

Synthesis and Characterization of Trinuclear Nickel (II) Complexes using Mononuclear Metal Complexes as Ligands

Satyam Kumar Singh & Naresh Kumar

University Department of Chemistry,
B.N. Mandal University, Madhepura - 852113, Bihar, India.
E-mail: drnareshchem@gmail.com

Abstract: A series of trinuclear nickel (II) complexes of the type $[Ni_3(Salen)_2(GDH)_2X_2]$ where $X=Cl^-$, Br^- , I^- , NO_3^- , SCN^- , and BF_4^- have been synthesized by union of mononuclear nickel (II) chelates $[Ni(Salen)]$ and $[Ni(GDH)_2X_2]$ in which unutilized $-NH_2$ groups of the hydrazone complexes has condensed with aldehydic oxygen of the $[Ni(Salen)]$ complex. The molar ratio between hydrazone complex and Salen complex has been 1:2. $[Ni(Salen)]$ complex has been synthesized by the metal ion catalyzed template synthesis allowing salicylaldehyde and ethylenediamine to react together in the presence of nickel acetate in butanol medium. The complex is stable and can be stored for long periods without decomposition. The electronic spectra and magnetic moment data show that the nickel ions are present in two types of environments. The central nickel ion is octahedrally coordinated while terminal nickel ions are present in square planar environments.

Keywords: Trinuclear Nickel (II) Complexes, Schiff-base Ligands, Spectral Study.

1. Introduction:

Multinuclear nickel (II) complexes have become a central theme of current research because of their potentially useful properties. They are involved in some notable catalytic processes. Their important use for modeling the metal active sites of metalloproteins and their recent applications in the area of nanoscience have drawn the focus of modern chemist towards the synthesis and characterization of such metal complexes¹⁻⁷.

In this present communication, we report synthesis and characterization of a series of trinuclear nickel (II) complexes of the type $[Ni_3(Salen)_2(GDH)_2X_2]$ using mono nuclear metal chelates as ligands.

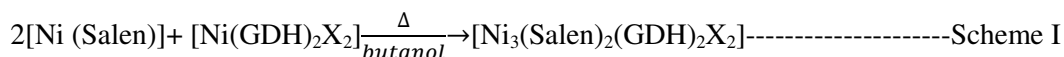
2. Experimental:

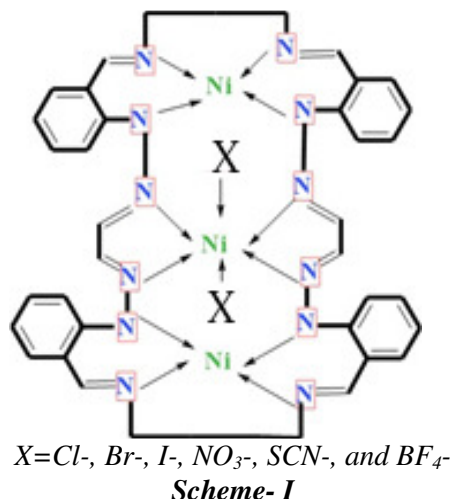
All the reagents were purchased commercially and are used without further purification.

2.1 Synthesis of Trinuclear Nickel (II) Complexes:

The trinuclear nickel (II) complexes of the type $[Ni_3(Salen)_2(GDH)_2X_2]$ were synthesized by Schiff base condensation and concerted template synthesis using the nickel (II) complex $[Ni(Salen)]$ and a complex of the type $[Ni(GDH)_2X_2]$ in the molar ratio 2:1 in butanol medium.

The $[Ni(Salen)]$ complex was prepared by the literature method reported by T. Tsumaki⁸ and $[Ni(GDH)_2X_2]$ by Sahoo et al⁹. The reaction taking place during the synthesis of complexes may be represented as shown in scheme I.





3. Results And Discussion:

Preparation in aqueous ethanolic medium also gives satisfactory results. The macrocyclic complexes were prepared under high dilute condition.

