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Synthesis, spectral characterization and thermo-kinetics of Cr(III) and Th(IV) complexes derived from hydrazones

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Abstract: The thermo-kinetics of Cr(III) and Th(IV) complexes derived from two different hydrazone Schiff bases was investigated by thermogravimetric analysis (TGA). The thermodynamic analysis shows that the complexes lose hydrated and/or coordinated water molecules in the first step; followed by decomposition of ligand moiety in the further steps leading to formation of stable metal oxide. The decomposition steps were analyzed and the parameters like order of reaction(n), energy of activation (Ea), entropy change (ΔS), free energy change (ΔF) and apparent entropy (S*) were calculated by using Freeman-Carroll (FC) and Horowitz-Metzger (HM) methods. The activation energy for complexes obtained in the two sets are in good agreement with each other. On the basis of half decomposition temperature, the thermal stability of the complexes was determined.

Keywords: Hydrazone, Metal complexes, Thermal decomposition, Thermodynamic parameters.

INTRODUCTION

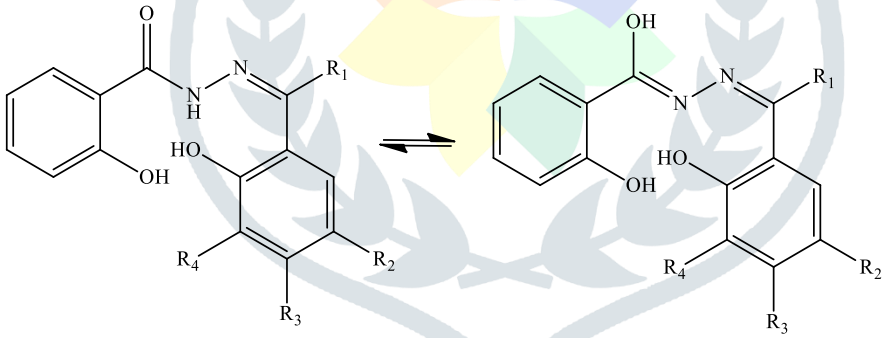
Schiff base complexes derived from hydrazone ligands, consisting strong donor sites like oxygen and azomethine nitrogen are widely studied due to their diverse metal binding, spectroscopic properties, and biological versatility. [1-3], but also due to their remarkable thermal stability as compared to the Schiff base ligands [4-7]. In spite of the relatively large number of reports on Schiff base metal complexes, less work has been published on thermal stability of the complexes and calculation of their kinetic and thermodynamic parameters of decomposition. In this paper we report kinetics of the thermal decomposition pattern of Cr(III) and Th(IV) complexes prepared by using two different hydrazone Schiff bases. The thermal parameters were calculated using Freeman-Carroll (FC) and Horowitz-Metzger (HM) [8] methods. The complexes are thermally stable and their thermal decompositions are multistage processes. The complexes are subjected to TG analysis from 50-850°C.

MATERIAL AND METHODS

All the chemicals used for the synthesis of the ligand and their metal complexes were of AR grade or chemically pure, solvents were purified and dried before use. The ligands used in the work were not commercially available, hence were synthesized in our laboratory. The metal complexes were prepared by mixing the ethanolic solution of metal salt with the ethanolic solution of ligands by setting the suitable reaction conditions. The Cr(III) and Th(IV) metal salts used for the preparation of complexes were chromium(III) chloride [$CrCl_3$] and thorium nitrate tetrahydrate [$Th(NO)_3.4H_2O$] respectively. The ^1H NMR spectra of the ligands were taken using TMS as the internal standard on a 90 MHz on a Perkin Elmer R-32 spectrometer. IR spectra (KBr) were recorded on a Perkin Elmer-842 spectrophotometer in the region 400-4000cm^{-1} at RSIC, Punjab University, Chandigarh. Thermal analysis results of the complexes were obtained at a rate of 10^0C per minute on a Rijaku-Thermo plus EVO2 thermodilatometer.

Synthesis of the Schiff base ligands:

All the ligands: SSH (Salicylaldehyde salicyloyl hydrazone) and DHASH (2,4-dihydroxyacetophenone salicyloyl hydrazone were prepared by the addition of hot ethanolic solution of salicyloyl hydrazide (0.05 mol) into hot ethanolic solution of respective aldehyde/acetophenone (0.05 mol). The reaction mixture was refluxed in a water bath for 4-6 hrs. The colored products so obtained were filtered off and recrystallized from dimethyl formamide.



Ligand	R_1	R_2	R_3	R_4
SSH	H	H	H	H
DHASH	CH_3	H	H	OH

Synthesis of Cr(III) and Th(IV) Complexes:

Equimolar quantities of respective metal salt (0.02 mol $CrCl_3$ or $Th(NO)_3.4H_2O$) and the ligands were dissolved separately in absolute ethanol (25 ml). Both the solutions were filtered and mixed in hot condition. The reaction mixture was refluxed for 4-6 hrs in a water bath. The colored products obtained were filtered, washed several times with hot water followed by ethanol and diethyl ether and finally dried over fused calcium chloride.

