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Spectral and thermal studies for some transition metal complexes of bis(benzylthiocarbohydrazone) focusing on EPR study for Cu(II) and VO²⁺

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Abstract

The coordination behavior of bis (benzylthiocarbohydrazone) as a macrocyclic ligand (H₂BBTC), towards Co(II), Ni(II), Cu(II) nitrates, Cd(II) and Pt(IV) chlorides as well as VO²⁺ sulphate has been investigated. The elemental analysis, magnetic moments, spectral (UV–vis, IR, ¹H NMR and EPR) with thermal studies were used to characterize the isolated complexes. The IR spectra showed that the ligand acts as a binegative hexadentate donor through NH groups and thiol S atoms. Electronic and magnetic data proposed the octahedral structure for all complexes under investigation, except VO²⁺, is a square-pyramidal geometry. EPR spectra for VO²⁺ and Cu(II) reveal data confirmed the proposed structures. The ionization constants ($pK_1 = 8.3$ and $pK_2 = 7.7$) of the ligand and the stability constants of its complexes in solution were determined. The TG analysis for most complexes supports the absence of solvent molecules in or out the coordination sphere through the high thermal stability observed on the thermal curves for the investigated complexes.

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1. Introduction

Formerly the complexes containing four or two nitrogen and oxygen atoms in an equatorial plane was extensively studied [1-3]. The macrocyclic ligands containing nitrogen and oxygen atoms are of great interest due to their elaborated versatility [4], through the flexibility and the ability to coordinate in either neutral or deprotonated form [5].

They also contain N=C-C=N structure unit, which displays a strong chelating ability through the electron delocalization, which associated with extended conjugation, that may affect on the nature of the complex formed. They can yield mono or polynuclear complexes, some of which are biologically relevant [6]. Particularly, first row of transition metal complexes with such ligands have a wide range of biological properties [7–11]. The ligand under investigation is expected to form additional complexes. The ligitional behavior appeared with the prepared nitrogen–sulphur ligand (Scheme 1) with some 3d metal ion

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complexes was elucidated. In which, the ligand coordinated in protonated and deprotonated forms by losing of hydrazinic protons (Scheme 1).

2. Experimental

All chemicals used $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $Cu(NO_3)_2 \cdot 2.5H_2O$, $VOSO_4 \cdot 2H_2O$, $CdCl_2 \cdot 2.5H_2O$, H_2PtCl_6 , benzyl, ethanol, diethylether, DMF and DMSO were of analytical reagent grade (BDH) and used as supplied.

2.1. Synthesis of ligand

An ethanolic solution of benzyl (40 mmol, 8.40 g) was added to thiocarbohydrazide, which was prepared using a published procedure [12], in glacial acetic acid (80 mmol, 8.48 g). The reaction mixture was refluxed on a hot plate for 1 h. The orange precipitate formed was separated out, filtered off, recrystallized from ethanol, and dried in desiccators over anhydrous CaCl₂. The proposed chemical structure of the ligand is in a good agreement with the stoichiometry abstracted from its analytical data and confirmed from the IR, ¹H NMR and mass spectral data.



Scheme 1. Thione form of H₂BBTC.

2.2. Synthesis of complexes

The solid complexes were prepared by the reaction of calculated amount for 1:1 (M:L) ratio of both metal salts and ligand in ethanol–water (v/v) solution. The reaction mixture was heated under reflux on a water bath for 2–3 h. During the preparation of Pt(IV) and VO²⁺ complexes sodium acetate was added by about 0.3 g. The reaction product was filtered immediately, washed several times with hot EtOH followed by diethylether and dried in a desiccator over anhydrous CaCl₂. The analytical and physical data are given in Table 1.

