Complexes of *meso*- and (±)-Butane-2,3-diamine with Manganese-, Cobalt-, Nickel-, Copper-, Zinc-, and Lead-(II): A Potentiometric, Calorimetric, and Spectroscopic Study †

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The formation constants of complexes of *meso*- and (±)-butane-2,3-diamine with Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+} have been measured potentiometrically at 25 °C and I = 0.10 mol dm^{-3} (K[NO_3]), and the enthalpy changes on complex formation with Ni^{2+}, Cu^{2+}, and Zn^{2+} have been measured calorimetrically. The results are interpreted in terms of the possible conformational differences in the chelate rings and the formation of square-planar bis complexes with Ni^{2+} (particularly with the *meso* isomer of the ligand) and of tetrahedral bis complexes with Zn^{2+}. The existence of square-planar bis complexes of Ni^{2+} has been confirmed spectroscopically, and the square-planar–octahedral equilibrium constants have been estimated.

COREY and Bailar[1] first applied the method of conformational analysis to the stable five-membered chelate rings formed between ethylenediamine (en) and metal ions in 1959. They concluded that the ring is not planar, unlike cyclopentane, but puckered with a dihedral angle, θ, greater than zero. This angle was calculated to be 49°, and found to be 48° in an early crystal-structure analysis.[2] In general the dihedral angle was found to lie

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† No reprints available.

[1] E. J. Corey and J. C. Bailar, *J. Amer. Chem. Soc.*, 1959, **81**, 2620.

[2] Y. Saito, K. Nakatsu, M. Shiro, and H. Kuroya, *Bull. Chem. Soc. Japan*, 1957, **30**, 795.

in the range 45—55°.[3] Planar bis complexes of en with metal ions can exist as two diastereoisomeric conformational isomers, the λλ-[ML_2] (or δδ-[ML_2]) species of D_2 symmetry and the centrosymmetric *meso* isomer λδ-[ML_2] of C_{2h} symmetry.[4] The relative energies of the two isomers in solution will depend on different hydrogen–hydrogen interactions and may be calculated.[1,3] The difference is found to be small. In octahedral tris complexes more severe non-bonded interactions are present due to steric crowding so that larger differences in energy between the various isomers may be expected.

When the carbon atoms of the diamine ring are substituted with bulky substituent groups it is reasonable to expect these groups to adopt equatorial positions to minimise steric interference; such equatorial orientation is found in the crystal structures of complexes of propane-1,2-diamine[5] and is supported by ^1H n.m.r. studies.[6] However, detailed calculation of repulsion energies showed that the difference in energy between equatorial and axial orientations is small or non-existent.[3] What is more, small increases in the M–N bond length cause any apparent selectivity to vanish very rapidly.[7] When two substituent groups are introduced into the diamine chelate ring, as in butane-2,3-diamine (bn), both *meso* and optically active forms of the ligand are possible. Optically active butane-2,3-diamine, (±)bn, can adopt the normal puckered chelate ring with a metal ion with both methyl groups equatorial. The *meso* isomer, (*m*)bn, is unable to adopt such a favourable conformation. The formation constants of both the mono and bis complexes of (*m*)bn with bivalent transition-metal ions have been shown to be significantly smaller than those of the optically active analogues,[4] and this has been interpreted as confirming the preference of bulky substituent groups for an equatorial conformation.

The aim of the present study is to extend the thermodynamic data on complex formation of (*m*)- and (±)-bn to include data on enthalpy changes and to cover the formation of tris complexes in more detail. Complexes with Mn^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Pb^{2+} were studied, with particular emphasis on the complexes of Ni^{2+} and Cu^{2+}. Complexes with Ni^{2+} proved to be particularly interesting as a result of the planar–octahedral equilibria present with high ligand to metal ratios.

