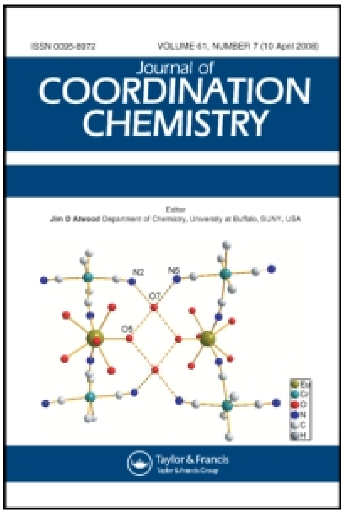

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Synthesis and spectroscopic characterization of cobalt(II) thiosemicarbazone complexes

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Synthesis and spectroscopic characterization of cobalt(II) thiosemicarbazone complexes

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Thiosemicarbazone derivatives are formed on reaction between acetophenone, salicylaldehyde, benzophenone and/or 2-hydroxy-4-methoxybenzophenone and thiosemicarbazide or its N^4H substituents (ethyl-, phenyl-, and *p*-chlorophenyl-). The ligands were investigated by elemental analysis and spectral (IR, ^1H NMR and MS) studies. The formulas of the prepared complexes have been suggested by elemental analyses and confirmed by mass spectra. The coordination sites of each ligand were elucidated using IR spectra revealing bidentate and tridentate coordination. Different geometries for the complexes were proposed on the basis of electronic spectra and magnetic measurements. The complexes have been analyzed thermally (TG and DTG) and the kinetic parameters for some of their degradation steps were calculated.

Keywords: Cobalt(II) complexes; Thiosemicarbazones; Spectra; Thermal studies

1. Introduction

Thiosemicarbazones and their complexes have been extensively studied owing to their pharmaceutical and biological properties such as antitumor [1–3], fungicidal [4], bactericidal and antiviral activities. They have also been used for analysis of metals, for device applications relative to telecommunications, optical computing, optical storage and optical information processing [1]. There has been considerable interest in thiosemicarbazones derived from salicylaldehyde [5], 2-hydroxyacetophenone [6], 2-aminobenzaldehyde, 2-aminoacetophenone [7], acetophenone [8] and in particular, those with substitution at the N(4) position of the thiosemicarbazone moiety [9]. The stoichiometry and stereochemistry of the metal complexes were found to be different for unsubstituted thiosemicarbazones compared to the N(4) substituted [10–13]. Transition metal complexes for several of these compounds have also been screened for their medicinal properties and possess cytotoxic activity [14]. In this work, we focus our interest on compounds having N(1) and N(4) substituted thiosemicarbazones

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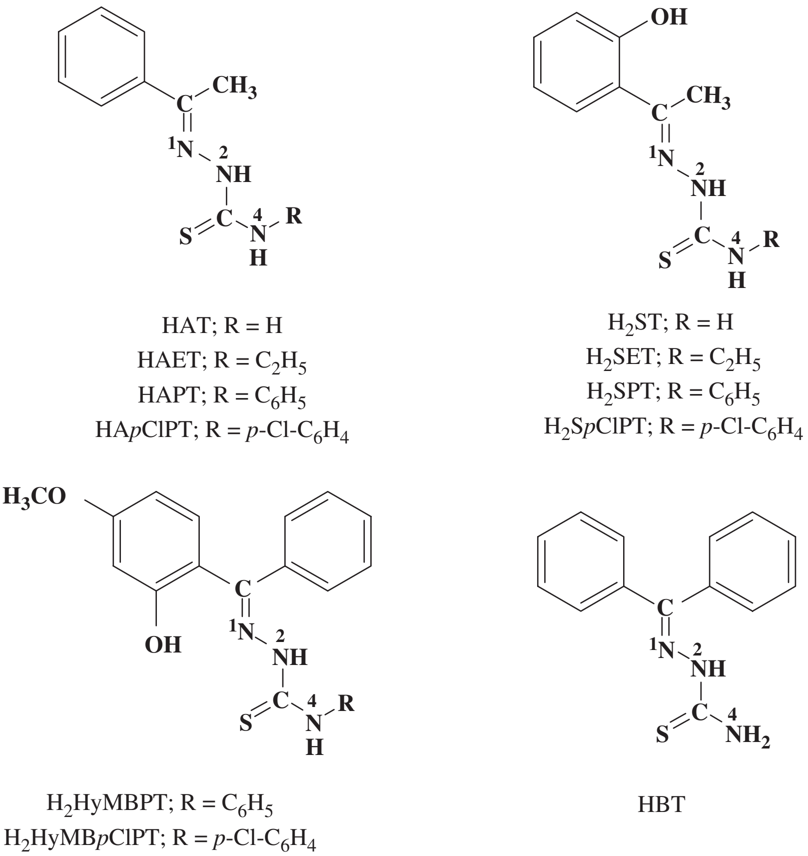


Figure 1. Structures of ligands.

(figure 1) and their Co(II) complexes. In addition, the decomposition steps of the complexes were studied thermally.

2. Experimental

Reagent grade (BDH) precursors to ligands and solvents were purified by the usual methods [15]. Cobalt acetate was purchased from Merck and used as received. All other chemicals were purchased from commercial sources and used without further purification. The abbreviations, full names, melting points and formula weights of the investigated ligands are listed in table 1.

2.1. *Preparation of ligands*

The ligands under investigation were prepared by the same procedure. The preparation of 1-acetophenone thiosemicarbazones (HAT) is explained in detail as an example. Equimolar amounts of acetophenone (12 mL, 0.1 mol) and ethanolic solution (50 mL)

Table 1. Abbreviations, full names, melting points, elemental analyses and formula weights of the ligands.