2.3. Procedure for the pH-metric titrations

The titrations were carried out at room temperature $(25 \pm 1 \,^{\circ}\text{C})$. The titrant was added from burette and the contents of the titration vessel were stirred magnetically. The titration was carried out for the following solutions:

- (1) $2.5 \text{ ml of HCl}(10^{-2} \text{ mol } 1^{-1}) + 1.25 \text{ ml KCl} + 10 \text{ ml ethanol.}$
- (2) 2.5 ml of HCl + 1.25 ml KCl $(6.1 \text{ mol } l^{-1}) + 0.25 \text{ ml}$
- $(10^{-2} \text{ mol } l^{-1})$ of ligand + 9.75 ml of ethanol.
- (3) Solution (2) + 0.05 ml $(10^{-2} \text{ mol } 1^{-1})$ of metal ion.

All the above solutions were completed to 25 ml with twicedistilled water and titrated against $0.978 \times 10^{-2} \text{ mol } \text{l}^{-1} \text{ NaOH}.$

Table 1
Analytical and physical data for the metal complexes

2.4. Physical measurements

Carbon and hydrogen contents were determined at the Microanalytical Unit in Cairo University. The analysis of metal and chloride ions was carried out according to the standard methods [13]. The infrared spectra, as KBr discs, were recorded on a Mattson 5000 FTIR Spectrophotometer. The electronic and ¹H NMR (200 MHz) spectra were recorded on UV₂ Unicam UV-vis, and a Varian Gemini Spectrophotometers, respectively. The mass spectra were recorded on a Varian MAT 311 instrument. The thermal studies were carried out on a Shimadzu thermogravimetric analyzer at a heating rate of $10 \,^{\circ}\text{C} \,^{\text{min}-1}$. The protonation constants of the ligand and the formation constants of its complexes were determined pH-metrically by Irving and Rossotti method. ESR spectrum was obtained on a Bruker EMX Spectrometer working in the X-band (9.78 GHz) with 100 kHz modulation frequency. The microwave power was set at 1 mW, and modulation amplitude was set at 4G. The low field signal was obtained after 4 scans with a 10-fold increase in the receiver gain. A powder spectrum was obtained in a 2 mm quartz capillary at room temperature.

3. Results and discussion

The macrocyclic ligand used in this study is elucidated by different tools as, the elemental analysis, which used to propose the ligand formulae and the molecular ion peak in mass spectrum supported this. ¹H NMR spectrum is the final confirming tool for the ligand structure and displayed a singlet peak at $\delta = 7.34$ by integration assigned to 20 H referring to the four phenyl groups. Also, the two singlet peaks at $\delta = 8.4$ and 8.8 each peak by integration assigned to the two hydrogen atoms aggregated from two similar NH groups. The relative down field appearance of the second peak ($\delta = 8.8$) may be due to the intramolecular hydrogen bonding between NH and C=S groups [14]. All the isolated complexes are stable under atmospheric conditions and insoluble in most common organic solvents except DMF and DMSO dissolved all of them except [Cu(C₃₀H₂₂N₈S₂)] which is partially soluble. The soluble complexes having a non-conducting feature. [Pt(BBTC)]Cl₂ deviates from this behavior by showing a relative high conductivity value $(110 \,\Omega^{-1} \,\mathrm{cm}^2 \,\mathrm{mol}^{-1})$ which may refer to the presence of two ionizable chloride ions in the crystal lattice. All the complexes have melting points above

No.	Complex	Color	Found (calcd.%	F.W. found ^a			
			С	Ν	Н	М	
1	$[C_{30}H_{24}N_8S_2]$	Yellow	65.2(64.3)	19.2(20.0)	4.75(4.32)	_	563(560.7)
2	$[Cd (C_{30}H_{22}N_8S_2)]$	Yellow	52.7(53.7)	15.9(16.7)	4.3(4.32)	17.2(16.7)	-((671.1)
3	$[Co (C_{30}H_{22}N_8S_2)]$	Brown	59.8(58.4)	17.8(18.1)	3.1(3.6)	9.6(9.5)	619(617.6)
4	$[Cu (C_{30}H_{22}N_8S_2)]$	Green	56.6(57.7)	17.5(18.0)	3.8(3.6)	10.9(10.2)	-((622.2)
5	[Pt(C ₃₀ H ₂₂ N ₈ S ₂)]Cl ₂	Green	44.0(43.7)	12.9(13.6)	3.2(2.7)	24.1(23.6)	-((824.7)
6	[Ni (C ₃₀ H ₂₂ N ₈ S ₂)]	Green	56.7(58.4)	17.5(18.1)	3.4(3.6)	9.8(9.5)	618(617.4)
7	$[(VO)_2 (C_{30}H_{22}N_8S_2) SO_4]$	Dark green	46.4(45.7)	14.9(14.2)	3.3(2.8)	12.1(12.9)	626(625.7)

