Pakistan J. Sci. Ind. Res., Vol. 14, Nos. 4–5, August–October 1971

STUDIES ON COORDINATION COMPOUNDS

Part III.—Nickel(II) Complexes of Acetamide

M. Arshad A. Beg and Mustahsan R. Farooqui

PCSIR Laboratories, Karachi 39

(Received March 18, 1971)

Acetamide complexes of the type $[Ni(Acetamide)_4.2H_2O]X_2$ (where X is chloride, bromide, iodide or nitrate ion) have been prepared. The IR spectra suggest a bonding through the carbonyl group. The magnetic studies indicate the presence of two unpaired electrons. From the visible spectra it seems that the compounds have a distorted octahedral arrangement. The $\nu(NH_2)$, the Dq value and the intensity of the 24000 cm^{-1} band is found to vary with the anion. The stability constant calculated from conductivity shows the same to have the following trend $Cl>Br>I>NO_3$.

We have recently reported the isolation of complexes from dihydrazides with nickel(II) and cobalt(II) salts.[1,2] In each case the compounds had two molecules of water coordinated to the metal. We have therefore attempted the preparation of such aquo-complexes with simple ligands. The hexaacetamido complex of nickel has already been reported.[3] We had noted the formation of some of the acetamide complexes from the study of such physical properties as the density and the viscosity of a univariant system of nickel chloride and acetamide and found the formation of complexes in the 1:4 and 1:6 proportion.[4] With these results in mind we report here the preparation and properties of the diaquotetracetamido complexes of nickel(II).

Experimental

The hydrated nickel chloride and bromide were partly dried at 110°C so as to obtain the dihydrates. Nickel iodide was prepared by refluxing the nitrate in 90% ethanol and adding potassium iodide in stoichiometric proportion. Nickel nitrate was partly dehydrated by refluxing its hexahydrate in butanol. The partly dehydrated nickel salt and acetamide in the 1:4 molar proportions were refluxed in butanol or methanol for 1 hr. The solution so obtained was concentrated by distilling off some of the alcohol. The tetracetamido complexes separated out as light green crystals from butanol but had to be precipitated by ether from methanolic solutions. The isolated compound was further purified by washing with chloroform to remove the traces of acetamide. The compounds were desiccated over sulphuric acid. No loss in weight was observed even when kept for several days.

It was not possible to crystallize these complexes from any solvent since in each case a displacement of the amide was observed. In the case of ammonia, aniline, pyridine and bipyridine the corresponding complexes were obtained which were identified spectroscopically but with acetonitrile, acetone, nitromethane and boiling chloroform acetamide was displaced giving anhydrous nickel salts. An aqueous solution gave free acetamide and the hydrated nickel salt. This was confirmed by the NMR spectrum recorded in D_2O which gave a broad band for the amide in the 100 c/s region. (Found: C, 23.65; H, 6.03; N, 13.6; Ni, 14.1; Cl, 17.43%; m.p. 115°C. Calc. for $[NiAcam_4(H_2O)_2]Cl_2$: C, 23.91; H, 6.02; N, 13.94; Ni, 14.61; Cl, 17.64%.) (Found: C, 19.93; H, 5.13; N, 11.45; Ni, 11.50; Br, 32.41, m.p. 132°C. Calc. for $[NiAcam_4(H_2O)_2Br_2$: C, 19.61; H, 4.82; N, 11.42; Ni, 11.96; Br, 32.56%.) (Found: C, 16.6; H, 4.1; 4.1; N, 9.3; Ni, 10.3; I, 43.13; m.p. 98–100°C. Calc. for $[NiAcam_4(H_2O)_2I_2$: C, 16.44; H, 4.21; N, 9.58; Ni, 10.02: I, 43.39%.) (Found: C, 21.6; H, 5.2; N, 18.7; Ni, 12.3; m.p. 102°C. Calc. for $[NiAcam_4(H_2O)_2]$ (NO_3); C,21.12; H, 5.32; N, 18.48; Ni, 12.29%.)

IR spectra were recorded on a Perkin Elmer Model 237 spectrophotometer using KBr pellets and nujol mulls. The visible spectra were recorded on Unicam SP 500 and Beckman DK2 spectrophotometers. The spectra were run in methanolic solutions and concentrations were adjusted so as to obtain the optical density at λ_{max} in the range of 0.5–1.0. Magnetic susceptibility measurements were made on a Gouy magnetic balance using powdered samples. Conductivity was measured on a WTW conductivity meter type LBr, using extra pure methanol as solvent.

