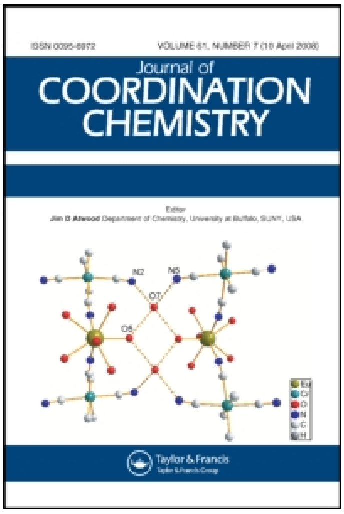

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Synthesis and spectroscopic characterization of new mono- and binuclear complexes of some NH(1) thiosemicarbazides

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Synthesis and spectroscopic characterization of new mono- and binuclear complexes of some NH(1) thiosemicarbazides

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4-Ethylthiosemicarbazide and its NH(1) derivatives have been prepared and confirmed by elemental analysis and ^{1}H NMR spectra to produce diverse complexes with Co(II), Ni(II) and Cu(II) ions. The obtained complexes have been investigated based on elemental and thermal analyses, spectral (UV/VIS, ESR, mass) studies and magnetic measurements. The IR data reveal the presence of variable modes of chelation for the investigated ligands. The electronic spectra of the complexes as well as their magnetic moments provide information about geometries. The ESR spectra give evidence for the proposed structure and the bonding for some Cu(II) complexes. Thermal decomposition of some complexes ended with metal or metal oxide as a final product.

Keywords: Thiosemicarbazides; Complexes; ^{1}H NMR; Mass; ESR spectra; Thermal analysis

1. Introduction

The chemistry of substituted thiosemicarbazides and their metal complexes has been a focus over the last three decades because thione compounds can act as anticarcinogenic or antitumour reagents [1–5]. Moreover, these compounds have priority for preconcentration of some pollutants and precious ions [6]. Our previous studies on thiosemicarbazides were focused on the NH(4) and NH(1) substitutents comprising aliphatic [7], aromatic [8] and/or heteroaromatic [9] ligands beside those containing bis-thiosemicarbazides [10]. Also, recently [11], new complexes of some thiosemicarbazides were characterized with VO^{2+} ions. Continuation by investigation for new Cu(II), Co(II) and Ni(II) complexes with 4-ethylthiosemicarbazide (HETS) and its NH(1) derivatives (figure 1) are reported herein.

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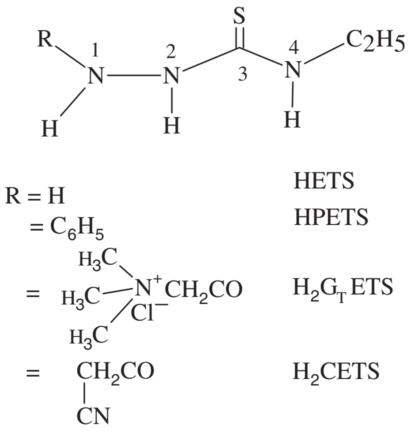


Figure 1. Formula of ligands.

2. Experimental

2.1. *Materials*

The acetate and chloride salts of Co(II), Ni(II) and/or Cu(II), ethylisothiocyanate, hydrazine hydrate, phenyl hydrazine, Girard's T, ethylcyanoacetate, DMF, DMSO and the other solvents were reagent grade (BDH or Merck).

2.2. *Preparation of ligands*

The thiosemicarbazide derivatives comprising 4-ethylthiosemicarbazide (HETS) and its NH(1) derivatives – phenyl (HPETS), trimethylammonium chloride acetyl (H_2G_TETS) and cyanoacetyl (H_2CETS) thiosemicarbazides – are shown in figure 1. The compounds were synthesized by reacting equimolar amounts of ethylisothiocyanate (0.1 mol) with hydrazine hydrate or its derivatives (phenylhydrazine, Girard T reagent or cyanoacetylhydrazine), 0.1 mol, in 20 mL absolute ethanol. The reactants were heated under reflux for ≈ 2 h. After cooling, white crystals were obtained for each prepared ligand. This procedure was used for all preparations except 4-ethylthiosemicarbazide, which was isolated directly by cooling the reactants without heating (this compound is also provided from Merck). The crystals were removed by filtration, washed with ethanol and diethyl ether, and finally dried. The ^1H NMR spectra of HPETS, H_2G_TETS and H_2CETS showed the following data:

- HPETS: (δ) 1.06 (t, CH_3CH_2); 3.43 (q, CH_2CH_3); 6.69–7.25 (m, C_6H_5); 7.85 (s, NHCS–); 8.13 (t, CH_2NH); 9.25 (s, NHPh–).
- H_2G_TETS: (δ) 1.06 (t, CH_3CH_2); 3.89 [s, s, $(CH_3)_3$]; 4.34 (s, N–CH_2); 8.43 (s, NH), 9.33 (s, N^2H).
- H_2CETS: (δ) 1.10 (t, CH_3CH_2); 3.22 (s, $(CH_2CN)_3$); 3.46 (q, CH_2CH_3), 7.79(s, N^4H), 9.10 (s, N^2H) and 9.98 (s, N^1H).

2.3. *Preparation of the metal complexes*

In this investigation, the chloride and/or the acetate salts of Cu(II), Co(II) and Ni(II) are used. The complexes were prepared by reacting the required amounts for 1 : 1

ratio from both the ligand (0.01 mol) and the metal salt (0.01 mol) in 50 mL of absolute ethanol. The reaction mixtures were heated under reflux for a time (1–4 h) depending on the metal salt used. The precipitate thus formed was filtered off, washed several times with ethanol and diethylether, and then dried.

