Octahedral Complexes of Nickel(II) Formate with Amines

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Three hexaco-ordinated complexes of nickel(II) formate 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. A discussion of the structure in the light of these transitions is presented.

A large number of nickel ammine complexes of inorganic salts have been prepared, but comparatively very little work has been done on organic salts of nickel.[1-3] Moreover, the nature of the anion is found to be a contributing factor to the stability of the complexes.[4] An attempt has, therefore, been made to prepare some amine complexes of nickel(II) formate and to study their absorption spectra and the effect of formate ions on the properties of the complexes.

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[1] H. Grossmann and G. Jagar, *Z. anorg. Chem.*, **73**, 48 (1912).

[2] C. S. Shaw, *Z. Physik. Chem.*, **204**, 194 (1955).

[3] P. Shukla et al., *Z. anorg. u. allgem. Chem.*, **333**, 165 (1964).

[4] T. Moeller, "Inorganic Chemistry" (1st. Indian printing) (1962), p. 237.

No.	Formula	In alcohol		In formamide	
		λ_{max}, mμ	Approximate frequency, cm^{-1}	λ_{max}, mμ	Approximate frequency, cm^{-1}
1	$[Ni(HCOO)_2(NH_3)_4]^0$	Insoluble		345	29000
				555	18020
				825	13000
				928	10700
2	$[Ni(HCOO)_2(en)_2]^0$	340	29400	350	28600
		550	18000	560	18700
		820	12200	825	13000
		915	10930	935	10700
3	$[Ni(HCOO)_2(pn)_2]^0$	355	28600	360	28600
		555	18000	560	18000
		825	13000	825	13000
		925	10700	925	10800

Experimental and Results

Synthesis.—*i) Biformatotetra(ammine)nickel(II).* —Five hundred milligrams of nickel(II) formate was placed in a calcium chloride tube fitted with a cotton wool plug at the bottom. The tube was then attached to the neck of a flask containing an excess of liquid ammonia and left overnight. The tube was taken out in the morning, and dried first over calcium chloride and then over phosphorus(V) oxide. The complex is blue in colour and is soluble in formamide. (Found: Ni, 26.89; N, 25.66; NH_3, 31.06. Mol. wt., 201. Cond., 0.43 mhos. Calcd. for $C_2H_{14}O_4N_4Ni$: Ni, 27.08; N, 25.8; NH_3, 31.33%. Mol. wt., 216.7)

ii) Biformatobis(ethylenediamine)nickel(II).—A five hundred milligrams portion of nickel(II) formate was shaken in acetone with a calculated quantity of amine for two hours; the reaction mixture was then left overnight, filtered the next morning, and dried over phosphorus(V) oxide. The complex is violet in color and is soluble in formamide and alcohol. (Found: Ni, 21.65; N, 20.58, en, 44.19. Mol. wt, 253. Cond., 0.51 mhos. Calcd. for $C_6H_{18}O_4N_4Ni$: Ni, 21.84; N, 20.84; en, 44.67%. Mol. wt, 268.7)

iii) Biformatobis(propylenediamine)nickel(II).—This was prepared as ii). The complex is violet in colour and is soluble in formamide and alcohol (Found: Ni, 19.4; N, 18.58; pn, 49.44. Mol. wt., 278. Cond., 0.26 mhos. Calcd. for $C_8H_{22}O_4N_4Ni$: Ni, 19.79; N, 18.87; pn, 49.9%. Mol. wt., 296.7)

The Determination of the Base and the Molecular Weight.—The methods used have already been outlined by the author.[5]

Visible Absorption Spectra.—The spectra were recorded on a Unicam S. P. 500 spectrophotometer in formamide and in alcohol.

Discussion

The results of analysis show the molecular formulae to be $Ni(HCOO)_2(am)_4$ and $Ni(HCOO)_2(am)_2$, where am represents ammonia, ethylenediamine and propylenediamine. The conductivity and molecular weight measurements in formamide indicate the complexes to be non-electrolytes; hence, it is suggested that formate ions, besides neutralizing the charge of the metal, are also coordinated to it. The formulae of the complexes are thus to be written as $[Ni(HCOO)_2(am)_4]^0$ and $[Ni(HCOO)_2(am)_2]^0$. The coordination number thus becomes six in all the cases. The violet colour of the bidentate amine complexes is in contrast with the blue or green colour observed for all other octahedral complexes. It is known that the greater the strength of the coordinate bond between a nickel atom and a ligand, the greater is the deviation from the usual colour.[6]

The terms arising from the d^8 ground state are:

$$3d^8 = F,\ P,\ G,\ D \text{ and } S$$

Ballhausen,[7] on the basis of a series of calculations, found that at least three of four transitions are to be expected for octahedral complexes. The complexes presently under investigation also show four sharp bands in alcohol and formamide. In alcohol the bands occur in the vicinity of 345, 550, 815 and 920 mμ while in formamide, they occur near 350, 560, 825 and 925 mμ. The slight positive shift in the positions of the bands results from the higher polarity of formamide; this changes the energies, which in their turn change the frequencies of the absorption bands.

Further, the comparison of these spectra with the spectra of other known octahedral nickel complexes (bands in the vicinity of 350, 550, 800 and

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[5] G. Narain, *Z. anorg. u. allgem. Chem.*, to be published.

[6] R. S. Nyholm, *Chem. Revs.*, **53**, 263 (1953).

[7] C. J. Ballhausen, *Dan. Mat-fys. Medal*, **29**, No. 4 (1954).

925 mμ) shows a fair agreement between the two. Moreover, as has been reported by Frenelius,[8)] the ν_3/ν_1 ratio is 1.82 for all octahedral nickel(II) complexes irrespective of the ligands used for coordination. If the 925 mμ band in this case is considered to be the ν_1 band, the ν_3/ν_1 ratio also turns out to be 1.82.

The four absorption bands arise from the following transitions of the electrons:

Position of the absorption band	Transition
925 mμ (ν_1)	$A_{2g} \rightarrow T_{2g}$
825 mμ (ν_2)	$A_{2g} \rightarrow E_g$
560 mμ (ν_3)	$A_{2g} \rightarrow T_{1g(F)}$
350 mμ (ν_4)	$A_{2g} \rightarrow T_{1g(P)}$

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8) C. Fernelius and W. Manch, *J. Chem. Ed.*, **38**, 192 (1961).