EXPERIMENTAL

The compounds (*m*)- and (±)-bn were prepared by reducing dimethylglyoxime with Raney nickel followed by fractional crystallisation of the hydrochlorides from anhydrous methanol.[8] The *racemic* (±)bn is considerably more soluble in this solvent (7 g per 100 cm^3) than the *meso* isomer (0.7 g per 100 cm^3). Product purity was checked by elemental analysis and melting points [Found for (*m*)bn·2HCl: C, 30.2; H, 8.65; Cl, 43.7%. M.p. 322 °C. Found for (±)bn·2HCl: C, 30.2; H, 8.7; Cl, 43.9%. M.p. 250 °C. $C_4H_{14}Cl_2N_2$ requires C, 29.8; H, 8.7; Cl, 44.1%].

Acid-dissociation constants and metal complex-formation constants were determined potentiometrically at 25.0 °C and $I = 0.10$ mol dm^{-3} (K[NO_3]) using a glass electrode calibrated in terms of hydrogen-ion concentrations. Calculations were carried out with the aid of the MINIQUAD computer program.[9] Calorimetric measurements were made at 25 °C and $I = 0.10$ mol dm^{-3} (K[NO_3]) in an LKB 8700 solution calorimeter using a range of metal : ligand ratios between 1 : 1 and 1 : 3 and adjusting the pH of the solutions to obtain a suitable degree of formation ($\bar{n}$) of the metal complexes. The enthalpy change on formation of the bis complex was calculated from the measured heat of reaction by allowing for: (*i*) the heat of formation of water due to the change in pH; (*ii*) the heats of protonation of the ligands; and (*iii*) the heat of dilution of the metal ions.[4]

Visible absorption spectra of the complexes of Ni^{2+} and Cu^{2+} were recorded using a Carey 14H spectrophotometer over the wavelength range 300—900 nm. Species distributions were calculated with the aid of the COMICS computer program.[10]

RESULTS AND DISCUSSION

Formation Constants.—Protonation and metal complex-formation constants are in Table 1.

TABLE 1

Metal complex-formation constants of (±)- and *meso*-butane-2,3-diamine (bn) at 25 °C and $I = 0.10$ mol dm^{-3} K[NO_3]. Standard deviations (σ values) are given in parentheses

	log β	
Complex species	(±)bn	(*m*)bn
Hbn^+	9.851(1)	9.824(1)
H_2bn^{2+}	16.525(2)	16.493(2)
$[Mn(bn)]^{2+}$	2.94(2)	2.64(5)
$[Co(bn)]^{2+}$	5.579(5)	4.84(1)
$[Co(bn)_2]^{2+}$	10.08(2)	8.88(3)
$[Ni(bn)]^{2+}$	7.640(6)	6.729(2)
$[Ni(Hbn)]^{3+}$	12.84(6)	12.7(1)
$[Ni(bn)_2]^{2+}$	14.01(2)	12.311(6)
$[Ni(bn)_3]^{2+}$	18.0(1)	14.86(7)
$[Cu(bn)]^{2+}$	11.265(3)	10.538(4)
$[Cu(Hbn)]^{3+}$	14.67(3)	13.91(8)
$[Cu(bn)_2]^{2+}$	20.92(1)	19.79(1)
$[Zn(bn)]^{2+}$	5.944(3)	5.45(1)
$[Zn(Hbn)]^{3+}$	11.59(6)	11.6(1)
$[Zn(bn)_2]^{2+}$	11.260(7)	10.77(2)
$[Zn(bn)_3]^{2+}$	14.76(3)	14.63(6)
$[Pb(bn)]^{2+}$	5.35(6)	5.45(5)
$[Pb(bn)_2]^{2+}$	10.4(1)	10.2(1)

The quoted standard deviations give an indication of the relative precision of the results, and the importance of the species. They do not include systematic errors.

The early observation that (±)bn is slightly more basic than (*m*)bn is confirmed,[11] the small difference

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[3] J. R. Gollogly and C. L. Hawkins, *Inorg. Chem.*, 1969, **8**, 1168; 1970, **9**, 576.

