Effect of Different Anions on the Structures of Some Mixed Ligand Complexes of Copper(II), Nickel(II) & Iron(II) with Various Amines

GOPAL NARAIN* & (Ku.) GEETA MISHRA

Chemistry Department, University of Saugar, Sagar 470 003

and

(Mrs) P R SHUKLA

Chemistry Department, Lucknow University, Lucknow 226 007

A series of copper(II), nickel(II) and iron(II) complexes have been prepared with different amines and various coordinating and non-coordinating anions. The analytical and molar conductance data of the complexes suggest their molecular formulae to be $[Cu(CH_2COO)_2(am)_2]$, $[Cu(dam)_2]$ $(CH_2COO)_2$, $[Cu(dam)_2]$ $(C_7H_6O_2N)_2$, $[Ni(C_4H_4O_2N)_2(dam)_2]$, $[Ni(dam)_3]$ $(C_7H_6O_2N)_2$, $[Ni(dien)_2]$ $(SCN)_2$, $[Ni(dien)_2]WO_4$, $[Ni(trien)_2(H_2O)_2]WO_4$ and $[Fe(dam)_3](C_7H_6O_2N)_2$, where am = ammonia or aliphatic amines; dam = en, pn, dipy or phen; dien = diethylenetriamine and trien = triethylenetetramine; and $(CH_2COO)_2$ = succinate; $(C_7H_6O_2N)_2$ = anthranilate ion. The magnetic and spectroscopic data indicate planar structures for copper(II), and octahedral structures for nickel(II) and iron(II) complexes. The effect of anions on the coordinating abilities of metals as well as the structures of complexes so formed is discussed.

In the last few years a large number of mixed ligand complexes derived from various nitrogen donors and anions have been reported[1-5]. In almost all the cases the anion was found to exert a profound influence on the coordination number of metal ion used. In this note an attempt has been made to correlate the effect of anion and ligand on the coordination number of metal ion by preparing a series of complexes with different mono- and diamines and various anions. The prepared complexes have been characterised on the basis of their analytical, molar conductance, magnetic moment, infrared and electronic spectral data.

The ligands used in the investigation were BDH reagents of AR grade. Copper(II) succinate and nickel(II) succinimide, thiocyanate and tungstate were supplied by M/s Alpha Inorganic Corporation and K & K Laboratories, USA, while copper(II), nickel(II) and iron(II) anthranilates were obtained by treating sodium anthranilate with the metal(II) sulphates in aqueous medium. The precipitates so obtained were filtered, washed repeatedly with water and dried *in vacuo* over $CaCl_2$. The analytical data are given in Table 1.

The complexes were prepared by treating stoichiometric quantities of the required amine with the metal salt in ethanol and refluxing the solution for 8-10 hr. These were crystallised by distilling off 50% of solvent and cooling the concentrated solution of reactants. The analytical, molar conductance and magnetic moment data are given in Table 1.

The molar conductance values of the complexes measured in nitrobenzene (Table 1) show that the metal succinate (succ) complexes with ammonia or aliphatic amines (am) are non-electrolytes thus suggesting the coordination of succinate ion, $[Cu(succ)_2(am)_2]$; on the other hand, when ethylene- or propylene-diamine is used the complexes become electrolytes and the succinate ion is not coordinated, and complexes have the formula $[Cu(en)_2$ or $(pn)_2]$ $(succ)_2$. These diamines are stronger ligands and thus replace succinate ion from coordination sphere. Succinimide ion, however, remains coordinated to metal as it has probably the same strength as the diamines e.g. $[Ni(succinimide)_2(en)_2$ or $(pn)_2]$. In the case of mononegative anthranilate ion (anthr), the chelating diamines do not permit its coordination to metal and hence it always remains outside the coordination sphere and compounds of formula $[M(dam)_n](anthr)_2$ where n = 2, dam = ethylene- or propylene-diamine when M = Cu; n = 3, dam = en, pn, dipy or phen when M = Ni; and n = 3, dam = dipy and phen when M = Fe are obtained. The anion tungstate, which is non-coordinating in nature, gives the expected electrolytic complexes. The results with nickel(II) thiocyanate are slightly unexpected and in spite of the strong tendency of NCS to coordinate, only electrolytic complexes are obtained.