RESULTS AND DISCUSSION

Infrared Spectra of the ligand:

The IR Spectra of the ligands were recorded for the identification of their donor sites and to compare the shifts in frequencies after their complexation with Cr(III) and Th(IV) metal ions. A broad and strong band in the spectra of complexes in the region 3365-3268 cm^{-1} is assigned to intramolecular hydrogen bonded phenolic OH, a sharp band between 3220- 3011 cm^{-1} is due to N-H Stretching. The other bands in the region 1649-1642, 1621-1618, 1301-1270 and 1031-962 cm^{-1} are assigned to ν(C=O), ν(C=N) ν(C-O) and ν(N-N) respectively [9-13].

^{1}H NMR Spectral data of ligands:

L1-SSH - δ 12.39 (2 H,S, phenolic OH); 11.44 (1H,S, Imino NH); 6.95 - 7.95 (8H,M, Aromatic proton); 8.94 (1H,s, Azomethine HC=N) [18-21].

L2-DHASH - δ 13.33 (2 H,S, Phenolic C_2-OH); 11.44 (1H,S, Imino NH); 6.98 - 7.99 (7H,M, Aromatic proton); 2.3 (3H,s, Methyl, N=CCH_3) ; 9.82 (1H,S, Phenolic C_4-OH).

Table 1. The analytical and physical data of the complexes.

Sr. No.	Complex	Formula Weight g mol^{-1}	Colour	Time of Reflux	M% Found (Calcd.)	C% Found (Calcd.)	H% Found (Calcd.)	N% Found (Calcd.)
1.	Cr-L1	341.69	brown	5 h	15.63 (15.22)	48.99 (49.21)	2.99 (2.95)	8.14 (8.20)
2.	Cr -L2	370.99	Brown	6 h	13.85 (13.99)	49.23 (48.47)	321 (3.25)	7.48 (7.54)
6.	Th–L1	578.29	Yellow	6 h	39.68 (40.12)	31.02 (29.08)	1.80 (1.74)	9.71 (9.69)
4.	Th –L2	608.32	Yellow	6 h	38.18 (38.14)	29.58 (29.62)	1.79 (1.99)	9.26 (9.21)

Thermogravimetric analysis of the complexes:

All the complexes are stable up to 650°C and are decomposed into two stages. The Cr(III) and Th(IV) complexes remain stable up to ~235°C indicating absence of coordinated and lattice water molecules. Elimination of ligand moiety takes place in the first step and a part of coordinate ligand decomposed in second step followed by horizontal level beyond 650°C in all the complexes due to formation of stable metal oxides. The above pattern confirms the formation of metal complexes. The half decomposition temperature, entropy change (ΔS), free energy change (ΔF) and frequency factor (Z) of compounds were calculated by employing using Freeman-Carroll (FC) and Horowitz-Metzger (HM) methods [14-16]. The kinetic parameter data for the complexes are given in the Table 3. On the basis of half decomposition temperature, the thermal stability of the Cr(III) and Th(IV) metal complexes is found to be: Cr-L_1 > Cr-L_2 > Th-L_2 > Th-L_1 respectively.

Table 2 Thermal decomposition data of Cr(III) and Th(IV) complexes.

Sr. No.	Complex	Half decomposition temperature (°C)	Activation Energy Ea (kJ mole^{-1})		(n)	Entropy Change -ΔS (J/mol/K)	Free Energy Change ΔF (kJ/mol)	Apparent Entropy Change S* (kJ)
			FC*	H-M**				
1.	Cr-L1	405	13.22	11.26	0.93	-311.28	113.33	-28.45
2.	Cr -L2	389	10.27	11.36	0.95	-310.25	107.52	-36.73
3.	Th–L1	352	15.23	14.12	0.96	-369.17	104.79	-32.47
4.	Th –L2	365	13.82	14.11	0.92	-312.74	110.34	-30.74

CONCLUSION

The activation energies calculated by the Freeman-Carroll (FC) and Horowitz-Metzger (HM) methods are in good agreement with each other. Thermodynamic parameters have been calculated on the basis of thermal activation energy and values are given in Table 2. The thermal stability of the compounds can be correlated with the substituent group attached to the ligands.

REFERENCES

1. Islam, M. T., Bitu, N. A., Chaki, B. M., Hossain, M. J., Asraf, M. A., Hossen, M. F., Kudrat-E-Zahan, M., & Latif, M. A. (2024). Water-soluble Schiff base ligands and metal complexes: an overview considering green solvent. RSC advances, 14(35), 25256–25272.

