# 97. 1,1′-*Diaminobicyclohexyl and the Stability of its Metal Complexes.*

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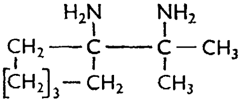
1-(2-Aminoisopropyl)cyclohexylamine and 1,1′-diaminobicyclohexyl (dabch) have been synthesised and the stability of complexes of the latter diamine with protons and the bivalent ions of cobalt, nickel, copper, and zinc measured potentiometrically at 20·0° and $\mu = 0{\cdot}1$M. With nickel it forms sparingly soluble yellow, diamagnetic complexes of the type Ni (dabch)$^{2+}X_2^-$ (where X = Cl, Br, I, or $NO_3$) and there is no tendency to co-ordinate a third molecule of diamine.

2-Cyclohexylamino-1,1-dimethylethylamine ($C_6H_{11}{\cdot}NH{\cdot}CH_2{\cdot}CMe_2{\cdot}NH_2$; chibn) has been prepared and the stability of its complexes with protons and with cupric ions shows the expected effect of an *N*-alkyl group in providing steric hindrance to co-ordination. In a preliminary investigation of its reactions with nickel, yellow compounds of the type Ni(chibn)$_2^{2+}X_2^-$,$2H_2O$ were isolated; there is evidence of the co-ordination of a third molecule of diamine in solution although this remains yellow and the preliminary stability constants are highly anomalous.

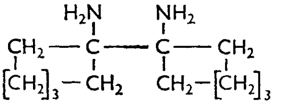
THE substitution of alkyl groups for the amino-hydrogen atoms of ethylenediamine (I) gives homologues of greater basicity, but owing to steric hindrance to co-ordination the complexes formed with copper and nickel become progressively weaker [1,2] and liable to hydrolysis and the formation of binuclear bridged complexes.[3] On the other hand progressive substitution on the carbon atoms of ethylenediamine (compounds (I) to (IV)) produces no very striking changes in either the basicity of the diamines or in the composition and stability of their metal complexes (cf. Table 1) until four alkyl groups have been introduced. Thus while ethylenediamine (I) and the lower homologues (II, III, and IV) form blue 1 : 1, 1 : 2, and 1 : 3, paramagnetic complexes with nickel(II), tetramethylethylenediamine (V; tetrameen) gives only a bis-complex, Ni(tetrameen)$_2^{2+}$, which is yellow and diamagnetic. This implies a change from $sp^3d^2$ to $dsp^2$ hybridisation.[4] Ethyltrimethylethylenediamine (2,3-diamino-2-methylpentane) and diethyldimethylethylenediamine (2,3-diamino-2,3-dimethylhexane) behave similarly.[5] Although no value for $K_1$, the stability constant of the 1 : 1 nickel complex, has been reported, values for $\beta_2$, the overall stability constants for the formation of biscomplexes (Table 1), suggest that both the copper and nickel complexes of tetrameen are more stable (relative to the strength of

$H_2N{\cdot}CR^1R^2{\cdot}CR^3R^4{\cdot}NH_2$

| | (I) | (II) | (III) | (IV) | (V) |
|---|---|---|---|---|---|
| $R^1$ ............................ | H | H | Me | H | Me |
| $R^2$ ............................ | H | H | H | H | Me |
| $R^3$ ............................ | H | H | H | Me | Me |
| $R^4$ ............................ | H | Me | Me | Me | Me |
| Abbrevn. .................... | en | meen | dimeen | *i*-bn | tetrameen |



(VI)



(VII) dabch

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[1] Irving and Griffiths, *J.*, 1954, **213**, and refs. therein.

[2] Basolo and Murmann, *J. Amer. Chem. Soc.*, 1952, **74**, 5243; 1954, 76, 211.

[3] Pfeiffer and Glasser, *J. prakt. Chem.*, 1938, **151**, 134.

