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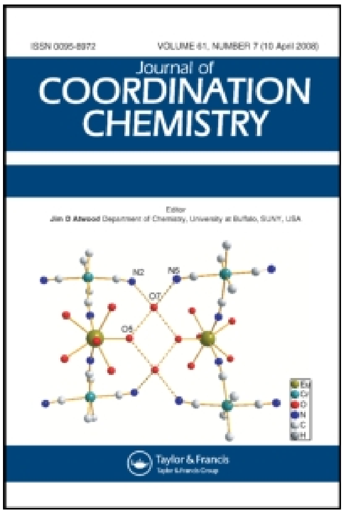

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Chelating activity of bis(diacetylmonoxime)thiocarbohydrazone towards VO^2, Co(II), Ni(II), Cu(II) and Pt(IV) ions

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Chelating activity of bis(diacetylmonoxime)thiocarbohydrazone towards VO^{2+}, Co(II), Ni(II), Cu(II) and Pt(IV) ions

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A new chelating agent, bis(diacetylmonoxime)thiocarbohydrazone (H_3DMT), has been synthesized from reaction between diacetylmonoxime and thiocarbohydrazide. The prepared ligand, characterized by elemental analysis, IR and ^1H NMR spectra, is a strong chelating agent and indicator. Its coordinating properties have been studied toward VO^{2+}, Co(II), Ni(II), Cu(II) and Pt(IV) ions. The data revealed the formation of mononuclear complexes with Co(II) and Pt(IV) and binuclear complexes with the rest. In all complexes, the ligand binds in its deprotonated form through the oxime and hydrazone nitrogens as well as the thiol or thione sulfur forming five- and six-membered rings. All complexes exhibit an octahedral structure except for the Cu(II) which has a square-pyramidal geometry based on the spectral and magnetic studies. The ESR spectra of the Cu(II) and VO^{2+} complexes are in good agreement with the structural results. The color change from acidic (yellow) to basic (reddish brown) media gives the ligand the ability to become as an analytical indicator for weak acid–weak base titrations.

Keywords: Thiocarbohydrazones; Complexes; ESR spectra; Acid–base indicator

1. Introduction

Oxygen, nitrogen and sulphur compounds are extensively studied [1], including the effect of active donors and electron delocalization in transition metal complexes [2–6] as well as antimicrobial activity. While thiosemicarbazones and their transition metal complexes have been studied for antimicrobial properties, little is known about thiocarbohydrazones. Some have been tested as fungicides for textile fabrics. 2-Acetylpyridine thiocarbohydrazones were found more active than 2-acetylpyridine thiosemicarbazones as inactivators of HSV-1 ribonucleotide reductase [7]. This work investigates the coordination behaviour of bis(diacetylmonoxime)thiocarbohydrazone, H_3DMT (figure 1) towards some metal ions using spectral, magnetic and thermal studies.

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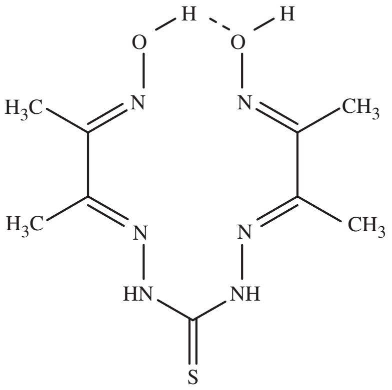

Figure 1. Formula of H_3DMT.

Table 1. Yield and elemental analysis of H_3DMT and its complexes.

		Analysis%, found (Calcd)			
Compound	Yield	C	H	M	Mol. wt.*
H_3DMT	87%	39.5(39.7)	5.7(5.9)	–	275(272.3)
$[Cu_2(HDMT)_2(H_2O)]$	64%	31.2(31.5)	4.0(4.4)	19.0(18.5)	684(685.7)
$[Ni_2(HDMT)_2(H_2O)_3]$	78%	30.4(30.3)	4.2(4.8)	16.2(16.5)	714(712.5)
$[(VO)_2(HDMT)_2(H_2O)]$	81%	32.9(31.2)	4.1(4.2)	15.0(14.7)	695(692.5)
$[Co(HDMT)(H_2O)_2] \cdot H_2O$	63%	30.2(30.4)	5.2(4.8)	16.9(16.5)	(712.1)
$[Pt(DMT)(OAc] \cdot 2H_2O$	89%	23.2(23.6)	2.9(3.6)	34.6(34.9)	(559.5)

*Values obtained from mass spectra.

Table 2. Infrared spectral bands of H_3DMT and its complexes.

