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Nickel Complexes with Induced Trigonal Prismatic Symmetry

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A synthetic procedure has been developed which affords a new series of six coordinate nickel(II) complexes distinguished by a bicyclic ligand framework which encapsulates the metal ion and imposes a trigonal prismatic (TP) or near TP stereochemistry. Electronic, infrared spectra and magnetic moments are discussed.

Introduction

One of the most important classes of metal template reactions is the formation of macrocyclic ring system which can function as multidentate ligand [1, 2]. The complexes having a characteristic trigonal symmetry were originally designed and synthesized by Lions and coworkers [3, 4]. Recently there has been renewed interest in trigonal sexadentate ligands arising from their potential capabilities to produce complexes with coordination geometries distorted from the typical octahedral arrangement. Holm [5, 6] and coworkers have reported geometrical and electronic features of trigonal prismatic, antiprismatic and intermediate complexes of some transition metals.

Experimental

Materials

Triamines were prepared by the standard methods reported in the literature [7, 8]. Glyoxal and biacetyl were distilled before use. All other chemicals used were of reagent grade.

Procedure for the Preparation of Complexes

Bis[1,1',1''-tris(glyoxaldiamino)methylethane] nickel(II) tetraphenylborate

To a 25 ml water solution containing 1.73 grams (0.01 mol) of 1,1,1-tris(aminomethyl)ethanetrihydrochloride, a 50 ml water solution containing 2.46 grams (0.03 mol) of sodium acetate was added. To the solution 0.87 grams (0.015 mol) of glyoxal was added as 25 ml ethanol solution. The mixture was refluxed for a while. To this, 30 ml of water solution containing 1.5 grams (0.005 mol) of $Ni(NO_3)_2 \cdot 6H_2O$ was added. The mixture was refluxed for about two hours with stirring and cooled to room temperature. To the cooled solution 3.42 grams (0.01 mol) of sodium tetraphenylborate was added. The precipitated complex was filtered, washed with methanol till it was free from the reagents and dried at 50 °C.

Bis[Cis,cis-1,3,5-tris(Glyoxaldiamino)cyclohexane] nickel(II) tetraphenylborate

A 30 ml methanol solution containing 1.5 grams (0.005 mol) of $Ni(NO_3)_2 \cdot 6H_2O$ was added slowly to a 25 ml methanol solution containing 1.2 grams (0.01 mol) of 1,3,5-triaminocyclohexane. The mixture was refluxed for a while with continuous stirring. To this mixture 0.87 grams (0.015 mol) of glyoxal was added and the mixture was refluxed for about two hours and cooled to room temperature. To this cooled solution sodium tetraphenylborate (0.01 mol) in 30 ml methanol was added. The complex separated was filtered washed with methanol till it was free from the reagent and dried at 50 °C.

Bis[1,1'1''-tris(2,3-butanediamino)methylethane]-nickel(II) perchlorate

A 30 ml methanol solution containing 1.5 grams (0.005 mol) of $Ni(NO_3)_2 \cdot 6H_2O$ was added to a 25 ml methanol solution containing 1.13 grams (0.01 mol) of 1,1,1-tris(aminomethyl)ethane (tame). To the mixture 1.32 grams (0.015 mol) of biacetyl in 25 ml of methanol was added and the mixture was refluxed with stirring about two hours and cooled to room temperature. To this cooled mixture sodium perchlorate (1.39 grams) in 30 ml of water (0.01 mol) was added. The complex separated was filtered, washed with methanol till it was free from the reagents and dried at 50 °C.