2.4. *Procedure for the pH-metric titration*

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

(1) 2.5 mL of HCl (10^{-2} mol L^{-1}) + 1.25 mL of KCl (1.0 mol L^{-1}) + 10 mL of ethanol.
(2) 2.5 mL of HCl + 1.25 mL of KCl + 0.25 mL (10^{-2} mol L^{-1}) of ligand + 9.75 mL of ethanol.
(3) Solution b + 0.05 mL (10^{-2} mol L^{-1}) of metal ion.

All the above solutions were completed to 25 mL with twice-distilled water and titrated against 0.99×10^{-2} mol L^{-1} NaOH.

2.5. *Measurements*

The infrared spectra of the ligands and their isolated solid complexes were recorded as KBr discs on a Mattson 5000 FTIR spectrophotometer. The ^{1}H NMR spectra in d$_6$-DMSO for the ligands were recorded on a Varian Gemini spectrometer (200 MHz) at Cairo University. Mass spectra for three Cu(II) complexes were recorded on a Varian MAT 311 instrument at the National Research Center, Cairo. The UV/VIS spectra of the complexes were recorded on a UV$_2$ Unicam UV/VIS spectrophotometer using a 1 cm stoppered silica cell at Mansoura University. The ESR spectra were recorded for $[Cu_2(ETS)(OAc)_3(H_2O)_2] \cdot \frac{1}{2}H_2O$, $[Cu(HPETS)_3(OAc)_2]$ and $[Cu(HCETS)_2(H_2O)]$ 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 the modulation amplitude was set at 4 Gauss. The low field signal was obtained after four scans with a 10-fold increase in the receiver gain. A powder spectrum was obtained in a 2 mm quartz capillary at room temperature. Thermogravimetric curves (TGA and DTG) between 20 and 1000°C were recorded on a Shimadzu thermogravimetric analyser, TGA-50 at Mansoura University. The nitrogen flow and heating rates were 20 mL min^{-1} and 10°C min^{-1}, respectively, using α-Al$_2$O$_3$ as a reference. The pH-metric titrations were performed using a Metrohm E$_{536}$ potentiograph equipped with a 665 DOSIMAT (Metrohm, Herisau, Switzerland). The combined glass electrode was standardized before using with buffer solutions produced by Fisher's (Fairlawn, NJ). Magnetic measurements were carried out on a Johnson Matthey magnetic balance, UK. The effective magnetic moments were evaluated by applying: $\mu_{\mathrm{eff}} = 2.828\sqrt{\chi_{\mathrm{M}}^{-} T}$ 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. Elemental analyses as carbon and hydrogen content for the investigated complexes were determined at the Microanalytical Unit, Cairo University, Egypt. The Ni(II), Co(II) and Cu(II) analysis was carried out complexiometrically by well-known standard methods [12]. The chloride content was gravimetrically determined as AgCl.

3. Results and discussion

Cobalt(II), nickel(II) and copper(II) chloride or acetate offer new complexes with 4-ethylthiosemicarbazide (HETS), 4-ethyl-1-phenylthiosemicarbazide (HPETS), 4-ethyl-1-tri-methylammonium chloride acetylthiosemicarbazide (H_2G_TETS) and 4-ethyl-1-cyanoacetyl-thiosemicarbazide (H_2CETS). All the isolated complexes are stable under atmospheric conditions and insoluble in most common organic solvents except dimethylformamide (DMF) and dimethylsulphoxide (DMSO), which dissolve the complexes without interaction. All have melting points above 300°C except $[Co(H_2G_TETS)(H_2O)Cl_2]\cdot C_2H_5OH$, which melts at 195°C. The molar conductivities of DMF soluble complexes were measured, and all show a non-conducting character except $[Cu(HPETS)_2(H_2O)Cl]Cl$, which measured $50\,\Omega^{-1}\,cm^2\,mol^{-1}$ corresponding to 1 : 1 electrolyte [13]. Moreover, the complexes containing Girard's T reagent have conductance values due to the chloride inside the ligand itself. The C, H and N analyses for the isolated complexes are consistent with those calculated for the suggested formulas and presented in table 1.

3.1. *IR spectra of metal complexes*

A careful comparison between IR spectra of the ligands and their complexes gave an insight into the modes of bonding. The conjugated anions allow the ligand to interact through the protonated and/or deprotonated form. The use of metal chloride or acetate shows different modes of chelation in such complexes.

Monodentate character through the thione sulphur occurs for $[Co(H_2G_TETS)(H_2O)Cl_2]\cdot C_2H_5OH$ (blue), $[Cu(HPETS)_3(OAc)_2]$ (dark green) and $[Cu(HPETS)_2(H_2O)Cl]Cl$ (olive green). This is supported by: (1) the lower shift of $\nu(C{=}S)$ from ≈ 770 to 719–760 cm^{-1}, (2) the lack of shift of the $\nu(C{=}O)$ band at 1700 cm^{-1}, ruling out its coordination in the first complex, and (3) the appearance of new bands

Table 1. Analytical and physical data for the metal complexes.

