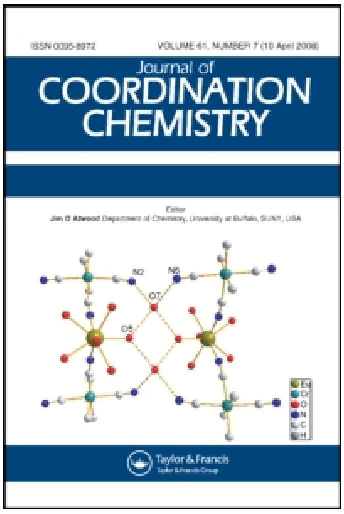

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Spectral, magnetic, thermal and electrochemical studies on phthaloyl bis(thiosemicarbazide) complexes

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Spectral, magnetic, thermal and electrochemical studies on phthaloyl bis(thiosemicarbazide) complexes

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The coordination behaviour of phthaloyl bis(thiosemicarbazide), H_4PBT, towards VO^{2+}, Co(II), Ni(II), Cu(II), Zn(II) and UO_2^{2+} ions has been investigated. The elemental analyses, magnetic moments, spectra [UV-Vis, IR, ESR and MS] and thermal studies were used to characterize the isolated complexes. Cyclic voltammetry was used to study the electrochemical behaviour of the Cu(II) complex. The IR spectra showed that the ligand is deprotonated in the complexes and acts as a binegative SSNN donor. The $f_{U\text{–}O}$ (mdyn $Å^{-1}$) and the length r_{U-O} (Å) of the UO bond are calculated spectroscopically from the IR data. The loss of thiol hydrogen during the formation of complexes was confirmed from the pH-metric titrations of the ligand and its metal(II) complexes. The protonation constants of the ligand ($pK_1 = 9.45$ and $pK_2 = 7.25$) as well as the stability constants of its complexes were calculated. The intensity and position of the V=O band in the IR spectra reflect the geometry of the formed complex. Also, its colour (dark green) is consistent with the suggested stereochemistry. The binuclear VO^{2+} complex was isolated and confirmed by ESR spectra. The TG analyses for the VO^{2+}, Co(II), Ni(II) and Zn(II) complexes suggest different decomposition steps. The Coats–Redfern and Horowitz–Metzger equations have been used to calculate the kinetic and thermodynamic parameters for the different thermal decomposition steps of some complexes. The redox properties, nature of the electroactive species and the stability of the Cu(II) complex toward oxidation were examined. The electrochemical data are discussed in terms of the kinetic parameters and the reaction mechanism.

Keywords: Bis(thiosemicarbazide); Complexes; Spectra; Thermal, redox behaviour

1. Introduction

Thiosemicarbazides are of interest in numerous coordination chemical studies since this class of compounds has remarkable properties [1]. The importance of these

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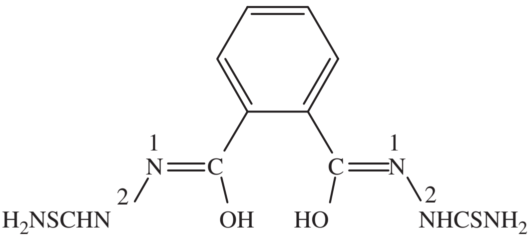


Figure 1. Enol/thione tautomeric form of H_4PBT.

compounds is mainly the result of their antimicrobial activities [2, 3]. The fungicidal activity of these compounds is due to their ability to form stable chelates with essential metal ions which fungi need for metabolism [4]. In the last decades, complexes of many thiosemicarbazides – especially those with bis(thiosemicarbazides) – have been prepared and characterized [5–7]. The work reported herein is focused on the synthesis, spectroscopic and electrochemical characterization of VO^{2+}, Co(II), Ni(II), Cu(II), Zn(II) and UO_2^{2+} complexes of phthaloyl bis(thiosemicarbazide) ligand (figure 1). The electrochemical behaviour of the Cu(II) complex was investigated by cyclic voltammetry for possible applications as a superoxide dismutase mimetic complex and as a copper sensor. In addition, the kinetics and thermodynamic characteristics of the decomposition steps of some of the complexes have been studied employing Coats–Redfern and Horowitz–Metzger equations.

2. Experimental

All chemicals used were of analytical reagent grade (BDH) and were used as supplied. Tetrabutylammonium tetraflouroborate ($TBA^+BF_4^-$) was used as a supporting electrolyte.

2.1. *Synthesis of ligand*

Phthaloyl bis(thiosemicarbazide) (figure 1) was prepared by reacting diethylphthalate (11.1 g, 0.5 mol) in 20 mL ethanol with an ethanolic solution of thiosemicarbazide (9.1 g, 0.1 mol). The reaction mixture was heated under reflux on a water bath for 2 h. The formed precipitate was separated by filtration, recrystallized from ethanol and dried. The proposed formula of the ligand ($C_{10}H_{12}N_6O_2S_2$, M.W. = 312.38) is in good agreement with the stoichiometry concluded from analytical data and mass spectra (e/m = 311 representing M^{+1}) and confirmed by IR spectral data. The ^{1}H NMR spectrum of the ligand in d_6-DMSO showed signals at δ 9.71(s, 1H), 9.39(s, 1H) and 8.05(s, 2H) ppm assigned to the OH, N(2)H and NH_2 protons, respectively. The presence of NH_2 and N(2)H signals at relatively higher values indicate strong hydrogen bonding.

