448. *Researches on Ammines. Part VI. Nickelammine Salts in Aqueous Solution.*

By HERBERT J. S. KING, ARTHUR W. CRUSE, and FREDERICK G. ANGELL.

AMMINES of bivalent metals usually differ from the more stable ammines of tervalent cobalt or chromium in that they smell of the co-ordinated base (ammonia, pyridine, etc.) both in the solid state and in aqueous solution. No exact information is available as to the extent to which the complex kation is decomposed in aqueous solutions of various concentrations. Dawson and McCrae (J., 1900, **77**, 1239) investigated the distribution of ammonia between chloroform and aqueous solutions of various metallic salts; they recorded no data for nickel sulphate, but concluded, from the amount of ammonia required to give a clear solution with the salt, that the nickel complex was considerably more decomposed in aqueous solution than was the copper complex. Dawson (J., 1906, **89**, 1666) recorded more exact distribution experiments with ammoniacal solutions of copper sulphate, but these usually contained considerable excess of ammonia.

In Part IV (J., 1930, 2307) values were obtained by one of us for the number of mols. of ammonia or pyridine combined with each g.-atom of copper in aqueous solutions of cuprammine nitrates, the excess freezing-point depressions of the pure salts over those of cupric nitrate at equivalent concentrations being attributed to free ammonia or pyridine, the concentration of which could then be calculated. For the hexapyridino-salt, the free pyridine per g.-atom of copper varied from 0·8 to 2·5 mols. between molar concentrations of 0·25 and 0·025. The hexammino-salt showed greater decomposition, to the extent of 5—6%, and the results for this complex were in excellent agreement with those of Dawson (*loc. cit.*) in the two cases where comparison was possible.

Similar determinations have now been made on solutions of *pentamminonickelous sulphate* and *hexammino-* and *hexapyridino-nickelous nitrates*, the proportion of free ammonia in the first case being 0·6—1·3 mols. (molar concentrations, 0·3—0·075), and in the second, 0·4—0·8 mol. (molar concentrations, 0·3—0·2). Thus hexamminonickelous nitrate in aqueous solution proved to be *more* stable than the hexammino-cupric salt, comparison with the data recorded in Part IV (*loc. cit.*) showing that its decomposition in 0·2*M*-solution was only about 60% of that for the cuprammine. On the other hand, the proportion of free pyridine in solutions of the third salt varied from 1·5 to 3·3 mols. (molar concentrations, 0·25—0·05), and was therefore some 50% greater than for hexapyridinocupric nitrate, for which the variation was 0·8—2·2 mols. between the same concentration limits.

The method of calculation of these values involves the assumptions that the complex salts ionise similarly to nickel sulphate and nitrate and that these nickel salts dissolve in water without co-ordination of water molecules. It was shown in Table III of Part IV (*loc. cit.*) that, if cupric nitrate dissolves in water as $[Cu(H_2O)_6](NO_3)_2$, the error introduced into the calculations is negligibly small at the lower concentrations and only reaches 1% in 0·175*M*-solution.

Pyridino-derivatives of both nickel and copper salts give clear aqueous solutions however low the concentration, but when solutions of the corresponding ammino-compounds are diluted, a point is always reached at which precipitation of hydroxide or basic salt occurs.

EXPERIMENTAL.

Amminonickelous Sulphates.—Ammines with 6, 4, and 2½ mols. of NH_3 in association with each Ni atom have previously been described. Rose (*Pogg. Annalen*, 1830, **20**, 151) prepared $[Ni(NH_3)_6]SO_4$ by treating anhyd. $NiSO_4$ with NH_3 gas. André (*Compt. rend.*, 1888, **106**, 937) and Erdmann (*J. pr. Chem.*, 1836, **7**, 264) claimed to have prepared $[Ni_2(NH_3)_5](SO_4)_2,7H_2O$ and $[Ni(NH_3)_4]SO_4,2H_2O$ respectively by treating $NiSO_4$ aq. with NH_3 aq., but we have obtained only the monohydrated pentammine by this method.