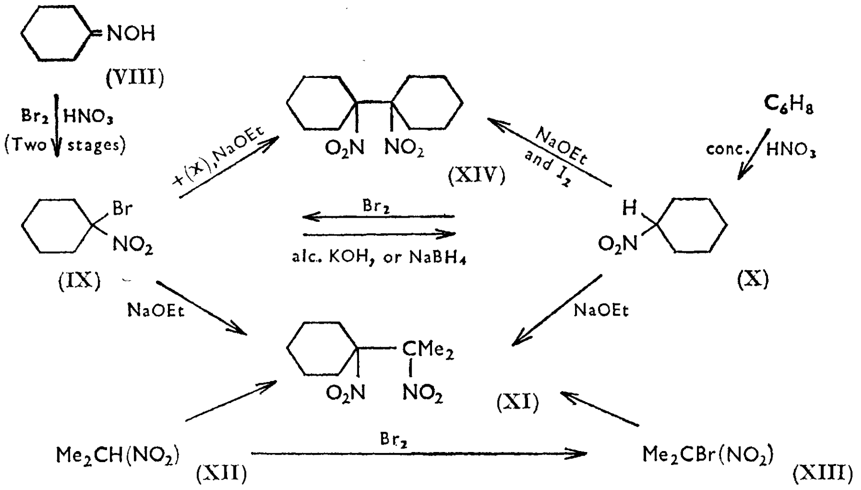
[4] Basolo, Murmann, and Chen, *J. Amer. Chem. Soc.*, 1954, **76**, 956.

[5] Wilkins, *J.*, 1957, 4521.

their proton complexes) than expected from the behaviour of the lower homologues, (I)—(IV). There is a strong presumption that the anomalous behaviour of tetrameen (V) derives from the steric effects of the four methyl groups [4] and this is supported by the kinetic stability of the nickel and copper complexes of this ligand and its higher homologues.[5] To obtain further information on this phenomenon we have prepared 1-(2'-aminoisopropyl)cyclohexylamine (VI) and 1,1'-diaminobicyclohexyl (VII; dabch), from the corresponding dinitro-compounds (XI) and (XIV).

A natural starting point for the synthesis of compound (XI) or compound (XIV) is 1-nitrocyclohexane (X) which has been prepared from cyclohexanone oxime (VIII) by a four-stage process (VIII ⟶ IX ⟶ X).[6,7] It can be more conveniently prepared by the direct nitration of cyclohexane [8] and although the batch yields are low ($\sim$3·5%) the starting materials are cheap, and unchanged material can readily be reprocessed.

1,1'-Dinitrobicyclohexyl (XIV) was obtained in 17% yield by the condensation of 1-bromo-1-nitrocyclohexane (IX) [7] with the sodium salt of the nitrocyclohexane (X). Poorer yields (7%) were obtained by a one-stage bromination and condensation process from nitrocyclohexane following Sayre's procedure.[9] The action of iodine upon sodium nitrocyclohexane in aqueous solution gave only an 8% yield of compound (XIV) but this was raised to 43% by changing the medium to a mixture of alcohol, ether, and water.



The preparation of 1-nitro-1-(2-nitroisopropyl)cyclohexane (XI) from the sodium salt of nitrocyclohexane and 2-bromo-2-nitropropane has been reported [10] but in our hands this reaction gave a mixture which could not readily be separated. The desired dinitro-compound (XI) was obtained in 20% yield from the corresponding bromonitroalkane (XIII) and also from the condensation of the sodium salt of (XII) with 1-bromo-1-nitrocyclohexane (IX).

The reduction of the dinitro-compound (XIV) by hydrazine and Raney nickel, hydrazine and palladium charcoal (cf. Dewar and Mole [11]), aqueous sodium polysulphide, or lithium aluminium hydride in ether or tetrahydrofuran gave little or none of the desired diamine

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[6] Iffland, Criner, Koral, Lotspeich, Papanastoussion, and White, *J. Amer. Chem. Soc.*, 1953, **75**, 4044.

[7] Iffland and Criner, *J. Amer. Chem. Soc.*, 1953, **75**, 4047.

[8] Personal communication, I.C.I. Dyestuffs Division, Blackley.

[9] Sayre, *J. Amer. Chem. Soc.*, 1955, **77**, 6689.

[10] Seigle and Hass, *J. Org. Chem.*, 1940, **5**, 100.

[11] Dewar and Mole, *J.*, 1956, 2556.

(VII), which was best obtained by reduction with finely divided tin and concentrated hydrochloric acid in glacial acetic acid. Diaminobicyclohexyl (VII) was unexpectedly volatile.