^a Values obtained from mass spectra.

Table 2 Significant IR spectral bands (cm⁻¹) of H₂BBTC and its metal complexes

Complex	$\nu(NH)$	$\upsilon(\mathrm{NH}{\cdots}\mathrm{S})$	v(C=N)	$v_{I}(C=S)$	$v_{IV}(C=S)$	v(N-N)	$\delta(NH)$	v(M-N)	v(M-S)
1	3220	3127	1640	1580	873	1025	1533		
2		_	1623	1485	_	1070		420	380
3	3059	_	1598	1482	_	1065	1482	400	340
4	3058	_	1600	1483	_	1098	1483	420	380
5	3100	_	1630	1556	_	1028	1500	420	394
6	3023	_	1619	1535	_	1105	1535	422	397
7	3060	-	1635	1538	-	1111		420	390

 $300 \,^{\circ}$ C. The elemental analysis and the color of the complexes are listed in Table 1.

3.1. IR spectral studies

The characteristic bands of the ligand and its complexes are collected in Table 2. The infrared spectrum of H₂BBTC shows bands at 3220 and 3127 cm^{-1} assigned for vNH groups, the lower appearance of the second NH (3127 cm^{-1}) group may support its participation in hydrogen bonding [15]. The two bands at 1640 and 1025 cm⁻¹ for ν (C=N) and ν (N–N) vibrations, respectively [16]. The band at 873 cm^{-1} is assigned to ν (C=S) vibration. The careful comparison between IR spectra of H₂BBTC and each complex spectrum reflects the following observations: (i) the negative shift $(50-90 \text{ cm}^{-1})$ observed on ν (C=N) band, (ii) the positive shift (40–80 cm⁻¹) observed for ν (N–N) band, (iii) the coordination of azomethine nitrogen is also consistent with the presence of new band at the range $(400-480 \text{ cm}^{-1})$ assignable to the ν (M–N) vibration [17]; and finally, (iv) the coordination via thiolate sulphur is indicated by the absence of ν (C=S) vibration with the simultaneous appearance of new bands at the ranges 619-697 and 340-420 cm⁻¹ attributed to the ν (C–S) [18] and ν (M–S) vibrations, respectively. Such observations proposed the binegative hexadentate feature of the ligand with all investigated metal ions in a mononuclear structure (Scheme 2) except with VO²⁺ ion, which appeared as a binuclear complex. In which, the band at 1190 and $1020 \,\mathrm{cm}^{-1}$ is assigned to $\nu(\mathrm{SO}_4)$ in its bidentate nature [19] as



Scheme 2. (a) The modeling for Co(II) complex in which the phenyl groups were excluded, after the minimization energy steps, to clarify the figure and (b) is the proposed structure for the complexes, where M = Co(II), Ni(II), Cu(II) and Cd(II).

well as the band at 1111 and 1040 cm^{-1} is due to $\nu(\text{V=O})$ and $\nu(\text{N-N})$ vibration, respectively. This is the further evidence for square-pyramidal geometry proposed for VO²⁺ complex [19].