Pentamminonickelous sulphate monohydrate, $[Ni(NH_3)_5]SO_4,H_2O$. 40 G. of cryst. $Ni(NO_3)_2$ (Co-free) were warmed with 120 c.c. of NH_3 aq. (*d* 0·880) till dissolved. To the cool filtered solution were added, drop by drop, 50 c.c. of EtOH satd. with NH_3. The ppt. was washed successively with ammoniacal EtOH and Et_2O, and left over-night in vac. over soda-lime. 25 G. of bright blue hexagonal plates were obtained (Found: Ni, 22·6; NH_3, 32·9; SO_4, 37·6. $[Ni(NH_3)_5]SO_4,H_2O$ requires Ni, 22·8; NH_3, 33·0; SO_4, 37·3%). Complete pptn. by adding excess of ammoniacal EtOH gave a less pure product. The *compound* dissolved in H_2O to a bright blue solution, which could be diluted to a concn. of 0·05*M* before becoming turbid. The solid, when heated at 85° for 3 hr. lost 7% of its NH_3 and 25% of its H_2O.

Amminonickelous Nitrates.—Erdmann (*J. pr. Chem.*, 1866, **97**, 395) and Laurent (*Ann. Chim. Phys.*, 1852, **36**, 353) stated that they obtained respectively $[Ni(NH_3)_4](NO_3)_2,H_2O$ and $[Ni(NH_3)_4](NO_3)_2,2H_2O$ by addition of NH_3 to $Ni(NO_3)_2$ aq. André (*loc. cit.*) obtained only the hexammine when NH_3 solutions of $Ni(NO_3)_2$ were cooled or treated with EtOH. We have confirmed André's results, and there appears to be no evidence for the existence of a tetrammine. Pyridino-derivatives of $Ni(NO_3)_2$ have not hitherto been described.

Hexamminonickelous nitrate, $[Ni(NH_3)_6](NO_3)_2$. 20 G. of cryst. $Ni(NO_3)_2$ (Co-free) were dissolved in 25 c.c. of hot H_2O, and the cooled solution was treated, drop by drop, with 25 c.c. of NH_3 aq. (*d* 0·880). The small bluish-violet octahedral crystals which were pptd. (8 g.) were washed and dried as above (Found: Ni, 20·6; NH_3, 35·9; N, 39·2. $[Ni(NH_3)_6](NO_3)_2$ requires Ni, 20·6; NH_3, 35·9; N, 39·4%). The *compound* dissolved fairly readily in H_2O, but the solution became turbid on dilution to 0·175*M*.

Hexapyridinonickelous Nitrate, $[Ni(C_5H_5N)_6](NO_3)_2$.—20 G. of pure cryst. $Ni(NO_3)_2$ were dissolved in 50 c.c. of hot C_5H_5N. The solution was filtered hot, and the supersaturated filtrate crystallised when scratched. The product was washed successively with a little EtOH and Et_2O (it was rather sol. in EtOH), and proved to be the required salt but in a hydrated and somewhat impure condition. The pure anhyd. *salt* was obtained from it as follows: H_2O was completely removed by 2 weeks' standing in vac. over H_2SO_4, and the dry product was then redissolved in boiling anhyd. C_5H_5N. The solution was left in vac. over soda-lime until the salt separated, as bright blue hexagonal plates, which were collected without washing, kept on a porous plate for a few days in vac. over soda-lime, and then transferred to a stoppered bottle which was kept in a desiccator containing C_5H_5N (Found: Ni, 8·9; N, 17·1; NO_3, 18·6. $[Ni(C_5H_5N)_6](NO_3)_2$ requires Ni, 8·9; N, 17·1; NO_3, 18·9%); NO_3 was estimated by the nitron method; and N by combustion, the substance being mixed with powdered $KHSO_4$ to prevent premature loss of C_5H_5N. The compound was very sol. in H_2O and its solutions did not become turbid on dilution.

TABLE I.