				Found (Calcd %)		F. W	
Abbreviated name	Full name	Color	M.P. (°C)	C	H	Found*	Calcd
HAT	1-Acetophenonethiosemicarbazone	White	132	55.8 (55.9)	5.7 (5.7)	–	193.3
HAET	1-Acetophenone-4-ethylthiosemicarbazone	White	145	60.0 (59.7)	6.4 (6.8)	221.0	221.3
HAPT	1-Acetophenone-4-phenylthiosemicarbazone	White	198	67.0 (66.9)	5.9 (5.6)	–	269.4
HA*p*ClPT	1-Acetophenone-4-*p*-chlorophenylthiosemicarbazone	Yellowish white	190	58.8 (59.3)	4.2 (4.6)	304.0	303.8
H_2ST	1-Salicylaldehydethiosemicarbazone	Yellow	245	49.3 (49.2)	5.0 (4.6)	–	195.2
H_2SET	1-Salicylaldehyde-4-ethylthiosemicarbazone	White	184	53.3 (53.8)	5.4 (5.9)	223.0	223.3
H_2SPT	1-Salicylaldehyde-4-phenylthiosemicarbazone	Yellowish white	205	61.0 (61.9)	4.8 (4.8)	–	271.3
H_2S*p*ClPT	1-Salicylaldehyde-4-*p*-chlorophenylthiosemicarbazone	Yellow	212	54.3 (54.9)	4.0 (3.9)	304.0	305.9
H_2HyMBPT	1-(2-Hydroxy-4-methoxybenzophenone) 4-phenylthio-semicarbazone	Yellow	110	66.0 (66.8)	4.8 (5.1)	377.0	377.5
H_2HyMB*p*ClPT	1-(2-Hydroxy-4-methoxybenzophenone) 4-*p*-chloro-phenylthiosemicarbazone	Yellow	135	61.2 (61.2)	4.3 (4.4)	412.0	411.9
HBT	1-Benzophenonethiosimecarbazone	White	191	66.6 (65.8)	4.6 (5.1)	255.9	255.3

*Values obtained from mass spectra.

of thiosemicarbazide (9.1 g, 0.1 mol) were heated at reflux on a water bath for 2 h. A few drops of glacial acetic acid were added at the onset of the reflux. The precipitate thus formed was removed by filtration, recrystallized from absolute ethanol and dried.

The yield of the prepared ligands was found in the range 65–80%. Identification of the ligands was confirmed by elemental analysis and mass spectra (table 1) as well as IR spectra (table 2).

2.2. *Preparation of complexes*

The preparation of $[Co_2(AT)_3(OH)(H_2O)]_2 \cdot 5H_2O$ is taken as a representative example. A solution of $Co(OAc)_2 \cdot 4H_2O$ (0.746 g, 3 mmol) in 30 mL aqueous-ethanol (1 : 1) solution was added dropwise with stirring to a solution of HAT (0.579 g, 3 mmol). The mixture was heated under reflux on a water bath for 4 h. The precipitate was filtered off, washed several times with hot water, hot ethanol and diethyl ether and finally dried in a vacuum desiccator.

All the other complexes were prepared by the same procedure.

2.3. *Physical measurements*

Carbon and hydrogen content was determined by the Microanalytical Unit at Cairo University. Analysis of cobalt ions carried out complexometrically using standard methods [16].

The infrared spectra in the region 200–4000 cm^{-1} were recorded, as KBr discs, on a Mattson 5000 FTIR spectrophotometer with a CsI beam splitter. The electronic spectra (Nujol mull and DMF solution) were recorded on a UV_2 Unicam UV/VIS Spectrophotometer. ^1H NMR spectra were recorded in DMSO-d_6 on a Varian Gemini Spectrophotometer (200 MHz). The mass spectra were recorded on a Varian MAT 311 instrument. The effective magnetic moments were evaluated using a Johnson Matthey magnetic susceptibility balance by applying: $\mu_{eff} = 2.828\sqrt{\chi_M^- T}$, 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 thermal studies were carried out on a Shimadzu thermogravimetric analyzer with a heating rate of 10°C min^{-1}.

3. Results and discussion

The Co(II) complexes of HAT, HAET, HAPT, HA*p*ClPT, H_2ST, H_2SET, H_2SPT, H_2S*p*ClPT, H_2HyMBPT, H_2HyMB*p*ClPT and HBT (see table 1 for abbreviations) are readily obtained by mixing aqueous-ethanol solutions of the ligands (figure 1) with $Co(OAc)_2 \cdot 4H_2O$. All the formed complexes are stable in atmospheric conditions, insoluble in water and common organic solvents, but completely soluble in dimethyl formamide (DMF) and dimethylsulphoxide (DMSO) except for $[Co(BT)(OAc)] \cdot 2H_2O$ which is insoluble and $[Co_2(AT)_3(OH)\text{-}(H_2O)] \cdot 2.5H_2O$, $[Co(APT)_2H_2O)_2]$, $[Co_2(ST)_2(H_2O)_2] \cdot 0.5H_2O$, $[Co(SPT)(H_2O)]$ and $[Co(S$*p*$ClPT)(H_2O)_2] \cdot H_2O$ which are partially soluble. The analytical data and some physical properties of the complexes are presented in table 2.

Table 2. Physical properties, elemental analysis and formula weights of the complexes.

