An Spectroscopic Investigation of Complex Formation in Nickel Sulphate-Aliphatic Amine System

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Summary

Visible absorption spectra of Nickel (II) sulphate and various aliphatic amines were analysed, in order to extract information regarding each of amine Nickel (II) complex. The presence of six different complexes i.e., mono, di, tri, tetra, penta and hexamines have been indicated by the shift of absorption maxima for these. The energy changes of complexes due to exchange of water ligands with amines have been calculated and an interpretation is offered for this shift in the observed position of absorption maxima.

Introduction

A survey of the literature shows that ammonia complexes of nickel (II) sulphate have been investigated in very great detail. However, aliphatic amines, have been given very little attention and only a few such complexes are known[1][2]. In the present paper, the results obtained by an systematic spectroscopic examination of nickel (II) sulphate solutions, with different molar quantities of various amines are reported. Amines used are, methyl, ethyl, propyl, butyl, amyl, dimethyl, diethyl, dipropyl and dibutyl amines.

Experimental

The spectra were obtained with a unicam SP 500 recording spectrophotometer on 2.10^2 M nickel sulphate solutions with different molar quantities of amines. The pH of the solution was buffered at low value with approximately 2M ammonium sulphate solution.

Results

The value of the calculated absorption maxima, energy in K. Cals absorbed per mole and intensity of various complexes are being given in the Tables 1 and 2.

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[1]) W. Peters, Z. anorg. Chem. 89, 191 (1914).
[2]) F. G. Mann, J. chem. Soc. London 2908 (1927).

Table 1

Amine used		Monoamine complex			Diamine complex		
		λ max	E	ε_0	λ max	E	ε_0
1. Ammonia	V_1	930 mμ	1.285×10^5	10	928 mμ	1.288×10^5	12
	V_2	825 mμ	1.449×10^5	10	820 mμ	1.458×10^5	10
	V_3	555 mμ	2.153×10^5	7	550 mμ	2.172×10^5	7
	V_4	400 mμ	2.987×10^5	8	398 mμ	3.003×10^5	6
2. Methylamine	V_1	930 mμ	1.284×10^5	9	925 mμ	1.292×10^5	9
	V_2	825 mμ	1.449×10^5	9	820 mμ	1.458×10^5	9
	V_3	560 mμ	2.134×10^5	6	555 mμ	2.153×10^5	6
	V_4	400 mμ	2.987×10^5	2	398 mμ	3.003×10^5	2
3. Ethylamine	V_1	930 mμ	1.295×10^5	10	928 mμ	1.288×10^5	10
	V_2	820 mμ	1.458×10^5	10	818 mμ	1.461×10^5	10
	V_3	550 mμ	2.172×10^5	6	545 mμ	2.193×10^5	6
	V_4	400 mμ	2.987×10^5	5	398 mμ	3.003×10^5	5
4. Propylamine	V_1	928 mμ	1.288×10^5	8	925 mμ	1.292×10^5	8
	V_2	830 mμ	1.440×10^5	8	825 mμ	1.449×10^5	8
	V_3	540 mμ	2.213×10^5	2	538 mμ	2.221×10^5	2
	V_4	395 mμ	3.028×10^5	1	390 mμ	3.064×10^5	1
5. Butylamine	V_1	925 mμ	1.292×10^5	7	920 mμ	1.299×10^5	7
	V_2	830 mμ	1.440×10^5	7	825 mμ	1.499×10^5	7
	V_3	545 mμ	2.193×10^5	6	540 mμ	2.213×10^5	6
	V_4	390 mμ	3.064×10^5	5	385 mμ	3.103×10^5	5

