Synthesis and Characterization of Metal Complexes with Mercaptosuccinic Acid and Hydrazine as Ligands

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Reaction of hydrazine and mercaptosuccinic acid with metal ion forms complexes with general formula, $[M(N_2H_4)_2\{CH_2(COO)CH(COOH)(S)\}]\cdot(H_2O)_n$ where n = 1 when M = Hg(II), Pb(II), n = 2 when M = Zn(II), Cd(II) and n = 3 when M = Co(II) at pH 4. The acid shows dianionic nature showing deprotonation in one of the -COOH groups and in -SH group in these complexes. The complexes have been characterized by analytical, IR and UV-visible spectroscopy and thermal studies. IR spectra show N-N stretching frequencies in the region 985-935 cm^{-1} indicates the nature of hydrazine in the complexes. Simultaneous TG-DTA analysis indicates that hydrazine complexes of Co(II), Cd(II), Pb(II) undergo endothermic dehydration in the range of 90-105 ºC followed by exothermic dehydrazination in the temperature range, 238-282 ºC and exothermic decomposition in the range of 290-467 ºC to the respective metal sulfide/sulfates as the end product. Zn complex shows a different thermal degradation pattern resulting in zinc oxide as an end product. SEM images and XRD pattern of the end products show that they are of nano size. X-Ray powder diffraction patterns show isomorphism among the complexes with similar molecular formulae. The kinetic parameters of the complexes have been computed by Coats-Redfern equation.

Key Words: Mercaptosuccinicacid, Hydrazine, IR, TG-DTA, SEM.

INTRODUCTION

Mercaptosuccinic acid, a potential tridentate ligand due to its three ionizable groups, two carboxylic acid and one thiol, has been put in use in analytical chemistry. A variety of metal chelates has been synthesized using metal ions Co(II)[1], Ni(II)[2], Zn(II)[3,4], Hg(II)[5], Pb(II)[6], gold[7], silver[8,9] and alkaline earth metals[10]. These complexes are particularly stable owing to the presence of two electron pair donor atoms that facilitate formation of chelate rings, differing characters of donor atoms and the stability of sulfur to accept electrons by back donation from metal *d* orbitals in the acid. It has been used as therapeutic agent as an antidote for metal poisoning[11]. Literature review indicated that it had also been used for synthesizing CdTe nanocrystals[12]. Further this acid plays a vital role in the synthesis of nano particles such as quantum clusters of gold[13], Ag-doped polyaniline nanoparticles[14] and CdSe quantum dots[15]. We have been synthesizing metal carboxylates complexes using hydrazine as a co-ligand in our laboratory[16-18]. Since no work has been published on the synthesis of mixed ligand metal complexes using hydrazine and mercaptosuccinic acid, we attempted this work. Here we have presented the synthesis of Co(II), Zn(II), Cd(II), Hg(II), Pb(II) complexes and their thermal characterization.

EXPERIMENTAL

The solvents were distilled prior to use and double distilled water was used for the preparation and chemical analyses. All the chemicals used were of AR grade received from Fluka Chemicals.

Preparation of $[M(N_2H_4)_2\{CH_2(COO)CH(COOH)(S)\}]\cdot(H_2O)_n$ where n = 1 when M = Hg(II), Pb(II), n = 2 when M = Zn(II), Cd(II) and n = 3 when M = Co(II): These complexes were prepared by adding a ligand solution which was obtained by mixing an aqueous solution (60 mL) of mercaptosuccinic acid (0.150 g, 1mmol) and hydrazine hydrate (0.1 g, 2 mmol), to a metal nitrate solution (*e.g.*, Co(NO₃)₂·6H₂O, 0.291 g, 1 mmol in 20 mL of distilled water) at pH 4. A crystalline product formed from the turbid solution while heating over water bath at 80 ºC for 1 h, was filtered, washed with absolute alcohol followed by ether and dried in a desiccator over anhydrous CaCl₂.