	Formula weight					Found (Calcd %)		
Complex/Formula	Found*	Calcd	Color	Yield (%)	M.P. (°C)	C	H	Co
$[Co_2(AT)_3(OAc)(H_2O)] \cdot H_2O$ $C_{29}H_{39}Co_2N_9O_{2.}S_3$	774.0	775.8	Dark brown	78	>300	45.2 (44.9)	5.2 (5.1)	15.6 (15.2)
$[Co(AET)_2(H_2O)_2]$ $C_{22}H_{32}CoN_6O_2S_2$	–	535.6	Brownish green	80	>300	49.7 (49.4)	5.6 (6.0)	10.7 (11.0)
$[Co(APT)_2(H_2O)_2]$ $C_{30}H_{32}CoN_6O_2S_2$	–	631.7	Dark brown	83	221	57.4 (57.0)	4.9 (5.1)	9.7 (9.3)
$[Co_2(A\textit{p}ClPT)(OAc)(OH)_2(H_2O)] \cdot H_2O$ $C_{17}H_{22}ClCo_2N_3O_6S$	548.0	549.8	Dark brown	81	>300	37.6 (37.1)	3.8 (4.0)	21.9 (21.4)
$[Co_2(ST)_2(H_2O)_2] \cdot 0.5H_2O$ $C_{16}H_{19}Co_2N_6O_{4.5}S_2$	548.0	548.8	Brown	71	>300	35.5 (34.9)	4.0 (3.5)	21.6 (21.5)
$[Co_2(SET)_2]C_2H_5OH$ $C_{22}H_{28}Co_2N_6O_3S_2$	606.0	606.5	Dark brown	86	>300	43.0 (43.6)	4.4 (4.6)	18.9 (19.4)
$[Co(SPT)(H_2O)]$ $C_{14}H_{13}CoN_3O_2S$	345.0	346.3	Yellowish brown	81	>300	47.9 (48.5)	3.8 (3.8)	16.6 (17.0)
$[Co(S\textit{p}ClPT)(H_2O)_2] \cdot H_2O$ $C_{14}H_{16}ClCoN_3O_4S$	415.0	416.8	Brown	78	>300	40.5 (40.3)	4.1 (3.9)	14.7 (14.1)
$[Co(HyMBPT)(H_2O)_3] \cdot H_2O$ $C_{21}H_{25}CoN_3O_6S$	–	506.4	Brown	75	>300	49.7 (49.8)	4.5 (4.9)	12.0 (11.6)
$[Co_2(HyMB\textit{p}ClPT)(OH)_2(H_2O)_3]$ $C_{21}H_{24}ClCo_2N_3O_7S$	615.0	615.9	Dark brown	76	>300	40.8 (40.9)	3.9 (3.9)	19.1 (19.1)
$[Co(BT)(OAc)] \cdot 2H_2O$ $C_{16}H_{19}CoN_3O_4S$	408.0	408.3	Dark brown	79	>300	46.7 (47.1)	4.3 (4.7)	13.7 (14.4)

*Values obtained from ms.

3.1. ^1H NMR spectra of ligands

The ^{1}H NMR spectra of HAET, HAPT and H_2HyMPT in d_6-DMSO show signals at δ 12.08–11.40 and 9.92–8.51 ppm, which are assigned to the N^2H and N^4H protons, respectively [8]. The ^{1}H NMR spectra of HAT and H_2ST show signals at δ 10.30, 10.07 and 8.09, 8.03 ppm which are assignable to the NH_2 and NH protons, respectively. However, the spectrum of H_2ST shows the OH signal [10] at 10.17 and the NH_2 at 10.07 ppm. The higher value of NH_2 signals may be due to intramolecular hydrogen bonding.

3.2. IR spectra of ligands and their complexes

The important IR bands of the ligands and their complexes are summarized in table 3. The mode of bonding of ligands to Co(II) was investigated. The data show the formation of two modes of chelation. The ligands in the first mode are mononegative bidentate and coordinate through the azomethine (C=N) and thiol (C–S) groups. This type of coordination was found in $[Co_2(AT)_3(OAc)(H_2O)] \cdot H_2O$, $[Co(AET)_2(H_2O)_2]$, $[Co(APT)_2(H_2O)_2]$, $[Co_2(A\textit{p}ClPT)(OAc)(OH)_2\text{-}(H_2O)] \cdot H_2O$ and $[Co(BT)(OAc)] \cdot 2H_2O$. The bonding sites are assigned based on the following evidence: (i) the disappearance of $\nu(N^2H)$, (ii) the shift of ν(C=N) to lower frequency by 11–66 cm^{-1} [16], (iii) the appearance of a new band due to ν(C=N)* at the same spectral region as for ν(C=N) of the thiosemicarbazone moiety, (iv) coordination of the azomethine nitrogen is also consistent with the presence of a new band at 402–470 cm^{-1}, assignable to ν(Co–N) vibration [17] and (v) the thioamide band (IV) is absent with the simultaneous appearance of new bands in the 606–662 and 346–383 cm^{-1} regions due to ν(C–S) [18] and ν(Co–S) vibrations [19], respectively. To confirm the coordination through the thiolato sulfur, the reduction of thioamide band(III) is possible if coordination occurs both through N and S atoms. The acetate ligand in $[Co_2(A\textit{p}ClPT)(OAc)(OH)_2(H_2O)] \cdot H_2O$ and $[Co(BT)(OAc)] \cdot 2H_2O$ is bidentate as indicated by the appearance of two new bands at 1348–1374 and 1417–1526 cm^{-1} due to symmetric and asymmetric stretching vibrations [20], respectively. In $[Co_2(AT)_3(OAc)(H_2O)] \cdot H_2O$, the acetate group is monodentate (two new bands with the difference of 157 cm^{-1} between the two bands). The bands observed at 485 and 506 cm^{-1} in the spectra of $[Co_2(AT)_3(OAc)(H_2O)] \cdot H_2O$ and $[Co_2(A\textit{p}ClPT)(OAc)(OH)_2(H_2O)] \cdot H_2O$ are assigned to ν(M–O) of coordinated water or OH.