Complex F. wt found (Calcd)	Colour	Elemental analysis (%) found (Calcd)			
		C	H	Cl	M
$[Co(ETS)_2]\cdot \frac{1}{2}C_2H_5OH$	Deep red	26.1 (26.3)	5.2 (6.0)	–	18.4 (18.4)
$[Co(PETS)(OH)(H_2O)]$	Dark green	37.0 (37.5)	4.9 (5.2)	–	21.1 (20.4)
$[Co(H_2G_TETS)(H_2O)Cl_2]\cdot C_2H_5OH$	Blue	27.5 (26.7)	5.0 (6.0)	22.8[a] (23.7)	13.1 (13.1)
$[Co_2(G_TETS)(OAc)(OH)(H_2O)_3]\cdot C_2H_5OH$	Dark brown	25.9 (26.3)	5.6 (6.1)	6.3[a] (6.5)	22.1 (21.5)
$[Co(HCETS)(OAc)(H_2O)_2]\cdot H_2O$	Brown	26.1 (26.8)	4.2 (5.1)	–	17.3 (16.4)
$[Ni(ETS)(OAc)(H_2O)_2]$	Green	21.2 (22.0)	5.6 (5.5)	–	21.3 (21.5)
$[Ni(PETS)(OAc)(H_2O)_2]\cdot \frac{1}{2}H_2O$	Dark green	38.0 (37.8)	4.8 (5.5)	–	16.6 (16.8)
$[Ni(G_TETS)(H_2O)]\cdot H_2O$	Dark brown	27.3 (27.5)	6.3 (6.1)	–	16.5 (16.8)
$[Ni(HCETS)(OAc)(H_2O)]\cdot H_2O$	Yellow	28.3 (28.2)	4.8 (4.7)	–	17.5 (17.3)
$[Cu_2(ETS)(OAc)_3(H_2O)_2]\cdot \frac{1}{2}H_2O$ 468 (468.4)	Dark blue	23.3 (23.1)	4.1 (4.7)	–	27.4 (27.1)
$[Cu(HPETS)_2(H_2O)Cl]Cl$ 542 (543.2)	Olive green	40.1 (39.8)	5.0 (5.2)	13.5 (13.1)	11.1 (11.7)
$[Cu(HPETS)_3(OAc)_2]$	Dark brown	48.3 (48.5)	5.2 (5.9)	–	8.5 (8.3)
$[Cu(H_2G_TETS)(H_2O)_2Cl_2]\cdot 1\frac{1}{2}H_2O$ 454 (453)	Green	22.1 (21.2)	5.4 (5.8)	23.1[a] (23.4)	14.5 (14.0)
$[Cu_2(HG_TETS)(OH)_3(H_2O)]\cdot \frac{1}{2}C_2H_5OH$	Green	23.3 (22.8)	4.5 (5.5)	5.7[a] (5.7)	27.2 (26.8)
$[Cu(HCETS)_2(H_2O)]$	Brown	31.3 (31.9)	4.3 (4.4)	–	14.8 (14.0)

[a] Cl^- of the ligand.

attributed to ν(M ← S) [14], (M–Cl) [15] and ν(M–O) [16] at ≈330, 290 and 470 cm^{-1}, respectively.

Bidentate nature in the neutral state is represented in $[Cu(H_2G_TETS)(H_2O)_2 Cl_2]\cdot 1\frac{1}{2}H_2O$ (green) or mononegative in $[Ni(ETS)(OAc)(H_2O)_2]$ (green), $[Ni(PETS)(OAc)(H_2O)_2]\cdot \frac{1}{2}H_2O$ (dark green), $[Co(ETS)_2]^{-}\cdot \frac{1}{2}C_2H_5OH$ (deep red), $[Co(PETS)(OH)(H_2O)]$ (dark green) and $[Cu(HCETS)_2(H_2O)]$ (brown). The neutral behaviour is based on: (1) the lower shift of ν(C=S) from 780 to 750 cm^{-1}; (2) the ν(NH) bands change in position or intensity, so the thione sulphur and NH group are the two sites of coordination. Mononegative coordination is confirmed by the supplementary data abstracted from a comparison between the complex and their relative ligands. 4-Ethylthiosemicarbazide coordinates via the thiol sulphur and either NH_2 with Ni(II) and Cu(II) or NH with Co(II). This is shown by the disappearance of ν(C=S) followed by the simultaneous appearance of ν(C–S) and ν(C=N) [17] bands at ≈640 and ≈1640 cm^{-1}, respectively, and the appearance of new bands characteristic for ν(M–N) and ν(M–S) at ≈450 and 360 cm^{-1}, respectively [16]. Also, the appearance of two new bands in the Ni(II) and Cu(II) spectra at ≈1420 and ≈1520 cm^{-1} is characteristic for the ν_s and ν_{as} of bidentate acetate [18].

4-Ethyl-1-phenylthiosemicarbazide (HPETS) is the other derivative which coordinates to the Co(II) and Ni(II) ions through two donation sites, thiol S and N^1H. This chelation mode is supported by the disappearance of ν(C=S) and the appearance of ν(C–S) and ν(C=N) bands at ≈660 and ≈1580 cm^{-1}, respectively, as well as the appearance of new bands for M–N and M–S stretching vibrations at ≈400 and 360 cm^{-1}, respectively. The nickel spectrum shows two additional bands at 1403 and 1532 cm^{-1} from bidentate acetate.