A similar combination of ligand solution with zinc nitrate trihydrate which resulted in clear solution, was evaporated to half of its volume by keeping it over boiling water bath. Zinc complex formed after 2 days, was filtered and washed as before.

Physico-chemical Techniques: The composition was fixed by chemical analysis. Hydrazine content was determined

by titrating against standard KIO_3 (0.025 mol L^{-1}) under Andrew's condition and metal contents were determined by titrating with EDTA (0.01 mol L^{-1}) after decomposing the complexes with 1:1 nitric acid[19].

IR spectra of the complexes in the region 4000-400 cm^{-1} were recorded as KBr pellets using Perkin Elmer 597 spectrophotometer. Electronic reflectance spectra for the solid state complexes were obtained using a varian, cary 5000 recording spectrophotometer. The magnetic susceptibility of the complexes was measured using a vibrating sample magnetometer, VSM EG and G model 155 at room temperature.

The X-ray powder diffraction patterns of the complexes were recorded using Philips X-Ray diffractometer (Model PW 1050/70) employing CuK_α radiation with nickel filter. The simultaneous TG-DTA experiments were carried out using SDT Q600 V8.3 instrument and Stanton 781 simultaneous thermal analyzer. Thermal analyses were carried out in N_2 atm at heating rate of 10 °C/min using 5-10 mg of the samples. Platinum cups were employed as sample holders and alumina as reference. The temperature range was ambient to 700 °C. The SEM images were recorded using a Cambridge scanning electron microscope.

RESULTS AND DISCUSSION

IR spectra: IR and analytical data of the complexes are listed in Table-1. In the IR spectra of the complexes, the broad band in the region 3340-3305 cm^{-1} is assigned to ν_{OH} vibrations of the associated water molecules. The ν(S-H) arising from sulphahydral group which appears at 2565 cm^{-1} for a free acid, is not found in the spectra of complexes, implying that mercapto group is ionized and coordinated. A free carboxylic group present unionised in the Co(II), Zn(II), Cd(II), Hg(II) and Pb(II) complexes is evidenced by the titration of the complexes against an alkali[20]. The hydrazine complexes display a N-N stretching frequency in the range of 985-937 cm^{-1} [21]. All the complexes show absorption in the range of 1658-1527 and 1369-1303 cm^{-1} corresponding to ν(C=O)(asym) and ν(C=O) (sym), respectively and their difference being greater than 200 cm^{-1}, unequivocally proving the monodentate coordination of carboxylate group to the metal[22].

Thermal analysis: TG-DTA of complexes are shown in Fig. 1a-b and the thermal data are given in Table-2. All the complexes excepting Hg complex starts losing H_2O from 50 °C and this slow dehydration show broad endotherms in the range of 78-105 °C. Subsequent decomposition seems to be a continuous process with exotherms at temperature ranging
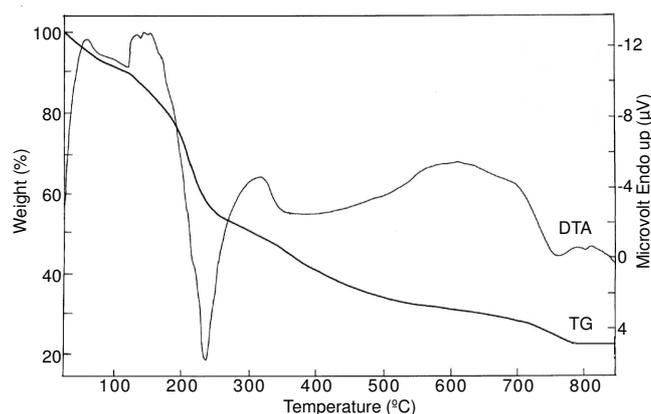
Fig. 1. (a) TG-DTA curves of $[Zn(N_2H_4)_2\{CH_2(COO)CH(COOH)(S)\}]\cdot(H_2O)_2$
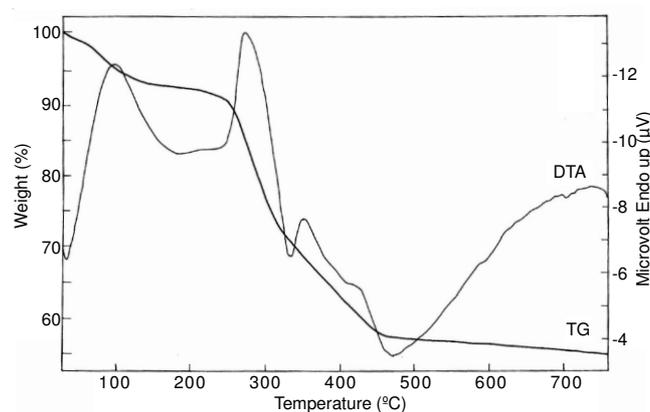
Fig. 1. (b) TG-DTA curves of $[Cd(N_2H_4)_2\{CH_2(COO)CH(COOH)(S)\}]\cdot(H_2O)_2$