A second mode of chelation was found through the C=N, C–S and phenolic oxygen groups in which the ligand is binegative tridentate. This behavior is found in the complexes $[Co_2(ST)_2(H_2O)_2] \cdot 0.5H_2O$, $[Co_2(SET)_2]C_2H_5OH$, $[Co(SPT)(H_2O)]$, $[Co(S\textit{p}ClPT)\text{-}(H_2O)] \cdot H_2O$, $[Co(HyMBPT)(H_2O)_3] \cdot H_2O$ and $[Co_2(HyMB\textit{p}ClPT)(OH)_2(H_2O)_3]$. Elucidation of this mode is proposed by: (i) the disappearance of $\nu(N^2H)$; (ii) the shift of ν(C=N) to lower frequency by 9–83 cm^{-1}; (iii) the phenolic oxygen of these ligands, on loss of the OH proton, occupies the third (through bridging) coordination site (disappearance of one of the ν(OH) band); (iv) a band at 486–505 cm^{-1} in the spectra of the complexes is assignable to ν(M–O) for the bridging phenolato oxygen; (v) the disappearance of ν(C=S) at 778–835 cm^{-1} in the complex spectra with the appearance of a new band at 606–638 cm^{-1} due to ν(C–S) vibrations, and new bands appeared in the low frequency region for ν(M–S) at 345–370 cm^{-1} and ν(M–N) at 405–453 cm^{-1}, evidence for S, N and O donors.

Table 3. IR spectral bands of the ligands and their complexes (cm^{-1}).

Compound	$\nu(NH_2)$	$\nu(OH)$	$\nu(N^4H)$	$\nu(N^2H)$	$\nu(C{=}N)$	$\nu(C{=}S)$	$\nu(C–S)$	$\delta(OH)$	$\nu(M–O)$	$\nu(M–N)$	$\nu(M–S)$
HAT	3409 3367	–	–	3223	1628	790	–	–	–	–	–
$[Co_2(AT)_3(OH)\ (H_2O)]\cdot 2.5H_2O$	3415 3368	3441	–	–	1611	–	606	1330	485	402	351
HAET	–	–	3319	3225	1630	788	–	–	–	–	–
$[Co(AET)_2(H_2O)_2]$	–	–	3316	–	1586	–	624	–	513	462	370
HAPT	–	–	3299	3250	1605	794	–	–	–	–	–
$[Co(APT)_2(H_2O)_2]$	–	–	3306	–	1594	–	610	–	–	405	352
Ha*p*ClPT	–	–	3292	3242	1635	797	–	–	–	–	–
$[Co_2(A\mathit{p}ClPT)(OAc)(OH)_2(H_2O)]\cdot H_2O$	–	3387	3290	–	1616	–	656	1390	506	446	346
H_2ST	3371 3317	3442	–	3166	1611	778	–	1366	–	–	–
$[Co_2(ST)_2(H_2O)_2]\cdot 0.5H_2O$	3377 3304	3426	–	–	1601	–	618	1327	486	430	350
H_2SET	–	3405	3353	3250	1607	791	–	1375	–	–	–
$[Co_2(SET)_2]C_2H_5OH$	–	3420	3365	–	1598	–	606	–	492	405	345
H_2SPT	–	3420	3381	3146	1621	835	–	1389	–	–	–
$[Co(SPT)\ (H_2O)]$	–	3417	3381	–	1610	–	638	1373	492	412	346
$H_2S\mathit{p}ClPT$	–	3333	3236	3154	1610	830	–	1331	–	–	–
$[Co(S\mathit{p}ClPT)(H_2O)_2]\cdot H_2O$	–	3314	3205	–	1608	625	625	1328	489	453	345
$H_2HyMBPT$	–	3470	3302	3162	1634	809	–	1327	–	–	–
$[Co(HyMBPT)(H_2O)_3]\cdot H_2O$	–	–	3305	–	1596	–	609	1319	502	405	350
$H_2HyMB\mathit{p}ClPT$	–	3439	3290	3181	1634	788	–	1348	–	–	–
$[Co_2(HyMB\mathit{p}ClPT)(OH)_2(H_2O)_3]$	–	–	3253	–	1597	–	623	1316	505	423	370
HBT	3364 3262	–	–	3175	1620	800	–	–	–	–	–
$[Co(BT)(OAc)]\cdot 2H_2O$	3329 3256	–	–	–	1554	–	662	–	525	470	383

3.3. *Magnetic and electronic spectral studies*

The investigated thiosemicarbazones have a ring $\pi \rightarrow \pi^*$ band at 32 790–40 820 cm^{-1} and $n \rightarrow \pi^*$ band at 28 570–30 960 cm^{-1}; little change in energies is seen for their complexes. Another $n \rightarrow \pi^*$ band in the spectra of the free thiosemicarbazones is also found in the spectra of the cobalt(II) complexes at 27 000–28 250 cm^{-1}. The band at 22 680–24 040 cm^{-1} in the spectra of the complexes may be due to LMCT. Previous studies on thiosemicarbazone complexes proved that a band in the region 25 000–26 040 cm^{-1} should be assigned to an O → M(II) transition [21] whereas a band in the range 21 790–24 750 cm^{-1} is due to S → M(II) transition [22]. All spectral measurements were carried out in Nujol and DMF; the medium has little effect.