The reduction of 1-nitro-1-(2-nitroisopropyl)cyclohexane (XI) was more troublesome and under the best conditions found (*viz.* iron powder in ethanol containing hydrochloric acid) the products were a nitrogen-free compound, $C_9H_{14}$ or $C_9H_{16}$, and a mixture of the desired diamine (VII) with ammonium chloride from which it was difficult to obtain analytically pure. The diamine (VII) was characterised as its dipicrate and by the formation of bis-[1-(2-aminoisopropyl)cyclohexylamine]nickel(II) halides.

For comparison with compound (VII) cyclohexylamino-1,1-dimethylethylamine ($C_6H_{11}\cdot NH\cdot CH_2\cdot CMe_2\cdot NH_2$; chibn) was prepared by the catalytic hydrogenation of 1-cyclohexylamino-2-methyl-2-nitropropane ($C_6H_{11}\cdot NH\cdot CH_2\cdot CMe_2\cdot NO_2$), itself prepared by the condensation of cyclohexylamine, formaldehyde, and 2-nitropropane.[12]

## EXPERIMENTAL

*Preparation of* 1,1′-*Dinitrobicyclohexyl* (XIV).—(*a*) *From nitrocyclohexane* (X). Nitrocyclohexane (12·9 g., 1 mol.) was added to an ice-cold solution of sodium ethoxide [from sodium (2·3 g., 1 mol.) and ethanol (50 ml.)]. After the addition of iodine (12·7 g., 0·5 mol.) in ether (30 ml.) followed by water (5 ml.) the mixture was stirred and heated on a water-bath. After 30 min. the mixture was cooled to 0° and the plates that separated overnight were washed with water. The filtrate was concentrated to *ca.* 50 ml. and decolourised with sodium thiosulphate; more plates separated overnight. The combined product (5·5 g., 43%) was recrystallised from ethanol and then from glacial acetic acid from which 1,1′-*dinitrobicyclohexyl* (XIV) separated as plates, m. p. 214·5° (decomp.) (Found: C, 56·5; H, 7·8; N, 10·6. $C_{12}H_{10}N_2O_4$ requires C, 56·2; H, 7·8; N, 10·9%).

(*b*) *From* 1-*bromo*-1-*nitrocyclohexane* (IX). 1-Bromo-1-nitrosocyclohexane, prepared from cyclohexanone oxime and sodium hypobromite [13] or, in higher yield, *N*-bromosuccinimide,[7] was oxidised to 1-bromo-1-nitrocyclohexane (IX), b. p. 116°/20 mm., with concentrated nitric acid.[7,13] The bromonitro-compound (8·5 g., 1 mol.) in ethanol (25 ml.) and water (6 ml.) was heated under reflux (3 hr.) with nitrocyclohexane (5·3 g., 1 mol.) in a solution of sodium hydroxide (1·65 g., 1 mol.) in the minimum amount of water. Crystals of 1,1′-dinitrobicyclohexyl separated on cooling and a second batch was obtained by careful dilution of the filtrate with water. The total yield was 1·8 g. (17%), m. p. 214° (decomp.).

1,1′-*Diaminobicyclohexyl* (VII).—1,1′-Dinitrobicyclohexyl (5 g., 1 mol.), concentrated hydrochloric acid (80 ml.), and glacial acetic acid (50 ml.) were heated on a steam-bath and vigorously stirred while fine-mesh tin powder (15 g., 6·5 mol.) was added in portions during 1 hr. The mixture was stirred and heated for 1 hr. more and the procedure repeated with more tin (15 g.). The mixture was then strongly basified (sodium hydroxide) and steam-distilled. The distillate was collected in dilute hydrochloric acid and concentrated to give 1,1′-*diaminobicyclohexyl dihydrochloride*, m. p. >240° (decomp.) after recrystallisation from concentrated hydrochloric acid–water (Found: C, 53·4; H, 9·8; N, 10·5. $C_{12}H_{24}N_2,2HCl$ requires C, 53·5; H, 9·7; N, 10·4%).

The *dipicrate* separated from aqueous ethanol as yellow needles, m. p. 219·5° (decomp.) (Found: C, 44·2; H, 4·5; N, 16·8. $C_{12}H_{24}N_2,2C_6H_3N_3O_7$ requires C, 44·0; H, 4·6; N, 17·1%).

