

Tetrahedral Complexes of Nickel(II) with Benzimidazole

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The preparations are described of the benzimidazole (=L) complexes, NiL_2X_2 (X = Br or I) and $(\text{Et}_4\text{N})(\text{NiLBr}_3)$. From their electronic spectra and magnetic properties these compounds are assigned pseudo-tetrahedral configurations, but with pronounced departures from T_d symmetry. The magnetic moments of NiL_2Br_2 and $(\text{Et}_4\text{N})(\text{NiLBr}_3)$ decrease from 3.46 and 3.57 B.M., respectively, at room temperature to about the spin-only value at ca. 4.2°K. The moments of $(\text{MePh}_3\text{As})_2\text{NiCl}_4$ and $\text{Ni}(\text{Ph}_3\text{P})_2\text{Cl}_2$, at ca. 4.2°K are 0.70 and 2.20 B.M., respectively. Solution equilibria between 2:1 and 4:1 complexes of L with the nickel halides are also reported.

DURING studies of some hexaco-ordinate complexes of benzimidazole (= L) with nickel(II) halides¹ it was found that on solution in solvents such as acetone or nitromethane, species having electronic spectra typical of tetrahedrally co-ordinated nickel(II) were formed. We report here the preparation and some physical studies of some solid tetrahedral complexes of nickel(II) with L, together with an investigation of the equilibrium occurring between them and the hexaco-ordinate complexes.

The compounds NiL_2X_2 (X = Br or I) were obtained as hygroscopic solids by rapid precipitation from hot solutions of the components in acetone. Attempts to prepare the analogous chloro-complex were unsuccessful, though it exists in solution; either the 4:1 or 1:1 complexes were obtained instead.

Electronic Spectra.—The electronic spectra of the solid compounds in the range 4000—20,000 cm^{-1} (Table 1) permit the assignment to them of essentially tetrahedral structures. The bands at 10,400 and 17,250 cm^{-1} for the bromo-, and at 10,000 and 16,200 cm^{-1} for the iodo-complex can be assigned as the ${}^3T_1(F) \longrightarrow {}^3A_2$ and ${}^3T_1(F) \longrightarrow {}^3T_1(P)$ transitions, respectively. The

transition to the 3T_2 level appears in the room-temperature spectra as a broad (half-width about 2000 cm^{-1}) band at surprisingly high energy (ca. 7000 cm^{-1}). The question arises as to whether a component of this transition, which is split into three components in C_{2v} symmetry, may lie below the range of measurement. The average energy of the components would then be much nearer to that expected for this type of ligand field.

At ca. 80°K, this broad band is resolved into two components for the bromide and three for the iodide. For the latter, at least, it seems unlikely that further components lie at lower energy, and, in view of the general similarity between the spectra, the same is assumed to be true for the bromide. The high average energy of this band is therefore probably due to the splitting of the ${}^3T_1(F)$ ground-state, as expected for a ligand field of C_{2v} symmetry.

For $(\text{Et}_4\text{N})(\text{NiLBr}_3)$, the transitions to the 3A_2 and ${}^3T_1(P)$ upper states occur at 8700 and 15,650 cm^{-1} , respectively, the ligand field being intermediate between

¹ D. M. L. Goodgame, M. Goodgame, and M. J. Weeks, *J. Chem. Soc. (A)*, 1967, 1125.

those of NiBr_4^{2-} and NiL_2Br_2 . At room temperature the transition to the 3T_2 state is observed only as a broad, weak band at about $4000\text{--}6500\text{ cm}^{-1}$. At *ca.* 80°K this is clearly resolved into the two components expected for