The magnetic moments and the electronic spectral bands of the complexes are listed in table 4. The complexes $[Co(AET)_2(H_2O)_2]$, $[Co(APT)_2(H_2O)_2]$ and $[Co(HyMBPT)(H_2O)_3] \cdot H_2O$ have magnetic moments of 4.82, 5.04 and 5.20 BM, respectively, which lie in the range reported for an octahedral geometry around the Co(II) [17]. Electronic spectra of the complexes recorded in Nujol and DMF are similar, characterized by two bands at 14 290–16 950 and 17 360–20 280 cm^{-1} attributed to the $^4T_{1g} \rightarrow {}^4A_{2g}(\nu_2)$ and $^4T_{1g} \rightarrow {}^4T_{1g}(P)(\nu_3)$ transitions, respectively. The observed bands are similar to those reported for octahedral complexes of Co(II) [23]. The ligand field parameters (B, β, 10Dq) are calculated by the equations used for the d^7 system [24] and are listed in table 4. The values agree fairly well with those reported for octahedral Co(II) complexes. Considerable reduction in the B value from 971 to 697–896 cm^{-1} and β (from unity to 0.718–0.922) indicates the covalent character of the L–M bond [8]. The color of these complexes is in good agreement with those reported for octahedral geometry.

The complexes $[Co_2(AT)_3(OAc)(H_2O)] \cdot H_2O$, $[Co_2(A\textit{p}ClPT)(OAc)(OH)_2(H_2O)] \cdot H_2O$ and $[Co(SPT)(H_2O)]$, have 4.02, 4.46 and 4.70 BM magnetic moments, respectively, which lie within the values reported for tetrahedral Co(II) complexes [25]. Other evidence is their electronic spectra which show one band at 15 625–16 050 cm^{-1} due to the $^4A_2 \rightarrow {}^4T_1$ transition in a tetrahedral structure [25]. The ligand field parameters of these complexes are also presented in table 4. The values of 10Dq may be taken as good criteria for the strength of the ligands based on crystal field. It is found that in the octahedral complexes, the order of ligands is: $H_2HyMBPT > H_2ST > HAET > HAPT$. The order of ligands in tetrahedral complexes is: HA*p*ClPT > HAT > H_2SPT.

The magnetic moment values of the complexes $[Co_2(SET)_2]C_2H_5OH$ (3.01 BM) and $[Co(BT)(OAc)] \cdot 2H_2O$ (2.80 BM) agree with the electronic spectra which showed one d-d transition at 18 900–19 100 cm^{-1} suggesting a square planar geometry around Co(II).

The 3.28 and 3.40 BM values measured for $[Co(ST)(H_2O)]_2 \cdot 0.5H_2O$ and $[Co_2(HyMB\textit{p}ClPT)(OH)_2(H_2O)_3]$ are less than reported for octahedral complexes (4.8–5.2 BM). The anomalous values may be due to cobalt–cobalt interaction or to high-spin–low-spin equilibrium. Their electronic spectra showed three bands at 16 000, 12 990 and 20 410 cm^{-1} attributed to the $^4A_2 \rightarrow {}^4A_2(P)$, $^4A_2 \rightarrow {}^4E$ and $^4A_2 \rightarrow {}^4E(P)$ transitions, respectively, perhaps a trigonal bipyramidal structure [26]. Figure 3 represents the geometry of $[Co(ST)(H_2O)]_2 \cdot 0.5H_2O$ in which sulphur bridged two cobalt atoms.

Table 4. Magnetic moments, electronic spectral bands and ligand field parameters of Co(II) complexes.

Complex	μ_{eff} (BM)	State	$\nu_{\max}$ (cm^{-1})	Ligand field parameters			Supposed structure
				B (cm^{-1})	β	10Dq (cm^{-1})	
$[Co_2(AT)_3(OH)(H_2O)] \cdot 2.5H_2O$	4.02	DMF	15 873	793	0.817	3172	Tetrahedral
		Nujol	15 847	757	0.780	3406	
$[Co(AET)_2(H_2O)_2]$	4.82	DMF	18 796, 16 000	836	0.860	8360	Octahedral
		Nujol	18 248, 15 923	795	0.818	8750	
$[Co(APT)_2(H_2O)_2]$	5.04	DMF	19 305, 16 000	859	0.884	8590	Octahedral
		Nujol	18 552, 16 000	795	0.819	8745	
$[Co_2(A\mathit{p}ClPT)(OAc)(OH)_2(H_2O)] \cdot H_2O$	4.46	DMF	16 050	666	0.686	4670	Tetrahedral
		Nujol	15 847	652	0.671	4670	
$[Co_2(ST)_2(H_2O)_2] \cdot 0.5H_2O$	3.20	DMF	19 305, 16 949	828	0.852	9108	Octahedral
		Nujol	20 150, 16 949	896	0.922	8967	
$[Co_2(SET)_2]C_2H_5OH$	3.01	DMF	19 047	–	–	–	Square planar
		Nujol	18 932				
$[Co(SPT)(H_2O)]$	4.70	DMF	15 625	763	0.785	3433	Tetrahedral
		Nujol	16 000	789	0.813	3156	
$[Co(S\mathit{p}ClPT)(H_2O)_2] \cdot H_2O$	4.16	DMF	17 667	–	–	–	Trigonal bipyramidal
		Nujol	20 610, 16 050, 13 050				
$[Co(HyMBPT)(H_2O)_3] \cdot H_2O$	5.20	DMF	17 361, 16 863	697	0.718	8940	Octahedral
		Nujol	20 283, 14 285	880	0.906	9213	
$[Co_2(HMB\mathit{p}ClPT)(OH)_2(H_2O)_3]$	3.40	DMF	16 666	–	–	–	–
		Nujol					
			20 405, 16 000, 12 990	–	–	–	Trigonal bipyramidal
$[Co(BT)(OAc)] \cdot 2H_2O$	2.80	Nujol	18 903	–	–	–	Square planar