Table 2

Amine used		Monoamine complex			Diamine complex		
		λ max	E	ε_0	λ max	E	ε_0
1. Amylamine	V_1	935 mμ	1.278×10^5	8	932 mμ	1.282×10^5	8
	V_2	830 mμ	1.440×10^5	7	825 mμ	1.449×10^5	7
	V_3	550 mμ	1.172×10^5	6	545 mμ	2.193×10^5	6
	V_4	390 mμ	3.064×10^5	8	385 mμ	3.103×10^5	8
2. Dimethylamine	V_1	930 mμ	1.285×10^5	7	928 mμ	1.288×10^5	7
	V_2	820 mμ	1.458×10^5	7	820 mμ	1.458×10^5	7
	V_3	550 mμ	2.172×10^5	6	545 mμ	2.193×10^5	6
	V_4	390 mμ	3.064×10^5	6	385 mμ	3.103×10^5	6
3. Diethylamine	V_1	930 mμ	1.285×10^5	10	928 mμ	1.288×10^5	10
	V_2	825 mμ	1.449×10^5	9	825 mμ	1.449×10^5	9
	V_3	560 mμ	2.134×10^5	6	555 mμ	2.153×10^5	6
	V_4	400 mμ	2.987×10^5	4	395 mμ	3.025×10^5	4
4. Dipropylamine	V_1	932 mμ	1.282×10^5	10	930 mμ	1.285×10^5	10
	V_2	820 mμ	1.458×10^5	10	818 mμ	1.461×10^5	10
	V_3	540 mμ	2.213×10^5	8	538 mμ	2.221×10^5	8
	V_4	400 mμ	2.987×10^5	6	395 mμ	3.025×10^5	6

Triamine complex			Tetramine complex			Pentamine complex			Hexamine complex		
λ max	E	ε_0	λ max	E	ε_0	λ max	E	ε_0	λ max	E	ε_0
925 mμ	1.292×10^5	12	920 mμ	1.299×10^5	10	920 mμ	1.299×10^5	10	915 mμ	1.307×10^5	10
818 mμ	1.461×10^5	10	815 mμ	1.466×10^5	10	810 mμ	1.475×10^5	10	805 mμ	1.484×10^5	10
545 mμ	2.193×10^5	7	545 mμ	2.193×10^5	7	540 mμ	2.213×10^5	7	520 mμ	2.299×10^5	9
395 mμ	3.025×10^5	6	390 mμ	3.064×10^5	8	385 mμ	3.103×10^5	8	380 mμ	3.145×10^5	6
925 mμ	1.292×10^5	10	923 mμ	1.295×10^5	12	920 mμ	1.299×10^5	10	918 mμ	1.302×10^5	9
818 mμ	1.461×10^5	9	815 mμ	1.466×10^5	9	815 mμ	1.466×10^5	9	810 mμ	1.475×10^5	8
550 mμ	2.172×10^5	6	545 mμ	2.193×10^5	6	540 mμ	1.213×10^5	6	530 mμ	2.254×10^5	6
395 mμ	3.025×10^5	2	390 mμ	3.064×10^5	2	385 mμ	3.103×10^5	2	380 mμ	3.145×10^5	2
925 mμ	1.292×10^5	12	920 mμ	1.299×10^5	12	915 mμ	1.307×10^5	10	913 mμ	1.309×10^5	9
815 mμ	1.466×10^5	10	815 mμ	1.466×10^5	10	810 mμ	1.475×10^5	10	805 mμ	1.484×10^5	10
540 mμ	2.213×10^5	6	535 mμ	2.234×10^5	6	530 mμ	2.254×10^5	6	525 mμ	2.276×10^5	6
395 mμ	3.025×10^5	5	390 mμ	3.064×10^5	5	385 mμ	3.103×10^5	5	380 mμ	3.145×10^5	5
923 mμ	1.295×10^5	10	918 mμ	1.302×10^5	12	915 mμ	1.307×10^5	9	910 mμ	1.313×10^5	12
820 mμ	1.458×10^5	8	815 mμ	1.466×10^5	8	810 mμ	1.475×10^5	8	805 mμ	1.484×10^5	8
535 mμ	2.224×10^5	2	530 mμ	2.254×10^5	4	525 mμ	2.276×10^5	2	520 mμ	2.299×10^5	2
385 mμ	3.103×10^5	1	380 mμ	3.145×10^5	1	375 mμ	3.187×10^5	1	370 mμ	3.230×10^5	1
920 mμ	1.299×10^5	10	918 mμ	1.302×10^5	12	915 mμ	1.307×10^5	10	913 mμ	1.308×10^5	9
820 mμ	1.458×10^5	7	820 mμ	1.458×10^5	7	815 mμ	1.466×10^5	7	810 mμ	1.475×10^5	7
538 mμ	2.234×10^5	6	530 mμ	2.254×10^5	6	525 mμ	2.276×10^5	6	520 mμ	2.299×10^5	6
385 mμ	3.103×10^5	5	380 mμ	3.145×10^5	5	375 mμ	3.187×10^5	5	370 mμ	3.230×10^5	5