3.2. Electronic spectra and magnetic measurements

The magnetic moments and the significant electronic absorption bands (in DMF) for all complexes under investigation are shown in Table 3. Nujol mull spectra for some complexes were done and displayed conformity for DMF results. The data abstracted reflect true insight about the geometry of the complexes which asserted by other tools. The magnetic moment of [Ni(BBTC)] is found to be 2.1 BM, which is not suitable with the normal values of Ni(II) geometries. This may suggest a mixed stereochemistry between octahedral and square-planar geometries [20] with ${}^{3}A_{2g}$ ground state term symbol. The electronic spectral bands support such postulation by the presence of 24,690 (ν_3) and 14,810 (ν_2) bands attributed to the ${}^{3}A_{2g}$ $(F) \rightarrow {}^{3}T_{1g}(F) \text{ and } {}^{3}A_{2g}(F) \rightarrow {}^{3}T_{1g}(P) \text{ transitions, respectively}$ in an octahedral structure. Also, the presence of $20,000 \,\mathrm{cm}^{-1}$ band in the spectrum assigned to the ${}^{1}A_{1g} \rightarrow {}^{1}A_{2g}$ transition in a square-planar [21] geometry. This verified the presence of square-planar by 25% in the geometry mix.

The electronic spectrum of the [Cu(BBTC)] complex, in DMF, shows band at 17,540 cm⁻¹ assigned to the ${}^{2}E_{g} \rightarrow {}^{2}T_{2g}$ transition which may suggest a distorted octahedral arrangement around the metal ion. The distortion may be due to Jahn Teller effect. The charge transfer band at 23,810 may be due to S \rightarrow Cu(II) which is previously mentioned [22] in which the S \rightarrow Cu(II) charge transfer band are in the region from 21,785 to 24,750 cm⁻¹. The normal magnetic moment (1.75 BM) supports the absence of any metal–metal interaction with the neighboring molecules, which appeared on the clear resolution of EPR spectrum.

The electronic spectrum of [Co(BBTC)] in DMF displays two bands at 19,455 and 14,830 cm⁻¹ assignable to the ${}^{4}T_{1g} \rightarrow {}^{4}T_{1g}(P) (\nu_{3})$ and ${}^{4}T_{1g} \rightarrow {}^{4}A_{2g} (\nu_{2})$ transitions, respectively corresponding to octahedral configuration [23]. The calculated values of $10D_{q}$, *B* and β (Table 3) lie in the range reported for the proposed structure. The magnetic moment value (3.4 BM) is near the spin only moment (3.87 BM) [24].

The electronic spectrum of $[(VO)_2(BBTC)SO_4]$ in DMF shows two bands at 12,370 and 16,000 cm⁻¹ may assign to ${}^2B_2 \rightarrow {}^2E$ and ${}^2B_2 \rightarrow {}^2B_1$, respectively, which are well characteristic for square-pyramidal geometry [25]. The magnetic moment value (1.4 BM) measured for the individual atom is

Complex	$\mu_{\rm eff}$ (BM)	$v_{\rm max}~({\rm cm}^{-1})$		Ligand field	Ligand field parameters			
				10 <i>D</i> _q	В	β		
2	Diamagnetic	17,857	24,570					
3	2.36	19,455; 14,830	25,125	4493	898	0.91		
4	1.75	17,540	23,810					
5	Diamagnetic	23,310; 12,195	25,000					
6	2.08	24,690; 20,000; 14,810	_	9031	903.1	0.88		
7	1.4	12,270; 16,000	29,410					

Table 3 Magnetic moments, electronic spectral data (in DMF) and ligand field parameters of some complexes