Table – I: Analytical Data of the Complexes $[Ni_3(Salen)_2(GDH)_2X_2]$

Complexes	Found (Calculated)				
	C %	H %	N %	Ni %	X %
$[Ni_3(Salen)_2(GDH)_2Cl_2]$	48.78 (49.02)	3.61 (3.63)	19.00 (19.09)	19.98 (20.11)	8.06 (8.07)
$[Ni_3(Salen)_2(GDH)_2Br_2]$	44.32 (44.58)	3.28 (3.30)	17.02 (17.33)	18.08 (18.26)	16.18 (16.51)
$[Ni_3(Salen)_2(GDH)_2I_2]$	40.12 (40.41)	2.98 (3.01)	15.30 (15.80)	16.38 (16.65)	23.80 (23.89)
$[Ni_3(Salen)_2(GDH)_2(NO_3)_2]$	46.08 (46.30)	3.42 (3.43)	20.96 (21.00)	18.83 (18.97)	- -
$[Ni_3(Salen)_2(GDH)_2(SCN)_2]$	46.32 (46.70)	3.45 (3.46)	17.98 (18.16)	19.00 (19.23)	12.48 (12.54)
$[Ni_3(Salen)_2(GDH)_2(BF_4)_2]$	43.52 (43.77)	3.18 (3.24)	16.98 (17.02)	17.68 (17.93)	17.59 (17.63)

3.1 Infrared Spectra:

Vibrational spectra of the complexes in the region $4000 - 200 \text{ cm}^{-1}$ have been recorded and presented in Table – II. General feature of the spectra of the macrocycles are quite complex to precursor complexes of dihydrazone and those of $[Ni(Salen)]$. Due to Schiff base condensation two significant aspects of the spectra are: - (1) The spectra for the macrocyclic structure and (2) several bands of structural significant characteristic of the precursors have disappeared from the spectra of the macrocycles.

There is no band in the regions 3300 – 3100 cm^{-1} which can be assigned to the stretching vibration of the $-\text{NH}_2$ groups of the precursor dihydrazones and suggest metal iron assisted template condensation of the $-\text{NH}_2$ group with dialdehyde $[\text{Ni}(\text{Salen})]$. A strong and sharp band is observed in the region 1605 – 1590 cm^{-1} in all the microcyclic complexes and is the only band of its kind in this region and it characterizes $\text{C}=\text{N}$ bands stretching vibrations. From structural considerations one might expect two kind of $\text{C}=\text{N}$ bands, one due to the imine groups that originally existed in hydrazonemotes and other due to diamine groups generated as a consequence of condensation of NH_2 groups of hydrazone with the precursor metal (II) aldehyde complex. But the appearance of alone $\text{C}=\text{N}$ bands gives us the impression that in the microcyclic complexes all imine groups are nearly of the same Vibrational energies which arises due to the high degree of conjugation or electron delocalization in the resultant microcyclic structure. A pair of bands which are clearly recognizable and have the characteristic features observed in the spectra of the dialdehydes are located at 1240 – 1225 cm^{-1} at 1060 – 1040 cm^{-1} respectively. These are asymmetric and symmetric ethereal $\text{C}-\text{O}-\text{C}$ stretching vibrations. From energy considerations they appear at a relatively lower frequency region in the microcyclic complexes compare to the corresponding vibrations observed for the free dialdehydes and the lowering of energy can be directly attributed to the involvement of ethereal oxygen atoms in coordination with the metal centres. In the lower energy region 900- 600 cm^{-1} there also appear a few bands which may be assign to the effect of substitutional on the phchyl rings and other skeletal modes of vibrations. The Vibrational spectra as a whole satisfy the microcyclic structure of the metal complexes of nickel (II).

3.2 Electronic Spectra and Magnetic Properties:

In order to elucidate the structural problems I.R and electronic spectra (Table II – III) of the precursors and tricyclomacrocyclic complex were recorded respectively on shimadza 160A and Beckan – 20 spectrophotometers. Conductivity and magnetic susceptibility have also been measured on systronics condtometer model – 303 and guuy balances respectively.

