

Electronic Spectra of Amminenickel(II) Halides and Pseudohalides

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Summary: Ligand field splitting parameters (10Dq) for the complexes $Ni(NH_3)_n X_2$ (X=Br, I, NCS; n=6,4,2) have been obtained from electronic spectra. The use of these results for the calculation of additional 10Dq values for $NiBr_2$, NiI_2 and $Ni(NCS)_2$ or $[Ni(NCS)_6]^{4-}$ is discussed. There is reasonable agreement between experimental and calculated values. A spectrochemical series for the ligands is presented.

Introduction

From the triplet terms arising from octahedral nickel(II) (d^8) complexes (see figure 1) are predicted only three spin allowed transitions having the energies

$${}^3A_{2g} \rightarrow {}^3T_{2g}, \nu_1 = 10Dq$$

$${}^3A_{2g} \rightarrow {}^3T_{1g} (F), \nu_2 = 15Dq + 15/2 B - 1/2 [(15B-6Dq)^2 + 64(Dq)^2]^{1/2}$$

$${}^3A_{2g} \rightarrow {}^3T_{1g} (P), \nu_3 = 15Dq + 15/2 B + 1/2 [(15B-6Dq)^2 + 64(Dq)^2]^{1/2}$$

Thus 10Dq (Dq is exchangeable with 0.1Δ) values are directly obtainable from the lowest band appearing in the electronic spectrum. Typically octahedral nickel(II) complexes such as $[Ni(NH_3)_6]^{2+}$ (4) give the characteristic spectrum shown (see figure 2- recorded by this author) In the present work, experimental 10Dq values were determined for $Ni(NH_3)_n X_2$ (X=Br⁻, I⁻; n=6,2) and $Ni(NH_3)_n(NCS)_2$ (n=4,2). Jorgensen's method (5) enables the calculation of 10Dq values for NiX_2 (X=Br⁻, NCS⁻) since these compounds have a polymeric octahedral structure (6,7) and therefore stereochemically equivalent to the former.

Experimental

Reagents

Hexamminenickel(II), bromide and iodide: These were prepared by literature methods (8) using nickel(II) bromide trihydrate and nickel(II) iodide hexahydrate as starting materials.

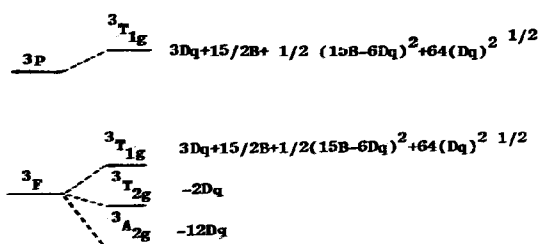


Fig. 1 : Triplet terms arising from nickel (II) ions in octahedral fields.

Diamminenickel (II) bromide and iodide: These were isolated from thermal decomposition of the respective hexammines at 132°C (boiling chlorobenzene) for $Ni(NH_3)_4 Br_2$ and 100°C for $Ni(NH_3)_2 I_2$. The preparation involves high vacuum techniques, details of which can be consulted elsewhere (7,9).

Amminenickel (II) thiocyanates: The starting material, nickel(II) thiocyanate was dried *in vacuo* at 140°C (10 hours). This was allowed to react with excess liquid ammonia (high vacuum techniques-reference 9) followed by evacuation at room temperature (22°C) for eight hours to yield $Ni(NH_3)_4(NCS)_2$. An alternative preparative route has been described by other workers (10). Thermal decomposition of the tetrammine at 77°C (boiling carbon tetrachloride) gave diamminenickel(II) thiocyanate.

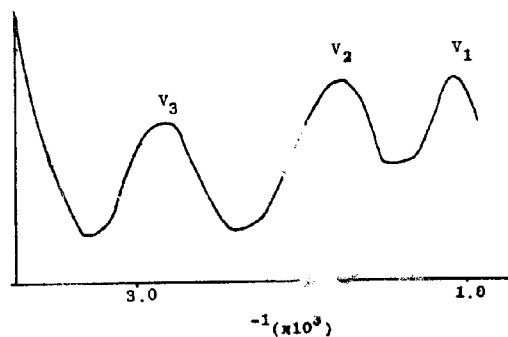
The analytical data for the compounds studied is summarised in Table 1.