2. Dinnimath, B., Palled, M., Sutar, S., Tashildar, S., Chavan, U., & Ganpule, S. (2024). Developing New Organometal Complexes of Schiff Base Derivatives with Anticancer Potentials. International Journal of Pharmaceutical Investigation, 14(3), 712–737.

3. Khan, H., Jan, F., Shakoor, A., Khan, A., AlAsmari, A. F., Alasmari, F., Ullah, S., Al-Harrasi, A., Khan, M., & Ali, S. (2024). Design, synthesis, molecular docking study, and α-glucosidase inhibitory evaluation of novel hydrazide-hydrazone derivatives of 3,4-dihydroxyphenylacetic acid. Scientific reports, 14(1), 11410. https://doi.org/10.1038/s41598-024-62034-x

4. Ahmad, N., Alam, M., Wahab, R., Ahmed, M. & Ahmad, A. (2020). Synthesis, spectral and thermo-kinetics explorations of Schiff-base derived metal complexes. *Open Chemistry*, *18*(1), 1304-1315.

5. Elemo, F., Gebretsadik, T., Gebrezgiabher, M., Bayeh, Y. & Thomas, M. (2019) Kinetics on thermal decomposition of Iron(III) complexes of 1,2-bis(imino-4'-antipyrinyl)ethane with varying counter anions. Advances in Chemical Engineering and Science, 9, 1-10. https://doi.org/ 10.4236/aces.2019.91001.

6. Sunjuk, M., Al-Najjar, L., Shtaiwi, M., El-Eswed, B. I., Sweidan, K., Bernhardt, P. V., Zalloum, H., & Al-Essa, L. (2023). Metal Complexes of Schiff Bases Prepared from Quinoline-3-Carbohydrazide with 2-Nitrobenzaldehyde, 2-Chlorobenzaldehyde and 2,4-Dihydroxybenzaldehyde: Structure and Biological Activity. Inorganics, 11(10), 412.

7. Komyha, E., Mahmoud, W., Hosny, W., & El-Sherif, A. (2023). Design, Structural Characterization, Molecular docking and Biomedical Applications Of Hydrazone-based Schiff base Metal Complexes. Egyptian Journal of Chemistry, 66(13), 1219-1230.

8. Auxier, J. D., Stratz, S. A., Shahbazi, S., Hanson, D. E., Cressy, D., & Hall, H. L. (2016). Thermodynamic analysis of volatile organometallic fission products. *Journal of radioanalytical and nuclear chemistry*, 307, 1621–1627. doi.org/10.1007/s10967-015-4653-9

9. Omar, M. M., Mohamed, G. G., & Ibrahim, A. A. (2009). Spectroscopic characterization of metal complexes of novel Schiff base. Synthesis, thermal and biological activity studies. *Spectrochim. Acta*, 73, 358-369. doi.org/10.1016/j.saa.2009.02.043

10. Refat, M. S., El-Sayed, M. Y., Adam, A. (2013). Cu (II), Co (II) and Ni (II) complexes of new Schiff base ligand: synthesis, thermal and spectroscopic characterizations. *J. Mol. Struct*., 1038, 62-72.
11. Li, J., Xu, B., Jiang, W., Zhou, B., Zeng, W. & Qin, S. (2008). Syntheses, spectroscopic characterization and metal ion binding properties of benzo-15-crown-5 derivatives and their sodium and nickel(II) complexes. *Transition Metal Chemistry*, 33(8), 975-979. doi.org/10.1007/s10847-011-9973-y
12. Maurya, M. R., Behl, S., Schulzke, C., & Rehder, D., (2001). Dioxo- and Oxovanadium(V) Complexes of Biomimetic Hydrazone ONO Donor Ligands: Synthesis, Characterisation, and Reactivity. *Eur. J. Inorg. Chem*, 3, 779-788.
13. Makhijani, R. M., & Barhate, V. D. (2014). Synthesis, characterization and study of microbiological activity of complexes of Fe(II) and Cu(II) with (N-(o-methoxy benzaldehyde)-2-aminophenol}(NOMBAP). *International Journal of ChemTech Research*, 6(2), 1003-1012
14. Abu-Melha, K. S., & El-Metwally, N. M. (2008). Spectral and thermal studies for some transition metal complexes of bis(benzylthiocarbohydrazone) focusing on EPR study for Cu(II) and VO^{2+}.*Spectrochimica Acta Part A*, 70(1), 277-283.
15. Borase, J. N., Mahale, R. G. & Rajput, S. S. (2021). Design, synthesis and biological evaluation of heterocyclic methyl substituted pyridine Schiff base transition metal complexes. *SN Appl. Sci.*, **3**, 197.
16. Thakare, K. A., & Aswar, A. S. (2021). Ti(III), VO(IV), Cr(III), Fe(III), MoO_2(VI) and WO_2(VI) complexes of new tridentate Schiff base ligand: synthesis, spectral characterization, thermal and biological studies. *Rasayan J. Chem*, 14(4), 2776-2789.