) COMPLEXES OF SOME SCHIFF BASE LIGANDS

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ABSTRACT

New Schiff base ligands, N-(3-methoxysalicylidene)-3,5-di(*tert*-butyl)-4-hydroxy aniline (HL³), N-(3-hydroxysalicylidene)-3,5-di(*tert*-butyl)-4-hydroxyaniline (HL³) and N-(4-hydroxysalicylidene)-3,5-di(*tert*-butyl)-4-hydroxyaniline (HL³) with their Cu(II), Pd(II) and VO(IV) complexes were synthesized and characterized by elemental analyses, IR, electronic absorption spectral data, magnetic moment and molar conductance. For the ligands and their Pd(II) complexes, ¹H and ¹³C NMR spectra were obtained. ¹H and ¹³C NMR spectra suggest that the ligands in the Pd(II) complexes coordinate through the nitrogen atom of the azomethine group and the oxygen atom of the phenolic (C-OH) group. All the compounds were found to be non-electrolytes in DMSO. However, the Pd(II) complexes exhibit low conductance in DMF due to solvolysis. Thermal studies show that the complexes decompose with the loss of water, followed by the organic ligand to give the corresponding metal oxides.

INTRODUCTION

Schiff bases and the corresponding metal ion complexes find interest in organic chemistry, biochemistry and inorganic chemistry. Enzymatic aldolization¹, enzymatic decarboxylation², and perhaps, even the visual process³, all appear to involve Schiff base formation and hydrolysis. Schiff base formation involves a two-step reaction between the carbonyl compound and the amino compound⁴. Metal ions contribute to the formation of Schiff bases by creating stable complexes. Furthermore, metals were found to catalyze these reactions by serving as a reaction template⁵ and acting as rudimentary enzymes.

In the present work, we describe the copper(II), palladium(II) and oxovanadium(IV) complexes with Schiff bases obtained from 3,5-di(*tert*-butyl)-4-hydroxyaniline and some derivatives of salicylaldehyde (Fig. 1). All compounds were characterized by means of elemental analyses, magnetic, electronic and IR spectral measurements. For the ligands and their Pd(II) complexes, ¹H and ¹³C NMR spectra were recorded. In order to confirm the results of the analytical and spectral studies and determine the order of the thermal stability of all compounds, thermogravimetric studies have been carried out.

EXPERIMENTAL

<u>Material</u>

The carbonyl compounds (3-methoxy, 3-hydroxy and 4-hydroxysalicylaldehyde) were obtained from Fluka and used without further purification. The metal salts were purchased from E. Merck and used as received, 3,5-di(*tert*-butyl)-4-hydroxyaniline was synthesized according to the known procedure⁶ and was used for ligand formation without further purification.

Preparation of Schiff Base Ligands

3,5-di(*tert*-butyl)-4-hydroxyaniline (1 mmol, 0.221 g), dissolved in ethanol (15 mL), was added with constant stirring to a solution of 3-methoxysalicylaldehyde (1 mmol, 0.152 g), 3-hydroxysalicylaldehyde (1 mmol, 0.138 g) or 4-hydroxysalicylaldehyde (1 mmol, 0.138 g) in ethanol (15 mL). The mixture was allowed to stir magnetically at



Fig. 1. General Structure of the Ligands

50 °C on a water bath for 30 min. After cooling, the resulting precipitate was collected on a filter and washed several times with methanol and recrystallized from acetone/hexane (1:1 by volume).

HL¹: ¹H NMR, in ppm (CDCl₃): δ 1.62 (s, 18H, *t*-butyl), δ 3.95 (s, 3H, OCH₃), δ 6.82-7.10 (m, 5H, Ar-H), δ 8.61 (s, 1H, CH=N). ¹³C NMR, in ppm (CDCl₃): δ 32.90 (*t*-butyl), δ 57.28 (OCH₃), δ 117.1-155.9 (aromatic), δ 163.32 (CH=N).