Compound	ν(NH)	$\nu(C{=}N_{hydrazone})$	$\nu(C{=}N_{oxime})$	ν(NOH)	$\nu(C{=}S)$
H_3DMT	3138	1627	1509	980	810
$[Cu_2(HDMT)_2(H_2O)]$	3135	1541	1484	1130	782
$[Ni_2(HDMT)_2(H_2O)_3]$	3139	1561	1501	1100	800
$[(VO)_2(HDMT)_2(H_2O)]$	3135	1598	1480	1141	756
$[Co(HDMT)(H_2O)_2] \cdot H_2O$	3170	1567	1430	1087	755
$[Pt(DMT)(OAc)] \cdot 2H_2O$	3103	1543	1437	1085	–

2. Experimental

2.1. *Synthesis of ligand*

H_3DMT was prepared by mixing 6.05 g of diacetylmonoxime with 3.18 g of thiocarbohydrazide (2 : 1 ratio) in glacial acetic acid. The reaction mixture was heated under reflux on a water bath for 10 h. After cooling, a brown precipitate separated, was filtered off, crystallized from ethanol and dried in a desiccator; its melting point is 130°C. The proposed formula of the prepared ligand is in good agreement with the stoichiometry concluded from its analytical data and mass spectrum (table 1) and confirmed through its IR spectrum (table 2).

2.2. *Synthesis of complexes*

All complexes were prepared by mixing equimolar amounts (3 mmol) of H_3DMT, in ethanol, and aqueous-ethanol solution of the acetate salt of Cu(II), Ni(II) or Co(II); the sulphate salt of VO^{2+} and H_2PtCl_6. Solid complexes were formed after 3 h of heating under reflex, directly with Cu(II), Ni(II) and Co(II) or by adding ca 0.5 g sodium acetate with Pt(IV) and VO^{2+}. The isolated complexes were filtered off, washed several times with hot ethanol, dried and stored.

2.3. *Equipment and measurements*

Carbon and hydrogen content was determined at the Microanalytical Unit of Cairo University. The analysis of metal ions was carried out according to standard methods [8]. The infrared spectra, as KBr pellets, were recorded on a Mattson 5000 FTIR spectrophotometer (with CsI splitter) in the range 200–4000 cm^{-1}. The electronic and ^1H NMR (200 MHz) spectra were recorded on UV_2 Unicam UV-Vis and Varian Gemini spectrophotometers, respectively. The mass spectra were recorded on a Varian MAT 311 instrument. The magnetic moment values were evaluated at room temperature (25 ± 1°C) using a Johnson Matthey magnetic susceptibility balance applying the $\mu_{eff} = 2.828\sqrt{\chi_M^- T}$ equation. The molar susceptibility, χ_M^-, is corrected for diamagnetism of all atoms in the ligands using Pascal's constants. The thermal studies were carried out on a Shimadzu thermogravimetric analyzer at heating rate of 10°C min^{-1}. The ESR spectra were obtained on a Bruker EMX spectrometer working in the X-band (9.78 GHz) with 100 kHz modulation frequency. The microwave power and modulation amplitude were set at 1 mW and 4 Gauss, respectively. The low field signal was obtained after 4 scans with 10 fold increase in the receiver gain. A powder spectrum was obtained in a 2 mm quartz capillary at room temperature.

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3. Results and discussion

3.1. *General*

The isolated complexes are stable in air, insoluble in common organic solvents, but are partially soluble in DMF and DMSO. The elemental analysis, color and melting points together with the formula weights obtained from mass spectra are listed in table 1.

3.2. *Mass spectra*

The mass spectra of most complexes were recorded and their molecular ion peaks have been used to confirm the proposed formulas. Calculated and found molecular weights are given in table 1. The mass spectrum of $[Ni_2(HDMT)_2(H_2O)_3]$ shows multi peaks (figure 2) corresponding to successive degradation of the molecule. The first peak at *m/e* 712 represents the molecular ion peak of the complex with 45% abundance. The sharp peak (base peak) with *m/e* 58 represents the stable species (Ni atom).

