

Study of Trinuclear Nickel Complexes of Nanodimension And Concerted Template Synthesis Using The Nickel(II) Complexes

SHAKTIDHAR JHA SUNIT, RAKESH RANJAN

Department of Chemistry, B. R. A. Bihar University, Muzaffarpur, Bihar, India

ABSTRACT - The branch of nanoscience and technology is truly multi-disciplinary and is an emerging technology with full of promises to have an impact on virtually every spectrum of civilization including communications, computing, textiles, cosmetics, sports, therapy, automotives, environmental monitoring, fuel cells and energy devices, water purification, food and beverage industry, etc. The ability to construct tiny objects atom-by-atom or molecule-by-molecule forms one of the exciting prospects of the research field in nano science. It shows great promise for providing us in the near future with many breakthroughs that will change the direction of nanotechnology advances in a wide range of applications.

KEYWORDS: Nanotech, Deposition, Bichelate, Hydrocarbons, Cobalt(II).

I. INTRODUCTION

The term “Nanotechnology” was first defined by **Norio Taniguchi** of the Tokyo Science University in 1974. Nanotechnology¹⁻³, shortened to “Nanotech” is the study of manipulating matter on an atomic and molecular scale. Generally nanotechnology deals with structures sized between 1 to 100 nm and involve developing materials or devices within that size. For comparison, 10 nanometers is 1000 times smaller than the diameter of a human hair. Nanotechnology has the capacity to improve our ability to prevent, detect, and remove environmental contaminants in air, water, and soil in a cost effective and environmentally friendly manner. Nanoscience and nanotechnologies are revolutionizing our understanding of matter and are likely to have profound implications for all sectors⁴⁻⁶ of the economy, including agriculture and food, energy production and efficiency, the automotive industry, cosmetics, medical appliances and drugs, household appliances, computers, and weapons.

II. SYNTHESIS OF NANOMATERIALS

Nanomaterials can be synthesised by only one of the several methods, i.e.,

Chemical vapour deposition

It involves decomposition of vapour of hydrocarbons such as methane, ethylene, acetylene, etc., at 1100°C in presence of catalysts like Ni, Co, Fe supported on MgO.

III. APPLICATIONS

Some commercial products on the market today utilizing nanomaterials include stain resistant textiles and reinforced tennis rackets. Companies like Kraft foods are heavily funding nanomaterials based plastic packaging. Food will

stay fresh longer if the packaging is less permeable to atmosphere.

Nanotechnology is already transforming our lives with new technologies and products. Nanotechnology exploits the novel phenomenon and properties of matter at nano scale and may offer new solutions of millions of people in developing countries who lack access basic services, such as safe water, renewable energy, health care and education. There is a steep rise in global funding for nanoscience and technology. There is also growing need to raise the level of awareness not only among scientists and industrial professionals but also among young students.

Although nanoscience has recently emerged as a unique discipline of research, the technology is still fairly young and the field remains loosely defined, presenting an opportunity to incorporate new concepts within the existing methodology. The future for the application of nanotechnology looks bright because of its efficiency and its potential to contribute to clean products.

Consequently, in continuation of our earlier interest in the field³⁵⁻³⁸, we, in the present programme propose to synthesize a series of coordination compounds of nanodimension by allowing small molecular components of a Schiff base ligand to assemble together in the presence of metal cations due to template effect and characterize them on the basis of special, magnetic and electrochemical technique leading to structural elucidation.

IV. RESULTS AND DISCUSSION

On the basis of elemental analysis (Table 1), stoichiometry of the macrocyclic precursors (Ni(dial) and (Ni(dial)'), bichelate non macrocyclic precursor (Ni-bis-dihydrazone) Br²) and tricyclomacrocyclic complex have been found to be

(Ni(C₁₆H₁₂N₂O₂Cl₂) (Ni(C₄H₈N₈R₄) Cl₂Br₂) and (Ni₃(Mc¹⁻⁸Br₂) respectively. In order to elucidate the structural problems, i.r. and electronic spectra of the precursors and

tricyclomacrocyclic complex were recorded respectively on Shiamadzu 160 A and Backman-20 spectrophotometers.