HL²: ¹H NMR, in ppm (CDCl₃): δ 1.45 (s, 18H, *t*-butyl), δ 6.68-7.25 (m, 5H, Ar-H), δ 8.59 (s, 1H, CH–N). ¹³C NMR, in ppm (CDCl₃): δ 32.09 (*t*-butyl), δ 119.0-154.95 (aromatic), δ 161.95 (CH=N).

HL³: ¹H NMR, in ppm (CDCl₃): δ 1.57 (s, 18H, *t*-butyl), δ 6.85-7.21 (m, 5H, Ar-H), δ 8.38 (s, 1H, CH–N). ¹³C NMR, in ppm (CDCl₃): δ 32.95 (*t*-butyl), δ 110.1-155.75 (aromatic), δ 164.75 (CH=N).

Preparation of the Cu(II) and VO(IV) Complexes

The Cu(II) and VO(IV) complexes were prepared by using similar methods. To a solution of the ligand (1 mmol) in hot methanol (20 mL) was added the appropriate metal salt (0.5 mmol, in 10 mL methanol). The reaction solution was heated to 70 °C for 1 h while stirring, then cooled. The precipitated complex was filtered and washed several times with cold methanol and dried in the vacuum desiccator over CaCl₂. The physical data of the complexes are listed in Table I.

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Compound	Empirical formula	Formula wt.	Colour	Yield	M. p.		Found (calc.) %		۸ _M
				(%)	(°C)	U	н	Z	
HL'	C ₂₂ H ₂₉ NO ₃	355	orange	84	131	74.21 (74.37)	7.83 (8.17)	3.51 (3.94)	1.0
[Cu(L ¹) ₂].H ₂ O	CuC ₄₄ H ₅₈ N ₂ O ₇	779.5	brown	68	243	66.79 (66.87)	7.46 (7.35)	3.47 (3.55)	4.2
[Pd(L ¹) ₂]	PdC ₄₄ H ₅₀ N ₂ O ₆	814.4	light yellow	66	162	65.07 (64.83)	6.95 (6.88)	3.32 (3.44)	4.3
[V0(L ¹) ₂] 2H ₂ O	VOC₄H₀N2Os	800.9	brown	73	268	65.20 (65.12)	7.21 (7.40)	3.61 (3.45)	5.8
HL ²	C ₂₁ H ₂₇ NO ₃	341	yellow	87	184	73.53 (73.90)	7.74 (7.90)	4.16 (4.10)	1.3
[Cu(L ²) ₂].3H ₂ O	CuC42H38N2O9	2.797	brown	74	235	62.98 (63.20)	7.40 (7.27)	3.64 (3.51)	7.5
[Pd(L ²),].2H ₂ O	PdC ₄₂ H ₃₆ N ₂ O ₅	822.4	light yellow	11	261	61.44 (61.28)	7.05 (6.81)	3.25 (3.41)	6.8
[V0(L ²) ₂].H ₂ O	VOC42H44N2O7	764.9	brown	80	>300	65.70 (65.89)	6.90 (7.06)	3.85 (3.66)	6.0
HL ³	C ₂₁ H ₂₇ NO ₃	341	yellow	86	163	73.97 (73.90)	7.74 (7.92)	3.88 (4.11)	1.2
[Cu(L ³) ₂] 2H ₂ O	CuC42H36N2O5	779.5	green	65	>300	64.81 (64.65)	7.02 (7.18)	3.50 (3.59)	5.4
[Pd(L ³) ₂].2H ₂ O	PdC ₄₂ H ₃₆ N ₂ O ₈	822.4	yellow	62	>300	61.33 (61.28)	6.65 (6.81)	3.15 (3.41)	6.3
[V0(L ³) ₂].2H ₂ 0	VOC42H56N2O8	782.9	brown	71	216	64.18 (64.37)	6.94 (7.15)	3.72 (3.58)	6.1
$a = \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$									

Preparation of the Pd(II) Complexes

The calculated amount of the ligand (HL^1 - HL^3 , 1 mmol) was added to Pd(II) acetate (0.5 mmol, 0.112 g) in a 1:2 (M:L) molar ratio in acetic acid (15 mL) as solvent. The solution was stirred for 3 h. The precipitated complex was filtered and washed with warm water (45 °C), several times with cold methanol and subsequently dried in a vacuum desiccator over CaCl₂.