Definite and conclusive evidence for the coordination of ligands is obtained by infrared spectra. (i) The evidence for the coordination of ammonia and aliphatic amines is obtained by a negative shift of νNH modes; the asymmetric and symmetric NH stretches appear near 3300 and 3200 cm^{-1}, respectively, in all the complexes[6]. The coordination of 2,2'-dipyridyl and 1,10-phenanthroline is indicated by the positive shifts of $C \doteq C$, $C = N$ and ring stretching modes[7,8]. (ii) The lattice held water molecules give asymmetric and symmetric OH stretches in the vicinity of 3500 cm^{-1}. The νOH mode of coordinated water molecules is seen at 3400 cm^{-1}, and in addition the rocking and wagging modes also appear at 900 and 775 cm^{-1} respectively. (iii) The succinate ion has C_{2h} symmetry in which the most important infrared active vibration is ν_s COO$^-$. This is observed in aliphatic amine complexes at 1390 cm^{-1}. Compared to free salts, it undergoes negative shift of the order of 60 cm^{-1} indicating the coordination of succinate ion. The ethylene- or

Table 1—Analytical, Conductance and Magnetic Moment Data of the Complexes

Complex	Found (calc.), %				Λ_M (in Ph-NO$_2$)	μ_{eff} (B.M.)
	M	C	H	N		
1 $[Cu(CH_2COO)_2(NH_3)_2]$	29.45 (29.75)	22.00 (22.49)	4.70 (4.71)	12.80 (13.12)	N.E.	1.89
2 $[Cu(CH_2COO)_2(CH_3NH_2)_2].H_2O$	24.01 (24.47)	28.22 (27.74)	5.80 (6.20)	10.41 (10.79)	Ins	1.93
3 $[Cu(CH_2COO)_2(C_2H_5NH_2)_2]$	23.22 (23.56)	35.18 (35.63)	6.28 (6.72)	9.98 (10.39)	Ins	2.04
4 $[Cu(CH_2COO)_2(n\text{-}C_3H_7NH_2)_2.3H_2O$	17.88 (18.08)	34.10 (34.10)	7.80 (8.02)	8.00 (7.96)	Ins	1.97
5 $[Cu(CH_2COO)_2 (i\text{-}C_3H_7NH_2)_2].H_2O$	19.61 (20.12)	37.68 (38.03)	7.12 (7.45)	9.30 (8.87)	Ins	1.87
6 $[Cu(CH_2COO)_2(n\text{-}C_4H_9NH_2)_2]$	19.23 (19.51)	43.88 (44.23)	7.82 (8.04)	8.22 (8.59)	Ins	1.92
7 $[Cu(CH_2COO)_2(i\text{-}C_4H_9NH_2)_2]$	19.86	44.40	7.69	8.89	Ins	1.89
8 $[Cu(C_2H_8N_2)_2] (CH_2COO)_2.2H_2O$	18.55 (18.93)	29.21 (28.62)	7.22 (7.20)	16.83 (16.69)	22.00	1.92
9 $[Cu(C_3H_{10}N_2)_2] (CH_2COO)_2.3H_2O$	16.22 (16.44)	31.02 (31.45)	8.01 (7.91)	14.44 (14.67)	24.00	1.90