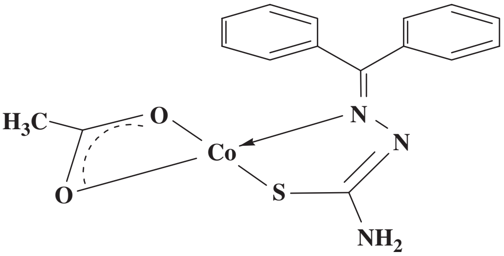


Figure 2. Structure of $[Co(BT)(OAc)] \cdot 2H_2O$.

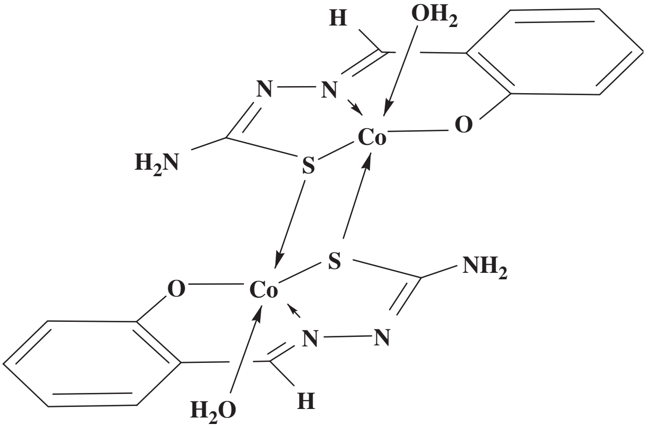


Figure 3. Structure of $[Co_2(ST)_2(H_2O)_2] \cdot 0.5H_2O$.

In the electronic spectrum of $[Co(SpClPT)(H_2O)_2] \cdot H_2O$, the d–d band is observed at $16\,610\,cm^{-1}$ and LMCT transition at $25\,000\,cm^{-1}$. The spectrum of this complex resembles five-coordinate cobalt(II) complexes [5, 27]. A square-pyramidal structure may be assigned for this complex, supported by its magnetic moment.

3.4. *Mass spectral studies*

The mass spectra of most complexes show molecular ion peaks in good agreement with the suggested formulas. The found and calculated molecular weights are presented in table 2. One spectrum is described in detail for $[Co(ST)(H_2O)]_2 \cdot 0.5H_2O$ (figure 4) showing multi peaks representing successive degradation of the molecule. The first peak at $m/e = 548.0$ (Calcd 549.3) represents the molecular ion peak of the complex with 90.59% abundance; this formula contains half water molecule. Scheme 1 demonstrates the proposed decomposition path for the complex. One of the strongest peaks (base beak) at $m/e = 370$, represents the stable species, $C_9H_{11}Co_2N_5O_2S$, after which many peaks are observed ending with Co at $m/e = 60$.

3.5. *Thermal studies*

The thermal decomposition steps for some complexes were analyzed applying Coats–Redfern [27] and Horowitz–Metzger [28] equations. The energy of activation (E),

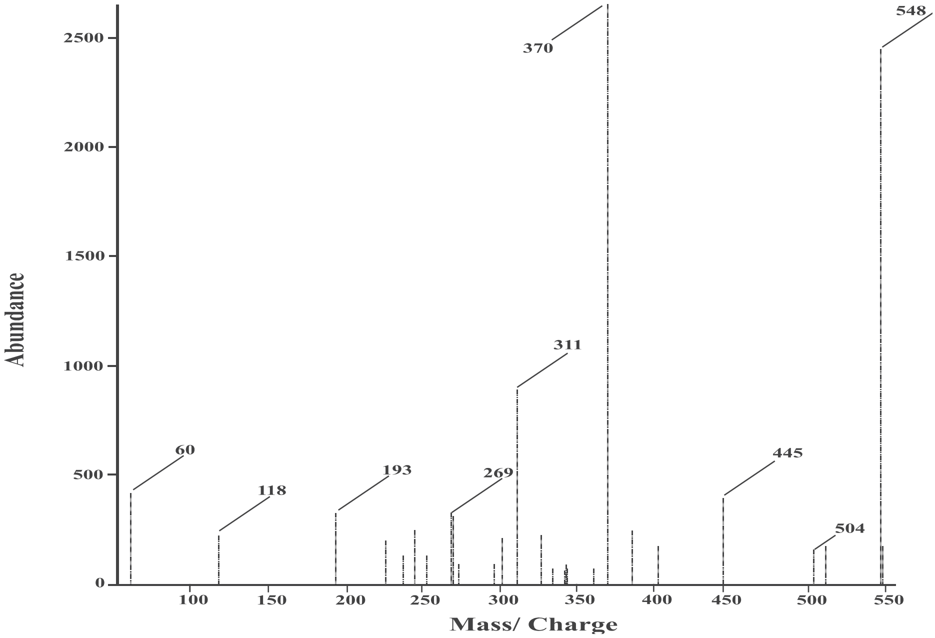


Figure 4. Mass spectrum of $[Co_2(ST)_2(H_2O)_2] \cdot 0.5H_2O$.