[Pd(L¹)₂]: ¹H NMR, in ppm (CDCl₃): δ 1.65 (s, 36H, *t*-butyl), δ 3.96 (s, 6H, OCH₃), δ 6.83-7.12 (m, 10H, Ar-H), δ 8.64 (s, 2H, CH=N). ¹³C NMR, in ppm (CDCl₃): δ 32.91 (*t*-butyl), δ 57.29 (OCH₃), δ 118.3-156.2 (aromatic), δ 165.6 (CH=N).

[Pd(L²)₂].2H₂O: ¹H NMR, in ppm (CDCl₃):δ 1.47 (s, 36H, *t*-butyl), δ 3.12 (s, 4H, H₂O), δ 6.69-7.26 (m, 10H, Ar-H), δ 8.62 (s, 2H, CH=N). ¹³C NMR, in ppm (CDCl₃): δ 32.13 (*t*-butyl), δ 120.3-155.63 (aromatic), δ 164.20 (CH=N).

[Pd(L³)₂].2H₂O: ¹H NMR, in ppm (CDCl₃): δ 1.58 (s, 36H, *t*-butyl), δ 3.21 (s, 4H, H₂O), δ 6.88-7.27 (m, 10H, Ar-H), δ 8.43 (s, 2H, CH=N). ¹³C NMR, in ppm (CDCl₃): δ 32.97 (*t*-butyl), δ 111.3-156.42 (aromatic), δ 166.47 (CH=N).

Physical Measurements

Elemental analyses (C, H, N) were performed by using a Carlo Erba 1106 elemental analyser. The infrared spectra were obtained using KBr discs (4000-400 cm⁻¹) on a Shimadzu 435 A spectrophotometer. The electronic spectra in the 200-900 nm range were obtained in CHCl₃ on a Shimadzu UV-160 A spectrophotometer. Magnetic measurements were carried out by the Gouy method using Hg[Co(SCN)₄] as calibrant. Molar conductances of the Schiff base ligands and their transition metal complexes were determined in DMSO (~10⁻³ M) at room temperature using a Jenway Model 4070 conductivity meter. The thermal analyses studies were performed on a Rigaku Thermal Analyzer using 10 mg samples. The DTA and TG curves were obtained at a heating rate of 10 °C min⁻¹. In all casec the 25-800 °C temperature range was studied in air atmosphere. The ¹H and ¹³C NMR spectra of the Schiff bases and their Pd(II) complexes were were recorded with a Varian XL-200 NMR instrument.

RESULTS AND DISCUSSION

The condensation of aldehydes with 3,5-di(tert-butyl)-4-hydroxyaniline readily forms the corresponding imines. These products are easily identified by spectral methods. The analytical results in Table I for the ligands and their metal complexes agree with the stoichiometry of the compounds. The analytical, spectral and other data favour complexes of the general formula [M(L)2] nH2O (n is 1, 2 or 3) for Cu(II), Pd(II) and VO(IV), except the Pd(II) complex of the ligand HL¹. TGA data show that the water molecules are outside of the coordination sphere. The ligands HL¹-HL³ were synthesized in good yields, but the yields of their complexes were not as good. The low yields for the complexes may be due to steric hindrance around the coordination center. All the compounds are very stable at room temperature in the solid state. The ligands are soluble in polar and nonpolar organic solvents and their complexes are only soluble in CHCl₃, EtOH, THF, DMSO and DMF. Because the complexes are readily soluble in a wide range of polar organic solvents, it is suggested that they are not polymeric. Solution conductivity measurements were performed to establish the electrolyte type of the complexes. The molar conductivities at 10⁻³ M concentrations for the complexes in DMSO are in the range expected for their formulation as 1:2 electrolytes7. The molar conductivity values of the Pd(II) complexes in DMF (in the range 25-35 Ω^{-1} cm² mol⁻¹) suggest partial solvolysis by DMF and it is reasonable to assume that the Pd(II) complexes are non-electrolytes.