Bis[Cis,cis,-1,3,5-tris(2,3-butanediamino)cyclohexane] nickel(II) perchlorate

To a 30 ml water solution containing 2.37 grams (0.01 mol) of aminetrihydrochloride was added a 50

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TABLE I. Elemental Analysis.[a]

S. No.	Complex	% Carbon	% Hydrogen	% Nitrogen	% Nickel
I	Bis[1,1′,1″-tris(glyoxaldiamino)-methylethane]nickel(II) Tetraphenylborate	77.32 (77.01)	6.64 (6.42)	8.64 (8.43)	4.92 (4.89)
II	Bis[*Cis,cis*-1,3,5-tris(glyoxaldiamino)-cyclohexane]nickel(II) Tetraphenylborate	77.54 (77.51)	6.19 (6.18)	8.31 (8.25)	5.88 (5.79)
III	Bis[1,1′,1″-tris(2,3-butanediamino)-methylethane]nickel(II) Perchlorate	41.25 (41.54)	5.71 (5.81)	12.61 (12.76)	8.89 (8.96)
IV	Bis[*Cis,cis*-1,3,5-tris(2,3-butanediamino)-cyclohexane]nickel(II) Perchlorate	37.63 (37.90)	5.66 (5.83)	13.49 (13.61)	9.25 (9.50)

[a]Values given in parentheses are calculated values.

ml water solution containing 2.46 grams (0.03 mol) of sodium acetate. To the solution 1.32 grams (0.015 mol) of biacetyl was added as 25 ml ethanol solution. The mixture was refluxed for a while. To this a 30 ml water solution containing 1.5 grams (0.005 mol) of $Ni(NO_3)_2 \cdot 6H_2O$ was added. The mixture was refluxed for about two hours with stirring and cooled to room temperature. To the cooled solution sodium perchlorate (1.39 grams) in 30 ml of water (0.01 mol) was added and the precipitated complex was filtered, washed with methanol till it was free from the reagents and dried at 50 °C.

Analysis

Nickel in the complexes was determined volumetrically with standard EDTA solution using Murexide indicator, and nitrogen by Kjeldahl method. The results of the elemental analysis are given in Table I.

Physical Measurements

The infrared spectra were obtained on a Beckman IR-8, recording spectrophotometer using nujol and potassium bromide pellets. The absorbance measurements and the spectra in the region 200–1000 nm were determined on a Cary-14 recording spectrophotometer using 1 cm quartz cells and concentrations of 10^{-3} to 10^{-5} *M*. Spectroscopic grade dimethyl sulfoxide was used for absorbance measurements in the region of 200–1000 nm.

The magnetic moments in the solid state were determined by Gouy's method using $HgCO(SCN)_4$ as the calibrant.

Results and Discussions

The complexes are not soluble in ordinary organic solvents but are soluble in DMF and DMSO to a limited extent. This limited solubility of the complexes has excluded the possibility of determining the molecular weights.

Infrared Spectra

The infrared frequencies of the complexes along with their tentative assignments are given in Table II.

The band appearing in the region 1643–1653 cm^{-1} in the complexes is assigned to the C=N stretching vibration. The shift of C=N stretching mode to the higher frequency is attributed to an increase in bond order of C=N and coordination of nitrogen of the azomethine group to nickel. This statement is in line with other workers [9, 10].

TABLE II. Infrared Absorption Maxima in cm^{-1}.[a]

I	II	Assignments	III	IV	Assignments
–	–	–	–	–	–
1653s	1651s	–C=N	1645s	1635s	–C=N
1500w	1495w	–C=C	1453sh	1447sh	–C=C
1425w	1425w			1393	
–	1270w		1195	–	
			1100b	1100b	Perchlorate
–	–		–	–	
733s	735s		–	–	
703s	704s	C–H (Aromatic)	635m	637m	

[a]Abbreviations: s = strong; m = medium; w = weak; b = broad; sh = shoulder.