Results

From the analytical data it is apparent that nickel is hexa-coordinated; the conductivity measurements which appear in Fig. 1 suggest the formulation $[Ni(Acetamide)_4.2H_2O]$ X_2 for these compounds. The bands in the IR spectra are listed in Table 1 along with their assignments. Fig. 2 depicts the absorption in the visible region of the spectrum and Table 2 lists the band assign-

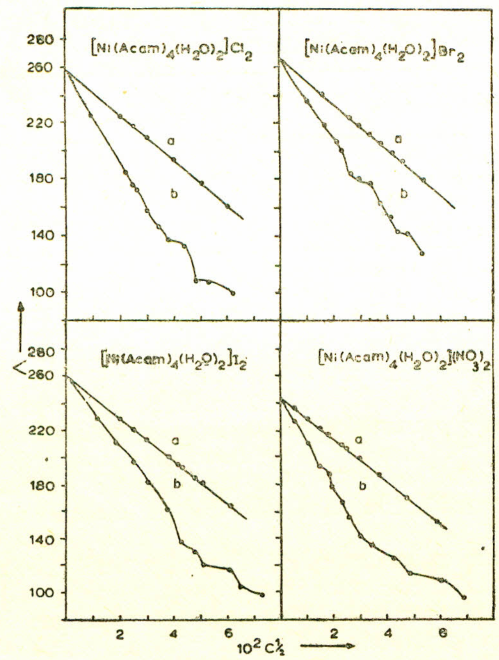

Fig. 1.—Conductance of nickel acetamide complexes.

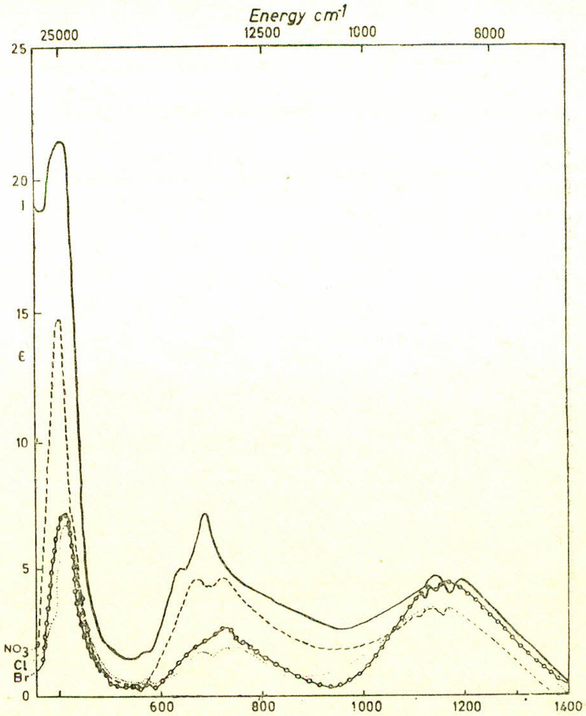

Fig. 2.—Electronic spectra of nickel acetamide complexes.

TABLE I.—IR ABSORPTION BANDS AND THEIR ASSIGNMENTS.