lower than that reported (1.7–2.1 BM), this may support the presence of vanadyl complex in a binuclear with strong interaction between the two VO²⁺ ions. The octahedral geometry is the most acceptable structure for [Pt(BBTC)]Cl₂ referring to the low spin d^6 system having ${}^1A_{1g}$ as ground state. Two spin allowed absorption bands at 23,310 and 12,195 cm⁻¹ are to be expected corresponding to transitions ${}^{1}A_{1g} \rightarrow {}^{1}T_{2g}$ and ${}^{1}A_{1g} \rightarrow {}^{1}T_{1g}$, respectively [26]. The spectrochemical parameters D_q , B and β of Co(II) and Ni(II) complexes are given in Table 3. the Dq values $(4.49 \times 10^3 \text{ and } 9.03 \times 10^3 \text{ cm}^{-1})$ are found close to that observed for the complexes containing oxygen, nitrogen and/or sulphur. The observed Dq values ordered the ligand in the middle range of the spectrochemical series and provides that the C=N and C=S of the ligand are complexed to the Co(II) and Ni(II) ions in an octahedral geometry. The Bvalues of the complexes were found by $\sim 90\%$, indicating considerable overlap with strongly ionic bond character [27]. The high B values are most likely associated with the unchangeable nuclear charge of the cation. The nephelauxetic parameter, β values (0.91 and 0.88 for Co(II) and Ni(II), respectively) are indicating that the ligand is in the middle of the nephelauxetic of other nitrogen and sulphur donor series. The values are higher than that reported for NiN₆ or NiO₆, confirming the coordination via N and S atoms (Scheme 2).

3.3. Thermal analysis

The thermogravimetric (TGA and DTGA) analysis for most investigated complexes was recorded at temperature range 25–800 °C. The thermograms exhibit several thermal events. The relative high thermal stability observed in all thermally investigated complexes, which may correspond to the absence of solvent molecules in/out the coordination sphere. This is proposed referring to the higher thermal stability observed for all investigated complexes in which the first decomposition step is started at relatively higher temperature. Also, the high weight percent of the residual part reflects the stability of the chelate structure, which is considered as a logical behavior especially with S and N sites.

The TG curves obtained for [Ni(BBTC)] showed high thermal stability up to 234 °C, followed by a sudden decomposition stage ended at 422 °C may be attributed to the removal of 4 ph groups by 49.4 (49.9%) weight loss. The second decomposition stage followed the previous one ended at 659.3 °C, also may be attributed to the removal of N₆H₂C₄ as the organic fragment. The residual part measured at 650 °C agrees with NiS + N_2C_2S fragment by 27.5(27.4).

The TGA curve of [Cu(BBTC)] shows a gradual degradation steps. The first started at 185.84 °C refers to the removal of 2(ph-C) by 28.4 (28.6%) weight loss as a terminal part in the ligand. The second decomposition step started at 330 °C is corresponding to the removal of another terminal part (2 ph + C) by 26.5 (26.7%) weight loss. The third decomposition step started at 485 °C is corresponding to the removal of another fragment (N₅H₂C₃) by 16.5(17.2%). The residual part observed at 660 °C by 27.5 (27.5%) is due to CuS beside N₃S fragment.

The TGA curve of [Co(BBTC)] shows three decomposition stages started at 210 °C corresponds to the dissociation of 3 ph groups by 36.4 (37.4%) weight loss, followed by C₂N₃H as a part expelled in the second step at 426 °C by 9.3 (10.8%) weight loss. The final step started at 529 °C represents the removal of ph + C₃N₃ fragment by 22.2 (23.1%) weight loss. The residual part representing CoS beside C₂H₂N₂S fragment is measured at 660 °C by 31.4 (28.7%) weight percent. The difference between the found and calculated values may be due to the overlapping between each successive steps.

The TGA curve of [Cd(BBTC)] showed three degradation steps started at 179 °C. The first step ended at 303 °C is attributed to the removal of phenyl group by 12.87 (11.50%) weight loss. The second step ended at 440 °C may attribute to the removal of 3 ph groups by 35.8 (34.4%) weight loss. The third step ended at 677 °C is attributed to the removal of N₄C₆H₂ fragment by 18.5 (19.3%). The final residue measured at 660 °C is due to CdS beside SN₄ fragment by 32.8 (34.6%).