Table-1: ANALYTICAL DATA THE COMPLEXES

SI. No.	Complexes	Colour	Found (Calc.)%					
			Ni	C	H	N	Cl	Br
1	Ni ₃ Mc ¹ Br ₂	Red	16.79 (16.84)	41.04 (41.10)	2.61 (2.66)	10.60 (10.66)	13.46 (13.51)	15.17 (15.22)
2.	Ni ₃ Mc ¹ Br ₂	Pink	15.93 (15.99)	43.31 (43.36)	3.21 (3.26)	10.08 (10.012)	12.78 (12.83)	14.40 (14.45)
3.	Ni ₃ Mc ² Br ₂	Violet	15.31 (15.36)	45.76 (45.82)	3.77 (3.82)	9.67 (9.71)	12.27 (12.32)	13.83 (13.88)
4.	Ni ₃ Mc ³ Br ₂	Yellowish	13.09 (13.14)	53.40 (53.45)	3.22 (3.27)	8.27 (8.31)	10.49 (10.54)	11.82 (11.88)
5.	Ni ₃ Mc ⁴ Br ₂	Red	15.27 (15.32)	45.66 (45.71)	2.68 (2.77)	9.65 (9.70)	12.23 (12.29)	13.79 (13.85)
6.	Ni ₃ Mc ⁵ Br ₂	Pink	14.66 (14.71)	47.85 (47.89)	2.94 (2.99)	9.26 (9.31)	11.75 (11.80)	13.25 (13.30)
7.	Ni ₃ Mc ⁶ Br ₂	Violet	14.12 (14.17)	49.91 (49.96)	3.46 (3.52)	8.91 (8.97)	11.32 (11.37)	12.76 (12.81)
8.	Ni ₃ Mc ⁷ Br ₂	Yellowish	12.21 (12.27)	56.50 (56.55)	3.00 (3.05)	7.71 (7.76)	9.78 (9.84)	11.02 (11.08)

Conductivity and magnetic susceptibility have also been measured on Synstronics conductometer model-303 and Guoy balance respectively, low value of molar conductivity in the range 10-15 ohm cm⁻² mol⁻¹ indicate the precursor and macrocyclic complex to be non-electrolytic in nature. The magnetic moment of precursors (Ni(C₁₆H₁₂N₂O₂Cl₂) and (Ni(C₂₀H₁₂N₂O₂Cl₂) indicated to be diamagnetic. Electronic spectrum with a broad band with low intensity at 20000 cm⁻¹ suggests the stereochemistry to be square planar. Non-macrocyclic precursor (Ni(C₄H₈N₈R₄)Br₂) (R=H, CH₃, C₂H₅ and C₆H₅) have μ_{eff} in the ranges 3.12-3.22 B.M. indicating them to be octahedral in nature. The electronic spectra are also in good agreement with the literature.

The μ_{eff} of tricyclomacrocyclic complex has been found to be 3.8 B.M. and is presumed to be due to central octahedral and terminal square planar environment of Ni(II) ions. The excess value is most presumably due to T.I.P contribution.

4.1 Infrared Spectra

Vibrational spectra of the complexes in the region 4000-300 cm⁻¹ have been recorded and presented in Table-2. General features of the spectra of the macrocycles are quite complex with respect to precursor complexes of dihydrazone and those of (Ni(dial) or (Ni(dial')). Two significant aspects of the spectra are :

- (1) The spectra for the macrocyclic structure and
- (2) Several bands of structural significance characteristic of the precursors have disappeared from the spectra of the macrocycles because of Schiff base condensation.

There is no band in the region 3300-3100 cm⁻¹ which can be assigned to the stretching vibrations of the-NH₂ groups of the precursor dihydrazones and suggests metal ion assisted template condensation of the-NH₂ groups with the dialdehyde (Ni(dial) or (Ni(dial')). In earlier reported spectra of (bis-(diacetyldihydrazone) M(II)²⁺ complexes, the NH₂ asymmetric and symmetric stretching mode of vibrations have been observed as two strong bands in the region 3300 to 3200 cm⁻¹. The C-H stretching vibrations of glyoxal, diacetyl and benzyl moieties and the phenyl groups of the dialdehydes are observed in the region 3060-2870 cm⁻¹. There appears a strong and sharp band in the region 1605-1590 cm⁻¹ in all the macrocyclic complexes and is the only band of its kind in this region and it characterizes C=N stretching vibrations. From Structural considerations one might expect two kinds of C=N bands, one due to the imine groups that originally existed in hydrozone moieties and the other due to the imine groups generated as a consequence of condensation of NH₂ groups of hydrazone with the precursor metal(II) aldehyde complex. But the appearance of a lone C=N band gives us the impression that in the macrocyclic complexes, all the imine groups are nearly of the same vibrational energies which arises due to high degree of conjugation or electron delocalization in the resultant macrocyclic 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 and at 1060-1040 cm⁻¹ respectively. These are asymmetric and symmetric ethereal C-O-C stretching vibrations. From energy considerations they appear at a relatively lower frequency region in the macro-cyclic complexes compared to the corresponding vibrations observed for the free dialdehydes and the lowering of energy can be directly attributed to involvement of ethereal oxygen atoms in coordination with the metal centres.