2.2. *Synthesis of the metal(II) complexes*

The complexes were prepared by reacting a molar mixture of the ligand (3 mmole) and the nitrate salt of Co(II), Ni(II), Cu(II) and Zn(II), the acetate salt of UO_2^{2+} and the sulfate salt of VO^{2+} (6 mmole). In preparation of the VO^{2+} complex, 0.1 g of sodium acetate was added as a buffering agent to raise the pH. The reaction mixture was heated under reflux on a water bath for 4–6 h. The precipitate was filtered off, washed with hot water, hot ethanol and diethylether and finally dried in a vacuum desiccator over anhydrous $CaCl_2$.

2.3. *Chemical and physical measurements*

Carbon, hydrogen and nitrogen contents were determined at the Microanalytical Unit of Cairo University. Co(II), Ni(II), Cu(II), Zn(II) and VO^{2+} analyses were carried out complexometrically according to the standard method [8]. UO_2^{2+} was determined gravimetrically [9] as U_3O_8. The infrared, as KBr discs, electronic, as DMF solutions, ^{1}HNMR in d_6-DMSO (200 MHz) and mass spectra were recorded on a Mattson 5000 FTIR Spectrophotometer, UV_2 Unicam UV/Vis, Varian Gemini and Varian MAT 311 Spectrometers, respectively. The magnetic moment values were evaluated at room temperature (25 ± 1°C) using a Johnson Matthey magnetic susceptibility balance. The effective magnetic moments were evaluated by applying: $\mu_{\text{eff}} = 2.828\sqrt{\chi_M^- T}$ where χ_M^- is the molar susceptibility corrected using Pascal's constants for the diamagnetism of all atoms in the complexes and T is the absolute temperature. The ESR spectra of the Cu(II) and VO^{2+} complexes were obtained on a Bruker EMX Spectrometer working in the X-band (9.78 GHz) with 100 kHz modulation frequency. The microwave power and the modulation amplitude were set at 1 mW and 4 Gauss, respectively. The low field signal was obtained after 4 scans with a ten-fold increase in the receiver gain. Powder ESR spectra for the Cu(II) and VO^{2+} complexes were obtained in 2 mm quartz capillaries at room temperature. The thermal studies were carried out on a Shimadzu thermogravimetric analyzer at a heating rate of $10^{\circ}C\,min^{-1}$ under nitrogen gas. The cyclic voltammetric measurements were carried out with a Potentiostat Wave Generator (Oxford press) equipped with a Phillips PM 8043 X–Y recorder. The electrochemical cell assembly consists of platinum wires of 0.5 mm diameter as working and counter electrodes and Ag/AgCl as a reference electrode. The protonation constants of the ligand and the formation constants of its complexes at 298 K were determined pH-metrically by the Irving–Rossotti method [9].

3. Results and discussion

The formulae of the complexes, together with the physical properties, elemental analyses and formula weights, obtained for some complexes from mass spectra are listed in table 1. The isolated solid complexes are stable at room temperature (25°C), non-hygroscopic and almost insoluble in water and in most organic solvents but are easily soluble in DMF and DMSO. Most of the complexes decomposed on heating at >300°C.

3.1. *IR spectral studies*

The most important infrared bands of the ligand and its metal(II) complexes with their probable assignments are given in table 2. Keto/thione, enol/thione, keto/thiol and

Table 1. Physical properties, analytical data and formula weights (F. W) of the complexes.

				Found (Calcd %)				F. W	
No.	Complex	Colour	M.P., °C	C	H	N	M	Found[a]	Calcd
1	$[(VO)_2(PBT)(C_2H_5OH)(H_2O)_2]$	Dark green	221	27.3(27.6)	4.0(3.5)	16.3(16.1)	19.3(19.9)	523.0	522.46
2	$[Co(H_2PBT)] \cdot 2H_2O$	Dark red	> 300	29.7(29.6)	3.7(3.5)	20.9(20.7)	14.7(14.5)	369.0	405.34
3	$[Ni(H_2PBT)]$	Brown	> 300	32.3(32.5)	2.9(2.7)	22.4(22.8)	15.8(16.0)	372.0	369.31
4	$[Cu(H_2PBT)(H_2O)]$	Green	> 300	30.6(30.6)	2.9(3.1)	21.1(21.4)	18.6(18.2)	–	391.93
5	$[Zn(H_2PBT)] \cdot C_2H_5OH$	White	198	34.5(34.2)	3.8(3.8)	19.1(19.9)	15.6(15.5)	–	421.82
6	$[UO_2(H_2PBT)(H_2O)]$	Orange	> 300	19.5(19.8)	2.4(2.2)	13.7(13.8)	40.1(39.1)	605.0	607.39

[a] Values obtained from mass spectra.

Table 2. Significant IR spectral data (cm^{-1}) of the complexes.

Compound	$\tilde{\nu}(NH_2)$	$\tilde{\nu}(OH)$	$\tilde{\nu}(N^2H)$	$\tilde{\nu}(C{=}N)$	$\tilde{\nu}(C{=}S)$	$\tilde{\nu}(C{-}S)$	$\delta(OH)$	$\tilde{\nu}(M{-}N)$	$\tilde{\nu}(M{-}S)$
H_4PBT	3260w 3235sh	3355s	3185w	1613vs	790m		1360sh		
1	3268m 3210m	3350m	–	1574br	–	603s	1330m	490w	360w
2	3265w 3221vw	3337vw	–	1596s	–	615br	1351w	465w	345w
3	3322br	3442m	–	1594s	–	694s	1382m	490w	360w
4	3261br	3324sh	–	1606s	–	670s	1384s	480m	370w
5	3262br	3343br	–	1602vs	–	694s	1340sh	485m	370w
6	3278vw	3351w	–	1575s	–	650w	1324s	470m	390w

s = strong, m = medium, w = weak, v = very, br = broad and sh = shoulder.