10 $Cu(C_7H_6O_2N)_2.3H_2O$	15.98 (16.30)	42.63 (42.88)	4.22 (4.65)	7.16 (7.18)	Ins	1.87
11 $[Cu(C_2H_8N_2)_2] (C_7H_6O_2N)_2.2H_2O$	12.83 (12.91)	44.25 (43.92)	6.12 (6.55)	17.00 (17.08)	22.00	1.94
12 $[Cu(C_3H_{10}N_2)_2] (C_7H_6O_2N)_2.4H_2O$	11.35 (11.42)	42.88 (43.19)	6.93 (7.24)	14.90 (15.11)	21.00	2.08
13 $[Cu(C_{10}H_8N_2)_2 (C_7H_6O_2N)_2$	9.44 (9.80)	63.34 (63.00)	4.01 (4.35)	12.72 (12.96)	20.50	1.98
14 $[Cu(C_{12}H_8N_2)_2] (C_7H_6O_2N)_2$	9.00 (9.12)	63.86 (64.07)	3.64 (4.05)	11.88 (12.07)	21.00	2.06
15 $[Ni(C_4H_4O_2N)_2 (C_2H_8N_2)_2].4H_2O$	12.98 (13.13)	31.73 (32.22)	6.82 (7.21)	19.11 (18.80)	N.E.	3.07
16 $[Ni(C_4H_4O_2N)_2(C_3H_{10}N_2)_2].3H_2O$	12.52 (12.84)	36.23 (36.77)	6.99 (7.49)	18.66 (18.38)	N.E.	3.11
17 $Ni(C_7H_6O_2N)_2.3H_2O$	15.02 (15.25)	43.02 (43.66)	4.21 (4.71)	6.89 (7.28)	N.E.	2.83
18 $[Ni(C_2H_8N_2)_3] (C_7H_6O_2N)_2.2H_2O$	10.44 (10.73)	44.22 (43.89)	6.98 (7.36)	20.83 (20.46)	26.00	2.99
19 $[Ni(C_3H_{10}N_2)_3] (C_7H_6O_2N)_2.2H_2O$	9.79 (9.96)	46.33 (46.87)	7.32 (7.86)	19.42 (19.01)	28.00	3.08
20 $[Ni(C_{10}H_8N_2)_3] (C_7H_6O_2N)_2.5H_2O$	6.46 (6.60)	58.84 (59.38)	4.96 (5.21)	12.40 (12.59)	31.50	3.12
21 $[Ni(C_{12}H_8N_2)_3] (C_7H_6O_2N)_2.2H_2O$	6.33 (6.46)	66.43 (66.17)	4.01 (4.44)	12.62 (12.34)	29.00	3.22
22 $[Ni(C_4H_{13}N_3)_2] (SCN)_2.2H_2O$	13.88 (14.07)	28.38 (28.78)	6.78 (7.24)	27.00 (26.84)	33.50	2.99
23 $[Ni(C_4H_{13}N_3)_2]WO_4.4H_2O$	9.73 (10.04)	16.12 (16.43)	5.33 (5.85)	13.90 (14.37)	21.00	3.28
24 $[Ni(H_2O)_2(C_6H_{18}N_4)_2]WO_4.6H_2O$	7.43 (7.90)	18.98 (19.39)	6.64 (7.05)	14.53 (15.07)	21.50 (15.07)	3.50
25 $Fe(C_7H_6O_2N)_2.2H_2O$	16.52 (16.81)	50.25 (50.62)	4.36 (4.85)	8.50 (8.44)	Ins	5.12
26 $[Fe(C_{10}H_8N_2)_3] (C_7H_6O_2N)_2.5H_2O$	5.98 (6.30)	59.12 (59.60)	4.77 (5.23)	12.60 (12.63)	32.00	Diam
27 $[Fe(C_{12}H_8N_2)_3] (C_7H_6O_2N)_2.5H_2O$	5.44 (5.82)	62.22 (62.63)	4.44 (4.83)	11.40 (11.68)	36.00	Diam

N.E. = non-electrolyte, Ins = insoluble, Diam = diamagnetic. The complexes are not soluble to the extent to allow the determination of molecular weights.