The curve of [Pt(BBTC)]Cl₂ showed stability till 170 °C above which a weight loss by 18.8 (17.8%) corresponds to the removal of ph+2Cl fragment. The second stage started at 282 °C is assigned to the elimination of 3 ph+N₈C₆H₂S by 53.7 (54.5%) as a residual organic fragment. The third step (458–618 °C) can be ascribed to the residual part (PtS) by 27.5 (27.8%) weight percent.

3.4. Mass spectra

The mass spectra for most investigated complexes and the molecular ion peaks confirmed the proposed formulae. Calculated and found molecular weights are given in Table 1. As a typical example, the mass spectrum (Fig. 1) of H₂BBTC shows peaks corresponding to the successive degradation of the molecule. The first peak at m/e = 563 (calcd. = 560.7) represents



Fig. 1. Mass spectrum of H₂BBTC.



Fig. 2. Solid state X-band ESR spectra for Cu(II) complex (a) and $\rm VO^{2+}$ (b) at room temperature.

the molecular ion peak of the complex $(M^+ + 2)$ with 9.2% abundance. The sharp peak (base peak) with m/e = 92 (calcd. = 91) may represent the residual part (C₆H₅N) of the ligand.

3.5. ESR spectra

The room temperature solid-state ESR spectrum of copper complex (Fig. 2a) exhibits axially symmetric *g*-tensor parameters with $g_{\parallel} > g_{\perp} > 2.0023$. The g values reflect that, the Cu(II) center has a tetragonal distorted octahedral geometry with

Table 4			
Spin-Hamiltonian	parameters	at room	temperature

 $d_x^2 - y^2$ orbital as a ground state [28]. No band corresponding to the forbidden magnetic dipolar transition for the complex was observed at half-field (ca. 1500 G, g = 4.0). This reveals the absence of any Cu-Cu interaction which supporting the mono nuclear complex. In axial symmetry the g-values are related to the G-factor by the expression, $G = (g_{\parallel} - 2)/(g_{\perp} - 2) = 4$, which measures the exchange interaction between copper centers in the solid. According to Hathaway [29], if the value of G is greater than 4, the exchange interaction between copper(II) centers in the solid state is negligible, whereas when it is less than 4, a considerable exchange interaction exists in the solid complex. The calculated G values are given in (Table 4). The G values are greater than 4, this supports the absence of exchange coupling between copper(II) centers in the solid state [30]. In hexacoordinated complex, tetragonal distortion from the octahedral symmetry due to the Jahn-Teller distortion is very common. The low g-value (g=2.17) obviously corresponds to regular octahedral Cu(II) complex. Superhyperfine structures for these complexes are not seen at higher fields excluding any interaction of the nuclear spins of the nitrogen (I = 1) with the unpaired electron density on Cu(II). Molecular orbital coefficients, a^2 (a measure of the covalence of the in-plane σ -bonding between the 3d orbital and the ligand orbitals) and β^2 (the covalent in-plane π -bonding), were calculated by using the following equations [31]:

$$\alpha^{2} = \left(\frac{A_{\parallel}}{0.036}\right) + (g_{\parallel} - 2.0023) + \frac{3}{7}(g_{\perp} - 2.0023) + 0.04,$$
$$\beta^{2} = \frac{(g - 2.0023)E}{-8\lambda\alpha^{2}}$$

where $\lambda = -828 \text{ cm}^{-1}$ for the free copper(II) ion and *E* is the electronic transition energy. The lower value of β^2 compared to α^2 indicates that the in-plane π -bonding is more covalent than the in-plane σ -bonding, the data in a good agreement with the data reported earlier [29]. The α^2 value for copper(II) complex indicates a considerable covalency in the bonding between the Cu(II) ion and the ligand.