The formation of the complexes may be represented as given in eqs (1-3) (x = 1, 2 or 3).

$$Cu(AcO)_{2}H_{2}O + 2HL^{x} \xrightarrow{MeOH} [Cu(L^{x})_{2}].nH_{2}O + 2AcOH (1)$$

$$n = 1, 2 \text{ or } 3$$

$$VO(SO_{4}).5H_{2}O + 2HL^{x} \xrightarrow{MeOH} [VO(L^{x})_{2}].nH_{2}O + H_{2}SO_{4} (2)$$

$$n = 1 \text{ or } 2$$

$$Pd(AcO)_{2} + 2HL^{x} \xrightarrow{AcOH} [Pd(L^{x})_{2}].nH_{2}O + 2AcOH$$
(3)

n = 2In the Pd(II) complex of the ligand HL¹, n is zero HL^x = HL¹, HL² or HL³

Infrared Spectra

The most characteristic bands of all the compounds are given in Table II. The free ligands have similar spectral bands. The solid state IR spectra of all complexes, compared with those of the ligands, indicate that the v(CH=N) band at 1640-1615 cm⁻¹ is shifted to lower values indicating that the ligands are coordinated to the metal ions through the nitrogen atom of the azomethine group⁸. The bands in 1360-1265 cm⁻¹ region in the spectra of the ligands are attributed to v(C-OH) stretching bands. There are no shifts in the bands at 1360 and 1265 cm⁻¹ in the spectra of the complexes of the ligands HL² and HL³. Therefore, it can be proposed that these bands are due to the stretching of 3-OH and 4-OH groups. On the other hand, the bands between 1280-1265 cm⁻¹ in the ligands are observed to shift towards lower wave lengths in the complexes, suggesting the involvement of the oxygen atom of the C-O moiety in coordination. These bands are attributed to the 2-OH group. All of these are in good agreement with the literature9. The spectra of the VO(IV) complexes contain bands in the 980-940 cm⁻¹ range. These bands are assigned to the v(V-O) group vibration¹⁰. In the spectra of the complexes containing hydrated water molecules, the diffused character and broadness of the bands in the 3350-3150 cm⁻¹ region in the Cu(II), Pd(II) and VO(IV) complexes are obviously due to the hydrated water molecules¹¹. The bands between 510-420 cm⁻¹ are assigned to vibrations that are probably coupled M-N and M-O modes, in accordance with literature data¹².

Electronic Spectra

The electronic absorption spectral data for all of the compounds are given in Table III. The spectra were recorded using CHCl₃ as solvent. The spectra of the free ligands HL¹-HL³ contain bands in the 225-461 nm range. The aromatic bands in the 225-297 nm range are attributed to benzene π - π * transitions¹³. The bands in the 336-461 nm

Compound	v(OH)/(H ₂ O)	v(C=N)	v(V=0)	v(M-N)	v(M-O)
HL'	-	1615	-	-	-
$[Cu(L^1)_2] H_2O$	3150	1600	-	498	420
$[Pd(L')_2]$	-	1605	-	505	415
$[VO(L^1)_2]_2H_2O$	3320	1603	980	504	430
HL ²	-	1640	-	-	-
$[Cu(L^2)_2]_3H_2O$	3350	1615	-	505	430
$[Pd(L^2)_2]_2H_2O$	3275	1625	-	500	415
$[VO(L^2)_2].H_2O$	3305	1630	940	495	420
HL ³	-	1625	-	-	-
$[Cu(L^3)_2]_2H_2O$	3215	1605	-	495	435
[Pd(L ³) ₂].2H ₂ O	3310	1605	-	500	420
$[VO(L^3)_2].2H_2O$	3250	1610	970	510	440

 Table II. The Infrared Absorption Spectral Data of the Schiff Base Ligands and Their

 Complexes (cm⁻¹).

range are assigned to the imine π - π * transitions. Compared to the free ligands, the imine π - π * transitions of the complexes were shifted to some extent, probably because of the coordination of the imine nitrogen to the metal ion¹⁴. The copper complexes show less intense shoulders at 647, 637 and 630 nm which are assigned as d-d transitions of the metal ion. The electronic spectra of the VO(IV) complexes show four bands in the 813-610 nm range, and these may be due to the transition corresponding to a square-pyramidal structure. Also, the presence of some strong bands in the region 390-465 nm, which were not observed in the free ligands, may be attributed to O(phenolate) \rightarrow M(II) ligand to metal charge-transfer bands (LMCT)¹⁵.