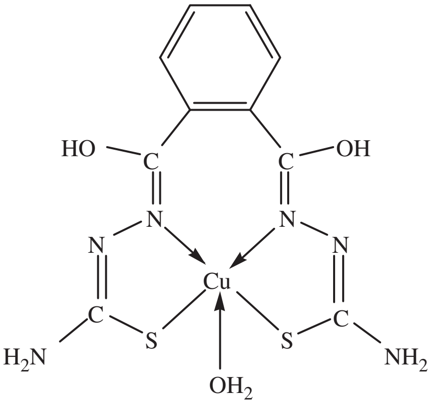


Figure 2. Structure of $[Cu(H_2PBT)(H_2O)]$.

enol/thiol are the four possible tautomeric forms for the ligand; in fact, the enol/thione form is predominant for the ligand in the solid state. Its IR spectrum exhibits bands at 3355, 3260, 3235, 3185, 3043 and 1023 cm^{-1} attributed to $\nu(OH)$, $\nu s(NH_2)$, $\nu as(NH_2)$, $\nu[N(2)H]$, $\nu(CH)_{aromatic}$, and $\nu(N{-}N)$, respectively. The azomethine band overlaps with both $\nu(C{=}C)$ and $\delta(NH_2)$ as a strong band at 1613 cm^{-1}. No band for the carbonyl group is detected. The appearance of the hydroxyl as well as the N(2)H bands at lower values suggests strong intramolecular hydrogen bonding. The thioamide [N(2)HCS] group has four bands (I–IV) observed at 1527, 1248, 940 and 785 cm^{-1}. These bands have contributions from $[\delta(C{-}H) + \delta(N{-}H)]$, $[\nu(C{=}S) + \nu(C{-}N) + \delta(C{-}H)]$, $[\nu(C{-}N) + \nu(C{=}S)]$ and $[\nu(C{=}S)]$, respectively [10]. The broadness of these bands, together with the absence of $\nu(SH)$, confirm the structure in figure 1.

The existence of numerous coordination sites in the ligand gives variable bonding modes, however comparison of the IR spectra of the ligand and its complexes revealed that the ligand is bonded to the M(II) ions in one coordination mode. The ligand is a quadridentate dibasic (NSSN) donor in $[Cu(H_2PBT)(H_2O)]$, $[Co(H_2PBT)] \cdot 2H_2O$, $[Ni(H_2PBT)]$, $[Zn(H_2PBT)]C_2H_5OH$ and $[UO_2(H_2PBT)(H_2O)]$, or tetrabasic in $[(VO)_2(PBT)\text{-}(C_2H_5OH)(H_2O)_2]$, forming two five- and one six-membered rings as shown in figure 2. The spectra proved that the C=N and C–S groups are the coordination centres. Strong evidence is: (i) the disappearance of $\nu(N^2H)$; (ii) the negative shift (10–65 cm^{-1}) of $\nu(C{=}N)$ [11]; (iii) the positive shift of $\nu(N–N)$; (iv) coordination of the azomethine nitrogen is also consistent with the presence of a new band at 410–445 cm^{-1} assignable to the $\nu(M–N)$ vibration [12]; and finally (v) coordination *via* thiolate sulfur is indicated by the absence of $\nu(C{=}S)$ vibration with the simultaneous appearance of new bands in the 610–690 and 325–370 cm^{-1} regions due to the $\nu(C–S)$ and $\nu(M–S)$ vibrations [13, 14], respectively. The existence of stretching and bending OH bands, which are more or less invariant, indicates that this group is not taking part in coordination.

The ^1H NMR spectra of the Zn(II) and $UO_2{}^{2+}$ complexes recorded in d_6-DMSO show the absence of the N(2)H signal due to its participation in enethiolization with the existence of the OH signal unaffected. The N(2)H, OH and NH_2 signals disappeared on adding deuterated water (D_2O). The ethanol molecule in the spectrum of the Zn(II) complex shows signals at 2.32 and 3.27 ppm which are absent in the spectrum of the uncomplexed molecule [15]. The spectrum of the UO_2^{2+} complex shows an additional band at 4.45 ppm which may be due to protons of coordinated water.

The complexes do not exhibit bands for nitrate (1350–1400 cm^{-1}), the sulfate (1117–1143 cm^{-1}, in VO^{2+} complex) or acetate (1345–1525 cm^{-1}, in UO_2^{2+} complex) indicating the absence of these anions.

The IR spectrum of $[UO_2(H_2PBT)(H_2O)]$ shows three bands at 855, 790 and 291 cm^{-1} attributed to ν_3, ν_1 and ν_4 vibrations of the dioxouranium ion, respectively. These bands suggest a linear UO_2 moiety. An increase in the electron density of uranium would lead to an increase in the repulsive force among the non-bonding electrons of UO_2 and thus weakens the U–O bond. The force constant (f) for $O{=}U{=}O$ was calculated by applying the equation of McGlynn [16] using the ν_3 band observed in the IR spectrum of the complex and is found to be 6.03 mdyn Å^{-1}. The U–O distance was also calculated with the help of Jones' equation [17, 18] and is found 1.69Å.