*Complexes of* 1,1′-*Diaminobicyclohexyl.*—(*a*) The free base (VII) was obtained by shaking the dihydrochloride (0·96 g.) overnight with water (10 ml.) and De-acidite FF anion exchange resin (10 g.) in the hydroxide form. After removal of resin a 0·004M solution of diaminobicyclohexyl was obtained (25% conversion).

(*b*) 1,1′-Diaminobicyclohexyl (0·99 g.) was added to a solution of potassium hydroxide (3 g.) in water (2·5 ml.) and the mixture distilled in steam in an all-glass micro-Kjeldahl apparatus. The concentration of diamine in the first 80 ml. of distillate was found to be 0·021M by titration with 0·1M-hydrochloric acid (Methyl Red); the concentration fell to 0·019M and 0·015M for total distillate volumes of 120 and 170 ml., respectively.

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[12] Jones and Urbanski, *J.*, 1949, 1766.

[13] Brown, Part II Thesis, Oxford University, 1958.

The absorbancies of mixtures of *x* ml. of 0·022M-diaminobicyclohexylamine with (10 − *x*) ml. of 0·022M-nickel sulphate were measured with a Unicam S.P. 500 spectrophotometer in 2·00-cm. cells at several wavelengths with the following results:

| | Absorbancies at | | | | | | |
|---|---|---|---|---|---|---|---|
| *x* | 400 mμ | 434 mμ | 476 mμ | *x* | 400 mμ | 434 mμ | 476 mμ |
| 0 | 0·213 | 0·048 | 0·008 | 6·5 | 0·575 | 1·102 | 0·372 |
| 2·5 | 0·360 | 0·416 | 0·121 | 7·0 | 0·458 | 0·935 | 0·322 |
| 5·0 | 0·398 | 0·870 | 0·302 | 8·5 | 0·290 | 0·482 | 0·166 |
| 6·0 | 0·575 | 1·090 | 0·375 | 10·0 | 0·00 | 0·010 | 0·010 |

The plots of the calculated Job ordinates against the mol. fraction gave maxima at $x = 6·5$ for each wavelength establishing the occurrence of a 2 : 1 complex.

*Bis*-(1,1'-*diaminobicyclohexyl*)*nickel*(II) *iodide* separated as a yellow precipitate when a slight excess of aqueous potassium iodide was added to a solution which was $3·75 \times 10^{-3}$M with respect to nickel ions and $8·21 \times 10^{-3}$M with respect to the diamine (VII). It was collected and dried at 80° for 1 hr. and then to constant weight *in vacuo* over phosphorus pentoxide (Found: C, 41·0; H, 6·5; Ni, 8·3. $C_{24}H_{48}NiI_2N_4$ requires C, 40·9; H, 6·9; Ni, 8·3%).

*Bis*-(1,1'-*diaminobicyclohexyl*)*nickel*(II) *nitrate* was prepared similarly (Found: C, 50·4; H, 8·5; Ni, 9·3. $C_{24}H_{48}N_6NiO_6$ requires C, 50·1; H, 8·4; Ni, 10·2%).

*Bis*-(1,1'-*diaminobicyclohexyl*)*nickel*(II) *chloride* was prepared by heating a solution of nickel acetate tetrahydrate (1·08 g.) in ethanol (25 ml.) with 1,1'-diaminobicyclohexyl dihydrochloride (1·56 g.) under reflux (30 min.). The orange crystals of $Ni(dabch)_2Cl_2$ that separated were recrystallised from aqueous ethanol (0·67 g.) (Found: C, 55·0; H, 9·4. $C_{24}H_{48}NiCl_2N_4$ requires C, 55·2; H, 9·2%). The magnetic susceptibility was measured on a Gouy balance (for which facility we are indebted to Dr. L. Venanzi) and gave the value $10^6\chi = -0·77$ comparable with values of similar complexes with hindered ligands, *e.g.*, for $Ni(tetrameen)_2Cl_2$, $10^6\chi = -0·615$.[4]

1-*Nitro*-1-(2-*nitroisopropyl*)*cyclohexane* (XI).—(*a*) *From* 2-*nitropropane* (*with L. R. Brown*).[13] 1-Bromo-1-nitrocyclohexane (IX) (0·1 mole) in ethanol (80%; 75 ml.) was heated under reflux (3 hr.) with a solution prepared from sodium hydroxide (0·1 mole) in the minimum amount of water to which 2-nitropropane (0·1 mole) had been added. After the mixture had been kept overnight 1-*nitro*-1-(2-*nitroisopropyl*)*cyclohexane* (XI) was collected, dissolved in acetone, reprecipitated by the addition of a large excess of water, collected, and recrystallised from ethanol; it had m. p. 139—142° (Found: C, 50·1; H, 7·3; N, 13·1. $C_9H_{16}N_2O_4$ requires C, 50·0; H, 7·5; N, 12·9%).