$[Ni(Acam)_4(H_2O)_2]Cl_2$ cm^{-1}	$[Ni(Acam)_4(H_2O)_2]Br_2$ cm^{-1}	$[Ni(Acam)_4(H_2O)_2]I_2$ cm^{-1}	$[Ni(Acam)_4(H_2O)_2](NO_3)_2$ cm^{-1}	Band assignments
3390 vs	3390 s	3448 vs broad	3333 vs	N—H stretching
3226 s	3279 s broad	3226 vs	3226 vs	N—H associated
	3175 s			
2985 m	2941 sh	2945	3030	C—H stretching
2958 sh	2778 m	2778 m	2778 m	
2817 m	2381 w	2381 w	2395 w	Coordinated water
	2299 w			
	2222 w		2227 w w(sh)	
2151 w	2128 w		2128 w	
2105 w				
1667 vs	1613 s	1667 vs	1770 m (sh)	C—O stretching
		1626 vs	1667 vs	
1575 vs	1587 s	1582 s broad	1587 s	—NH_2 bending
			1575 s	
1460 s	1481 m	1481 s	1493 m (sh)	CH_3 asymmetric bending
	1471 s	1460 s	1460 s broad	
1408 vs	1408 s	1408 vs	1408 vs broad	C—O bending and C—N asymmetric stretching
1307 m	1370 s	1143 s	1385 vs	CH_3 symmetric bending
1149 m	1149 m		1149 m	C—N asymmetric stretching
				C—H in plane vibration
1136 s	1136 s	1136 m	1136 m (sh)	
1099 w	1042 m	1097 m	1111 w	
1044 m			1045 m (sh)	
1020 w	1020 m	1026 w	1025 w	
			1015 w	
895 w	895 m	897 w	893 w	C—O deformation
		806 w	830 m	—NO_3
788–764 broad band	794–752 broad band	787–770 broad band	787–765 broad band	Coordinated water + —NH_2 wagging

vs=very strong; s=strong; m=medium; w=weak; sh=shoulder.

TABLE 2.—ABSORPTION BANDS IN THE VISIBLE REGION.

Compound	Concentration 10^{-2}M	Band cm^{-1}	Band ε	Band assignment
Ni(Acam)$_4$-(H_2O)$_2$ Cl_2	8.92	23980	6.79	$3A_{2g}(F)\rightarrow 3T_{1g}(P)$
		13790 13610	2.18 2.18	$\rightarrow 3T_{1g}(F)$
		9009 8658 8361	2.3 2.6 3.2	$\rightarrow 3T_{2g}(F)$
Ni(Acam)$_4$-(H_2O)$_2$ Br_2	9.3	24100	7.1	$3A_{2g}(F)\rightarrow 3T_{1g}(P)$
		13790 13070	2.6 2.1	$\rightarrow 3T_{1g}(F)$
		8696 8475 8368	4.19 4.29 4.26	$\rightarrow 3T_{2g}(F)$
Ni(Acam)$_4$-(H_2O)$_2$ I_2	4.5 4.5	24880	21.43	$3A_{2g}(F)\rightarrow 3T_{1g}(P)$
		15150sh 14710	5.00 7.10	$\rightarrow 3T_{1g}(F)$
		8772 8330	4.6 4.55	$\rightarrow 3T_{2g}(F)$
Ni(Acam)$_4$-(H_2O)$_2$ $(NO_3)_2$	5.9	24810	13.92	$3A_{2g}(F)\rightarrow 3T_{1g}(P)$
		14810 14470	4.6	$\rightarrow 3T_{1g}(F)$
		9050sh 8850 8439	3.1 3.4 3.4	$\rightarrow 3T_{2g}(F)$

ments. The calculated ligand field parameters are recorded in Table 3. The magnetic susceptibility measurements are listed in Table 4 which indicates the presence of two unpaired electrons. The series of compounds under study is therefore a tetragonal system.[5]

Discussion

The assembly of Fisher–Taylor–Hirschfelder model for this series of complexes indicates the following: (1) The acetamide molecules have to be twisted along the Ni—O—C bonds so as to minimize the mutual repulsions of the adjacent groups (2) the rotation of the amino groups is restricted, there is a possible interaction of the amino groups with the hydroxyls at the apical position and (3) at least two amino groups are above and two below the base of the octahedron. This arrangement gives a symmetrically distorted octahedral framework. The physical studies which follow support this structure.

IR Spectra.—The spectra of these compounds may be conveniently assigned to the three groups: —CH_3, —NH_2 and —C=O. These spectra are not much different from those of the copper and cadmium complexes which have already been reported.[6] The main difference from these spectra is in two consistent bands occurring at 2200 and 780 cm^{-1}. Both of them have been assigned to coordinated water.[7] This confirms the presence of the molecules of water in the coordination sphere.

TABLE 3.—THE CALCULATED LIGAND FIELD PARAMETERS.

Compound	E(P)-E(F) cm^{-1}	Dq*	β %
[Ni(Acam)$_4$(H_2O)$_2$]Cl_2	13170	850.8	16.9
[Ni(Acam)$_4$(H_2O)$_2$]Br_2	13270	851.3	16.28
[Ni(Acam)$_4$(H_2O)$_2$]I_2	14040	855.1	11.42
[Ni(Acam)$_4$(H_2O)$_2$(NO_3)$_2$	13830	864.4	12.75

* Average of the band positions in this region.

