994. *Complexes Formed by α-Hydroxy-amidines with Transition-metal Ions. Part III.*[1] *Complexes with Nickel*(II).

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The formation of α-hydroxy-amidine complexes and the function of α-hydroxy-groups in complex formation is discussed further with respect to the stable, uncharged complexes of nickel with three such amidines. The stability constants for the complexes in aqueous solution are reported, and the visible-region spectra are discussed with respect to the magnetic properties of the complexes.

THE dissociation of the α-hydroxy-α-phenylamidinium ions, $HO{\cdot}CPhR{\cdot}C(NH_2){:}NH_2^+$, as dibasic acids[2] and the formation of 2 : 1 complexes between the resulting anions and copper(II)[1] has been described for R = H (mandelamidinium ion, abbreviated to mdH_2^+), Me (atrolactamidinium ion, alH_2^+), and Et (α-hydroxy-α-phenylbutyramidinium ion, hbH_2^+). The rapid addition of an excess of sodium hydroxide, to a mixture containing these amidinium ions and nickel(II) in a ratio in excess of 3 : 1, results in a clear pink solution from which the complex, like that formed by copper(II), can be extracted by immiscible alcohols, but not by less polar solvents.

RESULTS

Formation and Stoicheiometry of the Complexes.—The amidine : nickel ratio in the complexes was demonstrated by Job's method of continuous variations. The solutions gave good agreement with Beer's law at the wavelength of maximum absorption of visible light (about 490 mμ for all complexes), the absorption being proportional to nickel content for all solutions containing a nickel : amidine ratio less than 1 : 3. At higher ratios, precipitation of nickel hydroxide occurs, but if this precipitate is removed the absorption–concentration plot reaches a maximum at a nickel : amidine ratio of 1 : 2, decreasing linearly with amidine concentration at ratios higher than 1 : 1. The presence of very large excesses of sodium hydroxide caused slightly more precipitation in the central portion of the plot, but did not alter the position of the maximum.

The amount of hydroxide ion used in complex formation could not readily be found by pH titrations (cf. Fig. 1), as no definite break occurred in the curves obtained by titrating mixtures of nickel and amidinium ions with sodium hydroxide. The titration can, however, be followed photometrically, by using a No. 603 filter, since the absorption of nickel ions is negligible at the wavelength of maximum absorption of the complex. When at least a five-fold excess of amidine is present, only slight absorption is observed until two moles of hydroxide per mole of nickel have been added. There is then a linear increase in absorbance, the extrapolation of

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[1] Part II, *J.*, 1963, 15.
[2] Part I, *J.*, 1962, 296.

which gives a good intersection with the horizontal line, corresponding to complete complex-formation, at four moles of hydroxide added per mole nickel.

Like those with copper, the nickel complexes could be readily extracted from aqueous solution by immiscible alcohols, and their electrical neutrality was confirmed by their failure to migrate when subjected to electrophoresis. The crystals deposited by the pentanol solution of the mandelamidine complex alone lose solvent readily (Found: C, 53·1; H, 5·5; N, 15·6; Ni, 16·4. Ni md_2 requires C, 53·8; H, 5·1; N, 15·7; Ni, 16·4%). When this solid was recrystallised from benzyl alcohol, the solvated crystals were more stable, and it was possible to determine the molecular weight by *X*-ray methods,[3] the value obtained (466) indicating that only one solvent molecule was associated with each nickel ion (calc. for Ni md_2,Ph·CH_2·OH: *M*, 465·3).