from 235-282 °C associated with hydrazine removal with no distinct intermediate formation and broad exotherms at around 290-467 °C. The end product were analyzed to be CoS, ZnO, $CdSO_4$, $PbSO_4$ for Co, Zn, Cd, Pb complexes, respectively, by XRD of residues and comparison with JCPDS values.

Hg complex differs in its decomposition pattern from other complexes by the display of the weight losses due to dehydration at 158 °C followed by the decomposition to metallic Hg showing exotherms and endotherms at 390, 433 and 453 °C, respectively, due to the phase changes of liquid mercury to mercury vapour. This thermal behaviour is normally observed in Hg complexes[23].

Scanning electron microscopy: The final product formed after the incineration of the Zn complex in N_2 atmosphere at its decomposition point found from DTA, followed by sintering at the same temperature for about 3-4 h was found to be pure and uniform in nano scale (*ca.* 46 nm) as found from XRD

TABLE-1
ANALYTICAL AND IR DATA

Molecular formula of complexes	Colour	Yield (%)	d.p. (°C)	Analytical data (%): Found (calcd.)						IR spectral data (cm^{-1})							
				C	H	N	S	Hydrazine	M	ν(O-H) (H_2O)	ν(S-H)	ν(C=O) sym	ν(C=O) asym	ν(C=O) asym-sym	ν(COOH)	ν(N-N)	ν(NH)
$[Co(N_2H_4)_2\{(CH_2(COO)CH(COOH)(S)]\cdot(H_2O)_3$	Dark brown	50	90	14.8 (14.2)	5.5 (5.0)	17.2 (17.8)	9.8 (9.3)	19.2 (19.6)	18.8 (18.1)	3317 (b)	–	1303 (s)	1569 (s)	266	1780 (m)	937 (m)	3263 (b)
$[Zn(N_2H_4)_2\{(CH_2(COO)CH(COOH)(S)\}]\cdot(H_2O)_2$	Light brown	60	78	15.3 (14.8)	5.1 (4.6)	17.9 (17.3)	10.2 (9.7)	24.4 (20.4)	22.3 (20.8)	3334 (b)	–	1361 (s)	1645 (s)	284	1716 (s)	945 (m)	3267 (b)
$[Cd(N_2H_4)_2\{(CH_2(COO)CH(COOH)(S)\}]\cdot(H_2O)_2$	White	75	100	13.3 (12.8)	4.4 (3.9)	15.5 (15.0)	8.9 (8.3)	17.9 (17.7)	30.9 (31.1)	3305 (b)	–	1307 (s)	1550 (s)	243	1780 (m)	948 (m)	3265 (b)
$[Hg(N_2H_4)_2\{(CH_2(COO)CH(COOH)(S)\}]\cdot(H_2O)$	Dull white	75	158	8.3 (8.4)	3.5 (3.3)	13.5 (13.0)	7.8 (7.4)	14.5 (14.9)	47.0 (46.4)	3340 (b)	–	1369 (s)	1658 (s)	289	1703 (s)	985 (m)	3260 (b)
$[Pb(N_2H_4)_2\{(CH_2(COO)CH(COOH)(S)\}]\cdot(H_2O)$	White	75	105	11.0 (10.4)	3.2 (3.5)	12.8 (12.2)	7.3 (7.8)	14.9 (14.6)	47.8 (47.3)	3330 (b)	–	1301 (s)	1527 (s)	226	1676 (s)	941 (m)	3267 (b)