TABLE 1
Electronic spectra of the compounds

Complex	State *	$\nu_{\text{max.}}$ (cm. ⁻¹) (ϵ_{molar} for solutions)
NiL_2Br_2	Solid	$\sim 21,700\text{sh}, 17,250,$ $\sim 11,700\text{sh}, 10,420, 6800\text{br}$
	Solid 80°K	$24,000\text{w}, \sim 21,600\text{sh}, 17,300,$ $\sim 11,700\text{sh}, 10,500, 7800,$ 6300
	Acetone (0.0025M)	$17,500$ (200), $\sim 11,900\text{sh},$ $10,350$ (60)
	MeNO_2 (0.0025M)	$17,500$ (170), $\sim 11,900\text{sh},$ $10,370$ (50)
NiL_2I_2	Solid	$16,200, \sim 10,800\text{sh}, 9950,$ 6800br
	Solid 80°K	$16,300, \sim 10,950\text{sh}, 9900,$ $7620, 6470, \sim 5600\text{sh}$
	Acetone (0.0025M)	$16,600$ (280), $\sim 15,400\text{sh},$ $\sim 10,900\text{sh}, 10,050$ (80)
	MeNO_2 (0.0025M)	$16,700$ (200), $\sim 15,400\text{sh},$ $\sim 10,900\text{sh}, 10,050$ (55)
$(\text{Et}_4\text{N})(\text{NiLBr}_3)$	Solid	$15,650, 8700, 5100\text{br}$
	Solid 80°K	$15,700, \sim 10,800\text{sh}, 8700,$ $6300, \sim 4400\text{br}$
	Acetone (0.001M)	$15,900$ (210), 8700 (40)
	MeNO_2 (0.001M)	$16,250$ (210), $\sim 10,200\text{sh},$ 8800 (40)
" NiL_2Cl_2 "	Acetone (0.0025M)	$\sim 19,000\text{sh}, 17,700$ (140), $\sim 12,100\text{sh}, 10,500$ (50)

* At room temperature unless otherwise stated.

C_{3v} symmetry. It appears that in this compound also the low-symmetry component of the ligand field is appreciable.

Magnetic Results.—If the ligand field in the NiLBr_3^- anion has C_{3v} symmetry, the temperature-dependence of the magnetic moment should give some information concerning the degree of distortion from tetrahedral configuration.² The magnetic susceptibility of $(\text{Et}_4\text{N})(\text{NiLBr}_3)$ obeys the Curie-Weiss law over the range $80\text{--}300^\circ\text{K}$, with μ_{eff} at $295^\circ = 3.57$ B.M. and $\theta = -11^\circ$. While the negative Weiss constant implies a fall in the magnetic moment with temperature, this fall is no greater than observed for many octahedral nickel(II) complexes. Attempts to explain these results using the approach of Figgis *et al.*² suggested that the best parameters would be $\lambda = -220\text{ cm}^{-1}$; $\nu = \text{ca. } -3$; $A = 1.5$; $K = \text{ca. } 0.7$. However, the fit obtained was not really satisfactory, and in order to check it, the susceptibility was measured (by courtesy of Dr. M. J. Leask, Clarendon Laboratory, Oxford) at liquid-helium temperature (Table 2). The magnetic moment at *ca.* 4.2°K (2.84 B.M.) is much higher than that predicted by the theory. The deviation of this low-temperature value from the graph of $1/\chi$ against T extrapolated from the high-temperature points (Figure 1) is small and in the opposite direction from that expected from the theory.²

² B. N. Figgis, J. Lewis, F. E. Mabbs, and G. A. Webb, *Nature*, 1964, **203**, 1138.

The magnetic behaviour of the compounds NiL_2Br_2 and NiL_2I_2 between 100 and 300°K can also be adequately described by the Curie-Weiss law. Their room-temperature moments of 3.46 and 3.28 B.M., respectively, drop to 3.34 and 3.17 B.M. at 100°K . Similar behaviour has been observed³ for other tetrahedral nickel(II) complexes of this stoichiometry, and the temperature

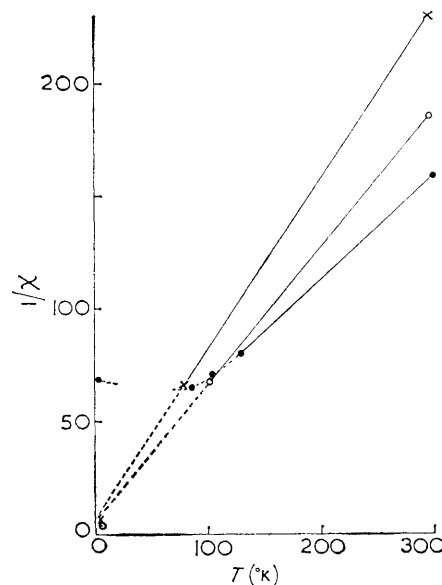
TABLE 2

Magnetic susceptibilities at *ca.* 4.2°K

Compound	χ_m (c.g.s.u.)	μ_{eff} * (B.M.)
$(\text{Et}_4\text{N})(\text{NiLBr}_3)$	0.238	2.84
NiL_2Br_2	0.240	2.85
$\text{Ni}(\text{Ph}_3\text{P})_2\text{Cl}_2$	0.140	2.20
$(\text{MePh}_3\text{As})_2(\text{NiCl}_4)$	0.0146	0.70