The aqueous solutions containing the other amidines deposited crystalline dihydrates, except that with amidine : nickel ratios higher than 20 : 1 no solid separated. The hydroxyphenylbutyramidine *complex* (Found: C, 52·9; H, 6·8; N, 12·6; Ni, 13·1. Ni hb_2,$2H_2O$ requires C, 53·5; H, 6·8; N, 12·6; Ni, 13·1%) and atrolactamidine *complex* (Found: C, 51·5; H, 6·1; N, 13·2; Ni, 14·0. Ni al_2,$2H_2O$ requires C, 51·3; H, 6·2; N, 13·3; Ni, 13·9%) both lose water of crystallisation at high temperatures. The hydroxyphenylbutyramidine complex lost its water in a vacuum (Found: H_2O, 7·9. Ni hb_2,$2H_2O$ requires H_2O, 8·0%); the atrolactamidine complex lost water quantitatively at atmospheric pressure on being dried for 2 hr. at 120° (Found: H_2O, 8·6. Ni al_2,$2H_2O$ requires H_2O, 8·5%). As was the case with the corresponding copper complex, mandelamidine–nickel solutions did not yield crystalline products before the amidine decomposed. The solid compounds were soluble in alcohols, formamide, and piperidine, and also in hot pyridine, but they separated again from the last on cooling; they were not soluble in less polar solvents.

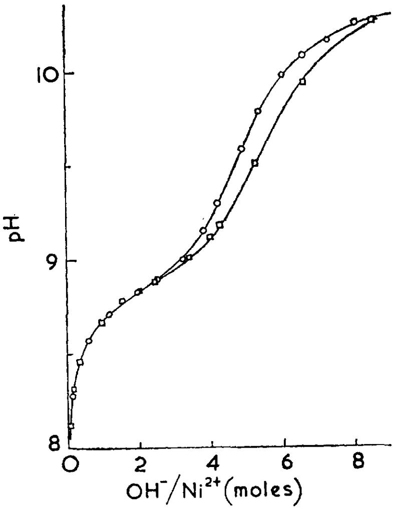

FIG. 1. pH-Titrations of solutions containing 0·001M-Ni^{2+} and 0·02M-alH_2^+, showing formation (○) and dissociation (□) of complexes.

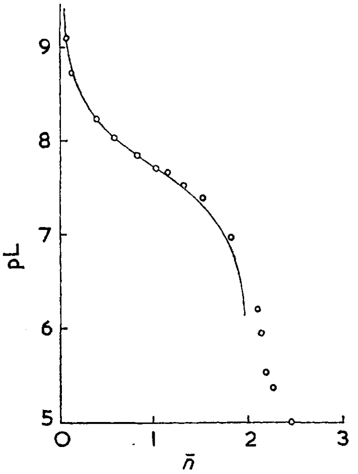

FIG. 2. Formation curve for nickel–atrolactamidine complex. Theoretical curve (calculated from log *K* values in Table 2) giving best fit at low values of $\bar{n}$ and sufficient experimental points to show deviation as $\bar{n}$ increases.

Stability Constants of the Complexes.—pH-titrations of mixtures of nickel and amidinium ions were carried out as for the copper solutions. In this case, as the midpoint of the formation curve occurred at pH ~9, base-catalysed decomposition of amidine was significant.[2] Since, however, the solutions did not appear to come to immediate equilibrium, batch methods could not be used as described earlier, and direct titrations were employed, only those results at low pH being relied on for calculations.

[3] Iball and Morgan, personal communication.

The method of carrying out the titrations has been given in Part II;[1] for the nickel solutions, amidine : metal ratios of at least 20 : 1 were required before the solutions remained clear throughout the titration. There was little discontinuity in the titration curves when four moles of hydroxide per mole of nickel had been added, no discontinuity being found for the mandelamidine–nickel system. The back-titration technique described in Part II was also applied to these complexes, and the forward- and back-titration curves for an identical mixture of nickel and atrolactamidinium ions are shown in Fig. 1. It will be seen that the curves can be superimposed only in the region of low pH.

TABLE 1.

Stability constants of nickel complexes with some α-hydroxy-amidines at 25° and an ionic strength of 0·1M.