[4] A. T. Advani, D. S. Barnes, and L. D. Pettit, *J. Chem. Soc.* (*A*), 1970, 2691.

[5] Y. Saito and M. Iawasaka, *Bull. Chem. Soc. Japan*, 1966, **39**, 92.

[6] S. Yano, H. Ito, Y. Koike, J. Fujita, and K. Saito, *Chem. Comm.*, 1969, 460.

[7] J. R. Gollogly, C. J. Hawkins, and J. K. Beattie, *Inorg. Chem.*, 1971, **10**, 317.

[8] F. H. Dickey, W. Ficket, and H. J. Lucas, *J. Amer. Chem. Soc.*, 1952, **74**, 944.

[9] A. Sabatini, A. Vacca, and P. Gans, *Talanta*, 1974, **21**, 53; P. Gans, A. Sabatini, and A. Vacca, *Inorg. Chim. Acta*, 1976, **18**, 237.

[10] D. D. Perrin and I. G. Sayce, *Talanta*, 1967, **14**, 833.

[11] F. Basolo, R. K. Murmann, and Y. T. Chen, *J. Amer. Chem. Soc.*, 1953, **75**, 1480.

being almost entirely in the first protonation constant. In the presence of metal ions, hydrolysed species were found to be unimportant over the concentration and pH ranges studied, *i.e.* below pH 9.5. In the case of Ni^{2+}, Cu^{2+}, and Zn^{2+} at pH <5, a marked improvement in the fit of the experimental data was found when the formation of monoprotonated complexes, $[M(HL)]^{3+}$, was taken into account. These contributed up to 10% of the total metal-ion concentration in the pH 4—5 region. The formation of unidentate protonated complexes has not been reported previously with 1,2-diamines.

TABLE 2

	Mn^{2+}	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}
$\log K_1(\pm) - \log K_1(m)$	0.30	0.74	0.91	0.73	0.49
$\log K_2(\pm) - \log K_2(m)$	(precipitation)	0.48	0.79	0.41	0.0

TABLE 3

Enthalpy changes (kJ mol^{-1}) accompanying complex formation of ($\pm$)- and (m)-bn at 25.0 °C and $I = 0.10$ mol dm^{-3} $K[NO_3]$. Standard deviations (σ values) are given in parentheses

	($\pm$)bn	(m)bn
$Hbn^+(\Delta H_1)$	−47.8(5)	−49.5(5)
$H_2bn^{2+}(\Delta H_{1-2})$	−94.3(3)	−94.7(3)
ΔH_2	−46.5(6)	−45.2(6)
$[Ni(bn)]^{2+}(\Delta H_1)$	−32.5(3)	−28.2(3)
$[Ni(bn)_2]^{2+}(\Delta H_{1-2})$	−62.0(5)	−51.9(5)
$[Ni(bn)_3]^{2+}(\Delta H_{1-3})$	−81.7(10)	−63.2(9)
$[Cu(bn)]^{2+}(\Delta H_1)$	−52.7(3)	−46.9(3)
$[Cu(bn)_2]^{2+}(\Delta H_{1-2})$	−100.0(5)	−96.8(4)
$[Zn(bn)]^{2+}(\Delta H_1)$	−18.0(7)	−13.9(7)
$[Zn(bn)_2]^{2+}(\Delta H_{1-2})$	−29.9(5)	−30.3(5)

A comparison of the formation constants reported here with those reported for complexes of propanediamine[4] (pn) and ethylenediamine[12] (en) shows that, for a number of bivalent transition-metal ions, the stabilities decrease in the order ($\pm$)bn > en > pn > (m)bn. When en is selected as a reference ligand and values for log β_{ML_x} were plotted against log $\beta_{M(en)_x}$ straight lines of unit gradient were obtained with ($\pm$)bn and pn while the points for (m)bn were scattered. This suggests that the ΔG values for the (m)bn complexes are anomalous, perhaps because of similar geometry in the ($\pm$)bn and pn complexes and varying geometry in (m)bn complexes.