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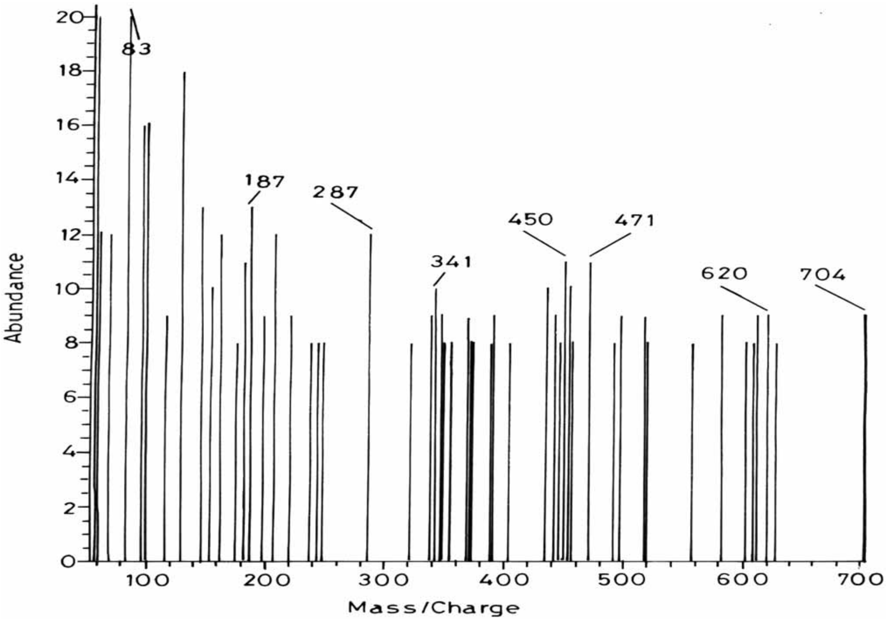

Figure 2. Mass spectrum of $[Ni_2(HMT)_2(H_2O)_3]$.

3.3. *IR spectra*

The most characteristic bands of H_3DMT and its complexes are summarized in table 2. The coordination of the ligand was determined based on comparison between the ligand spectrum with those of its complexes. The data reveals that H_3DMT acts as a dibasic pentadentate ligand in $[Ni_2(HDMT)_2(H_2O)_3]$, $[Cu_2(HDMT)_2(H_2O)]$ and $[(VO)_2(HDMT)_2(H_2O)]$ and tribasic in $[Pt(DMT)(OAc)] \cdot 2H_2O$. The ligand is dibasic tetradentate in $[Co(HDMT)(H_2O)_2] \cdot H_2O$, coordinating through the $C{=}N_{hydrazone}$ and $C{=}N_{oxime}$ groups [9]. The thione and/or thiol group is the fifth coordination site bridging two molecules. The bonds caused a shift in $\nu(C{=}N_{hydrazone})$ band from 1627 to 1541 cm^{-1}, while the two covalent bonds formed through the $C{=}N_{oxime}$ groups, after deprotonation of oxime protons caused lower (72 cm^{-1}) and higher (130 cm^{-1}) shifts of both $\nu(C{=}N_{oxime})$ and $\nu(NO)$ bands, respectively [10] with disappearance of $\delta(OH)$ band. The lower shift of $\nu(C{=}S)$ in all investigated spectra, except $[Co(HDMT)(H_2O)_2] \cdot H_2O$, supports the coordination of the ligand in its thione form. In $[Pt(DMT)(OAc)] \cdot 2H_2O$, the $\nu(C{=}S)$ band disappears with the appearance of a new band at 635 cm^{-1} attributed to $\nu(C\text{–}S)$ indicating covalent attachment with Pt(IV) after thioenolization [11]. Also, the appearance of new bands at 1627 and 1437 cm^{-1}, assigned to $\nu_{as}(OAc)$ and $\nu_s(OAc)$, suggest monodentate attachment of the acetate group [12]. In VO^{2+}, the band at 1140 cm^{-1} was previously attributed to $\nu(V{=}O)$ in the octahedral structure [13]. This band overlapped with the $\nu(NO)$ in the present complex and appeared strong and broad confirming the proposed structure. The appearance of new bands assigned to $\nu(M\text{–}OH_2)$, $\nu(M\text{–}N)$ and $(\nu M\text{–}S)$ supports the suggested coordination sites [14].

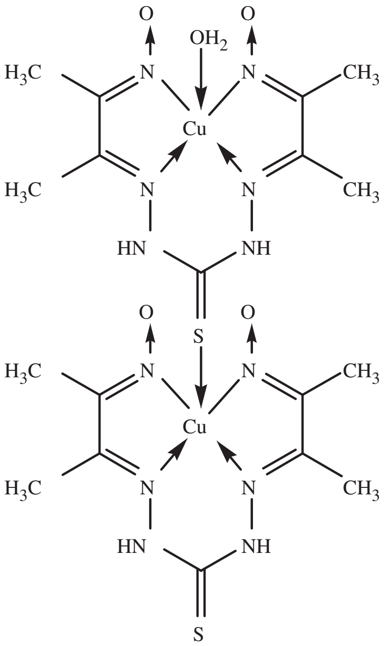

Figure 3. Structure of [$Cu_2(HDMT)_2(H_2O)$].

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3.4. *Electronic spectra and magnetic measurements*

The proposed structure for [$Cu_2(HDMT)_2(H_2O)$] is square pyramidal; based on the appearance of a band at 12 230 cm^{-1} assigned to the $^2B_1 \rightarrow {}^2E$ transition [15]. The magnetic moment value (2.1 BM) recorded for copper in the complex lies within the range reported for a d^9 system containing one unpaired electron. This value precludes a metal–metal interaction, perhaps because of the parallel arrangement of the two atoms in the complex (figure 3).