(*b*) *From* 2-*bromo*-2-*nitropropane*. Crude 1-nitro-1-(2-nitroisopropyl)cyclohexane, m. p. 125° (13 g., 23%), separated when bromonitropropane was condensed with nitrocyclohexane following Siegle and Hass.[10] The product recrystallised from ethanol as plates, m. p. 138—139°. (Siegle and Hass report a crude yield of 10% of material, m. p. 140—141°.)

1-(2-*Aminoisopropyl*)*cyclohexylamine* (VI).—A mixture of 1-nitro-1(-2-nitroisopropyl)cyclohexane (6 g.) in ethanol (300 ml.) and iron powder (10 g.; excess) was heated under reflux while dilute hydrochloric acid (100 ml.) was added gradually (1 hr.). The reduction was completed by adding concentrated hydrochloric acid (2 ml.) and heating for a further 3 hr.

The mixture was then made strongly alkaline and distilled in steam; hydrochloric acid was added as required to the distillate to maintain the pH just below 7. White fumes passed over with the alcohol at the beginning of the distillation and after the distillate had stood overnight needles separated. These had m. p. 53·5° after crystallisation from ethanol (Found: C, 86·9; H, 12·1. $C_9H_{16}$ requires C, 87·0; H, 13·0%). The remaining distillate was taken to dryness to give a crude mixture (3·8 g.) of the required diamine with ammonium chloride from which it could not be obtained analytically pure although substantial purification could be effected by recrystallisation from propanol, in which the diamine hydrochloride was more soluble than ammonium chloride. From the purest specimen of the hydrochloride were prepared the *dipicrate* [yellow needles, m. p. 232° (decomp.)] (Found: C, 41·3; H, 4·4. $C_9H_{20}N_2,2C_6H_3N_3O_7$ requires C, 41·4; H, 4·3%) and [yellow needles (from ethanol)] *bis*-(1-(2-*aminoisopropyl*)*cyclohexylamine*)*nickel*(II) *chloride dihydrate*] (Found: C, 45·4; H, 9·6; $C_{18}H_{40}N_4Cl_2Ni,2H_2O$ requires C, 45·2; H, 9·3%). The orange-yellow *iodide* was prepared similarly (Found: C, 31·6; H, 6·2. $C_{18}H_{40}N_4I_2Ni,2H_2O$ requires C, 32·7; H, 6·7%).

*Preparation of* 2-*Cyclohexylamino*-1,1-*dimethylethylamine*.—A solution in ethanol (200 ml.) of 1-cyclohexylamino-2-methyl-2-nitropropane hydrochloride (18·8 g. m. p. 201°), prepared in 59% yield by the condensation of cyclohexylamine, formaldehyde, and 2-nitropropane,[12] was reduced with Adams platinum oxide catalyst (0·8 g.) at room temperature and 2—4 atmospheres pressure (12 hr.). The catalyst was removed and the filtrate saturated with dry hydrogen chloride and concentrated to 50 ml. On the addition of ethyl acetate (200 ml.) 2-cyclohexylamino-1,1-dimethylethylamine dihydrochloride separated (10 g., 52%), m. p. 230—240°, when recrystallised from ethanol–ethyl acetate (Found: *M* (by titration), 244. $C_{10}H_{22}N_2,2HCl$ requires *M*, 243). For further purification the base was converted into its *dipicrate* which formed yellow needles, m. p. 252° (decomp.), from ethanol (Found: N, 17·6; $C_{10}H_{22}N_2,2C_6H_3N_3O_7$ requires N, 17·8%). The dipicrate was treated with concentrated aqueous potassium hydroxide and the ether extracts (5 × 50 ml.) were dried and saturated with dry hydrogen chloride. 2-*Cyclohexylamino*-1,1-*dimethylethylamine dihydrochloride* (VIII) (4·2 g., m. p. 256—260°) separated from ethanol–ethyl acetate as needles, m. p. 256—258° (Found: C, 49·6; H, 10·0; N, 11·1; Cl, 29·2. $C_{10}H_{22}N_2,2HCl$ requires C, 49·4; H, 9·9; N, 11·5; Cl, 29·2%).