The coordinating water in the VO^{2+}, Cu(II) and UO_2^{2+} complexes is characterized by the appearance of $\nu(OH)$, ${}^{\rho}r(H_2O)$ and ${}^{\rho}w(H_2O)$ vibrations at 3426–3460, 850–870 and ~665 cm^{-1}, respectively [19]. Also, the 500–525 cm^{-1} band, assigned to $\nu(M \leftarrow OH_2)$, is strong evidence for the participation of water in coordination.

3.2. *pH-metric studies*

The pH-metric titrations of the ligand and its M(II) complexes against 0.01 M^{-1} NaOH, in the absence of HCl in a ethanol–water system (50% v/v) at $\mu = 0.1\,M^{-1}$ adjusted by KCl were carried out. The values of the average number of protons (n_A^-), the average number of ligand molecules attached per metal ion (n^-) and the free ligand exponent (pL) were calculated at different pH values. Plotting of n_A^- versus pH gives the proton–ligand formation constants ($\log K_1$ and $\log K_2$). The data calculated from the half and least square methods [15] are summarized in table 3. The $\log K$ values of the ligand reveal that the ligand has two ionization constants due to the liberation of the two symmetrical hydrogen atoms of OH and N(2)H on both thiosemicarbazide sides. The OH proton is more easily removed than the N(2)H proton.

The metal–ligand stability constants were determined by applying the curve fitting method to the data of n^- versus pL and the results are summarized in table 3.

Table 3. The protonation constants of H_4PBT and the formation constants of its complexes.

	Half-method			Least-square method		
Compound	pK_1	pK_2		pK_1	pK_2	
H^+	9.45	7.25		9.45	7.20	
	β_1	β_2	β^*	β_1	β_2	β^*
1	8.20	4.13	12.33	8.20	4.18	12.38
2	4.70	3.90	8.60	4.75	3.90	8.65
3	7.16	4.00	11.16	7.15	4.33	11.48
5	7.40	5.80	13.20	7.86	5.95	13.81

β^* is the overall stability constant.

Table 4. Magnetic moment, electronic spectra (cm^{-1}) in DMSO and ESR data of the complexes.

Complex	μ_{eff}, B.M	d–d transition, cm^{-1}	$g_{\parallel}$	$G_{\perp}$	G
1	2.20	11935	1.970	2.037	–
2	1.90	18860	–	–	–
3	1.72	15385, 21050, 24390	–	–	–
4	2.32	10740,18590	2.100	2.030	3.50

The data revealed that the values of $\log K_1$ are higher than those of $\log K_2$ for the same complex because all the available sites for binding the first ligand are free which is not the case for binding the second one. According to the values of β^* ($\log K_1 + \log K_2$), the stability of the complexes varied with the metal ions in the following sequence:

$$\mathrm{Zn(II)} > \mathrm{VO^{2+}} > \mathrm{Ni(II)} > \mathrm{Co(II)}$$

3.3. *Electronic spectra and magnetic studies*

The magnetic moments and the significant electronic absorption bands of the VO^{2+}, Co(II), Ni(II) and Cu(II) complexes, recorded in DMF solution, are given in table 4. The thiosemicarbazide has a ring $\pi \rightarrow \pi^*$ band at 32,785–40,815 cm^{-1} and $n \rightarrow \pi^*$ band at 28,570–30,960 cm^{-1} [20]; little change in their energies are recorded for the complexes. Another $n \rightarrow \pi^*$ band in the spectrum of the free thiosemicarbazide is also found in the spectra of its M(II) complexes at 27,000–28,250 cm^{-1}. The band at 22,220–26,040 cm^{-1} in the spectra of the complexes may be due to LMCT [21]. Previous studies proved that a band in the region 25,000–26,040 cm^{-1} should be assigned to a O → Cu(II) transition [22] whereas a band in the range 21,785–24,750 cm^{-1} is due to S → Cu(II) transition [23]. The CT band of the complexes is therefore due to S → M(II) charge transfer.

The electronic spectrum of $[(VO)_2(PBT)(C_2H_5OH)(H_2O)_2]$ recorded in DMSO shows the well characteristic band for the square–pyramidal [24] configuration at 11,935 cm^{-1}. The band is assigned to the $^2B_2 \rightarrow {}^2E$ (ν_1) and $^2B_2 \rightarrow {}^2B_1$ (ν_2) transitions. It was proposed earlier that the band at 970 cm^{-1} in the IR spectra of the VO^{2+} complexes is characteristic for the aforementioned structure [25]; the present complex shows this band at 985 cm^{-1}. The colour (dark green) is good evidence for the proposed structure.

$[Co(H_2PBT)] \cdot 2H_2O$ measured (1.99 B.M) magnetic moment value is close to the values reported for the presence of one unpaired electron in a square–planar geometry. Its electronic spectrum shows a broad band centered at 18860 cm^{-1} which is characteristic for the proposed geometry [26].

The magnetic moment value (1.19 B.M) measured for $[Ni(H_2PBT)]$ is subnormal compared with the values reported for Ni(II) complexes in its different stereochemistries. The anomalous value may suggest the existence of a mixed stereochemistry; a similar proposal was reported for many Ni(II) complexes [27]. Qualitatively, from the decrease in the moment, one can calculate that the octahedral isomer is present at a level of 37% (1.19/3.2 B.M) and the planar isomer as 63%. The electronic spectrum of this complex recorded in DMSO shows bands at 15,385 and 24,390 cm^{-1} characteristic for the octahedral geometry and attributed to the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2) and $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3) transitions, respectively. The ligand field parameters were calculated ($10\,Dq = 9960$ cm^{-1}, $B = 664$ cm^{-1} and $\beta = 0.684$). The values are lower than reported for regular octahedral proving the suggested mixed structure. An additional band is also observed at 21,050 cm^{-1} attributed to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition in the square–planar stereochemistry.