The magnetic moment of [$Ni_2(HDMT)_2(H_2O)_3$] is 2.91 BM, indicating octahedral geometry with a $^3A_{2g}$ ground term [16]. In its electronic spectrum, two bands at 22 220(ν_3) and 14 290 cm^{-1}(ν_2) are observed and attributed to the $^3A_{2g} \rightarrow {}^3T_{1g}$ (P) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) transitions [17] respectively. The spectral data are utilized to compute important ligand field parameters using the spin allowed transitions of the d^8 configuration. The values of B (529 cm^{-1}) and 10 Dq (9524 cm^{-1}) are used to calculate β and ν_1 ($^3A_{2g} \rightarrow {}^3T_{2g}$) to be 0.51 and 9530 cm^{-1} respectively. The electronic spectral data together with the reported magnetic moment value of the Ni(II) complex suggest an octahedral geometry.

The electronic spectrum of [$Co(HDMT)(H_2O)_2$] · H_2O, in DMF, displays two bands at 17 540 and 21 980 cm^{-1} assignable to $^4T_{1g} \rightarrow {}^4A_{2g}$ (ν_2) and $^4T_{1g} \rightarrow {}^4T_{1g}$ (P)(ν_3) transitions [18]. The calculated values of 10 Dq, B and β lie in the range reported for octahedral structures. The magnetic moment (3.6 BM) is found near the spin only value (3.86 BM) with no orbital contribution.

The electronic spectra of [$(VO)_2(HDMT)_2(H_2O)$] in DMF and Nujol mull show two bands at 11 850 and 26 460 cm^{-1} due to $^2B_2 \rightarrow {}^2E$ (ν_1) and charge transfer

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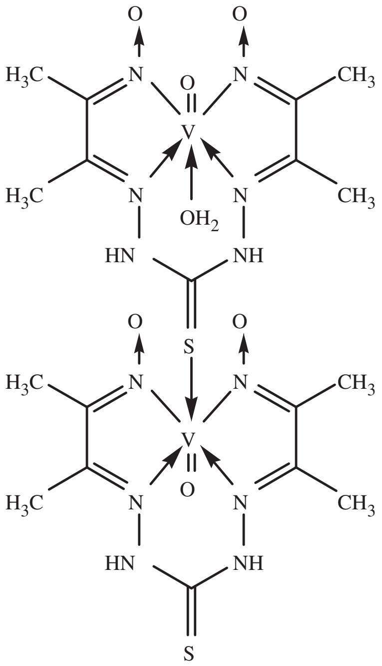

Figure 4. Structure of [$(VO)_2(HDMT)_2$ (H_2O)].

transitions [13], respectively, in an octahedral geometry (figure 4). The spectra were unchanged in the two media indicating that DMF has no effect on the geometry.

The octahedral geometry is preferred for [Pt(DAMT)(OAc)]$\cdot$$2H_2O$ as a characteristic for the d^6 system. The absorption band observed at 26 460 cm^{-1} is attributed to a charge transfer transition, probably O → Pt [19a]. The structure of this complex is represented in figure 5.

Some complexes exhibit a band in the range 23 450–26 320 cm^{-1} which may be due to S → M charge transfer transition [19b]. Electronic spectral data and magnetic moments are given in table 3.

3.5. *ESR Spectra*

The spin Hamiltonian parameters of Cu(II) and VO^{2+} complexes were calculated (table 4). The ESR spectrum of [$Cu_2(HDMT)_2(H_2O)$] (figure 6a) exhibits axially symmetric g-tensor parameters with $g_{\parallel} > g_{\perp} > 2.0023$ indicating that $dx^2 - dy^2$ is the ground state [20]. The $g_{\parallel} = (2.26) > g_{\perp}$ (2.06) $> g_o$ (2.0023) agrees with a square-pyramidal geometry of CuN_4O coordination [21]. A band corresponding to the forbidden magnetic dipolar transition is observed at half-field (ca 1500 G, $g = 4.0$), but the intensity is very weak, indicating that the complex is binuclear [22]. In axial symmetry, the G [$=(g_{\parallel} - 2)/(g_{\perp} - 2)$] value is 4.3 suggesting the absence of exchange coupling between the Cu(II) centers in the solid state [23]. The tendency of $A_{\parallel}$ to decrease with increasing $g_{\parallel}$ is an index for the increase of the tetrahedral distortion in the coordination sphere of Cu [24]. In order to quantify the degree of distortion of the

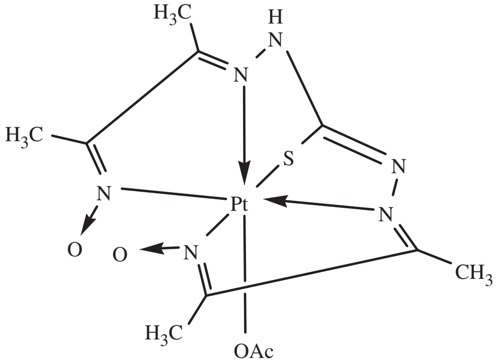

Figure 5. Structure of [Pt(DMT)(OAc]2H$_2$O.