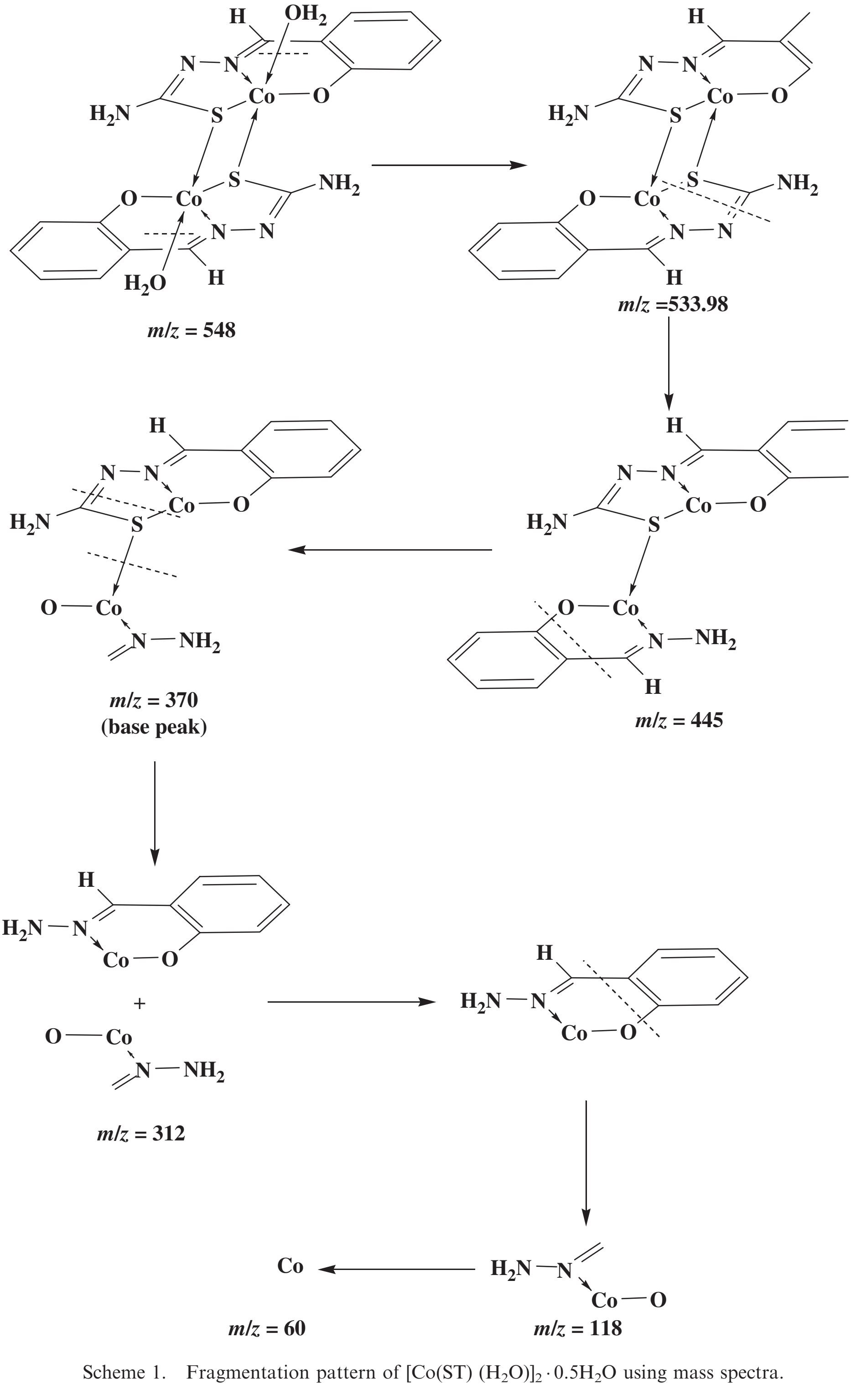
enthalpy (ΔH^*), entropy (ΔS^*) and the free energy (ΔG^*) were calculated (table 5). The relatively high E values (41.5–151.3 kJ mol^{-1}) indicate strong bonds to Co(II) ions while the negative ΔS^* values indicate that the activated complexes have more ordered structure than the reactants.

The TG thermograms of the complexes were studied in the temperature range 30–800°C.

As a representative example for the decomposition of these complexes, the TG of $[Co(AET)_2(H_2O)_2]$, shown in figure 5, is described. Its thermogram reveals four decomposition stages (scheme 2). The two coordinated water molecules may be eliminated in the first step which is major together with another decomposition product (Calcd 50.9%, Found 50.3%) with an activation energy of 78.2 kJ mol^{-1} and a first-order reaction. The third step suggests the expulsion of two HNC_2H_5 (Calcd 16.5%, Found 17.4%) which may dimmerize or abstract hydrogen before decomposition (this step is second order with activation energy of 76.3 kJ mol^{-1}). A continuous decomposition takes place until 800°C. The residue is CoS (Calcd 16.9%, Found 16.1%).

4. Conclusion

Although the same preparative technique was used, isolation of different Co(II) complexes of some N^4H thiosemicarbazone derivatives was surprising. Different geometries were proposed for these complexes based on electronic and magnetic data. All complexes have thermal stability. The existence of ligand tautomers



Scheme 1. Fragmentation pattern of $[Co(ST)(H_2O)]_2 \cdot 0.5H_2O$ using mass spectra.

Table 5. Kinetic parameters of the thermal decomposition of the complexes[a].

