

Anionic Complexes of Nickel(II)

C M DANİ

Research and Control Laboratory
Rourkela Steel Plant, Rourkela 769 011

and

A K DAS*

Bonaigarh College, Bonaigarh, Orissa

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Eight anionic complexes of nickel(II) having the compositions, $[LH_2][NiCl_4]$ and $[LH_2][NiCl_2Br_2]$, where L = ethylenediamine, *o*-phenanthroline, bipyridyl or *o*-phenylenediamine have been prepared and characterised. Tetrahedral stereochemistry around nickel(II) has been proposed for these anionic complexes.

Several reports¹⁻¹⁰ have been made earlier on the isolation and characterisation of anionic complexes of different transition metal ions involving different cations. Eight complexes having the general formulae $[LH_2][NiCl_4]$ and $[LH_2][NiCl_2Br_2]$, where L = ethylenediamine(en), *o*-phenanthroline(*o*phen), bipyridyl(*bipy*) or *o*-phenylenediamine(*opd*), have been prepared and characterised in the present investigation.

All the chemicals used were of A R grade (BDH).

Preparation of the complexes of the type $[LH_2][NiCl_4]$

To an ethanolic solution (0.01 mol) of ethylenediamine, bipyridyl, *o*-phenanthroline or *o*-phenylenediamine, dil. HCl was added till the solution became acidic (*pH* ~ 5). The resulting solution was then added to an ethanolic solution of nickel chloride (0.01 mol) and refluxed for half an hour. The solution

was slightly evaporated over a waterbath and kept overnight. The crystalline coloured compound that separated was filtered, washed repeatedly with ethanol, ether and finally dried *in vacuo*.

Preparation of anionic complexes of the type $[LH_2][NiCl_2Br_2]$

To an ethanolic solution of ethylenediamine, bipyridyl, *o*-phenanthroline or *o*-phenylenediamine (0.01 mol), dil. HBr was added till the solution became acidic (*pH* ~ 5). The resulting solution was then added to an ethanolic solution of nickel chloride (0.01 mol) and refluxed for half an hour. The solution was evaporated slightly over a waterbath and kept overnight. The crystalline coloured compound that separated was filtered, washed repeatedly with ethanol, ether and finally dried *in vacuo*.

The relevant physical and analytical data are recorded in Table 1.

Analytical data are in good agreement with the proposed formulations of the complexes. All the complexes are crystalline and coloured having high melting points (> 250°C). The molar conductance values in methanol (120.7 – 142.3 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$) indicate 1:1 electrolytic nature of the complexes. The magnetic moment values of the complexes lie in the range 3.51-3.88 B.M., which definitely suggest¹¹ tetrahedral environment around nickel(II) ion. The higher magnetic moment values of the complexes than the spin-only value may be attributed to large orbital contribution to the magnetic moment in the tetrahedral stereochemistry.

Table 1—Analytical and Physical Data of Anionic Complexes of Nickel(II)

Compound (Colour)	Found (Calc.), %						$\mu_{\text{eff.}}$ (B.M.)
	Ni	Cl	Br	C	H	N	
$[enH_2][NiCl_4]$ (Green)	21.85 (22.36)	53.18 (54.02)	—	8.78 (9.14)	3.20 (3.80)	9.90 (10.66)	3.88
$[enH_2][NiCl_2Br_2]$ (Green)	15.98 (16.70)	19.80 (20.17)	45.10 (45.47)	6.12 (6.82)	2.20 (2.84)	7.35 (7.96)	3.76
$[o\text{phen}H_2][NiCl_4]$ (Blue)	14.04 (14.64)	34.46 (35.39)	—	36.90 (37.61)	2.21 (2.61)	6.85 (7.31)	3.62
$[o\text{phen}H_2][NiCl_2Br_2]$ (Light blue)	12.82 (11.98)	14.20 (14.48)	31.84 (32.63)	29.88 (30.52)	1.90 (2.12)	5.20 (5.93)	3.80
$[bipyH_2][NiCl_4]$ (Blue)	15.42 (16.36)	39.12 (39.53)	—	33.04 (33.45)	2.22 (2.78)	7.36 (7.80)	3.51
$[bipyH_2][NiCl_2Br_2]$ (Green)	12.21 (13.11)	15.24 (15.84)	35.02 (35.70)	26.24 (26.80)	1.90 (2.23)	5.84 (6.25)	3.68
$[opdH_2][NiCl_4]$ (Pink)	19.72 (18.90)	44.78 (45.67)	—	22.90 (23.18)	2.80 (3.22)	8.48 (9.01)	3.67
$[opdH_2][NiCl_2Br_2]$ (Reddish brown)	14.21 (14.69)	16.98 (17.75)	39.60 (40.01)	17.65 (18.02)	1.85 (2.50)	6.39 (7.00)	3.60

Involvement of cations in the complexes is well substantiated by the IR spectra of some of the complexes. The IR spectra of the complexes, $[\text{enH}_2][\text{NiCl}_2\text{Br}_2]$ and $[\text{opdH}_2][\text{NiCl}_2\text{Br}_2]$ exhibit bands in the range 3100-3260 and 2780-2850 cm^{-1} which may be assigned¹² to the first overtone or combination bands of the deformation vibration in the region 1600-1500 cm^{-1} and CH_2 , CH and NH_3^+ stretching vibrations respectively. Besides, a band at 2575 cm^{-1} , attributed to combination bands involving fundamentals of NH_3^+ deformation vibration, has been observed in the IR spectrum of the complex, $[\text{opdH}_2][\text{NiCl}_2\text{Br}_2]$. The broad bands at 2775 and 2795 cm^{-1} in the complexes $[\text{ophenH}_2][\text{NiCl}_2\text{Br}_2]$ and $[\text{bipyH}_2][\text{NiCl}_4]$ respectively may be assigned¹² to N-H^+ stretching frequencies. The $\nu(\text{Ni-Cl})$ and $\nu(\text{Ni-Br})$ bands are observed in the ranges 265-290 and 238-240 cm^{-1} , respectively, indicating¹³⁻¹⁵ metal-halogen bonding in the complexes.

In general, tetrahedral nickel(II) complexes display two characteristic electronic spectral bands around 15.8 kK and 7.0-8.0 kK corresponding to ${}^3T_1(F) \rightarrow {}^3T_1(P)(\nu_3)$ and ${}^3T_1(F) \rightarrow {}^3A_2(F)(\nu_2)$ transitions, respectively. The electronic spectra of the present complexes in methanol display spectral bands in the region 15,800-16,200 cm^{-1} which may be assigned¹⁶ to ${}^3T_1(F) \rightarrow {}^3T_1(P)(\nu_3)$ transition in a tetrahedral field. The other band (ν_2) could not be detected due to the limitations of the instrument used. The present complexes have μ_{eff} values ranging between 3.51 and 3.88 B.M. indicating the presence of two unpaired electrons with a large orbital contribu-

tion, as expected for a tetrahedral nickel(II) complex^{11,17}.

In view of the above spectral behaviour and high magnetic moment values, tetrahedral stereochemistry has been proposed¹⁸ for these anionic complexes of nickel(II).

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