Table 3. Magnetic moments and electronic spectral data of complexes.

Compound	Color	μ_{eff} (BM)	State	d–d bands (cm^{-1})	Charge transfer (cm^{-1})	Supposed structure
[$Cu_2(HDMT)_2(H_2O)$]	Blue	2.10	DMF	12230	26320	Square-pyramidal
[$Ni_2(HMT)_2(H_2O)_3$]	Dark green	2.91	DMF	14290, 22220	–	Octahedral
[$(VO)_2(HDMT)_2(H_2O)$]	Green	0.68	DMF	11850	26460	Octahedral
[$Co(HAM)(H_2O)_2$] · H_2O	Brown	3.60	DMF	17540, 21980	23450	Octahedral
[Pt(DMT)(OAc)] · $2H_2O$	Brown	0.00	DMF	–	26460	Octahedral

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Table 4. ESR data of Cu(II) and VO^{2+} complexes.

Complex	$g_\parallel$	$g_\perp$	$A_\parallel \times 10^{-4}$	g	$g_\parallel/A_\parallel$	α^2	β^2
[$Cu_2(HDMT)_2(H_2O)$]	2.26	2.06	160	4.3	141	0.76	0.85
[$(VO)_2(HDMT)_2(H_2O)$]	1.96	2.04					

Cu(II) complexes, the **f** factor, $g_\parallel/A_\parallel$ (an empirical index of tetrahedral distortion) [25] was selected from the ESR spectra. Although its value ranges between 105 and 135 for square-planar complexes, the values can be much larger in the presence of a tetrahedral distorted structure [24]. For the investigated complex, the $g_\parallel/A_\parallel$ quotient is $141\,cm^{-1}$ supporting the presence of significant dihedral angle distortion in the xy-plane and indicating a tetrahedral distortion from square-planar geometry. Molecular orbital coefficients, α^2 (covalency of the in-plane σ-bonding) and β^2 (covalency of the in-plane π-bonding) were calculated [26, 27]. The α^2 value is found lower than β^2 indicating more covalent character of σ-bonding. The data agree with other reported values [28].

The X-band ESR spectrum (figure 6b) of the VO^{2+} complex gave a single broad line centered around $g = 1.96$, without resolved hyperfine structure. The absence of V hyperfine coupling is common in solid state samples and is attributed to the simultaneous flipping of neighboring electron spins [29] or due to strong exchange interactions, which average out the interaction with the nuclei. The shape of the ESR spectrum corresponds to a paramagnetic species with an axially symmetric g-tensor. A fit of the line shape gives axial g-tensor parameters of $g_\parallel = 1.96$ and $g_\perp = 2.04$; the values agree with those reported for distorted octahedral complexes [30].