Complex	Ni md_2	Ni al_2	Ni hb_2
log K_1	7·38	7·87	8·06
log K_2	7·02	7·53	7·74

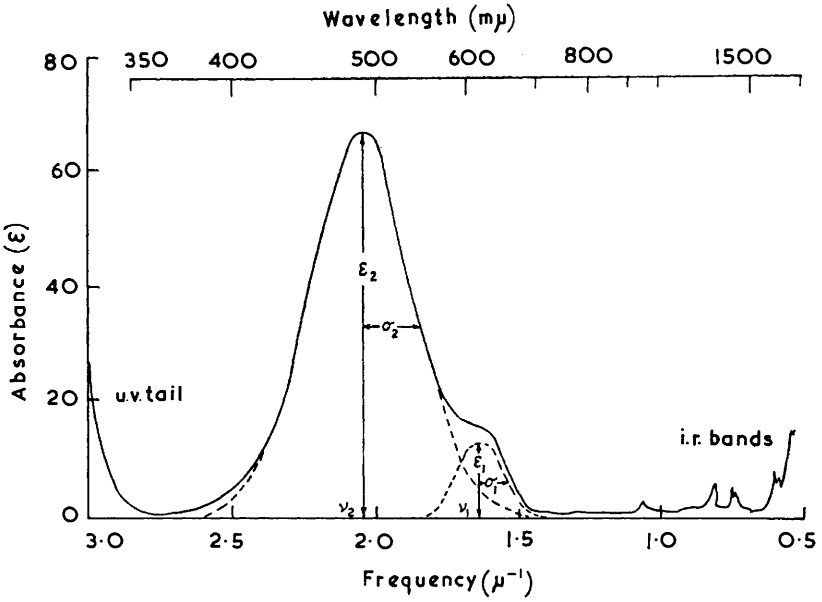

FIG. 3. Visible spectrum of Ni hb_2 solution in pentanol, showing division into gaussian components, with the frequency of maximum absorption, ν, maximum molar absorbance, ε, and half-band width, σ, for each component.

Calculation of Stability Constants.—Because of the evidently lower stability of the complexes, their formation curves cannot be calculated by using the approximations employed for the copper complexes,[1] but must be carried out rigorously.[4] The experimental points for the formation of the Ni–al complex corresponding to the titration curve in Fig. 1 are shown in Fig. 2, and the best theoretical curve corresponding to the formation of a 2 : 1 complex has been fitted to the points, those corresponding to low pH being weighted. From these formation curves for the three complexes, the stability constants given in Table 1 were deduced.[4]

Optical Studies.—As a check on these values, a simple spectrophotometric method was employed whereby measurements at higher pH could be used to obtain K_2 for the complexes. Solutions containing varying ratios mdH_2Cl : nickel were prepared, and sufficient sodium hydroxide was added to convert nearly all the metal ions into the doubly complexed form. The pH and the optical density of the solution were then measured as soon as possible, and, on

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[4] Bjerrum, Schwartzenbach, and Sillén, "Stability Constants," *Chem. Soc. Special Publ. No.* 6, Part I, p. viii.

TABLE 2.

Gaussian components of visible spectra of nickel(II) complexes with some α-hydroxy-amidines in various solvents; the meaning of the parameters is shown in Fig. 3.

Complex	Solvent	$\nu_1(\mu^{-1})$	ε_1	$\sigma_1(\mu^{-1})$	$\nu_2(\mu^{-1})$	ε_2	$\sigma_2(\mu^{-1})$
Ni md_2	Aq. alkali	1·65	8	0·10	2·02	52	0·21
	Pentanol	1·65	9	0·10	2·02	59	0·21
Ni al_2	Aq. alkali	1·68	9	0·10	2·04	53·5	0·21
	Pentanol	1·62	10	0·10	2·04	64	0·21
	Formamide	1·63	8	0·10	2·08	51	0·22
Ni hb_2	Aq. alkali	1·67	11·5	0·10	2·04	55·5	0·21
	Pentanol	1·62	12	0·10	2·04	67	0·21
	Formamide	1·63	9	0·10	2·08	50	0·22