*Dissociation Constants.*—The dissociation constants of the acids conjugate to the new diamines and the stability constants of their metal complexes were measured at 20·0° by potentiometric titration using conventional apparatus [1] (save that the microburette was replaced by an Agla microsyringe) and the customary methods of calculation were facilitated by the University's " Mercury " computer and programmes devised by Dr. M. Stacey. The ionic strength was maintained at 0·1M with potassium chloride (or potassium sulphate in specific cases).

## RESULTS AND DISCUSSION

1,1′-Diaminobicyclohexyl reacts with nickel ions to give yellow solutions with a single absorption band ($\lambda_{max.} = 432$ mμ, $\varepsilon_{max.} = 71{\cdot}4$) which does not change its position when the molar concentration of ligand to metal is increased from 1·09 : 1 to 5·83 : 1. This behaviour resembles that of analogous hindered diamines for which the values reported are for tetrameen [4] $\lambda_{max.} = 434$ mμ, $\varepsilon_{max.} = 63{\cdot}8$; [13] for 2,3-diamino-2,3-dimethylpentane $\lambda_{max.} = 430$ mμ; [13] for 2,3-diamino-2,3-dimethylhexane, $\lambda_{max.} = 425$ mμ; and for meso-stilbenediamine $\lambda_{max.} = 444$, $\varepsilon_{max.} = 74{\cdot}7$.[14] By Job's method of continuous variations this spectrum was shown to be due to a 2 : 1 complex and no evidence was obtained for lower or higher complexes. Sulphate and acetate ions form soluble salts with the bis-(1,1′-diaminobicyclohexyl)nickel(II) ion but the addition of chloride, bromide, iodide, nitrate, or perchlorate ions produced very insoluble, yellow compounds of which the iodide, $(C_{12}H_{24}N_2)_2NiI_2$, nitrate, $(C_{12}H_{24}N_2)_2Ni(NO_3)_2$, and chloride $(C_{12}H_{24}N_2)_2NiCl_2$ were obtained analytically pure; the last-named was shown to be diamagnetic.

An examination of " Catalin " molecular models showed that the most likely conformation of the diamine moieties in the nickel complex is that with both cyclohexane rings are in the " chair " form (Fig. 1) and slightly skew to one another. Of other possible conformations the " chair–boat " form presented a large degree of interference between hydrogen atoms at the side of the molecule remote from the plane of the chelate ring whereas the " boat "–" boat " form placed the co-ordination valencies of the nitrogen atoms at a large angle (~120°) inappropriate for the formation of square-planar complexes. In the most favoured position the methylene groups adjacent to the nitrogen atoms are in close proximity to the nitrogen atoms of the chelated ligands and the annulus of eight hydrogen atoms (Fig. 2) on each side of the central metal will certainly hinder the co-ordination of other molecules. With nickel ions there will therefore be a change from paramagnetic six-co-ordinate $Ni(H_2O)_6^{2+}$ to diamagnetic four-co-ordinate $Ni(dabch)_2^{2+}$ and a change in hybridisation from $d^2sp^3$ to $dsp^2$.

By conventional potentiometric titrations [1,13] the dissociation constants of the conjugate acids $dabch.H_2^{2+}$ and $dabch.H^+$ were found to be $10^{-5{\cdot}62}$ and $10^{-10{\cdot}41}$ at 20° ($\mu = 0{\cdot}1$M-KCl). Comparison (Table) with data for tetramethylethylenediamine (tetrameen) shows that it is easier to remove the first proton from $dabch.H_2^{2+}$ than from $tetrameen.H_2^{2+}$: the reverse

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[14] Goodgame, D.Phil. Thesis, Oxford, 1959.

is true for the dissociation of dabch.H$^+$ and tetrameen.H$^+$, owing probably to the conformation of the cyclohexyl groups shielding the proton from the solvent. The successive formation constants for the copper complex (Table 1) are both larger than for tetrameen.