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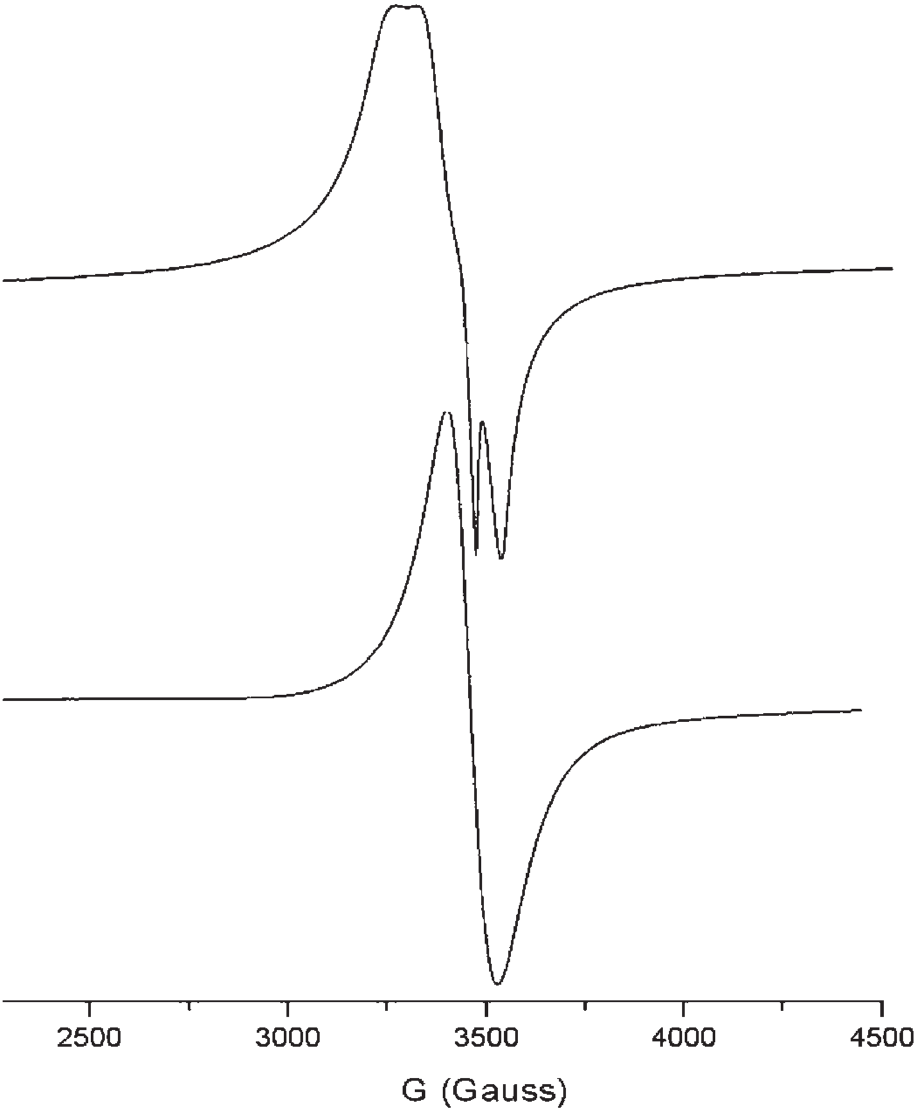

Figure 6. Solid state ESR spectra for the Cu(II) (a) and VO^{2+} (b) complexes at room temperature.

3.6. *Thermal studies*

The TG analysis for the studied complexes displayed high residual at the end of the decomposition indicating high thermal stability. This behaviour may be explained by the existence of five- and six-membered rings. The TG thermogram of $[Cu_2(HDMT)_2(H_2O)]$ shows thermal stability till 184°C. A decomposition stage with weight loss of 30.0 (Calcd 31.5%) is attributed to the removal of $4(C_4H_6)$ from the ligand. In the thermal curve of $[Ni_2(HDMT)_2(H_2O)_3]$, the first step (5.2% weight loss) corresponds to removal of two coordinating water molecule. The second (32.2% weight loss) results from expelling H_2O,o $8CH_3$ and N_2H_2CS at 236–394°C. The TGA curve of

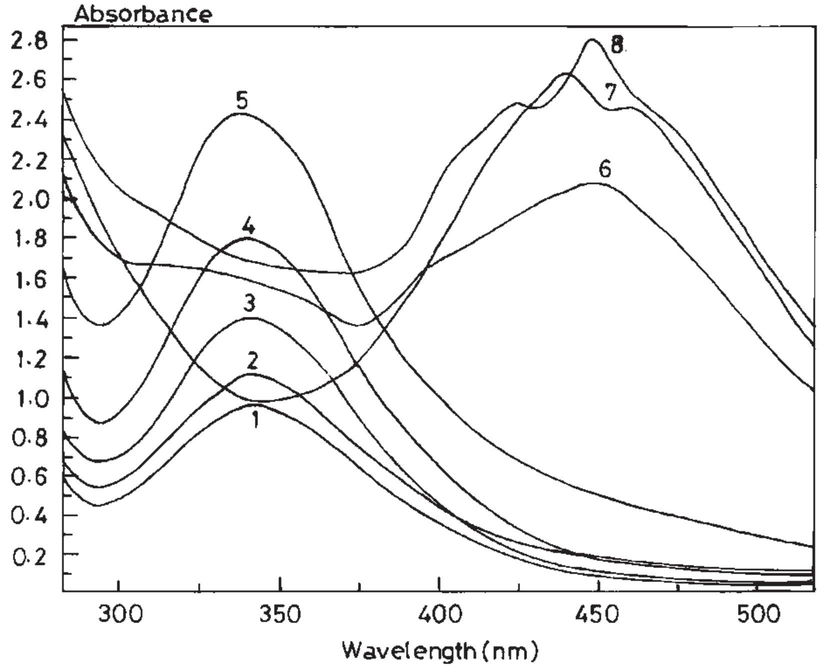

Figure 7. Absorption spectra of the indicator at different pH's: 2.86 (1); 3.90 (2); 4.50 (3); 5.30 (4); 6.00 (5); 7.80 (6); 8.10 (7) and 9.30 (8).