Spectral measurements

Diffuse reflectance spectra of powdered samples with added magnesium oxide diluent were recorded on a Unicam SP700C spectrophotometer.

Table 1. Analytical data for amminenickel(II) halides and pseudohalides

Compound	Found (%)					Calculated (%)						
	Ni	C	N	H	X	NH ₃	Ni	C	N	H	X	NH ₃
Ni(NH ₃) ₄ (NCS) ₂	24.33	9.78	34.55	4.80		27.82	24.17	9.88	34.58	4.94		27.99
Ni(NH ₃) ₂ (NCS) ₂	28.41	11.30	26.71	3.58		16.45	28.10	11.49	26.81	3.87		16.28
Ni(NH ₃) ₆ Br ₂					49.52	31.50					49.86	31.80
Ni(NH ₃) ₂ Br ₂					62.96	13.18					63.29	13.46
Ni(NH ₃) ₆ I ₂					61.02	24.38					61.23	24.61
Ni(NH ₃) ₂ I ₂					73.25	9.54					73.25	9.81

Fig. 2 : Electronic spectrum of [Ni(NH₃)₆]I₂Table 2: 10Dq values (cm⁻¹) for octahedral Ni²⁺ with various ligands.

	Ni(NH ₃) ₆ X ₂	Ni(NH ₃) ₄ X ₂	Ni(NH ₃) ₂ X ₂	NiX ₂
X=Br ⁻	11000	—	7800	6200
X=I ⁻	10900	—	7600	5950
X=NCS ⁻	—	10800	10200	9600

Results and Discuss

Energies of the $3A_{2g} \rightarrow 3T_{2g}$ band^a (equivalent to 10Dq) as determined from the electronic spectra of the amminenickel(II) complexes are summarised in Table 2. Additional calculated 10Dq values for NiBr₂, NiI₂ and Ni(NCS)₂ (or [Ni(NCS)₆]⁴⁻) using Jorgensen's method are included.

The following 10Dq values are reported in the literature: [Ni(NH₃)₆]²⁺, 10750 cm⁻¹ (4); NiBr₂, 6800 cm⁻¹ (6); [Ni(NCS)₆]⁴⁻, 9600 cm⁻¹ (11); Ni(NCS)₂, 9600 cm⁻¹ (7).

No literature value is available for NiI₂ (presumably the bulky iodide ion is ill-suited for six co-ordination). There is reasonable agreement between literature values and those obtained in this work; some of the calculated NiX₂ 10Dq values may show significant differences and this is partly attributable to departures from perfect octahedral geometry. On the basis of this work, the spectrochemical series for the ligands is arranged thus: NH₃ > NCS⁻ > Br⁻ > I⁻.

References

1. L. Sacconi, *Transition Metal Chem.*, **4**, 199 (1968).
2. A.B.P. Lever, "Inorganic Electronic Spectroscopy" Elsevier (1968).
3. C.J. Ballhausen, "Introduction to Ligand Field Theory", McGraw-Hill (1962).
4. O. Bostrup and C. K. Jorgensen, *Acta Chem. Scand.*, **11**, 1223 (1957).
5. C. K. Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes", Pergamon (1962) p. 109.
6. A. Ludi and W. Feitknecht, *Helv. Chim. Acta*, **46**, 2226 (1963).
7. D.M.S. Mosha, Ph.D. Thesis, University of Liverpool (1978).
8. G.W. Watt, *Inorg. Syn.*, **3**, 195 (1950).
9. D. Nicholls, "Inorganic Chemistry in Liquid Ammonia" Elsevier (1979).
10. E.K. Yukhno and M. A. Porai-Koshits, *Kristallografiya*, **2**, 239 (1957).
11. D. Foster and D. M.L. Goodgame, *Inorg. Chem.*, **4**, 823 (1965).