A square–pyramidal structure (figure 2) is proposed for $[Cu(H_2PBT)(H_2O)]$ based on the presence of two bands at 10,740 and 18,590 cm^{-1}. These may be assigned to the $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively [28]. Due to the low intensity of the $^2B_{1g} \rightarrow {}^2B_{2g}$ transition, it is not observed as a separate band in the tetragonal field.

3.4. *Mass spectra*

The recorded mass spectra and the molecular ion peaks for most of the complexes have been used to confirm the molecular formulae. Calculated and found molecular weights are given in table 1. The mass spectrum (figure 3) of $[Co(H_2PBT)] \cdot 2H_2O$ shows multi peaks corresponding to the successive degradation of the molecule. The first peak at m/e 369 represents the molecular ion peak of the complex $(M–2H_2O)$ with 33.33% abundance. The sharp peak (base peak) with m/e 135 represents the stable species $(CoNS_2)$ while that observed at 59 represents the final residue (Co). Scheme 1 demonstrates the proposed degradation steps for the investigated complex.

3.5. *ESR spectra*

A powder ESR spectrum of the Cu(II) complex, $[Cu(H_2PBT)(H_2O)]$ (figure 4a) at room temperature was recorded at 9.7 GHz with field set at 3250 G. The spectrum reveals a broad line with poorly resolved hyperfine structure. No band corresponding to $\Delta ms = \pm 2$ forbidden transition was observed in the spectrum, ruling out any Cu–Cu interaction and revealing that the complex is mononuclear. The unresolved hyperfine splitting can be attributed to dipolar effects caused by mutual interactions between paramagnetic Cu(II) ions. The g tensor values of the Cu(II) complex can be used to derive the ground state. In tetragonal and square–planar complexes, the unpaired electron lies in the $d_{x^2-y^2}$ orbital giving $^2B_{1g}$ as the ground state. From the observed

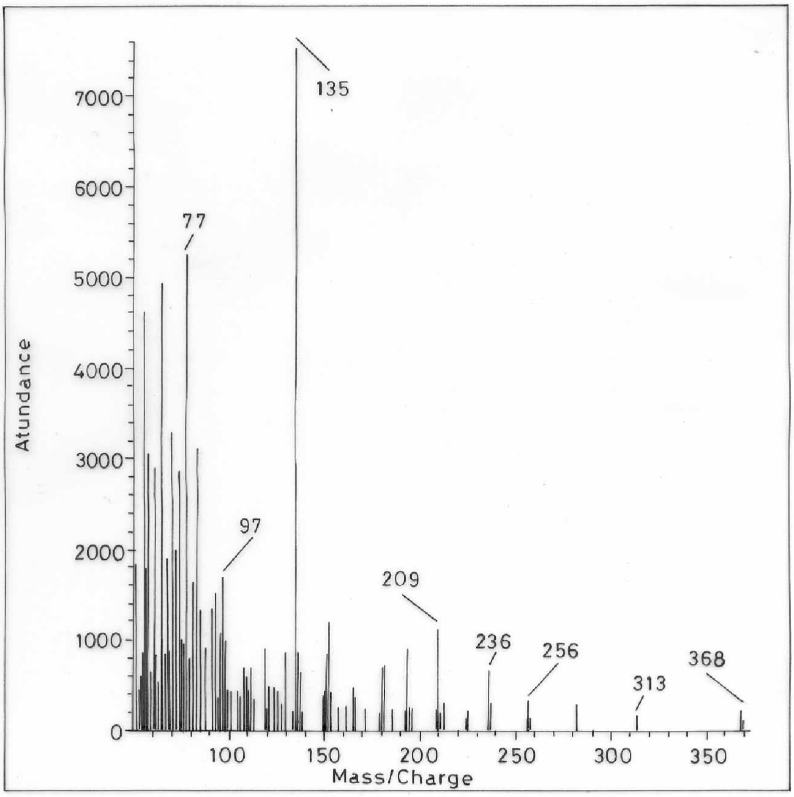
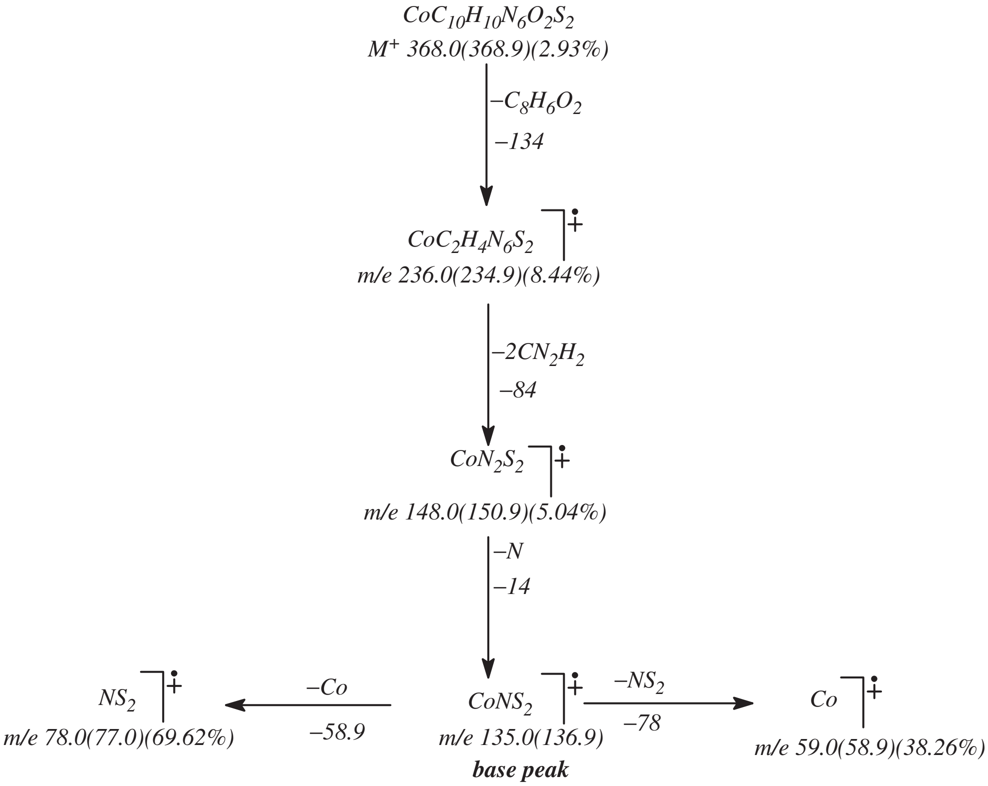