The difference in stability between complexes of ($\pm$)- and (m)-bn may be expressed quantitatively as the ratio of the stepwise constants, *i.e.* $\log K_n(\pm) - \log K_n(m)$. Values calculated are shown in Table 2. These differences must result from differences in the energy between the axial and equatorial methyl substituents on the chelate rings, and differences in solvation or hydrogen bonding between the two structures (expected to be small). In general it is found that the greater stability of the ($\pm$)bn chelate ring is more marked in the formation of the first chelate ring (corresponding to K_1) than the second. In fact, with Zn^{2+} there is no significant difference in the second step.

Enthalpy Changes.—Calculated enthalpy changes are reported in Table 3. Enthalpy changes for the stepwise complex-formation reactions are represented as ΔH_n, corresponding to K_n, and for the overall reactions as ΔH_{1-n} corresponding to β_n. Thermodynamic quantities calculated from values in Tables 1 and 3 are shown in Table 4.

The ($\pm$)- and (m)-bn complexes would be expected to differ in ΔH values as a result of different conformational energies. Different entropy contributions, arising from different ring-deformation vibrations, are also to be expected. *A priori* calculation on the model complex $[M(bn)(OH_2)_4]^{2+}$ with M–N and M–O bond distances of 200 pm resulted in the values for $\Delta G[(\pm)bn] - \Delta G[(m)bn]$ of −3.4 kJ mol^{-1} and $\Delta H[(\pm)bn] - \Delta H[(m)bn]$ of −2.3 kJ mol^{-1}.[13] These values are consistent with those calculated from Table 4 and suggest that the differences in enthalpy and entropy changes found experimentally may be explained satisfactorily in terms of differing conformational energies and associated vibrational entropies.

TABLE 4

Thermodynamic values (kJ mol^{-1}) for the formation of complexes of ($\pm$)- and (m)-bn at 25.0 °C

	($\pm$)bn			(m)bn		
Reaction	ΔG	ΔH	$T\Delta S$	ΔG	ΔH	$T\Delta S$
$H^+ + bn \longrightarrow Hbn^+$	−56.2	−47.8	8.4	−56.1	−49.5	6.6
$2H^+ + bn \longrightarrow H_2bn^{2+}$	−94.3	−94.3	0	−94.1	−94.7	−0.6
$Ni^{2+} + bn \longrightarrow [Ni(bn)]^{2+}$	−43.6	−32.5	11.1	−38.4	−28.2	10.2
$[Ni(bn)]^{2+} + bn \longrightarrow [Ni(bn)_2]^{2+}$	−36.3	−29.5	6.8	−31.8	−23.7	8.1
$[Ni(bn)_2]^{2+} + bn \longrightarrow [Ni(bn)_3]^{2+}$	−22.6	−19.7	2.9	−14.6	−11.7	2.9
$Ni^{2+} + 2bn \longrightarrow [Ni(bn)_2]^{2+}$	−79.9	−62.0	17.9	−70.2	−51.9	18.3
$Ni^{2+} + 3bn \longrightarrow [Ni(bn)_3]^{2+}$	−102.5	−81.7	20.8	−84.8	−63.6	21.2
$Cu^{2+} + bn \longrightarrow [Cu(bn)]^{2+}$ *	−64.3	−52.7	11.6	−60.1	−46.9	13.2
$[Cu(bn)]^{2+} + bn \longrightarrow [Cu(bn)_2]^{2+}$	−54.8	−47.3	7.5	−52.8	−49.9	2.9
$Cu^{2+} + 2bn \longrightarrow [Cu(bn)_2]^{2+}$ *	−119.1	−100.0	19.1	−112.9	−96.8	16.1
$Zn^{2+} + bn \longrightarrow [Zn(bn)]^{2+}$	−33.9	−18.0	15.9	−31.1	−13.9	17.2
$[Zn(bn)]^{2+} + bn \longrightarrow [Zn(bn)_2]^{2+}$	−30.4	−11.9	18.5	−30.4	−16.4	14.0
$Zn^{2+} + 2bn \longrightarrow [Zn(bn)_2]^{2+}$	−64.3	−29.9	34.4	−61.5	−30.3	31.2