Magnetic Moment

The magnetic moments of the Cu(II) complexes at room temperature have values between 1 81-1.90 B.M. and lie in the interval expected for the square-planar complexes

Compo	ounds.	
Compound	μ _{eff}	λ_{max} (ϵ , M ⁻¹ cm ⁻¹)
	(B.M.)	
HL		420 (1.5 x 10 ³), 373 (1.3 x 10 ³), 339 (1.7 x 10 ³),
		280 (1.6 x 10 ³), 240 (2.1 x 10 ³)
$[Cu(L^1)_2] H_2O$	1.90	630 (167), 460 (1.8 x 10 ³), 334 (1.4 x 10 ³), 265 (2.3 x 10 ³)
$[Pd(L^1)_2]$	diamag.	409 (1.9 x 10 ³), 381 (1.2 x 10 ³), 267 (2.5 x 10 ³),
		230 (2.8 x 10 ³)
$[VO(L^1)_2]_2H_2O$	1.81	754 (174), 610 (246), 460 (2.6 x 10^3), 340 (4.0 x 10^3),
		268 (4.3 x 10 [°])
HL ²		461 (1.2×10^3), 345 (1.1×10^3), 271 (1.5×10^3),
		257 (1.3 x 10 ³)
$[Cu(L^2)_2].3H_2O$	1.81	647 (162), 460 (5.1 x 10 ³), 336 (3.2 x 10 ³), 270 (2.8 x 10 ³)
$[Pd(L^2)_2] 2H_2O$	diamag.	414 (2.0×10^3), 401 (2.1×10^3), 341 (2.7×10^3),
		297 (5.0 x 10 ³), 254 (7.0 x 10 ³)
$[VO(L^2)_2]_H_2O$	1.78	730 (459), 465 (1.0×10^3), 348 (3.6×10^3), 256 (4.0×10^3)
HL ³		430 (2.7×10^3), 341 (1.7×10^3), 275 (1.3×10^3),
		225 (1.5 x 10 ³)
$[Cu(L^3)_2].2H_2O$	1.83	645 (162), 415 (2.0 x 10 ³), 348 (3.0 x 10 ³), 278 (2.5 x 10 ³),
		254 (2.5 x 10 ³)
$[Pd(L^3)_2]_2H_2O$	diamag.	392 (2.0 x 10^3), 297 (5.0 x 10^3), 259 (9.0 x 10^3)
$[VO(L^3)_2]_2H_2O$	1.77	813 (127), 498 (495), 420 (9.2 x 10 ³), 348 (3.6 x 10 ³),
		278 (3.7 x 10 ³), 255 (3.6 x 10 ³)

Table III. The Electronic Absorption Spectral Data and Magnetic Moments of the

of Cu(II)¹⁶. The magnetic moment values for the VO(IV) complexes are 1.77, 1.79 and 1.81 B.M., consistent with a square-pyramidal geometry¹⁷. However, the Pd(II) complexes are diamagnetic have square-planar geometry around the metal ion.

¹H and ¹³C NMR Spectra

The ¹H and ¹³C NMR spectra of the ligands and their Pd(II) complexes were recorded using CDCl₃ as solvent. In the case of the ligands and their metal complexes, it is particularly important to establish whether the molecules are in the keto form. The most useful techniques to investigate the tautomeric forms of these derivatives are UV and NMR spectroscopy, while IR spectroscopy seems of limited value here because the location of the v(C=O) and v(C-O) stretches in the spectra are obscured by the abundance of aromatic skeletal modes.