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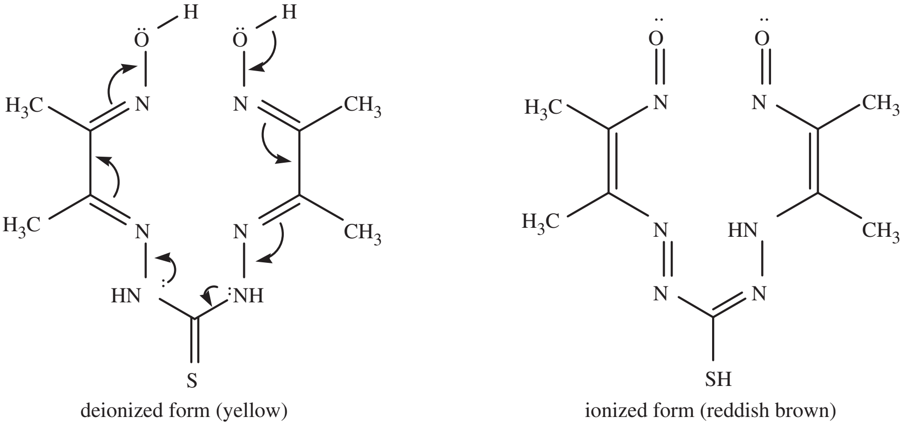
$[Co(HDMT)(H_2O)_2]H_2O$ shows a gradual weight loss (8.7%) due to the loss of two water molecules. The stage ended at 332°C (36.1% weight loss) due to removal of the last coordinating water and $C_4H_6N_2O_2$ as a ligand fragment. The final step ended at 586°C (28.6% weight loss) is corresponding to the removal of $2(CH_3) + N_2H_2CS$. $Co(CN)_2$ is the residual part leaving 26.4% weight loss. $[Pt(DMT)(OAc)] \cdot 2H_2O$ shows a decomposition stage (37–138°C) corresponding to removal of the hydrated water molecules (4.4% weight loss). The stage ending at 377°C (12.6%) is correlated to removal of N_2H_2CS. The final stage ending at 527°C (15.3%) is due to the loss of $2CH_3$ and OAc. The residue reflects a higher stability of such complexes upon heating.

3.7. *Analytical application*

The ligand is brown in the solid state but absorption spectra of the ligand at different pH's (figure 7) show bands at 340 nm (acidic, faint yellow) and 450 nm (basic, reddish brown). The band in basic medium may be due to electron transfer after deprotonation of OH group leading to azo formation (scheme 1) causing darkness of the color. In acidic medium, the faint yellow color may be due to the protonation of the donor groups (OH, NH and/or NH_2) with the absence of azo group. The data abstracted from the figure between pH and the relative absorbance gives the pH interval (6.0–7.8) for the instantaneous color change in acidic and basic media.

The use of such compound in detecting different types of acid–base titrations is promising. For strong acid and base titrations (HCl, NaOH) for $10^{-3}\,g\,eq\,L^{-1}$,



Scheme 1. The ionized and deionized forms of the indicator.

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the proposed indicator reveals a higher conformity with the results of official indicators (pH.pH and M.O). Also, this indicator is better for strong acids and weak bases and vice versa in dilute solutions till $10^{-3}\,\mathrm{g\,eq\,L^{-1}}$ than the usual indicators. The advantage is the higher detection ($10^{-2}\,\mathrm{g\,eq\,L^{-1}}$) of acetic acid and ammonium hydroxide end point; a few mixed indicators are suitable. However, their use is very tedious and requires storage in the dark.

The color change of the present indicator may be understood if Bronsted and chromophore theories are taken into consideration. Bronsted theory refers the color to the ionization: $HI_n \rightarrow H^+ + In^-$ and the chromophore theory to modifications inside the molecule leading to the formation of –N=N– in the ionized form. The proposed mechanism may be explained through scheme 1.

4. Conclusion

H_3DMT is a strong chelating agent coordinating to metal ions as a polydentate ligand, with different tautomeric forms and as a bi and/or trinegative molecule. The complexes have been characterized and their molecular weights evaluated from mass spectra. The Cu(II) complex was square pyramidal while the rest were octahedral. The complexes were stable and their thermal degradation was studied. The deep color of the ligand introduced it as an analytical reagent for weak acid-weak base titrations.

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References

[1] (a) A.A. Abou-Hussen, A.A. Emara. *J. Coord. Chem.*, **57**, 973 (2004); (b) V.Yu. Kukushin, A.J.L. Pombeiro. *Coord. Chem., Rev.*, **181**, 147 (1999).