Figure 3. Mass spectrum of $[Co(H_2PBT)] \cdot 2H_2O$.

values, it is clear that $g_{\parallel} > g_{\perp}$ (2.1 > 2.03) indicating that the complex is axially symmetric and its unpaired electron is in $d_{x^2-y^2}$ orbital characteristic of square–planar or square–pyramidal geometry. The $g_{\parallel}$ value is an important function for indicating covalent character of M–L bonds [29]; for ionic character, $g_{\parallel} > 2.3$ and for covalent character $g_{\parallel} < 2.3$. In the present complex, the $g_{\parallel}$ is more than 2.3 indicating appreciable covalent character for the Cu–L bond. In addition, exchange coupling interaction between the two copper centres is explained by the Hathaway expression (if G is greater than 4, the exchange interaction in the solid state is negligible, whereas when it is less than 4, a considerable exchange interaction is noticed in the solid complex). The calculated G value of the complex $[Cu(H_2PBT)(H_2O)]$ suggests some interactions between the Cu(II) centers.

The X-band ESR spectrum (figure 4b) of a powdered sample of $[(VO)_2(PBT)(C_2H_5OH)(H_2O)_2]$ gave a single broad line centred around $g = 1.97$, without resolved hyperfine structure. In particular, the hyperfine coupling with the nearby ^{51}V ($I = 7/2$) nucleus is not observed. The absence of vanadium hyperfine coupling is common in solid state samples [30] and is attributed to the simultaneous flipping of neighbouring electron spins [31] or due to strong exchange interactions, which average out the interaction with the nuclei. The shape of the ESR spectrum corresponds to the powder spectrum of a paramagnetic species with an axially symmetric g-tensor.



Scheme 1. Proposal degradation of $[Co(H_2PBT)] \cdot 2H_2O$ by mass spectra.

A fit of the line shape gives axial g-tensor parameters of $g_{\parallel} = 1.97$ and $g_{\perp} = 2.037$. These values agree with the g-tensor parameters reported for vanadium complexes with square–pyramidal geometry [32].

3.6. *Thermal studies*

Non-isothermal calculations were used extensively to evaluate the thermodynamic and kinetic parameters for the different thermal decomposition steps in the complexes employing the Coats–Redfern [33] and Horowitz–Metzger equations [34]. The results of activation enthalpy ($\Delta H^{\#} = E - RT$); the activation entropy ($\Delta S^{\#} = 2.303 [\log(Zh/KT)]R$) and the free energy of activation ($\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$) are given in table 5, where Z, K and h are the pre-exponential factor, Boltzman and Plank constants, respectively [35]. The kinetic parameters calculated by the Horowitz–Metzger method revealed no significant difference with that evaluated by the Coats–Redfern method. The activation energy values, the high value of E for the complex $[Co(H_2PBT)] \cdot 2H_2O$, indicates that the removed part is strongly bonded to the Co(II) ion. The E value observed for the fourth decomposition stage of $[Co(H_2PBT)] \cdot 2H_2O$ was found higher than that of the third in [Ni(PBT)] and the second in $[(VO)_2(PBT)(C_2H_5OH)(2H_2O)]$ indicating a low rate of decomposition.