In the ¹H NMR spectra of the ligands, the signal for the proton of the -NH(R) group was not found. Therefore, we suggest that the Schiff base ligands do not undergo ketoenol tautomerism (see Fig. 2). The spectra of the ligands HL¹-HL³ contain singlets at 8.38, 8.59 and 8.61 ppm, and these can be attributed to the protons of the azomethine groups. In the Pd(II) complexes, these are shifted downfield (at 8.43, 8.62 and 8.64 ppm) and indicate that complexation occurs via the nitrogen atom of the azomethine group. The spectrum of the ligand HL¹ contains a singlet at 3.95 ppm and this may be due to the protons of the methoxy group. In the complex, this singlet shifts downfield to 3.96 ppm. In the spectra of the ligands, the singlets in the region 1.45-1.62 ppm and the multiplets in the 6.68-7.25 ppm region may be attributed to the protons of the tert-butyl groups and the aromatic rings, respectively. In the spectra of the Pd(II) complexes, compared to the free ligands, these signals are shifted downfield which confirm the complexation of palladium by the imine nitrogen and phenolic oxygen atom. The spectra of the $[Pd(L^2)_2]_2H_2O$ and $[Pd(L^3)_2]_2H_2O$ complexes show two singlets at 3.03 and 3.11 ppm, and these may be due to the protons of the hydrated water molecules¹⁸. These protons have been easily identified by their disappearance upon D₂O exchange.

The ¹³C NMR spectra of the ligands HL¹-HL³ contain three signals at 32.09, 32.95 and 32.9 ppm, which are due to the carbon atoms of the *tert*-butyl groups. In the spectra



R = 3,5-di(*tert*-butyl)-4-hydroxymethyl $R' = 3-OCH_3 (HL^1), 3-OH (HL^2) and 4-OH (HL^3)$

Fig. 2. Tautomeric Forms of the Ligands

of the Pd(II) complexes, these signals shift slightly downfield to the range 32.11-32.97 ppm. The spectrum of the ligand HL¹ shows one signal at 57.28 ppm and this can be attributed to the carbon atom of the methoxy group. This signal has been observed at 57.29 ppm in the Pd(II) complex. The signals of the aromatic ring carbon atoms of the free ligands are shown in the 110.1-155.9 ppm range, but, in the Pd(II) complexes, these signals shift downfield to the 111.3-156.42 ppm range. The spectra of the ligands show three signals at 161.95, 163.32 and 164.75 ppm and these are assigned to the carbon atoms of the azomethine groups. When the Pd(II) complexes are formed, these signals shift downfield to the 163.32-166.3 ppm range indicating that the nitrogen atom of the azomethine group is coordinated to the Pd(II) ion.

As seen from the above results, the ¹H and ¹³C NMR spectra of the ligands and their Pd(II) complexes provide further evidence for the proposed structures (Fig. 3) of the complexes.

Thermal Studies

The thermal analyses of the ligands and their complexes have been performed. The TG curves for the ligands HL^1 - HL^3 demonstrate that these compounds are thermally stable up to 132, 164 and 185 °C, respectively. Their pyrolytic decomposition starts in the 136-190 °C temperature range, and is completed in the 350-400 °C range with the total loss of the samples. The thermal stability of the ligands decreases as follows:



 $R' = 3-OCH_3$ (HL¹), 3-OH (HL²) and 4-OH (HL³) M = Cu(II), Pd(II) and VO(IV)

Fig	. 3.	Suggested	Structure o	ft	he	Comp	lexes.
		<u> </u>					

Table IV. Thermal Degradation of the Ligands and Their Complexes.

Compound	Dehydration		Decomposition of complexes		Final
	mass loss	T/°C	mass loss	T/⁰C	product
	Found (calc*.)%		Found (calc ^b .)%		
$[Cu(L^1)_2]H_2O$	2.2 (2.3)	55-60	92.0 (92.2)	334-578	CuO
[Pd(L ¹) ₂]			87 2 (87 1)	290-592	PdO
[VO(L ¹) ₂] 2H ₂ O	4.6 (4.4)	48-53	91.6 (91.4)	327-597	V ₂ O,
[Cu(L ²) ₂] 3H ₂ O	4.7 (4.5)	65-70	89.2 (89.3)	315-592	CuO
$[Pd(L^2)_2] 2H_2O$	4.5 (4.4)	60-65	86.5 (86.5)	300-581	PdO
[VO(L ²) ₂] H ₂ O	2.2 (2.4)	58-65	91 5 (91 4)	299-611	V ₂ O,
[Cu(L ³) ₂].2H ₂ O	4.5 (4.6)	50-55	91.4 (91.5)	309-610	CuO
[Pd(L ³) ₂] 2H ₂ O	4.3 (4.4)	33-37	86.7 (86.5)	277-583	PdO
[VO(L ³) ₂] 2H ₂ O	4.4 (4.6)	35-43	91.1 (91.0)	310-568	V_2O_3