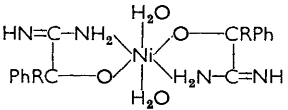
the assumption that the concentration of free metal ion would be negligible under these circumstances, the relative concentrations of the species Ni md_2 and Ni md^+ were calculated by comparison with the optical density of a solution in which complete complex-formation could be assumed. The quantity log $[L^-]$($= -pL$, as defined before [1]) may then be obtained from the pH values by successive iterations of the relation: log $[HL] = \log [H_2L^+] + pH - pk_1$ (with the assumption that $[L^-]$ will likewise be negligible in comparison with $[HL]$ and $[H_2L^+]$). Calculated in this manner, log K_2 is *ca.* 7·1, in close agreement with that determined under similar conditions by the pH method (above).

Visible Spectra of the Complexes.—Since, like the copper complexes, the nickel–α-hydroxy-amidine complexes were soluble only in the most polar solvents, little study could be made of the effect of solvents on the visible-region spectra. All those studied gave an unambiguous division into two components, similar to those shown in Fig. 3 for the nickel–hydroxyphenylbutyramidine complex in pentanol. The important features of the visible spectra of all the complexes in aqueous alkali, pentanol, and formamide are given in Table 2. A similar division could be made for the spectra obtained from the solutions in pyridine before they crystallised, although here the ultraviolet tail is shifted considerably into the visible region. The powder spectrum of a liquid paraffin mull of the anhydrous complexes also showed a peak at about 2·1 μ^{-1}, although no resolution into components could be shown.

Magnetic Properties of the Complexes.—The magnetic susceptibilities of the crystalline dihydrate complexes and of the dehydrated residues were measured at room temperature by the Gouy method. All specimens were diamagnetic.

DISCUSSION

Formation and Structure of the Complexes.—The above studies prove that the only chelate between nickel(II) and the α-phenyl-α-hydroxy-amidines which is significantly stable in aqueous solution involves four hydroxide and two amidinium ions per metal ion, as did the copper complexes. As similar complexes are not formed by phenylacetamidine, and as the solvent molecules are held very loosely, similar arguments to those suggested for the copper complexes [1] indicate that the dihydrate crystals are probably best represented by the structure (I).



(I)

The function of aliphatic hydroxyl groups in chelate formation with copper(II) has been discussed earlier,[1] and the same confusion is found in the case of nickel(II) complexes. With ethanolamine, some workers report a 2 : 1 chelate, $Ni(H_2N{\cdot}[CH_2]_2{\cdot}O)_2$ [5] or a hydroxy-complex, $Ni(H_2N{\cdot}[CH_2]_2{\cdot}OH)_2(OH)_2$,[6] while others report only a 3 : 1 doubly charged complex.[7] However, some of the hydroxy-derivatives of ethylenediamine and glycine

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[5] Rivkind, *Zhur. neorg. Khim.*, 1956, **2**, 1263.

[6] Subrahmanya, *Proc. Indian Acad. Sci.*, 1957, **45**, *A*, 184.

[7] Hieber and Levy, *Z. anorg. Chem.*, 1934, **219**, 225; Luz, Fallab, and Erlenmeyer, *Helv. Chim. Acta*, 1955, **38**, 1114; Sychev and Gerbeleu, *Russ. J. Inorg. Chem.*, 1962, **7**, 138.

form complexes with nickel in which the hydroxy-groups participate, notably *NNN'N'*-tetrakishydroxypropylethylenediamine, which can form a 1 : 1 neutral nickel complex with the ionisation of two protons.[8]

While some workers [9] have reported only two stability constants for nickel complexes with common amino-acids, there seems little doubt, from continuous-variation [10] and conductimetric [11] experiments, that 3 : 1 anionic complexes predominate in any excess of amino-acid and alkali. Even here, however, the similarity between the spectra of solutions of 2 : 1 and normal 3 : 1 complexes [11] suggests that the third amino-acid ion is not chelated, and so does not distort the essentially square-planar configuration, as would be necessary were the bidentate ligands to occupy octahedral positions.