* Values reported for butane-1,2-diamine [H. K. J. Powell and N. F. Curtis, *J. Chem. Soc.* (*A*), 1967, 1441] are:

	ΔG	ΔH	$T\Delta S$
$[CuL]^{2+}$	−57.4	−49.2	8.2
$[CuL_2]^{2+}$	−109.1	−99.6	9.5

In general, the differences in entropy changes are small,

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[12] T. Davies, S. S. Singer, and L. A. K. Staveley, *J. Chem. Soc.*, 1954, 2304.

[13] J. R. Gollogly and C. L. Hawkins, personal communication.

the major stabilisation of the (±)bn compared to the (*m*)bn complexes being a more favourable enthalpy change. The co-ordination of a second molecule of (*m*)bn to form a bis complex with axial methyl substituents would be expected to involve a relative destabilisation comparable to (or greater than) co-ordination of the first molecule. The comparison of stepwise formation constants given in Table 2 shows the opposite to be the case. From this it can be inferred that the stereochemistry of the bis complexes of (*m*)bn must differ from that of (±)bn so as to reduce the steric interactions and encourage co-ordination of a second ligand molecule. In this connection, the enthalpy changes accompanying the formation of the stepwise complexes of nickel are particularly interesting (see Table 3).

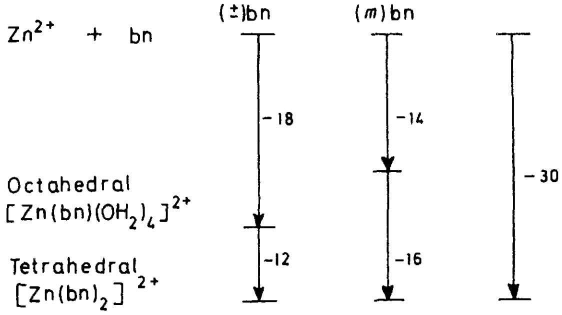
With en and Ni^{2+} the stepwise enthalpy changes are approximately equal at *ca.* -39 kJ mol^{-1}.[14] In contrast, each step for the butanediamine complexes is significantly less exothermic, the change being partly compensated by larger entropy changes. These changes are consistent with the endothermic displacement of co-ordinated water molecules of solvation by the axial methyl groups, causing a change in co-ordination number [equation (1)].

$$[Ni(bn)(OH_2)_4]^{2+} + bn \rightleftharpoons [Ni(bn)_2]^{2+} + 2H_2O \quad (1)$$

This is supported by the changes in colour found when the ratio of bn to Ni^{2+} is increased from 1 : 1 to 2 : 1, the solution becoming increasingly yellow. Spectral studies (see later) showed that this dehydration is incomplete at 25 °C, the octahedral and square-planar complexes existing in equilibrium with the planar bis complex $[Ni\{(m)bn\}_2]^{2+}$ being more important than planar $[Ni\{(\pm)bn\}_2]^{2+}$. As a result the tris complex $[Ni\{(m)bn\}_3]^{2+}$ has a markedly lower stability than $[Ni\{(\pm)bn\}_3]^{2+}$, the difference in stability being almost entirely due to the low value of ΔH_3 for the (*m*)bn complex. The ion $[Ni\{(m)bn\}_3]^{2+}$ must involve three axial methyl groups and space crowding makes conformational shifts to alleviate interference almost impossible. Hence the complex has a comparatively low stability, the square-planar bis complex, without water molecules on the *z* axis, being preferred. Since Cu^{2+} has little tendency to form octahedral complexes, square planar being the normal co-ordination, the trends in thermodynamic properties of the complexes with Cu^{2+} would not be expected to be similar to those with Ni^{2+}.