a : Calculated for the loss of all water molecules,

b : Calculated for the weight loss based on the dehydrated complexes

 HL^{1} > HL^{3} > HL^{2} . The TG curves of the complexes containing hydrated water molecules show two principal processes, a dehydration reaction that is followed by complete decomposition to the respective metal oxide. The release of the hydrated water molecules in the complexes occured in the 33-70 °C temperature range¹⁹.

Comparing the final temperatures of dehydration of the various complexes, it is possible to suggest that the hydrated water molecules are most strongly bonded in the Cu(II) complex of the ligand HL³ (see Table IV). Under the experimental conditions used, there was no evidence for the formation of stable compounds with intermediate degrees of hydration. The decomposition of the dehydrated complexes occurs in several poorly resolved steps over a vide and variable temperature range (277-611 °C). Subsequent decomposition to the respective metal oxides occurs in several overlapping steps indicating a complicated reaction mechanism.

REFERENCES

- J. C. Speck, P. T. Rowley and B. L. Horecker, J. Am. Chem. Soc., <u>85</u>, 1012 (1963).
- 2. I. Fridovich and F. H. Westheimer, J. Am. Chem. Soc., <u>84</u>, 3208 (1962)
- 3. T. Baosov, N. Friedman and M. Sheves, Biochemistry, 20, 3210 (1987)
- 4. W. P. Jencks, Prog. Phys. Org. Chem., 2, 63 (1964).
- 5. T. L. Taylor, S. C. Vergez and D. H. Busch, J. Am. Chem. Soc., 88, 3170 (1966).
- 6. A. Rieker, K. Scheffler, R. Mayer and E. Müller, B. Narr. Ann., 10, 693 (1966).
- 7. W. J. Geary, Coord. Chem. Rev., 7, 81 (1971).
- 8. P. Indrasenan and K. R. Sarojini, Indian J. Chem., 30A, 382 (1991).
- 9. M. M. Ayad, M. I. Ayad and I. A. Mansour, Monatsh. Chem., 124, 995 (1993).
- 10. R. W. Scheidt, Inorg. Chem., 12, 1758 (1973).
- A. C. Fabretti, W. Malavasi, D. Gatteschi and R. Sessoli, J. Chem. Soc., Dalton Trans., <u>9</u>, 2331 (1991).

- 12. D. X. West and R. J. Hartley, J. Inorg. Nucl. Chem., <u>42</u>, 1141 (1980).
- 13. L. Casella, M. Gullotti and G. Pacchioni, J. Am. Chem. Soc., 104, 2386 (1982)
- 14. S. S. Sandhu and N. S. Aulakh, J. Indian Chem. Soc., 66(11), 743 (1989)
- T. G. Fawcett, E. E. Bernaducci, K. Krogh-Jesperson and H. J. Schugar, J. Am. Chem. Soc., <u>102</u>, 2598 (1980).
- 16. B. N. Figgis and J. Lewis, Prog. Inorg. Chem., <u>6</u>, 37 (1964).
- 17. E. L. Muetterties and L. J. Guggenberger, J. Am. Chem. Soc., 96, 1748 (1974)
- J. D. Hoeschele, N. Farrell, W. R. Turner and C. D. Rithner, Inorg. Chem., <u>27</u>, 4106 (1988).
- M. Bombin, M. A. Martinez-Zaporta, A. Ramirez, A. Guerrero and A. J. Mendez, Thermochim. Acta, 224, 151 (1993).

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