Perturbation in the NH_2 frequency and splitting in the band corresponding to the carbonyl groups is also noticeable. These may be explained on the basis of the molecular model described above. Perturbations in the NH_2 frequency might be due to hydrogen bonding which in the present series is possible through the interaction of the amino with the hydroxyl groups. This interaction and the mutual repulsions of the molecules in the coordination sphere will result in a twisting of the acetamides along the Ni—O—C bond. The carbonyl groups are thus sterically different and hence would absorb differently producing split bands.

The amino group stretching frequency is seen to vary with the anion. It occurs at 3390 cm^{-1} for the chloride and bromide, at 3448 cm^{-1} for the iodide and at 3333 cm^{-1} for the nitrate.

Visible Spectra.—The notable features of the visible spectra are: (1) split bands at 8300–8700 cm^{-1} and (2) a doublet at 13000–15000 cm^{-1} and intense and sharp band at 24000–25000 cm^{-1}. The bands at 8300–8700 cm^{-1} may conveniently be assigned to the transition from the ground to the first excited state corresponding to the value of 10 Dq or Δ. The Dq values are found to be slightly higher than those of acetamide or water in the hexacetamido or hexaquo complexes. The larger Dq values may be a result of steric interaction as suggested by molecular models and also noted from the IR spectra. Water and acetamide being quite close in the spectrochemical series,[3] a large deviation from an octahedral structure is not expected. These compounds may therefore be safely treated as those having strong octahedral and weak tetragonal fields. The tetragonal perturbation implies either attraction or repulsion of electrons in the environment of the ligands which, in the present case, are placed on the apices of the octahedron. Water being above acetamide in the spectrochemical series would cause repulsion.[3,8]

TABLE 4.—MAGNETIC SUSCEPTIBILITY OF THE COMPOUNDS MEASURED AT 22°C.

Compounds	$X_g \times 10^6$	$X_M \times 10^6$	Corrected $X_M \times 10^6$	μ_{eff} B.M.
$[Ni(Acam)_4(H_2O)_2]Cl_2$	7.623	3064	3231.64	2.772
$[Ni(Acam)_4(H_2O)_2]Br_2$	7.549	3705	3895.04	3.04
$[Ni(Acam)_4(H_2O)_2]I_2$	7.518	4396	4618.04	3.3
$[Ni(Acam)_4(H_2O)_2(NO_3)_2$	7.254	2621	2779.64	2.62

TABLE 5.—CONDUCTIVITY OF THE COMPOUND IN METHANOL.

Compounds	$C \times 10^4$	Λ	α	$\Lambda°$	$\lambda°+$	K_s
$[Ni(Acam)_4(H_2O)]Cl_2$	37.88	99.86	0.402	248	130.7	2.2×10^6
$[Ni(Acam)_4(H_2O)_2]Br_2$	28.68	129.70	0.487	266	137.4	5.75×10^5
$[Ni(Acam)_4(H_2O)_2]I_2$	72.33	158.1	0.606	261	134.8	3.38×10^4
$[Ni(Acan)_4(H_2O)_2](NO_3)_2$	13.32	126.2	0.518	244	136.7	1.94×10^4

These parturbations together with the better donor capacity of water compared with acetamide would cause an increase in the value of Dq. Steric interactions and a consequent increase in the value of Dq were also noted in the case of the various hexaamido complexes prepared by Drago *et al.*[3]

The splitting of the band corresponding to 10 Dq orΔ cannot be explained by steric interactions alone since in spite of the same effect in the hexaamido complexes doublets were not observed by Drago *et al.* This may be accounted for if the local tetragonal symmetry is taken into consideration whereby the excited states T_1g and T_2g are split into A_2g+Eg and B_2g+Eg. The splitting, however, is not too large and it does not indicate a large tetragonal distortion. That the structure is close to octahedral is further supported by the ratio of the $^3A_2g(F) \rightarrow {}^3T_1g(P)$ to $^3A_2g(F) \rightarrow {}^3T_1g(F)$ which is 2.7–3.1. This is within the range for octahedral complexes.[9] The percentage lowering of the P–F term splitting is 11–16% which is of the same order as for the hexaacetamido complexes. The calculated position of the bands in Table 3 also corresponds to an octahedral arrangement.