TABLE III. Absorption Maxima and Magnetic Susceptibilities of Nickel(II) Complexes

S. No.	Solvent	Absorptions in nm	Absorptions in cm^{-1}	ϵ	μ_{eff} in B.M.
I	DMSO	270	37.04 x 10^3	1354	3.03
		330	30.30 x 10^3	392	
		940	10.64 x 10^3	5.538	
II	DMSO	273	36.36 x 10^3	822	2.95
		295	33.89 x 10^3	611	
		900	10.90 x 10^3	25.5	
		950	10.53 x 10^3	28.0	
III	DMSO	245	40.82 x 10^3	2327	2.98
		295	33.89 x 10^3	1730	
		960	10.31 x 10^3	20.38	
		900	10.90 x 10^3	19.23	
IV	DMSO	253	39.53 x 10^3	1577	2.93
		305	32.79 x 10^3	846	
		965	10.30 x 10^3	7.25	

It is established [11] that the free amine group exhibits two infrared absorption bands in the 3500–3350 cm^{-1}. The triamines in the present investigation show bands around 3500–3350 cm^{-1} due to the N–H stretching frequency. These bands are absent in the complexes. The conclusive assignment of the N–H deformation in the region 1600–1500 cm^{-1} cannot be made, as the C=N stretch and aromatic C=C stretching vibrations also occur in the same region.

The broad peak appearing in the region of 1100–1000 cm^{-1} in the complexes III and IV is assigned to perchlorate ion in the complexes. This is in line with previous workers [12]. The presence of perchlorate ion in the complexes is also confirmed by qualitative test [13]. This broad peak due to perchlorate ion did not show up in the complexes I and II, since they are precipitated as tetraphenylborates.

The low intensity broad bands appearing in the region of 700–800 cm^{-1} in the complexes I and II are assigned to aromatic C–H arising from tetraphenyl anion. Similar assignments were also made by earlier workers [11].

Electronic Spectra

The absorption maxima along with the ϵ values are listed in Table III.

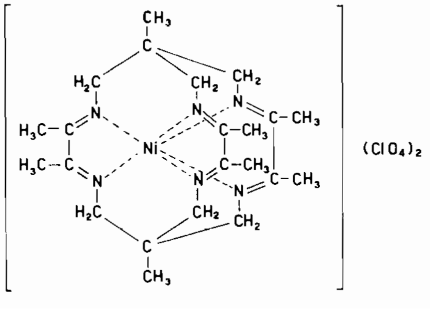
Robinson *et al.* [14(a)] have interpreted the results assuming octahedral symmetry and considered the band in the region 11,400–12,200 cm^{-1} as due to the spin-forbidden $3A_{2g} \rightarrow 1E_g(D)$ transition. Larsen and coworkers [6] have considered the complexes having TP or near TP symmetry in the light of octahedral ligand-field spectra of nickel(II) complexes and analysed them assuming octahedral microsymmetry. They have assigned the band around 11,500 cm^{-1} to the spin-forbidden band.

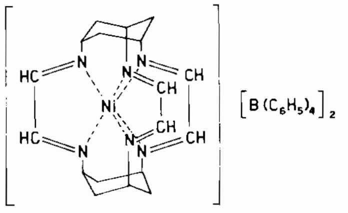
In these complexes we observe two bands for the complexes II and III, one around 10,900 cm^{-1} and the other around 10,530 cm^{-1} (Table III). These bands have almost equal intensities and can be looked upon as the characteristic bands of the complexes having TP geometry, and this trigonal prism component is responsible for the splitting of the band in the above region into two bands of almost equal intensities. It is rather difficult to find the band around 25,000 cm^{-1} as it is always buried underneath the high intensity charge transfer bands. The band around 15,000 cm^{-1} is observed as an influxion in the complex III.

All these evidences suggest that the complexes II and III have TP geometry. The ligand field spectra of the complexes I and IV resemble the spectra of octahedral nickel(II) complexes.

The magnetic measurements obtained at room temperature for these complexes fall in the range of 3.03–2.93 B.M. These values agree well with the values reported for the octahedral nickel(II) complexes. Larsen and coworkers [6] reported almost the same range for TP or near TP nickel(II) complexes.

Taking into consideration the evidences and usual hexacoordination of nickel(II) we propose the following structures for the complexes II and III, and complexes I and IV have usual octahedral structures.





Conclusion

Four nickel(II) complexes have been investigated. The spectral studies indicate that the authors have been successful in inducing the trigonal prismatic symmetry in two of the nickel(II) octahedral complexes.

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