

Preparation, Absorption Spectra and Electronic Configuration of some Amino Complexes of Nickel (II) Acetate

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Abstract

Three hexaco-ordinated complexes of nickel (II) acetate with ammonia, ethylenediamine and propylenediamine have been prepared. Conductivity measurements indicate the complexes to be non-electrolytes. Molecular weight measurements confirm this. The visible absorption spectrophotometric measurements show a number of bands corresponding to the various permitted transitions of the metal and a discussion of the structure in the light of these transitions is presented.

Introduction

Very little work has been done on organic salts of nickel with a view to study the relation between the colour and the stereochemistry of the complexes. Moreover, the nature of the anion is found to be a contributing factor towards the stability of the complexes¹⁾. Few of the nickel (II) acetate-ammonia complexes have been reported²⁾³⁾, but since then no attempt towards the assignment of the structures to these was made. Attempt has therefore, been made to prepare some amino complexes of nickel (II) acetate and study their absorption spectra.

Experimental and Results

A. Synthesis

1. Biacetate, tetra (ammine) nickel (II): — 500 mg of nickel (II) acetate were placed in a calcium chloride tube fitted with cotton wool plug at the bottom. The tube was attached to the neck of a flask containing excess of ammonia and was left over night. The tube was taken out in the morning, dried first over CaCl_2 and then over P_2O_5 . The complex is blue in colour and soluble in formamide (Found Ni = 24.2%, N = 22.58%, NH_3 = 27.56%.

¹⁾ T. MOELLER, Inorganic chemistry (First Indian Printing), p. 237 (1962).

²⁾ H. GROSSMANN and G. JÄGER, **73**, 48 (1912).

³⁾ C. S. SHAW, Z. physik. Chem. **204**, 194 (1955).

mole. wt. = 231, cond = 0.58 mhos; $C_4H_{18}O_4N_4Ni$ requires Ni = 24.0%, N = 22.88%, NH_3 = 27.8%, mol.wt. = 244.7).

2. Biacetato, bis (ethylenediamino) nickel (II): — 500 mg of nickel (II) acetate were shaken in acetone with calculated quantity of amine for two hours, the reaction mixture left overnight, filtered next morning, dried over P_2O_5 . The complex is violet in colour and soluble in formamide and water (Found Ni = 19.48%, N = 18.67%, en = 40.08%, mol.wt. = 278, cond = 0.36 mhos; $C_8H_{22}O_4N_4Ni$ requires Ni = 19.78%; 18.87%, en = 40.45%, mol.wt. = 296.7).

3. Biacetato, bis (propylenediamino) nickel (II): — Prepared as 2. and the complex is violet in colour, soluble in formamide and water (Found Ni = 18.26%, N = 17.40%, pn = 45.80%, mol.wt. = 304, cond = 0.14 mhos; $C_{10}H_{26}O_4N_4Ni$ requires Ni = 18.08%, N = 17.25%, pn = 45.59%, mol.wt. = 324.7).

B. Determination of base and molecular weight

Methods used as outlined by the author⁴).

C. Visible absorption spectra

Spectra were recorded on a Unicam S.P. 500 spectrophotometer in formamide.

No.	Formula	λ max	Frequency cm^{-1}
1	$[Ni(CH_3COO)_2(NH_3)_4]^0$	350 $m\mu$	28600 cm^{-1}
		560 $m\mu$	18700 cm^{-1}
		825 $m\mu$	12121 cm^{-1}
		925 $m\mu$	10800 cm^{-1}
2	$[Ni(CH_3COO)_2(en)_2]^0$	345 $m\mu$	29000 cm^{-1}
		555 $m\mu$	18020 cm^{-1}
		825 $m\mu$	12121 cm^{-1}
		928 $m\mu$	10700 cm^{-1}
3	$[Ni(CH_3COO)_2(pn)_2]^0$	350 $m\mu$	28600 cm^{-1}
		550 $m\mu$	18700 cm^{-1}
		825 $m\mu$	12121 cm^{-1}
		935 $m\mu$	10700 cm^{-1}

Discussion

The results of analysis show the molecular formulae to be $Ni(CH_3COO)_2(am)_4$ and $Ni(CH_3COO)_2(am)_2$, where am is any amine used. The conductivity and molecular weight measurements in formamide indicate the complexes to be non-electrolytes and hence it is suggested that acetate ion besides neutralizing the charge of the metal is also co-ordinated to it. The formulae of the complexes are thus to be written as $[Ni(CH_3COO)_2(am)_4]^0$ and $[Ni(CH_3COO)_2(am)_2]^0$. The co-ordination number thus becomes six in

⁴) GOPAL NARAIN, Z. anorg. allg. Chem. **347**, 215 (1966).

all the cases. The violet colour of the bidentate amine complexes is in contrast with the common blue or green colour observed for other octahedral complexes. It is known that the greater the strength of the co-ordinate bond between nickel atom and ligand, the greater is the deviation from the usual colour⁵⁾.

On exposure to light, the degenerate 3d orbitals show a number of transitions and by a series of calculations, BALLHAUSEN⁶⁾ has shown that at least three or four transitions are to be expected for octahedral complexes. Their position is theoretically shown to be:

$$V_1 = 10 Dq,$$

$$V_2 = 9/5 (10 Dq),$$

$$V_3 = 17000 + 6/5 (10 Dq)$$

The above complexes show four bands in the vicinity of 350, 560, 825 and 925 m μ .

The comparison of these with the spectra of other known octahedral nickel complexes (the bands in the vicinity of 350, 550, 800 and 925 m μ) shows a fair agreement between the two. Moreover, as given by FERNELIUS⁷⁾ the ratio V_3/V_1 is 1.82 for all octahedral complexes irrespective of the ligands used for co-ordination. The 925 m μ band in this case is considered to be V_1 band and the position of other bands is then calculated by above equation and it is thus found that V_3/V_1 is 1.82 in this case, and that there is a fair agreement between observed and calculated values.

The bands are proposed to correspond to the following transitions.

Frequency of the bands	Wave length	Transition
V_1 (10800 cm ⁻¹)	925 m μ	3 A _{2g} → 3 T _{2g}
V_2 (12121 cm ⁻¹)	825 m μ	3 A _{2g} → 1 E _g
V_3 (18700 cm ⁻¹)	560 m μ	3 A _{2g} → 1 A _{1g}
V_4 (28600 cm ⁻¹)	350 m μ	3 A _{2g} → 3 T _{eg}

⁵⁾ R. S. NYHOLM, Chem. Rev. **53**, 263 (1953).

⁶⁾ C. J. BALLHAUSEN, Dan Mat. fys. Medel **29**, No. 4 (1954).

⁷⁾ C. FERNELIUS and W. MANCH, J. chem. Educat. **38**, 192 (1961).

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