TABLE-2
THERMAL ANALYSIS OF COMPLEXES

Molecular formula of the complex	DTA peak Temp. (°C)	TG			Decomposition product
		Temp. range (°C)	Weight loss (%)		
			Obsd	Cald.	
[Co(N_2H_4)_2{CH_2(COO)CH(COOH)(S)}]·(H_2O)_3	90(+)	–	–	–	–
	282(-)	50-300	33	36	Co{CH_2(COO)CH(COOH)(S)}
	348(-)	300-600	71	72	Decomposition to cobalt sulfide
[Zn(N_2H_4)_2{CH_2(COO)CH(COOH)(S)}]·(H_2O)_2	78(+)	50-170	11	11	Zn(N_2H_4)_2{CH_2(COO)CH(COOH)(S)}
	235(-)	170-300	46	48	Decomposition to zinc sulfate
	350(-)	300-800	75	74	Decomposition to zinc oxide
[Cd(N_2H_4)_2{CH_2(COO)CH(COOH)(S)}]·(H_2O)_2	100(+)	50-170	9	9	Cd(N_2H_4)_2{CH_2(COO)CH(COOH)(S)}
	276(-)	170-300	27	27	Cd{CH_2(COO)CH(COOH)(S)}
	467(-)	300-700	42	42	Decomposition to cadmium sulphate
[Hg(N_2H_4)_2{CH_2(COO)CH(COOH)(S)}]·(H_2O)	158(+)	45-300	4	4	Hg(N_2H_4)_2{CH_2(COO)CH(COOH)(S)}
	390(-)	–	–	–	–
	433(+),453(+)	300-500	–	–	Liquid mercury to mercury vapour
[Pb(N_2H_4)_2{CH_2(COO)CH(COOH)(S)}]·(H_2O)	105(+)	50-170	4	4	Pb(N_2H_4)_2{CH_2(COO)CH(COOH)(S)}
	238(-)	170-280	18	18	Pb{CH_2(COO)CH(COOH)(S)}
	290(-)	280-700	31	31	Decomposition to lead sulfate

(+): Endotherm, (–): Exotherm.

using Scherer's formula[24], $D = K\lambda/\beta \cos\theta$ where λ is the X-ray wavelength, β is the full width of height maximum (FWHM) of a diffraction peak, θ is the diffraction angle and K is the Scherrer's constant of the order of 0.89. The SEM image of ZnO is shown in Fig. 2 as representative example.
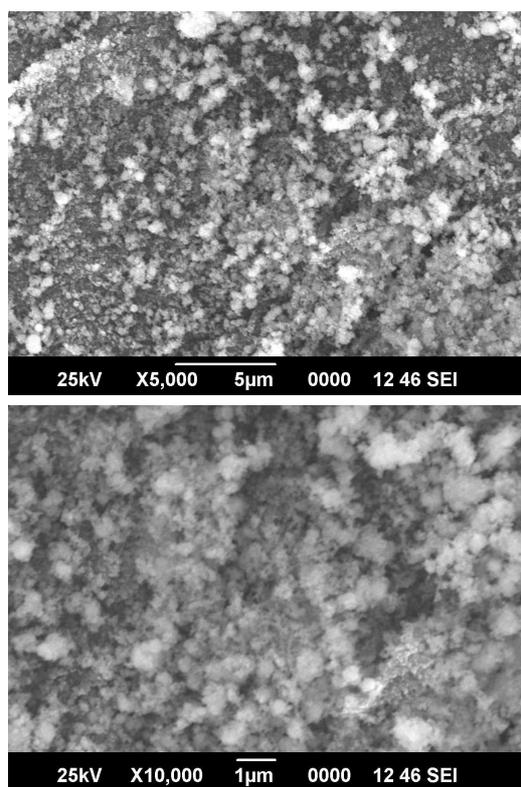
Fig. 2. SEM images of ZnO