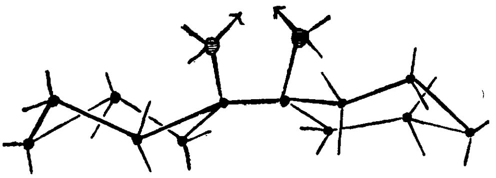

FIG. 1.

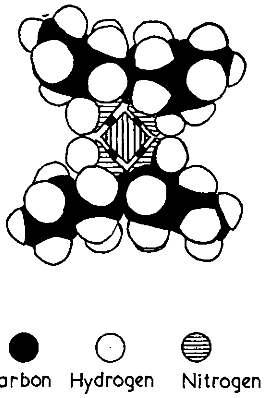

FIG. 2.

Again an examination of models shows that the steric requirements of the methylene groups adjacent to the four nitrogen atoms will cause less interference than the bulkier methyl substituents of tetrameen. Owing to the insolubility of the complex Ni(dabch)$_2$Cl$_2$ it was impossible to carry out a potentiometric titration of mixtures of nickel ions with diaminobicyclohexyl dihydrochloride. A solution of the sulphate, dadch.H$_2$SO$_4$ was therefore prepared by adding the equivalent of AnalaR silver sulphate to a solution of the dihydrochloride and removing silver chloride by centrifugation. The filtrate was diluted to $\sim 2 \times 10^{-3}$M and after standardisation had been carried out the ionic strength was brought to 0·1M with potassium sulphate. A redetermination of p$K_1$ and p$K_2$ in this medium gave identical results when allowance was made for junction potentials. However, equilibrium was established very slowly in the titration in the presence of nickel and up to 30 min. had to be allowed between successive increments of alkali before stable

TABLE 1.

Formation constants of complexes of *C*-substituted ethylenediamines with nickel and copper ions.

| | (I) | (II) | (III) | (IV) | (V) | (VI) | (VIII) |
|---|---|---|---|---|---|---|---|
| Diamine | en [a] | meen [b] | dimeen [b] | ibn [b] | tetrameen [b] | dabch [c] | chibn [c] |
| p$K_1$ ........... | 7·47 | 7·13 | 6·91 | 6·79 | 6·56 | 5·62 [c] | 6·77 |
| p$K_2$ ........... | 10·18 | 10·00 | 10·00 | 10·00 | 10·13 | 10·41 [c]<br>10·41 [d] | 10·18 |
| Copper(II) | | | | | | | |
| log $K_1$ ......... | 10·76 | 10·78 | 11·39 | 10·53 | 11·63 | 12·20 [c] | 9·01 |
| log $K_2$ ......... | 9·37 | 9·28 | 9·82 | 9·05 | 10·24 | 10·95 [c] | 7·14 |
| log $(K_1/K_2)$ ... | 1·39 | 1·50 | 1·57 | 1·48 | 1·39 | 1·25 | 1·87 |
| log $\beta_2$ ......... | 20·13 | 20·06 | 21·21 | 19·58 | 21·87 | 23·15 | 16·15 |
| Nickel(II) | | | | | | | |
| log $K_1$ ......... | 7·60 | 7·43 | 7·71 | 6·77 | | (7·5) | ~0 |
| log $K_2$ ......... | 6·48 | 6·19 | 6·48 | 5·40 | | (7·4) | ~9·6 |
| log $(K_1/K_2)$ ... | 1·12 | 1·24 | 1·23 | 1·37 | | | |
| log $\beta_2$ ......... | 14·08 | 13·62 | 14·19 | 12·17 | 14·68 | 14·9 [d] | ~9·6 |
| log $K_3$ ......... | 5·03 | 4·27 | 4·31 | 2·25 | — | — | ~3·9 |

[a] Basolo and Murmann, ref. 2. Data valid for 25° and $\mu$ = 0·5M-KNO$_3$. [b] Basolo, Murmann, and Chen, *J. Amer. Chem. Soc.*, 1953, **75**, 1478; 1954, **76**, 956. [c] Present work. Data valid for 20° and $\mu$ = 0·1M-KCl. [d] Present work. Data valid for 20° and $\mu$ = 0·1M-K$_2$SO$_4$.