Triamine complex			Tetramine complex			Pentamine complex			Hexamine complex		
λ max	E	ε_0	λ max	E	ε_0	λ max	E	ε_0	λ max	E	ε_0
930 mμ	1.285×10^5	9	930 mμ	1.285×10^5	12	925 mμ	1.292×10^5	10	920 mμ	1.299×10^5	9
820 mμ	1.458×10^5	7	820 mμ	1.458×10^5	7	815 mμ	1.466×10^5	7	810 mμ	1.475×10^5	7
540 mμ	2.213×10^5	6	535 mμ	2.234×10^5	6	530 mμ	2.254×10^5	6	525 mμ	2.276×10^5	6
380 mμ	3.145×10^5	8	375 mμ	3.187×10^5	8	370 mμ	3.230×10^5	8	370 mμ	3.230×10^5	8
925 mμ	1.292×10^5	10	923 mμ	1.295×10^5	9	920 mμ	1.299×10^5	12	915 mμ	1.307×10^5	10
815 mμ	1.466×10^5	7	815 mμ	1.466×10^5	7	810 mμ	1.475×10^5	8	805 mμ	1.484×10^5	8
540 mμ	2.213×10^5	6	535 mμ	2.234×10^5	7	530 mμ	2.254×10^5	7	525 mμ	2.276×10^5	7
385 mμ	3.103×10^5	5	380 mμ	3.145×10^5	6	380 mμ	3.145×10^5	5	375 mμ	3.187×10^5	5
925 mμ	1.292×10^5	2	920 mμ	1.299×10^5	8	918 mμ	1.302×10^5	9	915 mμ	1.307×10^5	7
825 mμ	1.449×10^5	9	820 mμ	1.458×10^5	9	815 mμ	1.466×10^5	9	810 mμ	1.475×10^5	7
550 mμ	2.172×10^5	6	545 mμ	2.193×10^5	6	540 mμ	2.213×10^5	6	535 mμ	2.234×10^5	6
395 mμ	3.025×10^5	4	390 mμ	3.064×10^5	4	385 mμ	3.103×10^5	4	380 mμ	3.145×10^5	4
928 mμ	1.288×10^5	12	928 mμ	1.292×10^5	10	923 mμ	1.295×10^5	12	920 mμ	1.299×10^5	10
815 mμ	1.466×10^5	10	810 mμ	1.475×10^5	9	805 mμ	1.484×10^5	9	805 mμ	1.484×10^5	10
535 mμ	2.234×10^5	8	530 mμ	2.254×10^5	6	525 mμ	2.276×10^5	6	520 mμ	2.299×10^5	6
390 mμ	3.064×10^5	6	390 mμ	3.064×10^5	4	385 mμ	3.103×10^5	2	380 mμ	3.145×10^5	2

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Discussion

It is reported that complex formation in solution is a stepwise process and many of the complexes, so formed are quite stable so that they can be studied upto certain extent[3]). It has therefore been found that gradual addition of ammonia to a nickel sulphate solution, results in the gradual displacement of water and formation of mono, di, tri, tetra, penta and hexamines.

If other aliphatic amines are added to the nickel sulphate solution, it has been observed that the colour of the solution changes from green to blue and ultimately becomes deep ink blue and any further addition of amine causes no change in the intensity of the amine. For spectroscopic study of the solutions exactly one mole of various amines are added to nickel sulphate solution in water. Since et each integral ratio a number of species exist in appreciable quantity, the value of the actual absorption maxima, was found as in case of copper complexes[4]), by plotting true absorptivity against wavelength, latter being obtained by solving the equation

$$AS_i^\lambda = b \sum_k a_k^\lambda C_{kl}$$

where AS_i^λ is the absorption at wavelength λ for the ith (Amine)$_0$/(Nickel)$_0$ ratio, b the cell thickness, a_k^λ is the absorptivity index for the kth species at λ and C_{ki} is the concentration of the kth compound at the ith ratio. Tables 1 and 2 summarise the spectral maxima for the complexes.