propylenediamine complexes have the corresponding band at 1440 cm^{-1}. As the band is present at almost the same position as in sodium(I) succinate, it is clear that the succinate ion is outside the coordination sphere[9-11]. (iv) All the complexes having anthranilate ions are electrolytes and hence the anthranilate ion possessing the free arylamine and carboxylic groups should show bands in all the complexes at positions similar to those observed in sodium anthranilate. The free aryl NH_2 absorption at 3400 cm^{-1} shifts to 3400 ± 25 cm^{-1} in diamine complexes, but it is observed very clearly in 2,2'-dipyridyl and 1,10-phenanthroline complexes at 3410 cm^{-1} showing its noninvolvement in coordination[11]. A band at 1525 cm^{-1} is due to ν_{as} COO^- of the free anthranilate ion[12]. (v) The succinimide complexes are also non-electrolytes. Its coordination is also indicated by a lowering in the CO stretch. (vi) The free thiocyanate ion shows three IR bands due to νCN, δSCN, and νCS modes. The first and the last bands occur at 2050 and 748 cm^{-1} respectively in the present complexes. The positions of these when compared to those in KSCN show no change and hence the ion is not coordinated. (viii) Tungstate ion belongs to point group T_a and four vibrations ν_1, ν_2, ν_3 and ν_4 are expected in its IR spectrum. Out of these, ν_1 and ν_3 are observed at 922 ± 10 cm^{-1} and 830 ± 10 cm^{-1} in the present complexes. These positions clearly indicate that the ion is not coordinated[13].

The copper(II) complexes are blue-violet in colour and paramagnetic with μ_{eff} in the range 1.70-2.20 B.M. indicating the presence of one unpaired electron. The tetracoordinated complexes are, therefore, assigned planar structure.

The Cu(II) complexes normally show only one band in 13.00-19.00 kK region, the position of which depends upon the ligand field strength. Thus, in aliphatic amine complexes it occurs at 13.70 kK, while in diamine complexes it occurs at 18.18 kK. The splitting of this band is not seen in any complex and the band is probably due to the simple $d_{z^2} \rightarrow d_{x^2-y^2}$ transition[14].

The nickel(II) complexes are paramagnetic with μ_{eff} values in the range 2.83-3.50 B.M. which are suggestive of octahedral geometry. The complexes are pink, violet or brown in colour and their diffuse reflectance spectra show three or four bands in the 10.00-30.00 kK region. These are assigned as: $^3A_{2g}(F) \rightarrow ^3T_{2g}(F), (\nu_1) (8.77-12.19$ kK); $^3A_{2g}(F) \rightarrow ^3T_{1g}(F), (\nu_2)$ (14.00-19.65 kK); and $^3A_{2g}(F) \rightarrow ^3T_{1g}(P), (\nu_3)$ (28.00-30.12 kK).

The positions of these bands as well as the values of various ligand field parameters have been determined. D_q, B, β and the ratio ν_2/ν_1 are 1064 cm^{-1}, 1100 cm^{-1}, 1.00 and 1.68, respectively, confirming the octahedral geometry. The splitting of ν_2 band is seen in those complexes where two ligands are present in the coordination sphere[15,16].

Both the hexacoordinated complexes of iron(II) prepared in this study are dark-red and diamagnetic. The amines, due to their very high ligand field strength, cause spin-pairing[17,18]. In low-spin iron(II) complexes, only two spin-allowed transitions $^1A_{1g} \rightarrow ^1T_{1g}$ and $^1A_{1g} \rightarrow ^1T_{2g}$ are possible which in the present complexes occur at 8.96 and 12.26 kK respectively. Due to the presence of some spin-forbidden transitions, a large number of shoulders are also seen and hence the calculation of ligand field parameters could not be accurately done[19,20].

It is apparent, therefore, that even the coordinating anions, in the presence of very strong amines, remain outside the coordination sphere and give electrolytic complexes, in which metal has the highest coordination number. Only the amines occupying lower positions in the spectrochemical series give non-electrolytic complexes.

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