UV-Visible spectroscopy and magnetic susceptibility: The absorptions in electronic spectra for cobalt complex at 19960, 15384 cm⁻¹ assigned to $^4T_{1g}(P) \rightarrow {}^4T_{1g}(F)$[25] and the effective magnetic moments for is 4.9, suggesting a high spin octahedral environment for the metal ion.

X-Ray diffraction: The X-ray powder diffraction data of the complexes are summarized in Table-3. The X-ray powder diffraction data of the complexes with formulation, $[M(N_2H_4)_2\{CH_2(COO)CH(COOH)(S)\}]\cdot(H_2O)_2$, where M = Zn(II)-Cd(II), $[M(N_2H_4)_2\{CH_2(COO)CH(COOH)(S)\}]\cdot(H_2O)$, where M = Hg(II)-Pb(II) show similarity among the individuals in each set, implying isomorphism.

TABLE-3
X-RAY DIFFRACTION DATA OF METAL COMPLEXES (D SPACING IN Å UNITS AND INTENSITY IN PARENTHESES)

[M(N_2H_4)_2{CH_2(COO)CH(COOH)(S)}].(H_2O)_2		[M(N_2H_4)_2{CH_2(COO)CH(COOH)(S)}].(H_2O)	
Zn	Cd	Hg	Pb
11.42	12.42	15.6	15.29
(7.74)	(7.11)	(5.30)	(5.74)
4.325	4.4	19.2	18.42
(20.52)	(21.14)	(4.40)	(4.80)
3.57	3.6	22.4	22.82
(24.92)	(24.26)	(3.70)	(3.80)
2.35	2.31	26.5	26.01
(38.16)	(38.94)	(3.10)	(3.01)
1.86	2.15	34.7	34.4
(48.80)	(41.89)	(2.40)	(2.64)
1.68	1.31	38.2	40.97
(54.47)	(71.79)	(2.10)	(2.20)
1.667	1.66	45.8	47.71
(55.03)	(55.27)	(1.99)	(1.90)
1.608	1.603	53.6	51.6
(57.24)	(57.44)	(1.81)	(1.76)

Kinetic studies: Dehydration and decomposition kinetics of complexes were followed using TG. Their parameters have been computed using integral method developed by Coats-Redfern[26]. The equation used for calculation of the E and A parameters is $\log[1 - (1 - \alpha)^{n-1}/(1 - n)T^2] = \log AR/\phi E [1-2RT/E] - E/2.303RT$ where a is the fraction reacted in time (t), T is temperature in K, A is the pre-exponential factor in min⁻¹, ϕ is the heating rate, E is the activation energy in KJ/mole and R is the gas constant. Plotting Y vs. 1/T gives a straight