Each complex exhibits 4 absorption bands and their relative band shifts if compared to nickel sulphate by the addition of 1, 2, 3, 4, 5 and 6 molar quantities of amine solutions, indicate the gradual formation of mono, di, tri, tetra, penta and hexamine nickel (II) complexes. Later on, no change occurs in the position of any band, even if amine is added in excess. These results indicate the formation of these six compounds, as shown below, but actually at each ratio, a mixture and not a single ion is supposed to be present.

$$[Ni(H_2O)_6]^{+2} \rightleftharpoons [Ni(H_2O)_5\, am]^{+2} \rightleftharpoons [Ni(H_2O)_4\, am_2]^{+2}$$
$$\Updownarrow$$
$$[Ni(H_2O)_3\, am_3]^{+2}$$
$$\Updownarrow$$
$$[Ni\,(am)_6]^{+2} \rightleftharpoons [Ni(H_2O)\, am_5]^{+2} \rightleftharpoons [Ni(H_2O)_2\, am_4]^{+2}$$

The energy in K. Cals absorbed per mole of these complexes for each absorption band, has been calculated by the equation $E = N\,h\,C/\lambda$ where N is AVOGADRO's Number, h is PLANK's constant, C velocity of light and

[3]) J. BJERRUM, Metal amine formation in aqueous solution, F. Hasse & Son, 1941.

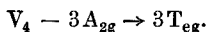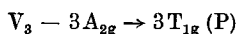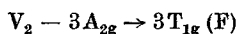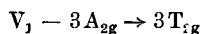[4]) GRANT and KOLLRACK, J. Inorganic and Nucl. Chem. **23**, 25 (1961).

λ the wave length of complex under consideration. It is observed that energy of these nickel amine complexes increases gradually as the water ligands in nickel (II) ion are replaced by amines. Further it is noted that these energy values in all the complexes of all the various amines are constant and that the increasing molecular weight of amine causes no change in the position of absorption maxima.

Nickel (II) sulphate exists in solution as the well known green $[Ni(H_2O)_6]^{+2}$ ion. In an octahedral field where the metal exhibits its maximum co-ordination number of 6 on the basis of energy level diagram, the terms arising fromthe d^8 ground state are

$$3 d^8 = 3F, 1D, 3P, 1G \text{ and } 1S.$$

Theoretically only three spin allowed transitions are expected, which occur in the spectra of all octahedral nickel (II) complexes. Many times the middle band of the spectrum is often splitted, due to spin-orbit coupling which mixes the $3T_{2g}$ (F) and 1 Eg states, which are very close in energy at the $\Delta 0$ value given by $6H_2O$. These bands are further characterised by very low intensity values.

These four bands are represented as V_1, V_2, V_3 and V_4 bands and are assigned as

$$V_1 - 3A_{2g} \rightarrow 3T_{ig}$$
$$V_2 - 3A_{2g} \rightarrow 3T_{1g} (F)$$
$$V_3 - 3A_{2g} \rightarrow 3T_{1g} (P)$$
$$V_4 - 3A_{2g} \rightarrow 3T_{eg}.$$

In case of hexaquo nickel (II) ion the solution is green in colour and the theoretical bands are observed at $V_1 = 9000 \text{ Cm}^{-1}$, $V_2 = 14000 \text{ Cm}^{-1}$, $V_3 = 17500 \text{ Cm}^{-1}$ and $V_4 = 25000 \text{ Cm}^{-1}$. When amines are added, the replacement of water ligands with amines, which lie toward the stronger end of spectrochemical series, begins and solution assumes a blue colour. The positions of the various absorption bands shifts to lower wavelength or higher frequency region, with a subsequent increase in ligand field than water and thus gives rise to an hyposochromic effect that causes the absorption bands to shift to lower wavelength, as in case of copper-amine complexes. This ultimately gives rise to a change in the colour of the solution, from green to faint blue and then to ink blue in hexamine, after which no change occurs. The energy now available for the electron to jump from one level into another is consequently increased, but this can not cause any aparent change in the magnitude of the transitions, because the above mentioned four transitions are the only spin-allowed transitions for a bivalent nickel ion in an octahedral field. Further the ratio V_3/V_1 is also equal to 1.82 for

all octahedral complexes irrespective of the ligand used for co-ordination[5]) is being observed here as well. It is thus concluded that the deepening of the colour in this particular case is due to the stronger ligand field environment produced around the metal, by the replacement of water ligands with various amines and the spectra confirm that metal remains hexaco-ordination in all the cases.

[5]) C. FERNELIUS and W. MANCH, J. chem. Educat. **37**, 193 (1960).

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