The EPR spectra of VO²⁺ complex at room temperature exhibit an eight-line pattern corresponding to the usual parallel and perpendicular components of g- and hyperfine (hf) *A*-tensors. As a representative, the EPR spectrum of the complex is shown in (Fig. 2b). It can be seen that the parallel and perpendicular components are well resolved. Nitrogen superhyperfine splitting is not observed in the complex, which indicates that the unpaired electron is in the d_{xy} orbital [30]. The pattern suggests that g and A are axially symmetric in nature. The spin Hamiltonian parameters derived from the spectrum are given in Table 4 with MO parameters computed from experimental data. The parameters A and g are found to be in agreement with the

Complex	g_{\parallel}	g_{\perp}	g_0	$A_{\parallel} \times 10^{-4}$	$g_{\parallel}/A_{\parallel}$	A_{\perp}	A_0	α^2	β^2
(4) (7)	2.17 1.937	2.03 1.964	2.12 1.955	187 -181.25	132.3	-70	-107.08	0.59 1.432	0.50 0.943

values generally observed for the vanadyl complex with squarepyramidal geometry [31]. The molecular orbital coefficient α^2 and β^2 were calculated using the following equations [32]:

$$\beta^{2} = \frac{7}{6} \left(-\frac{A_{\parallel}}{p} + \frac{A_{\perp}}{p} + g_{\parallel} - \frac{5}{14}g_{\perp} - \frac{9}{14}g_{e} \right),$$

$$\alpha^{2} = \frac{2.0023 - \Delta g}{8\beta^{2}\lambda} \quad \text{where} \ \Delta g = (g_{\perp} - g_{\parallel}) \times 10^{-3}$$

The negative values of β^2 lead to negative values of α^2 . Since hyperfine coupling constants are negative, calculations were done taking A_{\parallel} and A_{\perp} as negative, which gave positive values of β^2 and α^2 . In this study, α^2 is less than β^2 indicating that inplane σ -bonding is more covalent than in-plane π -bonding. The spectrum of the complex shows two bands at 16,000 cm⁻¹ (E_1) and 12,270 cm⁻¹ (E_2) which are assigned to ${}^2B_2 \rightarrow {}^2B_1$ and ${}^2B_2 \rightarrow {}^2E$, transitions, respectively. Assuming pure d-orbitals and using first- and second-order perturbation theory, the spin Hamiltonian parameters can be related to the transition energies by the following expressions:

$$g_{\parallel} = g_{\rm e} - \left(\frac{8\lambda}{E_1}\right)$$
 and $g_{\perp} = g_{\rm e} - \left(\frac{2\lambda}{E_2}\right)$

where g_e is the free-electron g value (2.0023). Using E_1 and E_2 values, the spin–orbital coupling constant (λ) value (182.79) is evaluated. A value for λ of 250 cm⁻¹ is reported [33] for the free V⁴⁺ ion. The reduction in the magnitude of λ for the double bonded oxovanadium complex (V=O)²⁺ is attributed to substantial π -bonding. While, the value is within the reasonable limits of predicated values.

3.5.1. Calculation of dipolar term (p)

The *p* value is calculated from the following equation:

$$p = \frac{7(A_{\parallel} - A_{\perp})}{6 + 3/2(\lambda/\Delta E_1)}$$

If A_{\parallel} is taken to be negative and A_{\perp} positive, the *p* value will be more than 270 G, which is far from the expected value. Thus, the signs of both A_{\parallel} and A_{\perp} are taken as negative and are indicated in the form of isotropic hf constant (A_0). McGarvey theoretically calculated the value of p to be +136 G for vanadyl complexes [34] and the value (129.42) of this complex do not deviate much from this expected value.

3.5.2. Calculation of MO coefficients and bonding parameters

The g values observed so far for most vanadyl complexes are generally lower than 2.0023 and the data in this work support this observation. This lowering is related to the spin–orbit interaction of the ground state d_{xy} level with low-lying excited states. The isotropic and anisotropic (g and A) parameters have been calculated from equations:

$$A_0 = \frac{A_{\parallel} + 2A_{\perp}}{3}, \qquad g_0 = \frac{g_{\parallel} + 2g_{\perp}}{3}$$

Taking A_{\parallel} and A_{\perp} to be negative values the expression for *K* is [35]:

$$K = -\left(\frac{A_0}{p}\right) - (g_e - g_0)$$

Thus K (Fermi-contact term) can be evaluated (0.88).