Diamine complexes of Zn^{2+} are known to undergo changes in stereochemistry during the course of stepwise complex formation, the stereochemistry often depending on the nature of the background electrolyte.[15] A comparison of ΔH and ΔS values for the stepwise formation of $[Zn(en)_2]^{2+}$ in $K[NO_3]$ and KCl solutions has been interpreted as demonstrating a change from octahedral to tetrahedral stereochemistry $\{$*i.e.* $[Zn(en)(OH_2)_4]^{2+} + en \longrightarrow [Zn(en)_2]^{2+} + 4H_2O\}$ in a nitrate background, while octahedral stereochemistry is maintained in a chloride medium $\{$presumably as $[ZnCl_2(en)_2]\}$. The ΔG and ΔH values for formation of $[Zn\{(\pm)bn\}]^{2+}$ are similar in magnitude to those obtained by Bertsch *et al.*[16] for the complex $[Zn(en)(OH_2)_4]^{2+}$. A similar octahedral co-ordination sphere can, therefore, be assumed. The complex $[Zn\{(m)bn\}]^{2+}$ is less stable, as expected as a result of steric interference from the axial methyl group.

The co-ordination of a second (±)bn ligand to Zn^{2+} is characterised by a smaller enthalpy change ($-\Delta H_2$) compared with $-\Delta H_1$ or with $-\Delta H_2$ for the en complex, and by a large positive entropy change ($\Delta S_2 > \Delta S_1$). The complex $[Zn\{(m)bn\}_2]^{2+}$ is anomalously stable, as indicated by the low value of $\log K_1 - \log K_2$ from Table 1 (0.13), and the numerically large value for $-\Delta H_2$ (such that $-\Delta H_2 > -\Delta H_1$) compared with values for (±)bn. All these results are consistent with tetrahedral co-ordination in both $[Zn\{(m)bn\}_2]^{2+}$ and $[Zn\{(\pm)bn\}]^{2+}$, according to the following scheme of enthalpy changes (kJ mol^{-1}):



The five-membered diamine chelate ring on an octahedral metal ion is known to be puckered. However, when the metal ion is in a tetrahedral environment the tetrahedral N–M–N bond angle causes a flattening of the ring, so destroying the distinction between axial and equatorial substituents. Hence the overall enthalpy change for formation of tetrahedral $[Zn(bn)_2]^{2+}$ would be expected to be similar for both (*m*)- and (±)-bn.

Spectroscopic Studies.—The colours of solutions of Ni^{2+} with simple 1,2-diamines (*e.g.* en) change from the pale green of $[Ni(OH_2)_6]^{2+}$ through blue to purple as the diamine to Ni^{2+} ratio is increased to 3 : 1. The spectra of the various stepwise complexes have been fully interpreted and are consistent with those expected for d^8 octahedral ions. Qualitatively a marked departure from this optical behaviour was observed for solutions of Ni^{2+} and (*m*)- and (±)-bn. At diamine : Ni^{2+} ratios of *ca.* 2 : 1 the solutions are yellow and almost colourless for the (*m*)- and (±)-bn ligands respectively, both reverting to purple when the ratio is increased to 3 : 1. Similar colour changes have been noted previously.[17]

There are three major peaks in the spectra of en and pn with Ni^{2+} corresponding to the three possible *d–d* transitions for a d^8 ion in an octahedral field. Examination of the spectra of mixtures of Ni^{2+} and (*m*)- or (±)-bn shows that three of the absorption maxima (ν_1, ν_2, and

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[14] F. Holmes and D. R. Williams, *J. Chem. Soc.* (*A*), 1967, 1702.