3.2. *Electronic and magnetic studies*

The electronic spectra of the complexes as well as their magnetic values (table 2) offer good evidence for variable structures. Hexa-coordination for the brown Co(II) complexes, $[Co_2(G_TETS)(OAc)(OH)(H_2O)_3]\cdot C_2H_5OH$ and $[Co(HCETS)(OAc)(H_2O)_2]\cdot H_2O$, is suggested, based on the appearance of 19,455 and (14,790–16,290) cm^{-1} bands in the spectra recorded in DMSO. The bands are almost the same as those in the spectra recorded in nujol mull. The bands are attributed to the $^4T_{1g} \rightarrow {}^4T_{1g}$ (p) and $^4T_{1g} \rightarrow {}^4A_{2g}$ transitions, respectively [19], in an octahedral structure around the Co(II) ion. Such octahedral structure mixed with square-planar is suggested for $[Co_2(G_TETS)(OAc)(OH)(H_2O)_3]\cdot C_2H_5OH$ (figure 2) and supported by the presence of an additional band at 21,270 cm^{-1} in its spectrum. The lower magnetic moment (2.96 B.M.) is good evidence for the proposed stereochemistry [20]. The second complex, $[Co(HCETS)(OAc)(H_2O)_2]\cdot H_2O$, has a (3.86 B.M.) magnetic moment value, close to the spin only moment [21]. The ligand field parameters (10 Dq = 4493 cm^{-1}, $B = 898$ cm^{-1} and $\beta = 0.91$) calculated for the second complex were similar to those reported previously [22]. The lower values (10 Dq = 4165 cm^{-1}, $B = 832$ cm^{-1} and $\beta = 0.86$) calculated for the first complex indicate the proposed mixed stereochemistry [17]. The β values (≈1) reveal more ionic bonding with the metal ions. The second complex has a more ionic character than the first. The tetra-coordination represented in a tetrahedral structure for $[Co(PETS)(OH)(H_2O)]$ and $[Co(H_2G_TETS)(H_2O)Cl_2]\cdot C_2H_5OH$ is observed in DMSO spectra. The bands at 13,050–14,790 cm^{-1} assigned to $^4A_2 \rightarrow {}^4T_1$ and at 21,645–18,115 cm^{-1} as a charge

Table 2. Magnetic moments, electronic spectral bands and ligand field parameters of the complexes.

				Ligand field parameters			
Complex	μ_{eff} (B.M.)	State	Charge transfer and d–d transition band (cm^{-1})	B (cm^{-1})	β	10 Dq (cm^{-1})	Suggested geometry
$[Co(ETS)_2] \cdot \frac{1}{2}C_2H_5OH$	3.09	Nujol	18,620	–	–	–	–
		DMSO		–	–	–	Square-planar
$[Co(PETS)(OH)(H_2O)]$	4.49	DMSO	21,640, 13,050	700	0.72	4444	Tetrahedral
$[Co(H_2G_TETS)(H_2O)Cl_2] \cdot C_2H_5OH$	4.70	DMSO	18,115, 14,790	903	0.93	3320	Tetrahedral
$[Co_2(G_TETS)(OAc)(OH)(H_2O)_3] \cdot C_2H_5OH$	2.96	DMSO	21,270, 19,455, 16,290	832	0.86	4165	Square-planar + octahedral
$[Co(HCETS)(OAc)(H_2O)_2] \cdot H_2O$	3.86	DMSO	19,455, 14,830	898	0.91	4493	Octahedral
$[Ni(ETS)(OAc)(H_2O)_2]$	2.90	DMSO	15,380, 26,525	589	0.60	10,525	Octahedral
$[Ni(PETS)(OAc)(H_2O)_2] \cdot \frac{1}{2}H_2O$	1.05	DMSO	16,360, 21,880, 25,910	678	0.65	10,705	Octahedral + square-planar
$[Ni(G_TETS)(H_2O)]H_2O$	3.59	DMF	18,000	–	–	–	Tetrahedral
$[Ni(HCETS)(OAc)(H_2O)] \cdot H_2O$	2.00	DMF	14,510, 19,340	–	–	–	Tetrahedral + square-planar
$[Cu_2(ETS)(Oac)_3(H_2O)_2] \cdot \frac{1}{2}H_2O$	1.69	DMSO	19,230, 10,740	–	–	–	Square-pyramid
		Nujol	19,230, 10,990	–	–	–	–
$[Cu(HPETS)_2(H_2O)Cl]Cl$	1.33	DMSO	21,185, 15,410	–	–	–	Square-pyramid
		Nujol	22,025, 15,770	–	–	–	
$[Cu(HPETS)_3(OAc)_2]$	1.13	DMSO	21,000, 14,285	–	–	–	Octahedral
		Nujol	20,370, 14,280	–	–	–	–
$[Cu(H_2G_TETS)(H_2O)_2Cl_2] \cdot 1\frac{1}{2}H_2O$	1.35	DMSO	22,760, 17,540, 13,930	–	–	–	Octahedral
		Nujol	184,800, 13,370	–	–	–	–
$[Cu_2(HG_TETS)(OH)_3(H_2O)] \cdot \frac{1}{2}C_2H_5OH$	0.95	DMSO	14,140	–	–	–	Distorted octahedral
		Nujol	21,830, 16,980	–	–	–	–
$[Cu(HCETS)_2H(H_2O]$	1.90	DMSO	22,220, 16,390	–	–	–	Square-pyramid
		Nujol	16,660	–	–	–	–

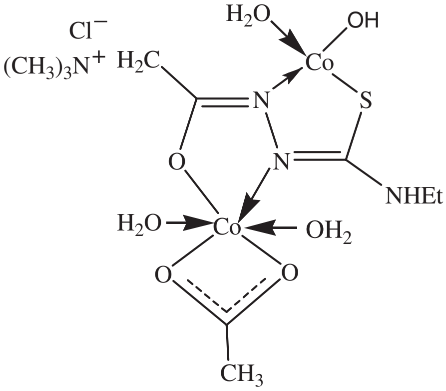


Figure 2. Proposed structure of $[Co_2(G_TETS)(OAc)(OH)(H_2O)_3]\cdot C_2H_5OH$.

transfer are suggested for the two complexes [23]. The magnetic moment values (4.49 and 4.70 B.M.) are good evidence for this proposal. The ligand field parameters (table 2) reveal an ionic character for $[Co(H_2G_TETS)(H_2O)Cl_2]\cdot C_2H_5OH$ and a high splitting energy (10 Dq) for $[Co(PETS)(OH)(H_2O)]$. Square-planar geometry is proposed for $[Co(ETS)_2]\cdot {}^1\!/\!_2C_2H_5OH$ through the presence of a characteristic band at $18650\,cm^{-1}$ as well as its magnetic moment (3.09 B.M.) value [24].