Table – II: Structurally Important I. R. Spectral bands (cm^{-1})

Complexes	$\nu_{\text{C-H}}$	$\nu_{\text{C=N}}$	$\nu_{\text{Ni-N}}$	$\nu_{\text{Ni-X}}$
$[\text{Ni}_3(\text{Salen})_2(\text{GDH})_2\text{Cl}_2]$	3015	1605	612	418
$[\text{Ni}_3(\text{Salen})_2(\text{GDH})_2\text{Br}_2]$	2995	1598	618	405
$[\text{Ni}_3(\text{Salen})_2(\text{GDH})_2\text{I}_2]$	3012	1595	610	398
$[\text{Ni}_3(\text{Salen})_2(\text{GDH})_2(\text{NO}_3)_2]$	3018	1602	615	415
$[\text{Ni}_3(\text{Salen})_2(\text{GDH})_2(\text{SCN})_2]$	3005	1608	609	418
$[\text{Ni}_3(\text{Salen})_2(\text{GDH})_2(\text{BF}_4)_2]$	3014	1610	618	408

Table – III: Electronic Spectral bands (cm^{-1}) and magnetic moment (B.M)

Complexes	${}^3\text{B}_{1g} \rightarrow$	${}^3\text{B}_{1g} \rightarrow$	${}^3\text{B}_{1g} \rightarrow$	${}^3\text{B}_{1g} \rightarrow$	Magnetic Moment
	${}^3\text{E}_g$	${}^3\text{B}_{2g}$	${}^3\text{A}_{2g}$	${}^3\text{E}_g({}^3\text{T}_{2g})$	
$[\text{Ni}_3(\text{Salen})_2(\text{GDH})_2\text{Cl}_2]$	8400	10,500	18,300	27,600	2.85
$[\text{Ni}_3(\text{Salen})_2(\text{GDH})_2\text{Br}_2]$	8700	11,200	19,200	28,300	2.65
$[\text{Ni}_3(\text{Salen})_2(\text{GDH})_2\text{I}_2]$	8200	10,800	18,600	29,000	2.72
$[\text{Ni}_3(\text{Salen})_2(\text{GDH})_2(\text{NO}_3)_2]$	9000	11,600	18,900	28,100	2.78
$[\text{Ni}_3(\text{Salen})_2(\text{GDH})_2(\text{SCN})_2]$	8520	10,600	19,100	27,900	2.68
$[\text{Ni}_3(\text{Salen})_2(\text{GDH})_2(\text{BF}_4)_2]$	8800	11,500	19,400	27,800	2.70

Low value of molar conductivity in the range $10 - 15 \text{ mho cm}^2 \text{ mole}^{-1}$ indicates the precursor and microcyclic complex to be non-electrolytic in nature. The magnetic moment of microcyclic precursor $[\text{Ni}(\text{C}_{20}\text{H}_{12}\text{N}_2\text{O}_2\text{Cl}_2)]$ indicated to be diamagnetic.

Electronic spectrum with a broad band with low intensity at 20000 cm^{-1} suggests the stereochemistry to be square planar.

Magnetic moment of the complex was found in the range 2.65 to 2.85 B.M. indicating central Ni_2 ion to be present in tetragonally distorted octahedral environment and terminal ones to be present in square planar environment.

4. Acknowledgements

Authors are thankful to Prof. H. C. Rai, Ex-Head, Univ. Department of Chemistry, B. R. A. Bihar University of Muzaffarpur.

References:

1. Iskander M.F and Saddeck S, *InorgChimActa*, 22 (1977) 141.
2. Elshazly M.F, *Transition Met Chem*, 6 (1981) 8.
3. Iskander M.F, Elsayeed L and Saddeck S, *Transition Met Chem*, 8 (1981) 32 and References Therein.
4. Stoufer RC and Burch DH. *J AM Chem Soc.*, 82 (960) 4834.
5. Chakrabarty J & Sahoo B, *Indian Chem*, 19 A (1980) 441.
6. Rai H.C & Sahoo B, *J Indian Chem Soc*, L111 (1976) 646.
7. Goedkon. VL & Pong S, *JCS ChemCommun*, (1973) 62.
8. Tsumaki, T., *Bull. Chem. Soc., Japan*, 13 (2), (1938) 252-260.
9. Sahoo Bhagirathi, Rout A. K., and Sahoo B. *Ind. J. Chem.*, 25A, (1986) 609-614.