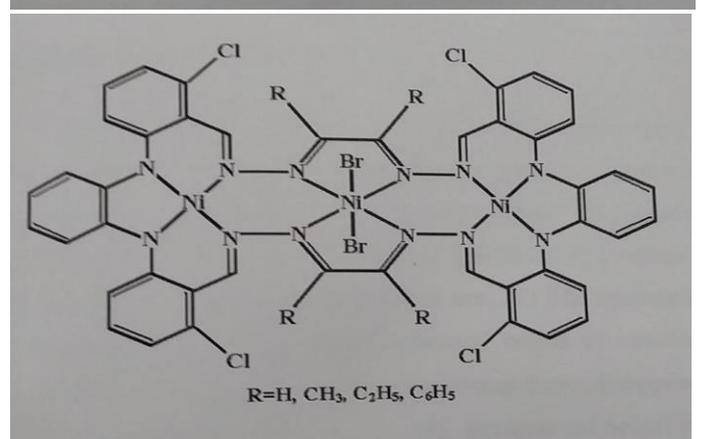
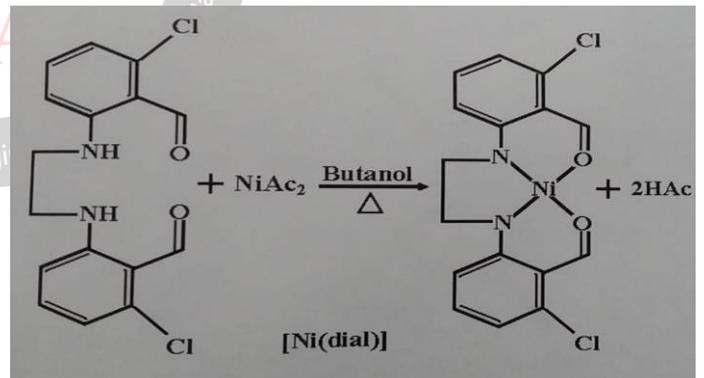
Table-2:Structurally important infraed bands (in-cm⁻¹) of the trinuclear nickel(II) Macrocylic complexes.

(Ni ₃ Mc ¹ Br ₂)	(Ni ₃ Mc ² Br ₂)	(Ni ₃ Mc ³ Br ₂)	(Ni ₃ Mc ⁴ Br ₂)	Bands assigned	
2975	965	3037	2945	U(C-N)	
2868	2872	2928			
1590	1595	1592	1600	U(C-N)	
1482	-	-	1490	Skeletal vibrations of phenyl and furyl groups and de-formation mode of vibrations of CH ₃ - and CH ₂ - groups	
1465	1460	1455	1450		
1390	1391	1391	-		
1295	1293	1294	1294		
1240	1244	1220	1245		
1055	1052	1057	1045	u _{as} (C-O-C)	
960	957	942		Bands due to effect of substitution on the phenyl rings and other skeletal modes vibrations.	
845	846	833	850		
812	810	755	756		
765	760	657	679		
620	619	529			
440	445	466	476		
(Ni ₃ Mc ⁵ Br ₂)	(Ni ₃ Mc ⁶ Br ₂)	(Ni ₃ Mc ⁷ Br ₂)	(Ni ₃ Mc ⁸ Br ₂)		Bands assigned
3060	3060	2952	3000		u(C-N)
2935	2934	2925	2940		
2873	2878				
1602	1605	1605	1610	v(C-N)	
1484	1484	1463	1475	Skeletal vibrations of phenyl and furyl groups and de-formation mode of vibrations of CH ₃ - and CH ₂ - groups	
1448	1452	-	1450		
1342	1390		1335		
1283	1346	1309			
	1293				
1244	1244	1236	1240	u _{as} (C-O-C)	
1053	1048	1044	1050	u _s (C-O-C)	
980	976	948	970	Bands due to effect of substitution on the phenyl rings and other skeletal modes vibrations.	
920					
863	869		860		
750	755	746	739		
690	690				
660	653	566	560		
483	479	473	475		