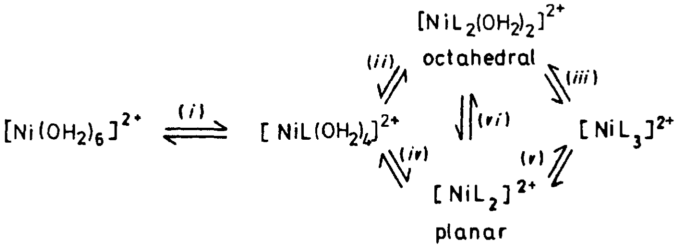
[15] M. Ciampolini, P. Paoletti, and A. Vacca, *J. Chem. Soc.*, 1960, 4553.

[16] C. R. Bertsch, W. C. Fernelius, and B. P. Block, *J. Phys. Chem.*, 1958, **62**, 444.

[17] F. Basolo, Y. T. Chen, and R. K. Murmann, *J. Amer. Chem. Soc.*, 1954, **76**, 956.

ν_3) resemble closely those found for normal octahedral fields round the Ni^{2+}, while an additional absorption band remained at a fixed wavelength of $\lambda_{max.}$ 440 nm and had a maximum intensity at the 2 : 1 ratio. This band was more intense with (*m*)- than (±)-bn. Spectral peaks for the various octahedral complexes can be assigned unambiguously to the ν_1, ν_2, and ν_3 transitions, the peak maxima being very close to those predicted by Jørgensen's ' rule of average environments '.[18]

The band at 440 nm was assigned to a transition in the square-planar complex $[Ni(bn)_2]^{2+}$ rather than a tetrahedral complex since such complexes only form under severe steric requirements and are intensely blue in colour ($\varepsilon_{max.}$ *ca.* 20 m^2 mol^{-1}). Similar octahedral–planar equilibria in complexes of Ni^{2+} have been reported with 1,1,2,2-tetramethylethylenediamine[17] and *meso*-1,2-diphenylethylenediamine [(*m*)dpen].[19] Two equilibrium patterns could be involved: octahedral bis(diamine) complexes $[Ni(bn)_2(OH_2)_2]^{2+}$ may exist in equilibrium with the square-planar complex; or the absorptions may be due solely to stepwise equilibria between $[Ni(bn)(OH_2)_4]^{2+}$, planar $[Ni(bn)_2]^{2+}$, and octahedral $[Ni(bn)_3]^{2+}$. The absence of clearly defined isosbestic points in the spectra of Ni^{2+} and (*m*)- or (±)-bn indicates that at no stage of the stepwise complex formation do simple two-species equilibria describe the system, so supporting the former equilibrium pattern shown in the Scheme. This was confirmed in a detailed analysis of the spectra when peaks characteristic of $[Ni(bn)_2(OH_2)_2]^{2+}$ were found. In the case of the more highly substituted 1,1,2-trimethylethylenediamine $[NiL_2(OH_2)_3]^{2+}$ apparently cannot be formed and so the equilibria (*ii*), (*iii*), and (*vi*) cannot be set up.[17]



SCHEME Possible equilibria involved in nickel(II)–diamine complex formation

An approximate value for the equilibrium constant for reaction (2), K' = [octahedral]/[planar], was calculated