	$[Ni(NH_3)_5]SO_4$ (M = 239·9).			$[Ni(NH_3)_6](NO_3)_2$ (M = 284·9).			$[Ni(C_5H_5N)_6](NO_3)_2$ (M = 657·0).		
C_w.	Δ*t*.	Δ*t*′.	*a*.	Δ*t*.	Δ*t*′.	*a*.	Δ*t*.	Δ*t*′.	*a*.
0·050	—	—	—	—	—	—	0·583°	0·345°	2·74
0·075	0·377°	0·186°	3·75	—	—	—	0·789	0·397	3·19
0·100	0·452	0·236	3·91	—	—	—	0·983	0·463	3·50
0·125	0·531	0·248	4·00	—	—	—	1·183	0·535	3·65
0·150	0·604	0·273	4·09	—	—	—	1·342	0·568	3·91
0·175	0·670	0·291	4·17	—	—	—	1·488	0·596	4·11
0·200	0·723	0·306	4·23	1·326°	0·318°	5·20	1·630	0·622	4·26
0·225	0·798	0·337	4·25	1·436	0·302	5·33	1·787	0·653	4·37
0·250	0·849	0·345	4·31	1·557	0·298	5·40	1·942	0·683	4·46
0·275	0·907	0·358	4·35	1·668	0·279	5·49	2·052	0·663	4·65
0·300	0·960	0·361	4·40	1·784	0·263	5·56	2·152	0·631	4·82

Freezing-point Depressions.—The Beckmann apparatus was used. Solutions of analysed samples of the solid salts were employed, and an independent solution was prepared in duplicate for each concn. The f. p. depressions were measured immediately after the solutions had been prepared, and the values recorded are the means of two identical or closely concordant results.

TABLE II.

	$NiSO_4$.		$Ni(NO_3)_2$.	
C_w.	Δ*t*.	Δ*t*/C_w.	Δ*t*.	Δ*t*/C_w.
0·050	—	—	0·266°	5·32
0·075	0·191°	2·55	0·392	5·23
0·100	0·236	2·36	0·520	5·20
0·125	0·283	2·26	0·648	5·18
0·150	0·331	2·21	0·774	5·16
0·175	0·379	2·17	0·892	5·10
0·200	0·417	2·09	1·008	5·04
0·225	0·461	2·05	1·134	5·04
0·250	0·504	2·02	1·259	5·04
0·275	0·549	2·00	1·389	5·05
0·300	0·599	2·00	1·521	5·07

	NH_3.	
C_w.	Δ*t*.	Δ*t*/C_w.
0·0667*	0·131°	1·96
0·111*	0·220	1·98
0·149*	0·298	2·00
0·186*	0·375	2·02
	C_5H_5N.	
0·157*	0·308°	1·96
0·179*	0·340	1·90
0·208	0·392	1·88
0·260	0·479	1·84
0·320	0·580	1·81
0·370	0·659	1·78
0·400	0·705	1·76

In the tables M indicates the calc. mol. wt., C_w the concn. (g.-mols. added to 1000 g. H_2O), Δt the f. p. depression of H_2O, $\Delta t'$ the excess f. p. depression due to the ammine over that due to the corresponding Ni salt, and a the number of mols. of NH_3 or C_5H_5N still associated with the Ni atom. Blanks in Table I indicate that the compound was decomp. by H_2O.

Table II gives the f. p. depressions for $NiSO_4$, $Ni(NO_3)_2$, NH_3, and C_5H_5N which were used in calculating the a values; *e.g.*, for $[Ni(C_5H_5N)_6](NO_3)_2$ and $Ni(NO_3)_2$ at a concn. of 0·2M, the values of Δt are 1·630° and 1·008° respectively; the difference of 0·622° corresponds to a free C_5H_5N concn. of 0·347M (by extrapolation from the C_5H_5N data, $0{\cdot}622/C_w$ is found to be 1·79); hence the concn. of free C_5H_5N is $0{\cdot}347/0{\cdot}2 = 1{\cdot}74M$, and that of combined C_5H_5N is $6 - 1{\cdot}74 = 4{\cdot}26M$.

The solutions of $NiSO_4$ and $Ni(NO_3)_2$ were prepared by dilution from solutions of known Ni content. The NH_3 and C_5H_5N values indicated by an asterisk are taken from Part IV (*loc. cit.*); the others were determined experimentally.

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