TABLE-4
KINETIC PARAMETERS OF THE COMPLEXES

Complex	Reaction	E (KJ/mol)	A (min^{-1})	n	ΔS (KJ/K)
[Co(N$_2$H$_4$)$_2$\{CH$_2$(COO)CH(COOH)(S)\}]·(H$_2$O)$_3$	Dehydration	13.101	3.0246×10^7	0.1	0.06137
	Decomposition	15.1925	6.7757×10^8	0.9	0.05815
[Zn(N$_2$H$_4$)$_2$\{CH$_2$(COO)CH(COOH)(S)\}]·(H$_2$O)$_2$	Dehydration	12.8006	6.0269×10^9	0.1	0.05529
	Decomposition	49.4434	8.9273×10^6	3.0	0.0316
[Cd(N$_2$H$_4$)$_2$\{CH$_2$(COO)CH(COOH)(S)\}]·(H$_2$O)$_2$	Dehydration	13.4742	1.5700×10^9	3.0	0.05043
	Decomposition	80.93	1.0577×10^6	3.0	0.02387
[Hg(N$_2$H$_4$)$_2$\{CH$_2$(COO)CH(COOH)(S)\}]·(H$_2$O)	Dehydration	38.7265	4.5687×10^7	3.0	0.03768
	Decomposition	62.2205	2.0796×10^6	0.1	0.02641
[Pb(N$_2$H$_4$)$_2$\{CH$_2$(COO)CH(COOH)(S)\}]·(H$_2$O)	Dehydration	14.2198	2.7971×10^9	3.0	0.05249
	Decomposition	95.6478	6.3445×10^6	3.0	0.03035

line for a parameter, n where $Y = 1 - (1 - \alpha)^{n-1}/(1-n)T^2$. The activation energy E can be calculated from the slope and the A factor from the intercept. Kinetic studies reveal that all the complexes follow same mechanism of decomposition as inferred from their computed E values. The activation energy for dehydration of the complexes are found to almost similar in the range of 12.8-14.2 KJ/mol except that of Hg complex which works out to be 38.7 KJ/mol. Activation energies of decomposition of anhydrous complexes are found to be varying from 15.1-95.6 KJ/mol. Table-4 shows the computed kinetic parameters and the dehydration and decomposition steps for all the metal complexes.

Conclusion

The reaction of metal nitrate with mercaptosuccinic acid and hydrazine hydrate yields the complexes of formula [M(N$_2$H$_4$)$_2$\{(CH$_2$(COO)CH(COOH)(S)\}]·(H$_2$O)$_n$ where n = 1 when M = Hg(II), Pb(II), n = 2 when M = Zn(II), Cd(II), n = 3 when M = Co(II) at pH 4. Analytical data confirm their formulations. The ν(N-N) frequencies in IR spectra of the complexes in the range of 937-985 cm^{-1} evidence the presence of hydrazine as a neutral bidentate ligand. The absence of ν(S-H) of sulphahydral group in case of complexes indicates the deprotonation of SH group by metal. Electronic spectra of the complexes confirm the distorted octahedral geometry for Co with coordination number six. The proposed structure of the Co complex is shown in Fig. 3. The thermoanalytical data evince that the complexes are stable upto 158 ºC. complexes
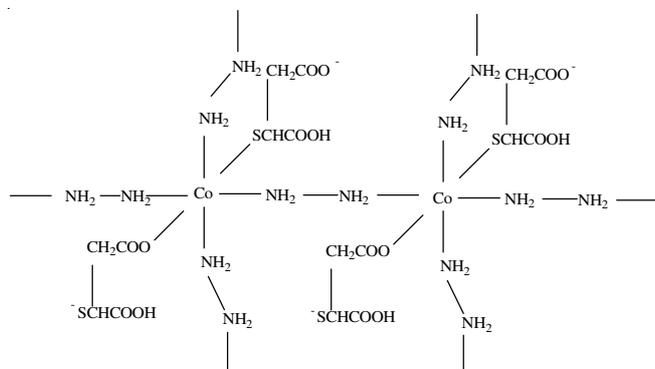
undergo complete decomposition in the range of 290-350 ºC (in the case of Co(II), Zn(II) and Pb(II)) and 433-467 ºC (in the case of Cd(II), Hg(II) complexes) resulting in CoS, ZnO, PbSO$_4$, CdSO$_4$, mercury vapour residues, respectively. SEM image of ZnO residue shows its nano sized clusters suggesting that the complex may be used as a precursor for nano ZnO.