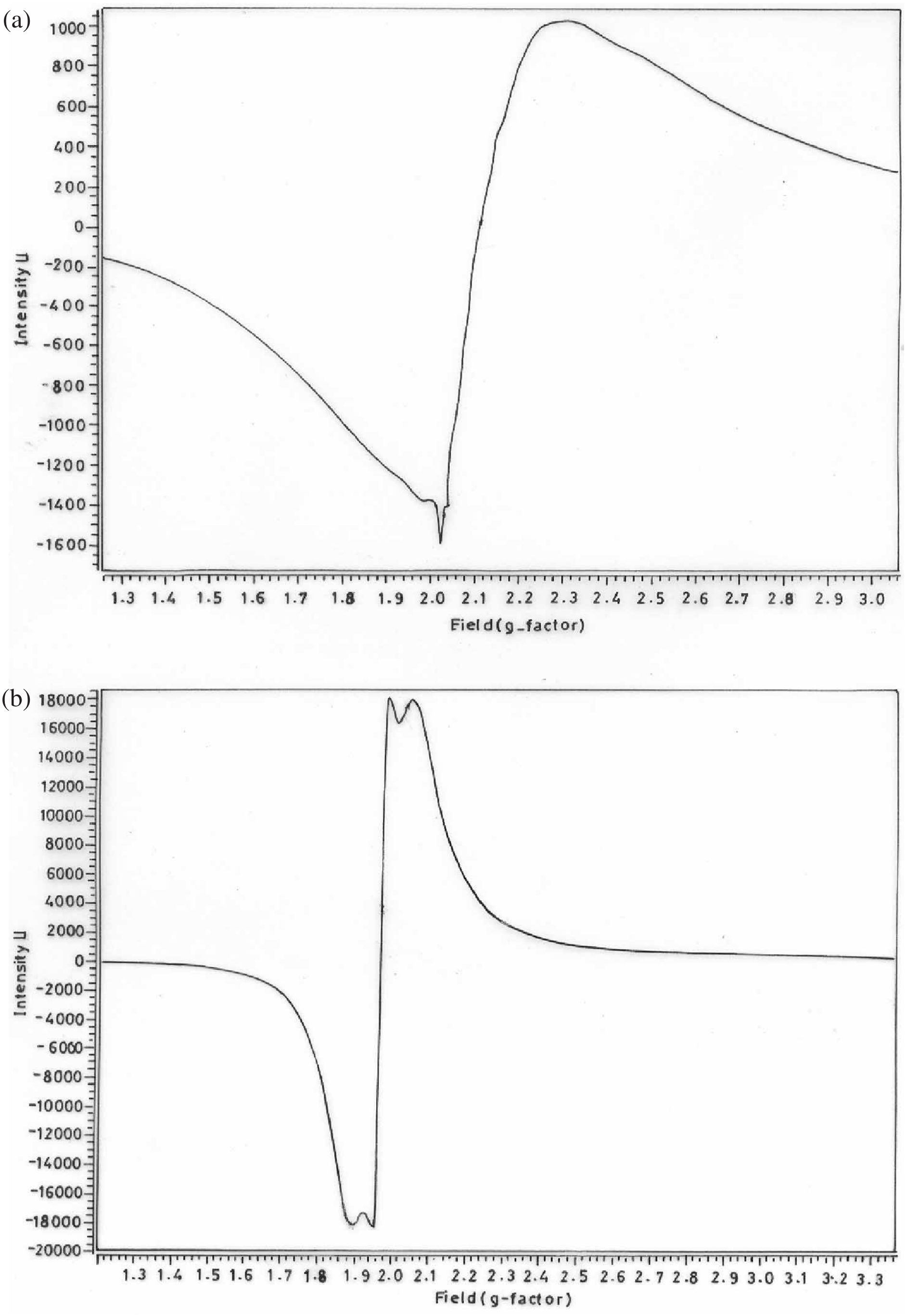


Figure 4. ESR spectra of: (a) [Cu(H_2PBT)(H_2O)]; (B) [$(VO)_2$(PBT)(H_2O)(C_2H_5OH)].

Table 5. Kinetic and thermodynamic parameters for some decomposition steps of some of the complexes.

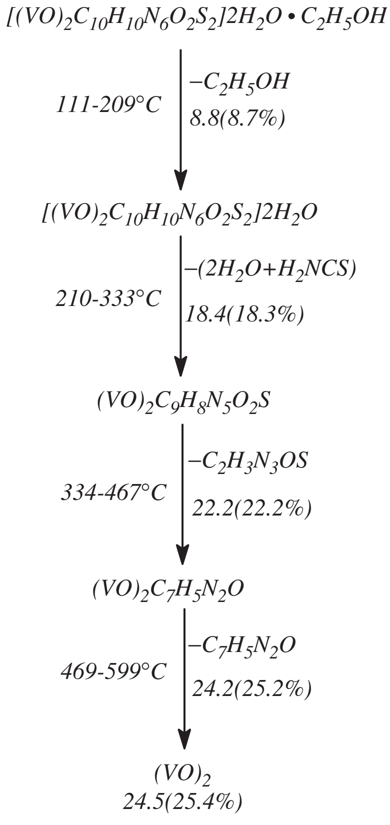
		Coats–Redfern eqn.			Horowitz–Metzger eqn.					
Compound	Step	R	N	E	r	n	E	$\Delta S^{\#}$	$\Delta H^{\#}$	$\Delta G^{\#}$
[Ni(H_2PBT)]	3nd	0.9983	0.00	158.4	0.9998	0.00	156.7	−145.7	151.9	266.7
		0.9994	0.33	173.0	1.0000	0.33	170.1	−125.8	166.5	265.6
		0.9999	0.66	188.9	0.9997	0.66	184.5	−104	182.4	264.3
		0.9998	1.00	206.5	0.9990	1.00	200.9	−95.6	200.0	275.0
		0.9973	2.00	266.1	0.9981	2.00	260.7	2.2	259.6	257.8
[Co(H_2PBT)] · 2H_2O	4th	0.9998	0.00	252.2	0.9997	0.00	266.6	−17.4	245.6	259.5
		0.9999	0.33	291.4	1.0000	0.33	306.2	22	284.8	267.2
		0.9989	0.66	335.3	0.9993	0.66	351.0	80.6	328.7	264.4
		0.9971	1.00	387.6	0.9977	1.00	403.1	139.3	381.0	269.8
		0.9885	2.00	573.5	0.9899	2.00	589.7	391.4	566.9	254.5
[$(VO)_2$(PBT)(C_2H_5OH)$(H_2O)_2$]	2nd	0.9864	0.00	59.1	0.9860	0.00	70.6	−236.8	54.7	181.6
		0.9902	0.33	64.7	0.9889	0.33	76.0	−224.6	60.3	180.7
		0.9929	0.66	70.5	0.9916	0.66	82.5	−212.4	66.1	179.9
		0.9954	1.00	76.9	0.9939	1.00	89.1	−205.9	72.5	182.8
		0.9993	2.00	98.6	0.9983	2.00	111.9	−152.2	94.2	175.8