The electronic spectra of the Ni(II) complexes recorded in DMSO reveal different structures. An octahedral geometry is proposed for $[Ni(ETS)(OAc)(H_2O)_2]$ assigning the bands at 15,380 and $26{,}525\,cm^{-1}$ to the ${}^3A_{2g}\rightarrow{}^3T_{1g}$ (F) and ${}^3A_{2g}\rightarrow{}^3T_{1g}$ (P) transitions [25], respectively. The ligand field parameters (10 Dq, B and β) were calculated for the d^8 system, and their values ($10{,}525\,cm^{-1}$, $589\,cm^{-1}$ and 0.6) agree well with those reported for six coordination [26]. The magnetic moment value (2.90 B.M.) is further confirmation. The tetrahedral geometry in $[Ni(G_TETS)(H_2O)]\cdot H_2O$ is characterized by the $18{,}000\,cm^{-1}$ band, assigned to the ${}^3T_1\rightarrow{}^3T_1$ (P) transition, and a normal magnetic moment (3.59 B.M.). Mixed stereochemistry is suggested for the $[Ni(PETS)(OAc)(H_2O)_2]$ and $[Ni(HCETS)(OAc)(H_2O)]$–H_2O complexes, based on the appearance of bands at 21,880, 25,910 and $16{,}365\,cm^{-1}$ in the spectrum of the first complex consistent with square-planar + octahedral stereochemistry [27]. This is confirmed by the small 1.05 B.M. magnetic moment. Square-planar + tetrahedral is sugggested for the second complex indicated by the presence of two bands at 19,340 and $14{,}510\,cm^{-1}$. The first band is due to the ${}^1A_{1g}\rightarrow{}^1A_{2g}$ transition in a square-planar geometry [28] and the other to the ${}^3T_1\rightarrow{}^3T_1$ (P) transition in a tetrahedral configuration. The proposed structure is supported by a low magnetic moment (2.0 B.M.) measured for the complex.

The electronic spectra of the Cu(II) complexes recorded in Nujol and DMSO are similar, even with different geometries. Distorted octahedral geometry is suggested for $[Cu(HPETS)_3(OAc)_2]$ and $[Cu(H_2G_TETS)(H_2O)_2Cl_2]\cdot 1{}^1\!/\!_2H_2O$ based on the appearance of a broad band centred at 14,280 and $13{,}930\,cm^{-1}$, respectively, attributed to the ${}^2E_{2g}\rightarrow{}^2T_{2g}$ transition [29]. The distortion is due to the Jahn–Teller effect [30]. The two spectra show a broad band centred at 21,000 and $22{,}760\,cm^{-1}$, respectively, assigned to a charge transfer, probably LMCT [31]. Previous studies on Cu(II) complexes with thiosemicarbazones [32] proved that the $21{,}785$–$24{,}750\,cm^{-1}$ band

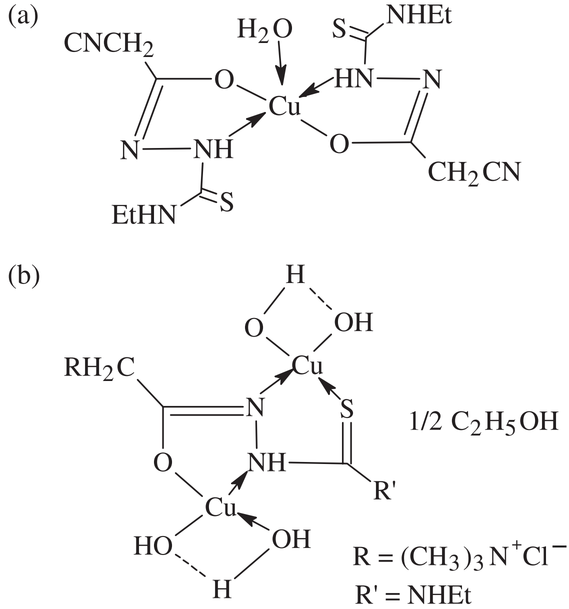


Figure 3. Proposed structure of: (a) $[Cu(HCETS)_2(H_2O)]$ and (b) $Cu_2(HG_TETS)(OH)_3(H_2O)] \cdot ½C_2H_5OH$.

is due to $S \rightarrow Cu(II)$ transition. Square-pyramidal geometry for $[Cu_2(ETS)(OAc)_3(H_2O)_2] \cdot ½H_2O$ and $[Cu(HCETS)_2H_2O]$ (figure 3a), is based on the presence of bands at 10,740 and 19,230 cm^{-1} for the first complex and at 16,390 and 22,220 cm^{-1} for the second. These are assigned to the $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively [30]. Because of the low intensity, the $^2B_{1g} \rightarrow {}^2B_{2g}$ transition is not observed as a separate band in the tetragonal field. Square-planar geometry is suggested for $[Cu(HPETS)_2(H_2O)Cl]Cl$ and $[Cu_2(HG_TETS)(OH)_3(H_2O)] \cdot ½C_2H_5OH$ (figure 3b) from the presence of bands at 15,770 and 22,025 cm^{-1} for the first complex and at 14,140 and 22,730 cm^{-1} for the second. The first band is assigned to the $^2B_1 \rightarrow {}^2E$ and $^2B_1 \rightarrow {}^2A_1$ transitions [30], while the second band is due to charge transfer. The magnetic moment values for the two Cu(II) complexes are normal and lower (1.9, 0.95 B.M.) than expected (1.7–2.2 B.M.) for one unpaired electron. The lower value may be due to strong interaction with the neighbouring molecule.