Several other vibrational bands which are self-consistent with the stretching vibrations of the macrocyclic skeleton are also observed in the infrared spectra of the complexes. The first group of bands is observed near 1480 and 1280 cm⁻¹. They arise due to skeletal vibrations of the phenyl and ethyl groups and the deformation mode of vibrations of -CH₃ and -CH₂- groups of the appropriate macrocycles. In the lower energy region 900-600 cm⁻¹ there also appear a few bands which may be assigned to the effect of substitution on the phenyl rings and other skeletal modes of vibrations. The vibrational spectra as a whole satisfy the macrocyclic structures of the metal complexes of nickel (II).

V. SYNTHESIS

The trinuclear nickel complexes of nanodimension were obtained by Schiff base condensation and concerted template synthesis using the nickel(II) complexes (Ni(dial) or (Ni(dial') and a complex of the type (bis-(dihydrazone) nickel(II)²⁺ in the mole ratio 2:1 in butanol. The synthesis is figuratively presented below.



Preparation in aqueous ethanolic medium also gives satisfactory results. The macrocyclic complexes were prepared under high dilute condition. The macrocycles with R=H went into solution and were obtained in the form of microcrystalline products on slow evaporation.

The complexes with R=CH₃, C₂H₅ and C₆H₅, on the other hand, were obtained more conveniently since they precipitate from butanol medium. They are stable and could be stored over long periods. All the complexes were isolated as dibromo salts.

5.2 Infrared Spectra:

Vibrational spectra of the complexes in the region 4000-300 cm⁻¹ have been recorded. General features of the spectra of the macrocycles are quite complex with respect to precursor complexes of dihydrazone and those of (Ni(dial) or (Ni(dial)'. Two significant aspects of the spectra are: (1) The spectra for the macrocyclic structure and (2) several bands of structural significance characteristic of the precursors have disappeared from the spectra of the macrocycles because of Schiff base condensation.

There is no band in the region 3300-3100 cm⁻¹ which can be assigned to the stretching vibrations of the -NH₂ groups of the precursor dihydrazones and suggests metal ion assisted template condensation of the -NH₂ groups with the dialdehyde (Ni(dial) or (Ni(dial)'. In earlier reported spectra of (bis-(diacetyldihydrazone) M(II)²⁺ complexes, the NH₂ asymmetric and symmetric stretching mode of vibrations have been observed as two strong bands in the region 3300 to 3200 cm⁻¹. The C-H stretching vibrations of glyoxal, diacetyl and benzil moieties and the phenyl groups of the dialdehydes are observed in the region 3060-2870 cm⁻¹. There appears a strong and sharp band in the region 1605-1590 cm⁻¹ in all the macrocyclic complexes and is the only band of its kind in this region and it characterizes C=N stretching vibrations. From structural considerations one might expect two kinds of C=N bands, one due to the imine groups that originally existed in hydrazone moieties and the other due to the imine groups generated as a consequence of condensation of NH₂ groups of hydrazone with the precursor metal (II) aldehyde complex. But the appearance of a lone C=N band gives us the impression that in the macrocyclic complexes, all the imine groups are nearly of the same vibrational energies which arises due to high degree of conjugation or electron delocalization in the resultant macrocyclic 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 and at 1060-1040 cm⁻¹ respectively. These are asymmetric and symmetric ethereal C-O-C stretching vibrations. From energy considerations they appear at a relatively lower frequency region in the macrocyclic complexes compared to the corresponding vibrations observed for the free

dialdehydes and the lowering of energy can be directly attributed to involvement of ethereal oxygen atoms in coordination with the metal centres.

Several other vibrational bands which are self-consistent with the stretching vibrations of the macrocyclic skeleton are also observed in the infrared spectra of the complexes. The first group of bands is observed near 1480 and 1280 cm⁻¹. They arise due to skeletal vibrations of the phenyl and ethyl groups and the deformation mode of vibrations of -CH₃ and -CH₂- groups of the appropriate macrocycles. In the lower energy region 900-600 cm⁻¹ there also appear a few bands which may be assigned to the effect of substitution on the phenyl rings and other skeletal modes of vibrations. The vibrational spectra as a whole satisfy the macrocyclic structures of the metal complexes of nickel (II).