r = Correlation coefficient, n = order of the decomposition reaction; E, $\Delta H^{\#}$ and $\Delta G^{\#}$ are in $kJ\,mol^{-1}$, $\Delta S^{\#}$ in $JK\,mol^{-1}$.

The negative $\Delta S^{\#}$ values for all decomposition steps in the complexes indicate that the complexes are more ordered [36]. The negative value is high in the VO^{2+} complex due to the calculation being done for the second step in which the removed part leaves a less ordered species while the low value calculated for the Co(II) complex (fourth step) indicates more order.

The TG thermogram of $[Zn(H_2PBT)(C_2H_5OH)]$ indicates stability till 152°C indicating that the ethanol participates in coordination or is inside the coordination with a hydrogen bond to one of the free coordination sites.

The TG thermogram $[(VO)_2(PBT)(C_2H_5OH)(H_2O)_2]$ is taken as a representative example for the decomposition of these complexes. It is characterized by four degradation steps in the range 111–209, 210–333, 334–467 and 468–599°C (scheme 2). Elimination of C_2H_5OH (Calcd 8.8, found 8.7%) is the first step. The second step consumed $2H_2O + H_2NCS$ radical (Calcd 18.4, found 18.3%). The first, third and fourth steps are not suitable for the kinetic analysis. The second step is slow with activation energy of 59.2 kJ mole^{-1} (Coats–Redfern equation) and first order. The radical $C_2H_3N_3OS$ is assumed to be evolved in the third step (Calcd 22.2, found 22.2%). Moreover, the fourth step in the thermogram shows removal of $C_7H_5N_2O$ up to 599°C after which a constant weight was observed and 2VO (Calcd 24.5%, found 25.4%) was the final residue.



Scheme 2. Proposed thermal decomposition pattern of $[(VO)_2(PBT)(C_2H_5OH)(H_2O)_2]$.

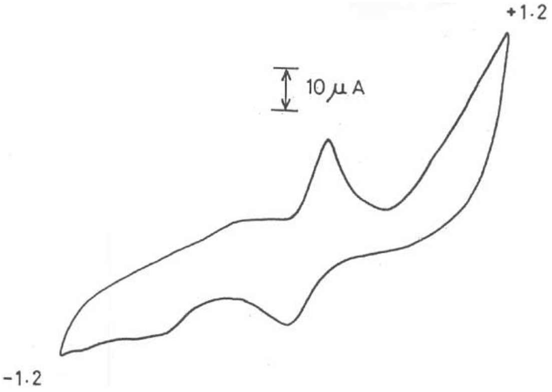


Figure 5. Cyclic voltammogram of [Cu(H_2PBT)(H_2O)] in DMF-TBA$^+$BF$_4^-$ *vs*. Ag/AgCl reference electrode at 100 mV s^{-1} scan rate.

3.7. *Electrochemical behaviour of [Cu(H_2PBT)(H_2O)]*

The electrochemical nature of the complex [Cu(H_2PBT)(H_2O)] was investigated in DMF-TBA$^+$BF$_4^-$ solution by cyclic voltammetry at incremental scan rates (10–200 mV s^{-1}) versus Ag/AgCl reference electrode (figure 5). The complex showed a potential at -1.2 V and displayed three well-defined reduction waves at -0.64, 0.04 and 0.68 V coupled with three anodic waves at -0.26, 0.17 and 0.78 with $E_{1/2} = -0.40$, 0.11 and 0.73, respectively. On comparison with analogous copper(II) complexes [37], the observed electrode couples are nearly irreversible ($\Delta E_p \geq 0.1$ V) and are safely assigned to one electron oxidation process Cu^o/Cu^I, Cu^I/Cu^{II} and Cu^{II}/Cu^{III}, respectively. The one electron nature of these irreversible electrode couples has been established by comparing its current height with similar copper(II) complexes [37].

The dependence of the cathodic peak current, $i_{p,c}$ of the electrode couple Cu^{III}/Cu^{II} on the square root of the sweep rate ($\nu^{1/2}$) for the investigated complex suggests a diffusion-controlled electrochemical process [38]. The cathodic peak potential ($E_{p,c}$) of this couple was shifted towards more negative values as ν increases indicating irreversible nature of the electrode couple. The irreversibility of this couple was also confirmed from the linear dependence of the cathodic peak potential, $E_{p,c}$ with log ν [39]. The product of the number of electrons involved in the reduction process (n) and the corresponding charge transfer coefficient (α) can be determined from the slope of this line. Assuming $n = 1$, the obtained α value (0.62) is in the expected range for a single one-electron transfer step [38].

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