3.3. *Mass spectra*

The mass spectra of $[Cu_2(ETS)(OAc)_3(H_2O)_2] \cdot ½H_2O$, $[Cu(HPETS)_2(H_2O)Cl]Cl$ and $[Cu_2(HG_TETS)(OH)_3(H_2O)] \cdot ½C_2H_5OH$ represented in table 1 provide confirmation for the suggested formula. The mass spectrum of $[Cu_2(ETS)(OAc)_3(H_2O)_2] \cdot ½H_2O$ is taken as a representative example (figure 4). It shows multiple peaks representing successive degradation of the molecule. The first peak at $m/e = 468$ (Calcd 468.4) represents the molecular ion of the complex with 19.77% abundance. The base peak (100% abundance) with $m/e = 64$ represents the final residue (Cu). Plausible degradation steps of the complex are shown in scheme 1.

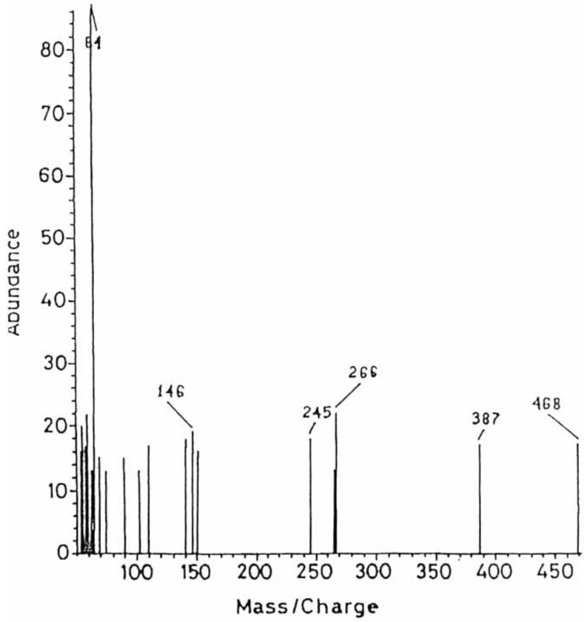


Figure 4. Mass spectrum of $[Cu_2(ETS)(OAc)_3(H_2O)_2] \cdot \frac{1}{2}H_2O$.

$[Cu_2(C_3H_9N_3S)(OAc)_3] \cdot 2H_2O$

↓ $-[2H_2O + C_2H_6N]$
81 (80)

$[Cu_2(CH_3N_2S)(OAc)_3]$

↓ $-2(OAc)$
121 (118)

$[Cu_2(CH_3N_2S)(OAc)]$

↓ $-Cu(OAc)$
120 (122.5)

$[Cu(CH_3N_2S)]$

↓ $-CH_3N_2S$
82 (75)

Cu 64 (63.5)

Scheme 1. Degradation scheme for $[Cu_2(ETS)(OAc)_3(H_2O)_2]$.

3.4. *ESR spectra*

To obtain further information about the stereochemistry and the metal ligand bonding, and to determine the magnetic interaction in the metal complexes, ESR spectra of $[Cu_2(ETS)(OAc)_3(H_2O)_2] \cdot \frac{1}{2}H_2O$ (**1**), $[Cu(HPETS)_3(OAc)_2]$ (**2**) and $[Cu(HCETS)_2(H_2O)]$ (**3**) were recorded in the solid state. The spin Hamiltonian parameters for the

Cu(II) complexes ($S = 1/2$, $I = 3/2$) were calculated (table 3). The room-temperature solid-state ESR spectra are quite similar and exhibit axially symmetric *g*-tensor parameters with $g_{\parallel} > g_{\perp} > 2.0023$ indicating that the copper site has a $d_{x^2-y^2}$ ground-state characteristic for square-planar, square-pyramidal or octahedral stereochemistry [33]. In axial symmetry, the *g*-values are related by the expression, $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$, where G is the exchange interaction parameter. According to Hathaway [34], the exchange interaction between copper(II) centres in the solid state is negligible if $G > 4$, but a considerable exchange interaction is indicated in the solid complex if $G < 4$. The calculated G values are given in table 3.

The powder ESR spectral profiles (figure 5) of complexes **1** and **3** are very similar and typical for square-pyramidal Cu(II) complexes [35–38]. A forbidden magnetic dipolar transition for complex **1** is observed at half-field (*c.* 1500 *G*, $g = 4.0$), but the intensity is very weak. Its spectrum is similar to that of binuclear Cu(II) complexes [39]. The appearance of a half-field signal confirms the binuclear unit with a magnetic interaction between the two Cu(II) ions; this is not observed in complex **2**, which is mononuclear.

The room-temperature ESR spectrum of complex **2** displayed a poorly resolved broad asymmetric signal with spin Hamiltonian parameters $g_{\parallel} = 2.34$ and $g_{\perp} = 2.07$.

Table 3. ESR data of some copper(II) complexes at room temperature.