5.3 Electronic spectra and magnetic properties:

In order to elucidate the structural problems, i.r. and electronic spectra of the precursors and tricyclomacrocyclic complex were recorded respectively on Shimadzu 160 A and Beckman-20 spectrophotometers. Conductivity and magnetic susceptibility have also been measured on Systronics conductometer model -303 and Guoy balance respectively. Low value of molar conductivity in the range 10-15 ohm cm⁻² mol⁻¹ indicates the precursor and macrocyclic complex to be non-electrolytic in nature. The magnetic moment of macrocyclic precursors (Ni(C₁₆H₁₂N₂O₂Cl₂) and (Ni(C₂₀H₁₂N₂O₂Cl₂)) indicated to be diamagnetic.

Electronic spectrum with a broad band with low intensity at 20000 cm⁻¹ suggests the stereochemistry to be square planar. Non-macrocyclic precursors (Ni(C₄H₈N₈R₄)Br₂) (R=H, CH₃, C₂H₅ and C₆H₅), have μ_{eff} in the ranges 3.12-3.22 B.M. indicating them to be octahedral in nature. The electronic spectra are also in good agreement with the literature.

For the present groups of macrocyclic complexes, the parameters D_q^{xy} and D_q^z which represent the crystal field strength of the macrocyclic ligands and the metal-ligand interaction (of Br ion) along the axial direction remain practically constant. The ligand field parameters have comparable magnitudes with the corresponding D_q^{xy} and D_q^z values for the bromo complexes of nickel (II) with 1, 2-diphenylethane-1, 2-dionehydrazone. The near constancy of the parameters along the series indicates that the metal-ligand interaction along the axial direction and in the plane do not mutually influence each other. It may be pointed out that the results for the tetragonal nickel (II) complexes show that the D_q^{xy} parameter is practically invariant for similar (Ni(Py)₄X₂) complexes (Py-is pyridine and X is a halide ion) and the ligand field effects are not transferable. But in the case of some carboxylate complexes, the parameter D_q^{xy} is found to be affected with the carboxylate

group and the effect has been attributed to the transferability of the ligand field effects.

The electronic spectra and the magnetic susceptibility show that the nickel ions are present in two types of stereochemical environments. The central nickel ion is octahedrally coordinated. It seems that a pair of Br ions is bonded to central nickel (II) ion. The terminal nickel ions are present in square planar environment.

VI. REFERENCES

- [1] Sundeep, H.; Yo, Hwei-Jang.; Huang, Jow-lay., *Int. J. Nanoscience*, 2010, 9(3), 225.
- A. Ravikrishna, *Engineering Chemistry*, Sri Krishna Hi-Tech Publishing Company, 10th Edition, Chennai, July (2009).
- [2] Arivalagan, K.; Karthikeyan, R., *Engineering Chemistry*, Shiv Publications, Chennai, July 2007.
- [3] Varma, R.S.; Saini, R.K. R. *Dahiya Tetrahedron Lett.* 1997, 38, 7823.
- [4] Kidwai, M.; Sapra, P., *Org. Prep. Proced. Int.* 2001, 33, 381.
- [5] Gedye, R.; Smith, F.; Westaways, K.; Ali, H., *Tetrahedron Lett.*, 1986, 27, 279.
- [6] Rajkumar, N; Umamaheswari, D.; Ramachandran, K., *Int. J. Nanoscience*, 2010, 9(3), 243.
- [7] Loupy, A., *Microwaves in Organic Synthesis* Wiley-VCH, Weinheim (2002).
- [8] Lidstrom, P.; Tierney, J.; Wathey, B., *Tetrahedron*, 2001, 57, 7764.
- [9] Kidwai, M., *Pure Appl. Chem.*, 2006, 78(11), 1983.
- [10] Sanghi, Rashmi., *Resonance*, March, 2000, 77.
- [11] Varma, R.S., *Tetrahedron*, 2002, 58, 1235.
- [12] Artman, D.D.; Williams, R.M., *J. Amer. Chem. Soc.*, 2007, 129, 6336.
- [13] Mohamed, A.E.; Rashad, R.M.; Bedway, M.K.; *Int. J. Nanoscience*, 2008, 8(3), 237.
- [14] Tans, S.J.; Verschueren, A.R. M.; Dekker, C. *Nature*, 1998, 393 49.
- [15] Bachtold, A.; Hadley, P.; Nakanishi, T.; Dekker, C., *Science*, 2001, 294, 1317.
- [16] Singh, B.P.; Varma, Amit, *Int. J. Nanoscience*, 2009 7(6), 305.