potentials were achieved. From the very steep formation curve log $\beta_2 = 14{\cdot}9$, but reliable values could not be calculated for $K_1$ and $K_2$. Since p[dabch] $\sim 7{\cdot}5$ when $\bar{n} = 0{\cdot}5$, log $K_1 \geqslant 7{\cdot}5$ and log $K_2$ will be of comparable magnitude. It can be shown that with such values of $K_1$ and $K_2$ the proportion of 1 : 1 complex cannot exceed 36% in a mixture with 32% of $Ni_{(aq.)}^{2+}$ and 32% of $Ni(dabch)_2^{2+}$ which would explain why it was not detected spectrophotometrically. Measurements with the zinc complex covered the range $0{\cdot}31 \geqslant \bar{n} \geqslant 1{\cdot}71$ and gave log $K_1 = 6{\cdot}35$, log $K_2 = 6{\cdot}95$, and log $\beta_2 = 13{\cdot}30$. With cobalt(II) the measurements ranged from $0{\cdot}39 \geqslant \bar{n} \geqslant 2{\cdot}63$ and gave log $K_1 = 5{\cdot}31 \pm 0{\cdot}2$, log $K_2 = 4{\cdot}8 \pm 0{\cdot}4$, and log $K_3 = 5{\cdot}3 \pm 0{\cdot}4$ when the data were processed by the " Mercury " computer using a programme devised by Dr. M. Stacey. An anomalous order of stability constants [$K_2 > K_1$ for zinc and $K_3 > K_2$ for cobalt(II)] is apparent; but the low precision of the measurements, which was a feature of work with this diamine and derives from the difficulty of securing equilibrium conditions, makes it unwise to lay overmuch emphasis on the relative magnitudes of the successive formation constants. The absolute values of the overall stability constants log $\beta_2 = 13{\cdot}3$ for zinc and log $\beta_3 = 15{\cdot}4$ for cobalt(II) are appreciably greater than literature values for the corresponding complexes of ethylenediamine (log $\beta_2 = 10{\cdot}37$ for $Zn^{2+}$ and log $\beta_3 = 13{\cdot}82$ for $Co^{2+}$). The acid dissociation constants (Table) of the species chibn.$H_2^{2+}$ and chibn.$H^+$ are very close to those of the simpler diamine ibn($H_2N{\cdot}CH_2{\cdot}CMe_2{\cdot}NH_2$). The effect of the *N*-cyclohexyl group is thus less than that of a methyl, ethyl, or isopropyl substituent.[1] However, the overall stability of the copper complex is much lower than that of ibn and the increased steric hindrance to co-ordination in the formation of a 1 : 2 complex, reflected in the high value of log $K_1$ − log $K_2 = 1{\cdot}87$, is comparable with the values of 1·99, 1·81, and 1·62 for the introduction of *N*-methyl, *N*-ethyl, and *N*-isopropyl groups in copper complexes of ethylenediamine.[1]

Solutions of nickel(II) and chibn were unexpectedly yellow ($\lambda_{max.} = 452$ mμ) and there was no change in the position of this maximum when the ratio of components was increased from 1 : 3·7 to 1 : 7·6 although the effective extinction coefficient increased from 50 to 90.

The time to reach equilibrium in potentiometric titrations was excessively long and the reproducibility was poor; the calculated formation curve rose as high as $\bar{n} = 2{\cdot}36$ before precipitation occurred, suggesting the presence of some 1 : 3 complex although the colour remained yellow throughout. For one run the values log $\beta_1 = 4{\cdot}5$, log $\beta_2 = 9{\cdot}8$, and log $\beta_3 = 13{\cdot}3$ represented the experimental formation curve; for five others the best fit was obtained with log $\beta_1 \sim 0$, log $\beta_2 = 9{\cdot}6 \pm 0{\cdot}4$, and log $\beta_3 = 13{\cdot}5 \pm 0{\cdot}2$. These results are quite unexpected for with other complexes of nickel with *N*-alkyl-substituted diamines log $\beta_1$ is always substantial and never more than three log units less than the value of log $\beta_2$ for the parent diamine (cf. ref. 1, Table 4); similarly $K_1$ is normally greater than $K_2$ and log $K_3 \sim 2$. Clearly these anomalies and the yellow colour of the solution demanded further investigation but this had to be discontinued. For the same reason the study of the diamine (VII) was limited to the preparation of the yellow bis-[1-(2′-aminoisopropyl)-cyclohexylamine]nickel(II) chloride (and iodide) dihydrates.

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