Complex	$g_{\parallel}$	$g_{\perp}$	$A_{\parallel} \times 10^{-4}$ (cm^{-1})	G	α^2	β^2
1	2.22	2.06	165	3.6	0.74	0.70
2	2.34	2.07	–	–	–	–
3	2.25	2.05	170	5.0	0.89	0.69

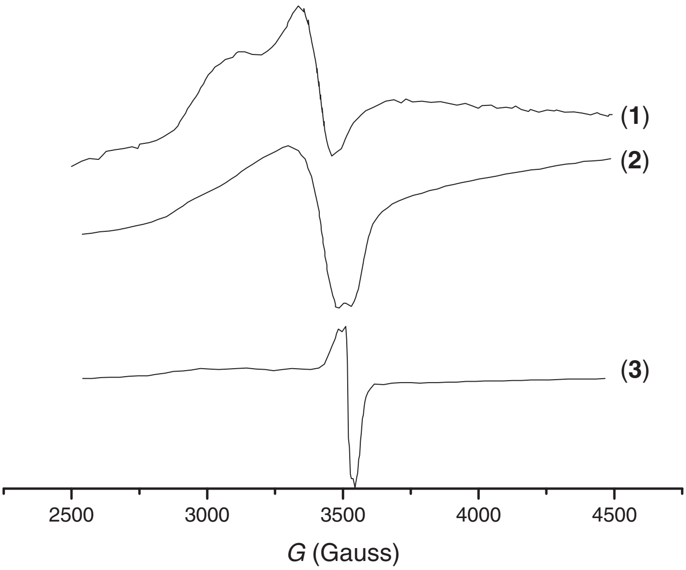


Figure 5. Solid state X-band ESR spectra for $[Cu_2(ETS)(OAc)_3(H_2O)_2] \cdot ½H_2O$ (**1**), $[Cu(HPETS)_3(OAc)_2]$ (**2**) and $[Cu(HCETS)_2(H_2O)]$ (**3**) at room temperature.

These values are consistent with a distorted octahedral complex [37] with no hyperfine splitting in the parallel feature. It is difficult to interpret quantitatively this broad band. Qualitatively, it is clear that these features were due to intramolecular spin–spin interaction arising from solid-state effects. This may be due to strong interactions persisting in the complex, where neighbouring magnetic dipoles tend to align in the opposite direction, resulting in a decrease in the magnetic moment. The low magnetic moment of complex **2** indicates the presence of a strong exchange interaction in the solid state, which may be due to the presence of sulphur coordination [40]. Superhyperfine structures for these complexes are not observed at a high field excluding any interaction of the nuclear spins of the nitrogen ($I = 1$) with the unpaired electron density on Cu(II). The exchange interaction parameter, G, in the first complex is less than four, suggesting that a copper–copper exchange interaction exists, while in complex **3**, the value ($G > 4$) suggests the absence of exchange coupling between copper(II) centres in the solid state [33].

Molecular orbital coefficients, α^2 (a measure of the covalency of the in-plane σ-bonding) and β^2 (covalent in-plane π-bonding) were calculated using the following equations [41]:

$$\alpha^2 = (A_{\parallel}/0.036) + (g_{\parallel} - 2.0023) + 3/7(g_{\perp} - 2.0023) + 0.04$$

$$\beta^2 = (g_{\parallel} - 2.0023)E/ - 8\lambda\alpha^2,$$

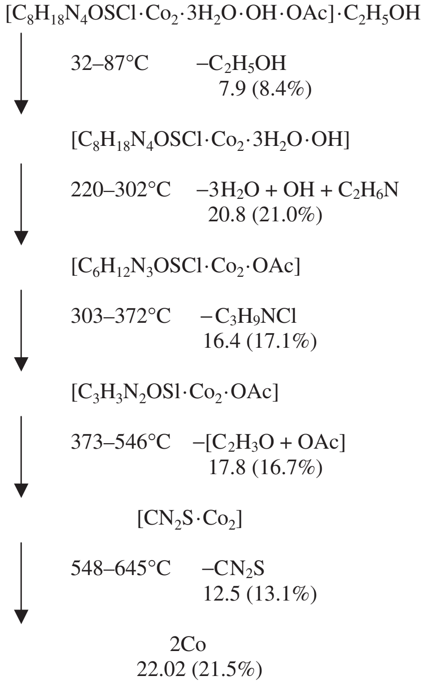
where $\lambda = -828\,\text{cm}^{-1}$ for the free copper ion, and E is the electronic transition energy.

As a measure of the covalency of the in-plane σ-bonding, $\alpha^2 = 1$ indicates a complete ionic character, whereas $\alpha^2 = 0.5$ denotes 100% covalent bonding, with the assumption of negligibly small values of the overlap integral. The smaller the β^2, the larger the covalency of the bonding. The values of α^2 and β^2 for complex **1** indicate that the in-plane σ-bonding and in-plane π-bonding are appreciably covalent, and are consistent with very strong in-plane σ-bonding in these complexes, whereas the in-plane π-bonding is almost covalent. These results are anticipated because there are appropriate ligand orbitals to combine with the d_{xy} orbital of the copper(II) ion. The lower values of β^2 compared with α^2 indicate that the in-plane π-bonding is more covalent than the in-plane σ-bonding. These data are consistent with other reported values [34, 41, 42].

3.5. *Thermal analysis*

The thermogravimetric (TGA and DTGA) analysis (25–1000°C) for some complexes was recorded to distinguish between the coordinated and hydrated solvents and to give an insight into the thermal stability of the studied complexes.

The curves obtained for $[Co(H_2G_TETS)(H_2O)Cl_2] \cdot C_2H_5OH$ showed thermal stability up to 180°C; the stability may be explained by hydrogen bonding of ethanol with sulphur. The first decomposition stage at 186–241°C is attributed to the removal of C_2H_5OH and H_2O with a weight loss of 16.0 (14.3%). The degradation steps for the complex end with CoS as a final product with a weight loss of 20.2 (21.1%).



Scheme 2. Degradation scheme for $[Co_2(G_TETS)(OAc)(OH)(H_2O)_3]\cdot C_2H_5OH$.

The decomposition curve of $[Co_2(G_TETS)(OAc)(OH)(H_2O)_3]\cdot C_2H_5OH$ begins by a step at 32–87°C displaying 7.9% weight loss corresponding to the removal of C_2H_5OH (Calcd 8.4%) followed by thermal stability at 220°C. The second weight loss stage at 220–302°C refers to the removal of the three coordinated waters, the bonded hydroxo group and C_2H_5NH as a fragment of the ligand decomposition. A gradual weight loss was recorded with a continuous increase in temperature and ended with two cobalt (2Co) by a percent of 22.02 (21.5%). Scheme 2 represents the degradation steps.