REFERENCES

1. G.E. Cheney, Q. Fernando and H. Freiser, *J. Phys. Chem.*, **63**, 2055 (1959).
2. R.S. Saxena, K.C. Gupta and M.L. Mittal, *Aust. J. Chem.*, **21**, 641 (1968).
3. R.S. Saxena, K.C. Gupta and M.L. Mittal, *Can. J. Chem.*, **46**, 311 (1968).
4. L.J. Porter and D.D. Perrin, *Aust. J. Chem.*, **22**, 267 (1969).
5. M. Maeda, K. Okada, K. Wakabayashi, K. Honda, K. Ito and Y. Kinjo, *J. Inorg. Biochem.*, **42**, 37 (1991).
6. V.K. Mathur and H.L. Nigam, *J. Fur. Prakti. Chem.*, **24**, 78 (1964).
7. L.F. Larkworthy and D. Sattari, *J. Inorg. Nucl. Chem.*, **42**, 551 (1979).
8. K.J. Ellis and A. McAuley, *J. Inorg. Nucl. Chem.*, **37**, 567 (1975).
9. K. Nomiya, K.-I. Onoue, Y. Kondoh, N.C. Kasuga, H. Nagano, M. Oda and S. Sakuma, *Polyhedron*, **14**, 1359 (1995).
10. P.R. Patil and V. Krishnan, *J. Inorg. Nucl. Chem.*, **41**, 1069 (1979).
11. M. Filella, A. Izquierdo and E. Casassas, *J. Inorg. Biochem.*, **28**, 1 (1986).
12. E. Ying, D. Li, S. Guo, S. Dong and J. Wang, *PLoS ONE*, **3**, e2222 (2008).
13. M.A.H. Muhammed, S. Ramesh, S.S. Sinha, S.K. Pal and T. Pradeep, *Nano Res.*, **1**, 333 (2008).
14. S.Y. Sim, Y.J. Gu, H.J. Ahn, C.S. Yoon and S.S. Im, *Polym. Degrad. Stab.*, **94**, 208 (2009).
15. S. Chen, X. Zhang, Q. Zhang, X. Hou, Q. Zhou, J. Yan and W. Tan, *J. Lumin.*, **131**, 947 (2011).
16. S. Vairam, T. Premkumar and S. Govindarajan, *J. Therm. Anal. Calorim.*, 100, 955 (2010)
17. S. Vairam, T. Premkumar and S. Govindarajan, *J. Therm. Anal. Calorim.* 101, 979 (2010).
18. N. Arunadevi and S. Vairam, *E-J. Chem.*, **6**, S413 (2009).
19. A.I. Vogel, A Textbook of Quantitative Inorganic Analysis Including Elementary Instrumental Analysis, The English Language Book Society and Longmans, Green Co., London, edn. 3, pp. 380 and 432 (1961).
20. P.R. Patil and V. Krishnan, *J. Inorg. Nucl. Chem.*, **40**, 1255 (1978).
21. E.W. Schmidt, Hydrazine and Its Derivatives-Preparation, Properties and Applications, Wiley Interscience, New York (1984).
22. K. Nakamoto, Infrared Spectra and Raman Spectra of Inorganic and Coordination Compounds, Wiley Interscience Co, New York, edn. 4 (1986).
23. N. Deb, S.D. Baruah and N.N. Das, *J. Therm. Anal.*, **45**, 457 (1995).
24. G. Cao, Nano Structures and Nano Materials, Synthesis, Properties and Applications, Imperial College Press, London (2004).
25. A.B.P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, p. 481 (1984).
26. A.W. Coats and J.D. Redfern, *Nature*, **201**, 68 (1964).

Fig. 3. Structure of [Co(N$_2$H$_4$)$_2$\{CH$_2$(COO)CH(COOH)(S)\}]·(H$_2$O)$_3$