$$[Ni(bn)_2]^{2+} + 2H_2O \rightleftharpoons [Ni(bn)_2(OH_2)_2]^{2+} \quad (2)$$

as follows. Solutions containing significant concentrations of the bis complexes will owe part of their intensity to the absorption by the octahedral species $[Ni(bn)_2(OH_2)_2]^{2+}$. The octahedral band ν_3 ($\lambda_{max.}$ 360 nm) is the sum of the absorption of all the octahedral species in solution and it is reasonable to suppose that absorption of planar $[Ni(bn)_2]^{2+}$ will be small at this wavelength. Concentrations of Ni^{2+}, $[Ni(bn)]^{2+}$, and $[Ni(bn)_3]^{2+}$ at each metal to ligand ratio used were calculated using the computer program COMICS,[10] and the absorption coefficients for the species Ni^{2+}, $[Ni(bn)]^{2+}$, and $[Ni(bn)_3]^{2+}$ were calculated (ε 0.1, 0.74, and 1.17 m^2 mol^{-1} respectively) from solutions of metal to ligand ratios of 1 : 0.5 and 1 : 5, when the species $[Ni(bn)_2(OH_2)_2]^{2+}$ is effectively absent. The observed optical density at 360 nm in each spectrum was then corrected for contributions from Ni^{2+}, $[Ni(bn)]^{2+}$, and $[Ni(bn)_3]^{2+}$, leaving the peak due to $[Ni(bn)_2(OH_2)_2]^{2+}$ which reached a maximum at the 1 : 2 ratio as expected. The absorption at 440 nm was corrected similarly and the residue was assumed to be due to planar $[Ni(bn)_2]^{2+}$. The absorption coefficient of octahedral $[Ni(bn)_2(OH_2)_2]^{2+}$ at 360 nm was estimated as 1.7 m^2 mol^{-1} from a comparison of the values for en and related ligands, and hence the concentration of $[Ni(bn)_2(OH_2)_2]^{2+}$, and of planar $[Ni(bn)_2]^{2+}$, was calculated. From these approximate calculations a value for $\varepsilon_{max.}$ at 440 nm of *ca.* 4.5 m^2 mol^{-1} was derived for (*m*)bn and a planar–octahedral equilibrium constant, K', of 0.7. For the (±)bn isomer the value of K' was 1.2. Recently, similar equilibria in aqueous solutions of polyamines with Ni^{2+} have been studied, and similar equilibrium constants found. It was suggested that the blue octahedral bis complexes may be *cis*-diaqua-species and that the yellow planar complex may not be completely devoid of axial water molecules.[20] The results are summarised in Table 5.

TABLE 5

Octahedral–square-planar equilibria at 25 °C and I = 0.10 mol dm^{-3}

Complex	K'	Octahedra (%)	Planar (%)	Ref.
$[Ni\{(m)bn\}_2]^{2+}$	0.7	42	58	*a*
$[Ni\{(\pm)bn\}_2]^{2+}$	1.2	55	45	
$[Ni(2Me\text{-}pn)_2]^{2+}$ [b]	1.3	56	44	*c*
$[Ni\{(m)dpen\}_2]^{2+}$	2.0	66	34	19
$[Ni(3,7NH\text{-}nd)_2]^{2+}$ [d]	3.7	78	22	20
$[Ni(3,6NH\text{-}od)_2]^{2+}$ [e]	83	99	1	20

[a] This work. [b] 2Me-pn = 2-Methylpropane-1,2-diamine. [c] M. E. Farago, J. M. James, and V. Trew, *J. Chem. Soc.* (*A*), 1968, 48. [d] 3,7NH-nd = 3,7-Diazanonane-1,9-diamine. [e] 3,6-NH-od = 3,6-Diazaoctane-1,8-diamine.

The difference in conformational energy between the (±)- and (*m*)-bn bis complexes of Ni^{2+} is small (*ca.* 5 kJ mol^{-1} per ring from Table 4), but is clearly enough to influence the position of the planar–octahedral equilibrium significantly so that, at room temperature, the planar bis (*m*)bn complex is predominant while the octahedral form of the bis (±)bn complex predominates. It is interesting to note that a 2 : 1 mixture of (±)bn and Ni^{2+} gave an excellent thermochromic effect at around room temperature, the solution being deep blue at 5 °C and changing reversibly through colourless to yellow at 35 °C; the planar complex is favoured at higher temperatures as a result of its more favourable entropy of formation.

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