The TGA thermogram of $[Co(HCETS)(OAc)(H_2O)_2]\cdot H_2O$ consists of four peaks. The first (38–125°C) is due to removal of the hydrated water molecule with a weight loss of 6.7 (5.0%). The second (127–310°C) with 23.7 (22.4%) weight loss is associated with the removal of two coordinated waters as well as C_2H_5NH from the ligand. The third (310–440°C) with 26.4 (27.6%) confirms elimination of the acetate molecule with CH_2CN as another part of the ligand. The final (446–632°C) step with a percent of 20.7 (23.7%) is attributed to complete decomposition of the complex leaving CoO residue with a percent of 22.9 (20.9%).

The curve for $[Ni(PETS)(OAc)(H_2O)_2]$ showed stability to 231°C, above which a weight loss by 12.7% corresponds to removal of two coordinated water molecules. The second stage ending at 442°C is assigned to the elimination of chelated acetate and C_2H_5 group from the ligand accompanied by a weight loss of 24.9%. The third step (442–550°C) can be ascribed to the removal of the remaining organic part ($C_7H_7N_3$) by a weight loss of 36.2%, leaving NiS as a residue with a percent of 26.0.

The degradation curve of $[Cu(HPETS)_3(OAc)_2]$ showed a peak centred at 210°C, corresponding to decomposition of (C_6H_5NHNH–) in the three ligands with a weight loss of 40.8 (Calcd 41.8%). The peak centred at 300°C corresponds to the loss of monodentate acetate, 8.3 (7.9%). The third stage in the 435–605°C range corresponds to loss of the bidentate acetate, as well as C_2H_5NH of the three ligands by a weight loss of 26.3 (24.7%). Finally, the residue at 520°C with a weight loss of 23.7 (25.5%) corresponds to the remaining complex CuS_3C_3. The unremovable C=S groups may be due to the strong coordinate bond with the Cu(II) ion. This is supported by the higher shift ($78\,cm^{-1}$) of the ν(C=S) vibration in its IR spectrum.

The curve for $[Cu_2(HG_TETS)(OH)_3(H_2O)] \cdot ½C_2H_5OH$ reveals stability to 200°C. The first stage displayed a weight loss of 21.5 (19.5%) at 200–333°C corresponding to the loss of 3(OH), H_2O and $0.5\,C_2H_5OH$, which hydrogen-bonds with the complex (figure 2b). The lower weight loss in the second stage and the higher residual weight percent indicate a higher thermal stability of the binuclear Cu(II) complex. Such stability may refer to the presence of two five-membered rings.

The difference between the observed and (calculated) percentages in some degradation stages may arise from overlap with the next step.

3.6. *pH-metric studies*

The ionization constant is an important property of organic molecules, related to solubility and extent of binding. It is used to measure the strength of acids, bases and different species formed in solution and to distinguish the structure of newly isolated substances. The ionization constant(s) of each of the investigated ligands was 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 [43]

$$\bar{n}_A = Y + \frac{(V_1 - V_2)([A] + [B])}{(V_0 + V_1)T_L},$$

where Y is the ionizable proton of the ligand, 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 ionization constants (pK_1 and pK_2) are determined by interpolation at $\bar{n}_A = 0.5$ and 1.5, respectively. The data reveal that the ligands have the following order: $H_2CETS > HETS > HPETS > H_2G_TETS$ according to the pK_1 values. This indicates a direct relation between the electron-withdrawing character for the neighbouring group and the facility of the ionization process. The values demonstrate the ability of ligands to complex with the metal ions through deprotonated forms of HETS and H_2CETS and the protonated and/or deprotonated forms of H_2G_TETS and HPETS.

The stability constants (table 4) of the Co(II), Ni(II) and Cu(II) complexes in solution were determined through the relation between the free ligand exponent (pL) and the

Table 4. Deprotonation constants of the investigated ligands and the formation constants of their Co(II), Ni(II) and Cu(II) complexes.

	H^+			Co(II)			Ni(II)			Cu(II)		
Compound	pK_1	pK_2	β_1	β_2	β*	β_1	β_2	β*	β_1	β_2	β_3	β*
HETS	10.70	–	7.90	6.40	14.30	8.20	7.10	15.30	9.75	8.65	3.80	22.20
HPETS	8.20	–	4.20	2.10	6.30	5.25	2.75	8.00	7.20	4.80	–	12.00
H_2G_TETS	6.35	5.30	5.40	4.90	10.30	9.20	8.60	17.82	10.50	9.15	–	19.65
H_2CETS	10.85	5.20	8.80	8.30	17.10	5.60	5.20	10.80	6.60	5.75	5.10	17.45

Note: β* is the overall stability constant.

average number of ligands attached per metal ion ($\bar{n}$). The values were evaluated applying the following equations:

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

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

$$pL = \log \frac{1 + K_1[H^+] + K_1K_2[H^+]^2}{T_L - \bar{n}T_M} \frac{V_3 + V_o}{V_o}, \quad \text{for a dibasic ligand,}$$

where V_3 is the volume of alkali required to reach the desired pH in the complex solution, and T_M is the initial concentration of the metal ion.

The data reveal a good agreement with the Irving and Williams [44] series with Cu(II) > Ni(II) > Co(II) order for the same ligand. For the Co(II) ion, the values of β* ordered the ligands as: H_2CETS > HETS > H_2G_TETS > HPETS; this order is reversed for both Ni(II) and Cu(II).

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