[2] H. Stunzi. *Aust. J. Chem.*, **35**, 1145 (1982).

[3] M.J.M. Campbell. *Coord. Chem. Rev.*, **5**, 279 (1973).

[4] S. Pandhey, G.B. Kauffman. *Coord. Chem. Rev.*, **63**, 127 (1985).

[5] D.X. West, S.B. Pandhey, P.B. Sonavane. *Struct. Bonding*, **76**, 1 (1991).

[6] D.X. West, A.E. Libertia, S.B. Pandhey. *Coord. Chem. Rev.*, **123**, 49 (1993).

[7] T.A. Blumenkopf, J.A. Hurrington, C.S. Bigham, V.L. Styles, Th. Spector. *J. Med. Chem.*, **35**, 2306 (1992).

[8] A.I. Vogel. *A Text Book of Quantitave Inorganic Analysis*, Longman, London (1994).

[9] U.I. El-Ayaan, G.M. Abou-El-Reash, I.M. Kenawy. *Synth. React. Inorg. Met.-Org. Chem.*, **33**, 327 (2003).

[10] A.A. El-Asmy, M.E. Khalifa, M.M. Hassanian. *Synth. Reac., Inorg. Met.-Org. Chem.*, **28**, 873 (1998).

[11] R.M. El-Shazly, G.A.A. Al-Hazmi, M.S. El-Shahawi, A.A. El-Asmy. *Spectrochimica Acta*, **61A**, 243 (2005).

[12] A.A. El-Asmy, M.E. Khalifa, T.H. Rakha, M.M. Hassanian, A.M. Abdallah. *Chem. Pharm. Bull.*, **48**, 41 (2000).

[13] N.M. El-Metwally, R.M. El-Shazly, I.M. Gabr, A.A. El-Asmy. *Spectrochimica Acta*, **61A**, 1113 (2005).

[14] J.P. Josinski, J.R. Bianchani, J. Cueve, F.A. El-Saied, A.A. El-Asmy, D.X. West. *Z. Anorg. Allg. Chem.*, **629**, 202 (2003).

[15] S. Chanda, X. Sangeetila. *Spectrochimica Acta*, **60A**, 147 (2004).

[16] N.K. Singh, S.B. Singh. *Transition Met. Chem.*, **26**, 487 (2001).

[17] A.A. El-Asmy, M.E. Khalifa, M.M. Hassanian. *Ind. J. Chem.*, **43A**, 92 (2004).

[18] A.A. El-Asmy, M.E. Khalifa, M.M. Hassanian. *Synth. React. Inorg. Met.-Org. Chem.*, **31**, 1787 (2001).

[19] (a) D.A. Skoog, D.M. West, F.J. Holler. *An Introduction of Analytical Chemistry*, Savrders College Publishing (1992); (b) S. Mostafa, M.M. Bekheit, M.M. El-Agez. *Synth. React. Inorg. Met. -Org. Chem.*, **30**, 2029 (2000).

[20] G. Speie, J. Csihony, A.M. Whalen, C.G. Pierpont. *Inorg. Chem.*, **35**, 3519 (1996).

[21] J.L. Mesa, J.L. Pizarro, M.I. Arriortua. *Cryst. Res. Technol.*, **33**, 3489 (1998).

[22] C.C. Wagner, E.J. Baran. *Acta Farm. Bonaerense*, **22**, 137 (2003).

[23] (a) B.J. Hathaway, D.E. Billing. *Coord. Chem. Rev.*, **5**, 143 (1970); (b) B.J. Hathaway. *Struct. Bonding*, **57**, 55 (1984).

[24] (a) J.A. Wellman, F.B. Hulsbergen. *J. Inorg. Nucl. Chem.*, **40**, 143 (1978); (b) U. Sagakuchi, A.W. Addison. *J. Chem. Soc. Dalton Trans.*, 660 (1979).

[25] H. Yokoi, A.W. Addison. *Inorg. Chem.*, **16**, 1341 (1977).

[26] K. Jayasubramanian, S.A. Samath, S. Thambidurai, R. Murugesan, S.K. Ramalingam. *Transition Met. Chem.*, **20**, 76 (1995).

[27] V.S.X. Anthonisamy, R. Anantharam, R. Murugesan. *Spectochimica Acta*, **55A**, 135 (1999).

[28] R.K. Ray, G.R. Kauffman. *Inorg. Chem. Acta*, **173**, 207 (1990).

[29] J. Costa Pessoa, I. Cavaco, I. Correia, D. Costal, R.T. Henriques, R.D. Gillard. *Inorg. Chim. Acta*, **305**, 7 (2000).

[30] R.C. Maurya, S. Rajput. *J. Molecular Structure*, **687**, 35 (2004).

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