The Dq values of these complexes vary with the anion and increase in the order: $Cl < Br < I < NO_3$. The P–F term splitting as also the intensity of the 24000 cm^{-1} band increase in the following sequence: $Cl < Br < NO_3 < I$. A similar trend was also noted in the ν (NH_2) frequency.

Conductance Measurements

The conductance data listed in Table 5 reveal certain interesting features. The plot of Λ_c vs. $C^{\frac{1}{2}}$ does not follow a straight line but is a curve with a steeper slope. There is a considerable deviation of the experimental values from those calculated by the Onsager equation. This type of deviation is characteristic of ionic association or ion pair formation.[10] The $\Lambda°$ values correspond to a bi-univalent electrolyte and depend on the anion. By subtracting the $\lambda°$ it is found that the $\lambda°+$is almost constant and can be assigned the value of 134 $ohms^{-1}$. Compared with the hexaminine cobalt salts which have a value of 99.2 $ohms^{-1}$ in aqueous solutions[11] this is quite reasonable.

The aqueous solutions of these complexes are more conducting than the alcoholic solutions. This must be because of the displacement of the amide by water. This is confirmed by the NMR spectrum of the complexes in D_2O which shows broad bands of the amide. Other solvents and ligands with better donor capacity also displace acetamide from the complex. Thus the complexes of ammonia, aniline, pyridine and bipyridine are easily obtained. On this basis it is possible to say that these are weak complexes. These displacement reactions must be attributed to a large gain in the crystal field energy in the formation of an amino or ammine complex since it has been shown earlier that Dq for these complexes is lower than for the amines and is of the same order as for water.

The conductances in alcoholic solutions suggest fairly reasonable dissociative equilibria and we have used the relation : [12]

$$K_s = \frac{C_{M_q A_r \pm}}{C^q_{M^+} + C^r_{A^-}} \qquad (1)$$

for the equilibrium

$$M_q A_r \pm \rightleftharpoons qM^+ + rA^-$$

for the calculation of the stability constant K_s.

This relation is valid for dilute solutions for which it is possible to know the degree of ionization, which in turn gives C_{complex} and the C_{cation} and C_{anion} can be calculated therefrom. The values of K_s obtained in this manner decrease in the following order $NO_3 < I < Br < Cl$. This trend is of the reverse order as observed for the Dq values.

At the present stage we would like to attach more importance to the trend in the stability constant values since the crystal field stabilization energy in these complexes is almost of the same order.

Acknowledgement.—Part of this work was carried out at the Department of Chemistry, University of Western Ontario, London, Canada, under the CIDA-NRC Research Associateship for which one of us (MAAB) is thankful to Professor H.C. Clark for offering all the facilities of the Department.

References

1. M.A.A. Beg and B. Bilquis, Pakistan J. Sci. Ind. Res., **12,** 339 (1970).
2. M.A.A. Beg and B. Bilquis, Rev. Roumaine de Chim., **15,** 1732 (1970).
3. R.S. Drago, D.W. Meek, M.D. Joesten and L. Laroche, Inorg. Chem., **2,** 124 (1963).
4. S.S. Ahmad and M.A.A. Beg, (unpublished results).
5. C. J. Ballhausen and A.D. Liehr, J. Am. Chem. Soc., **81,** 538 (1959).
6. W. Kutzelenigg and R. Meeke, Spectrochem. Acta., **18,** 549 (1962).
7. J. Fujita, K. Nakamoto and M. Koboyashi, J. Am. Chem. Soc., **78,** 4963 (1956).
8. W. Moffit and C. J. Ballhausen, Ann. Revs. Phys. Chem., **7,** 123 (1956).
9. W. Low, Phys. Rev., **109,** 247 (1958).
10. R.M. Fuoss and C.A. Kraus, J. Am. Chem. Soc., **55,** 1019 (1933).
11. I. J. Jenkins and C.B. Monk, J. Chem. Soc., 68 (1951).
12. S. Glasstone, *Introduction to Electrochemistry* (D. Van Nostrand, New York, 1942), p. 173.