		Coats–Redfern equation			Horowitz–Metzger equation					
Complex	Step	*R*	*N*	*E*	*r*	*N*	*E*	ΔS^*	ΔH^*	ΔG^*
$[Co_2(AT)_3(OH)(H_2O)] \cdot 2.5H_2O$	2nd	1	2	61.7	0.9989	2	71.5	−237.1	56.9	194.7
	3rd	1	1	206.5	1	1	220.9	−76.4	200.3	260.6
$[Co(AET)_2(H_2O)_2]$	1st	0.99931	1	78.2	0.9967	1	85.1	−197.9	73.7	176.6
	3rd	0.9997	2	76.3	0.9995	2	91.2	−243.3	70.1	252.5
$[Co(APT)_2(H_2O)_2]$	1st	0.9999	1	151.3	0.9997	1	166.9	−48.8	147	172.4
	2nd	0.9998	0.33	30.3	0.9984	0.33	44.7	−328.6	23.2	304.1
$[Co_2(ST)_2(H_2O)_2] \cdot 0.5H_2O$	1st	0.9849	2	177.3	0.9849	2	188.6	−96.1	172.7	164.6
	4th	0.9979	0.66	125.6	0.9982	0.66	139	−151.8	120.6	220
$[Co(HyMBPT)(H_2O)_3] \cdot H_2O$	2nd	0.9994	1	51.1	0.9993	1	58.8	−240.8	47.2	160.8
	3rd	0.9968	1	39.7	0.9941	1	54.2	−297.6	33.7	233
$[Co(BT)(OAc)] \cdot 2H_2O$	1st	0.9993	2	59.3	0.9982	2	63.5	−154.4	56.5	108.5
	3rd	1	0.33	109.5	0.9996	0.33	131	−206.2	102.9	264.9

[a] *r* = correlation coefficient, *n* = order of the decomposition reaction; *E*, ΔH^* and ΔG^* are in $kJ\,mol^{-1}$, ΔS^* in $JK\,mol^{-1}$.

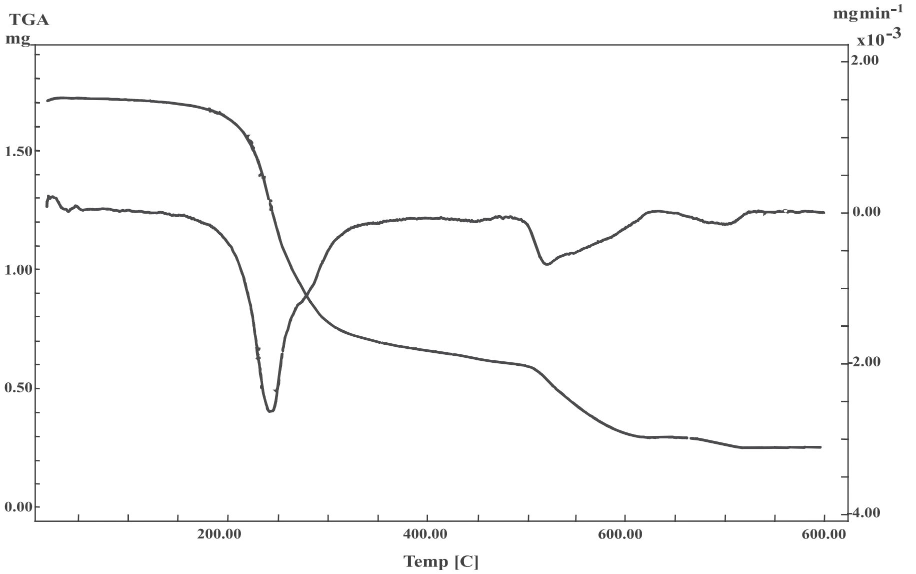
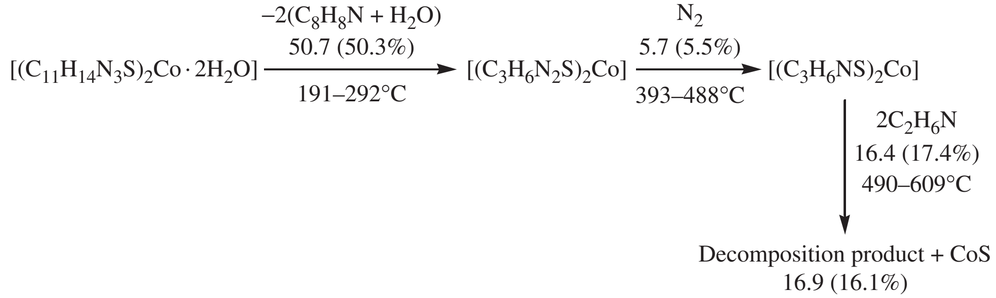


Figure 5. TG and DTG thermograms of $[Co(AET)_2(H_2O)_2]$.



$$[(C_{11}H_{14}N_3S)_2Co\cdot 2H_2O] \xrightarrow[191\text{–}292^\circ C]{-2(C_8H_8N + H_2O)\ \ 50.7\ (50.3\%)} [(C_3H_6N_2S)_2Co] \xrightarrow[393\text{–}488^\circ C]{N_2\ \ 5.7\ (5.5\%)} [(C_3H_6NS)_2Co]$$

$$\Big\downarrow\ 2C_2H_6N\ \ 16.4\ (17.4\%)\ \ 490\text{–}609^\circ C$$

Decomposition product + CoS
16.9 (16.1%)

Scheme 2. Thermal decomposition of $[Co(AET)_2(H_2O)_2]$.

may be significant. The ligands function as mononegative bidentate and binegative tridentate depending on the substitutent group of the ligands.

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