The existence of 5-co-ordinated nickel(II), as suggested here, is not at all uncommon,[12] $Ni(CN)_4^{2-}$ taking up only one more cyanide to form $Ni(CN)_5^{3-}$.[13] This may be explained, in terms of valence-bond theory, by the availability of a vacant *p*-orbital in low-spin d^8-complexes.[12] Ligand-field theory also affords an explanation in that it predicts that a d^8-ion in a square-planar complex would be slightly out of plane, and hence favour the co-ordination of one more group.[14] In this work, 5-co-ordination is suggested by the existence of crystalline Ni md_2,$Ph{\cdot}CH_2{\cdot}OH$, and it could be that the failure of solutions containing high ratios amidine : nickel to deposit crystals is due to the co-ordination of a third group in this way (see below).

Stability of the Complexes.—The stability constants in Table 1, like those reported for the copper complexes,[1] are based on predissociation of the hydroxyl group,[2] and cannot be directly compared with those of Hall and Jones.[8] A direct comparison may, however, be made with the nickel complex of 2-hydroxymethylpyridine, whose first stability constant is reported by Luz *et al.*[7] ($\log K_1 = 9$) on the assumption that the aliphatic hydroxyl group will have pK 14: the stabilities of these two similar chelate systems are of the same order of magnitude. Comparison with the nickel complexes of the α-amino-acids [15] shows that the greater stability of the amidine system is not so marked as it is in the case of the copper complexes. The formation curves for the α-hydroxy-amidine chelates, prepared from figures obtained from solutions of high amidine concentration, show that a third amidinate group must be attached very weakly, if at all, and thus show a difference from those of the α-amino-acids; [11] but that would not rule out some weak interaction between the 2 : 1 complexes and neutral amidine molecules in solutions of high pH.

The nickel complexes are less stable than the copper, as is predicted by the stability series of Irving and Williams.[16] The difference between the logarithms of the overall stability constants (about 9) is much larger than that for the 2 : 1 complexes of copper and nickel with α-amino-acids (about 4·5 for glycine) [15] but does accord with Chen's finding [17] that this difference increases among the amino-acids with increasing basic strength of the ligand. The relatively large drop in stability between the copper and the nickel complexes indicates that those of other bivalent ions of the first transition series would be still less stable; in fact, none were found, although a very stable complex with cobalt(III) is formed.[18]

[8] Hall and Jones, *Proc. West Va. Acad. Sci.*, 1957, **29**, 47 (*Chem. Abs.*, 1960, **54**, 3038c); Hall, Dean, and Pacofsky, *J. Amer. Chem. Soc.*, 1960, **82**, 3303; see also references in Part II.[1]

[9] Basolo and Chen, *J. Amer. Chem. Soc.*, 1954, **76**, 953; Irving, Williams, Ferrett, and Williams, *J.*, 1954, 3498.

[10] Gould and Vosburgh, *J. Amer. Chem. Soc.*, 1942, **64**, 1630.

[11] Pelletier, *J. Chim. phys.*, 1960, **57**, 287, 295, 301, 306, 311, 318.

[12] Nyholm, "Tilden Lecture," *Proc. Chem. Soc.*, 1961, 273; Miller, *Adv. Inorg. Chem. Radiochem.*, 1962, **4**, 133.

[13] McCullough, Jones, and Penneman, *J. Inorg. Nuclear Chem.*, 1960, **13**, 286.

[14] Jørgensen, *J. Inorg. Nuclear Chem.*, 1962, **24**, 1571; Liehr, *J. Phys. Chem.*, 1963, **67**, 389, 417.

[15] Bjerrum, Schwartzenbach, and Sillén, *op. cit.*, pp. 9, 15.