3.6. pH-metric studies

The association constant measured for organic molecules in solution is becoming important. This elaborates the insight during the investigation of their complexation behavior in aqueous or solid state. The protonation constants of the ligand were determined through a plot between pH and \bar{n}_{A} , where \bar{n}_{A} is the average number of protons associated per ligand molecule. This is easily calculated from the Irving and Rossotti equation [36]:

$$\bar{n}_{A} = Y + \frac{(V_{1} - V_{2})([A] + [B])}{(V_{0} + V_{1})T_{L}}$$

where Y is the ionizable proton of the ligand, $(2H^+) V_1$ and V_2 are the volumes of alkali required to reach the same pH value in the free acid and in the ligand mixture, respectively V_0 is the initial volume of the titrated mixture, T_L is the ligand concentration in the initial volume, and [A] and [B] are the concentrations of the free acid and the alkali, respectively. The association constants (pK_1 and pK_2) are determined [37] by interpolation at $\bar{n}_A = 0.5$ and 1.5, respectively. $pK_1 = 8.3$ and $pK_2 = 7.7$ is determined by indirect method using pK (at $\bar{n}_A = 1$) and pK₁ by applying this equation $pK_1 + pK_2 = 2 pK$ (at $\bar{n}_A = 1$). The low pK values may indicate the relative acidity of the ligand which facilitate the deprotonation as well as the little difference between the two values may refer to the stepwise deprotonation process even for the symmetric centers of ionization (NH–C=S). This may support the binegative behavior of the ligand which appeared, as the major trend towards the metal ions in the solid complexes. The stability constants (Table 5) of all metal ion complexes under investigation were determined. This by using the relation between the free ligand exponent (pL) and the average number of ligands attached per metal ion (\bar{n}_A). The values were evaluated applying the following equations:

$$\bar{n} = \frac{(V_3 - V_2)([A] + [B])}{(V_0 + V_1)^- n_A T_M}$$

Table 5

The association constants of the ligand and the formation constants of its complexes

System	Half method					
	$\log K_1$	$\log K_2$	$\log \beta^*$			
1	8.3	7.7	_			
2	4.6	2.2	6.8			
3	6.4	2.8	9.2			
4	9.6	8.7	18.3			
5	8.2	5.7	13.9			
6	8.5	5.3	13.8			
7	6.5	4.3	10.8			

 β^* is the overall stability constant.

pL = log
$$\frac{1 + K_1[H^+]}{T_L - \bar{n} T_M} \cdot \frac{V_3 V_0}{V_0}$$
 for a monobasic ligand

pL = log
$$\frac{1 + K_1[H^+] + K_1K_2[H^+]^2}{T_L - \bar{n}T_M} \cdot \frac{V_3V_0}{V_0}$$

for a dibasic ligand

where V_3 is the volume of alkali required to reach the desired pH in the complex solution, $T_{\rm M}$ the initial concentration of the metal ion. The data reveal a good agreement with the Irving and Williams [38] series with Cu(II) > Ni(II) > VO²⁺ > Co(II) > Cd(II) order in which, the stability of the complex increases with the size of metal ion decrease. The formation constants (8.2 and 5.7) for the Pt(IV) complexes in solution show a high stability for the different ratios (1:1 and 1:2 as M:L) appeared, which is the expected behavior for highly charged metal ion.

4. Conclusion

A series of novel complexes have been prepared and fully characterized. The ligand bind mainly as a binegative in all investigated complexes. The potentiometric studies supported the behavior of the ligand in solid complexes, also the formation constants for the complexes in solution proposed the high stability of Cu(II) an Pt(IV) complexes, which related to their smaller atomic size. EPR spectra for VO²⁺ and Cu(II) complexes supported the binuclear square pyramidal and mononuclear octahedral structures proposed for the two complexes, respectively. Proposed fragmentation and thermal decomposition patterns for some of the complexes are also given.

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