[16] Irving and Williams, *J.*, 1953, 3192.

[17] Chen, *Z. phys. Chem.*, 1962, **220**, 231.

[18] Gould and Jameson, unpublished work.

Spectrophotometric and Magnetic Properties of the Complexes.—The pink colour of the nickel–hydroxy-amidine complexes and their diamagnetism is in keeping with the classical observation that diamagnetic nickel complexes are normally red or yellow, while paramagnetic ones are green or blue. McKenzie *et al.*,[19] while pointing out several exceptions to this rule, showed that a sharp absorption band at 400 mμ was often associated with diamagnetic complexes, but this band, which has been variously interpreted,[20] appears to be missing from the spectra of the hydroxy-amidine complexes, unless it is related to the ultraviolet shoulder observed for the pyridine solutions. In any case, it is unlikely that this shoulder represents a *d–d* transition, since it is shifted so far in the other solvents.

Both the valence-bond and the ligand-field theory predict that diamagnetic complexes would have essentially square-planar symmetry, and this has largely been confirmed by structural data[21] (although the latter theory also allows paramagnetic square-planar complexes[22] and these have also been reported[23]). Here, the facts that water of crystallisation is so weakly held and that the powder and solution spectra agree suggest that the α-hydroxy-amidine complexes may be considered essentially square in all cases.

The assignment of spectra, however, is much more difficult. Ferguson, Belford, and Piper[20] studied the complex of nickel with salicylaldimine, using polarised light on single crystals, and showed that, for chelates of this type, the symmetry is lower than D_{4h}, and, as with the copper–hydroxy-amidine complexes,[1] symmetry and actual assignment must await the application of single-crystal work at low temperatures.[24] The present work does, however, support the general conclusions of Ballhausen and Liehr[25] that diamagnetic nickel complexes should have at most two bands in the visible region with maximum molar extinction coefficient less than 100.

EXPERIMENTAL

Apparatus.—The apparatus used for the measurement of pH, magnetic susceptibility, and visible spectra has been described previously.[1,2] The photometric titrations were followed with an EEL Quantitrator, adjusted to hold a beaker and fitted with a No. 603 filter.

Preparation and Analysis of Materials.—The preparation of the amidinium chlorides is described in Part I.[2] Standard 0·1M-nickel chloride in 0·5M-hydrochloric acid was standardised gravimetrically with dimethylglyoxime, the acid content being determined by ion-exchange, as described in Part II.[1] The solutions for spectrophotometry were analysed by Feigl's method,[26] the absorption of the oxidised nickel–dimethylglyoxime complex in ammoniacal citrate solution being measured at 530 mμ. The preparation of samples for analysis has been described in Part II,[1] and, as before, the presence of amidine residues and of small quantities of organic solvents did not alter the calibration curve.

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[19] McKenzie, Mellor, Mills, and Short, *Proc. Roy. Soc. New South Wales*, 1944, **78**, 70.

[20] Ferguson, *J. Chem. Phys.*, 1961, **34**, 611; Belford and Piper, *Mol. Phys.*, 1962, **5**, 251; Ferguson, Belford, and Piper, *J. Chem. Phys.*, 1962, **37**, 1569.

[21] Nyholm, *Chem. Rev.*, 1953, **53**, 263.

[22] Maki, *J. Chem. Phys.*, 1958, **28**, 651; 1958, **29**, 162, 1129.

[23] Sacconi, Paoletti, and Del Re, *J. Amer. Chem. Soc.*, 1957, **79**, 4062.

[24] Basu, Belford, and Dickerson, *Inorg. Chem.*, 1962, **1**, 438.

[25] Ballhausen and Liehr, *J. Amer. Chem. Soc.*, 1959, **81**, 538.

[26] Cf. Vogel, " A Textbook of Quantitative Inorganic Analysis," Longmans, Green and Co., London, 3rd edn., 1961, p. 794.