* Calc. from Curie law.

variations of the susceptibility of $\text{Ni}(\text{pyridine})_2\text{I}_2$ and $\text{Ni}(\beta\text{-picoline})_2\text{I}_2$, which have been interpreted³ according to the theory of Figgis *et al.*,² appear to be of the same type. The parameters used,³ however, would predict a magnetic moment below the spin-only value at 4.2°K ,



Comparison of magnetic susceptibilities at 4.2°K with those at $80\text{--}300^\circ\text{K}$ for: \circ $(\text{Et}_4\text{N})(\text{NiLBr}_3)$; \times $\text{Ni}(\text{Ph}_3\text{P})_2\text{Cl}_2$; \bullet $(\text{MePh}_3\text{As})_2\text{NiCl}_4$

whereas for NiL_2Br_2 at this temperature we find a moment of 2.85 B.M.

In compounds in which the ligand field experienced by the metal ion is of C_{2v} symmetry, when the $^3T_1(F)$ ground state is split into three orbital singlets, the theory of Figgis *et al.*² is not strictly applicable. It is therefore not surprising that the moment for NiL_2Br_2 fails to drop below the spin-only value at *ca.* 4.2°K . However, since no value below 2.8 B.M. appears to have been observed for tetrahedral nickel(II) complexes, it seemed desirable to obtain measurements at very low

³ B. N. Figgis, J. Lewis, F. E. Mabbs, and G. A. Webb, *J. Chem. Soc. (A)*, 1966, 1411.

temperature on some compounds known unequivocally to have this geometry. Susceptibilities at *ca.* 4.2°K were therefore measured for the compounds (MePh₃As)₂(NiCl₄), in which the nickel ion is surrounded by an almost exactly regular tetrahedron of chloride ions,⁴ and Ni(Ph₃P)₂Cl₂, in which the tetrahedron is seriously distorted.⁵

The moment of the former compound at *ca.* 4.2°K is indeed very low (Table 2). Although the susceptibility of Ni(Ph₃P)₂Cl₂ at this temperature is a power of ten higher than that of (MePh₃As)₂(NiCl₄) its magnetic moment is still below the spin-only value, and it seems that even with the considerable orbital splitting expected for this compound, the effect of spin-orbit coupling is still important. However, a graph of $1/\chi$ against T , in which this value of χ at 4.2°K, and higher-temperature values calculated from the data of Figgis *et al.*,³ are used, is once more a straight line, in contrast to the case for the NiCl₄²⁻ ion (Figure). The susceptibility of the phosphine complex remained essentially constant between *ca.* 4.2 and *ca.* 1.4°K.

Solution Behaviour.—The solution spectra (Table 1) of the compounds NiL₂Br₂ and NiL₂I₂ in acetone and in nitromethane closely resemble those of the solids, and show high molar extinction coefficients, indicating that the predominant species present is in each case tetrahedral NiL₂X₂. For the bromide this is borne out by the low electrolytic conductances of the solutions (Table 3), but for the iodide some dissociation of anions is indicated, though the conductance is much less than that expected for a 1:1 electrolyte.

TABLE 3

Electrolytic conductances for the complexes

Compound	Solvent	Concn. (M)	Λ_M (ohm ⁻¹ cm. ⁻¹)
NiL ₂ Br ₂	Acetone	0.0025	3
	MeNO ₂	0.005	1
NiL ₂ I ₂	Acetone	0.0014	62
	MeNO ₂	0.003	50
(Et ₄ N)(NiLBr ₃) ...	Acetone	0.001	125
	MeNO ₂	0.001	106

When benzimidazole is added to solutions of NiL₂Br₂ or NiL₂I₂ in either acetone or nitromethane, complexes, which may be solvated, containing four mol. of benzimidazole per nickel ion, crystallise out. These 4:1 complexes, on solution in the same solvents, give spectra identical, in both band position and band intensity, with those of the corresponding NiL₂X₂ compounds, and it was concluded that dissociation to the tetrahedral species was complete. Any of the forms of the 4:1 chloro-complex¹ dissolves in acetone to give a deep blue-purple solution, with an electronic spectrum (Table 1) very similar to that of NiL₂Br₂. It was concluded that dissociation of NiL₄Cl₂ into tetrahedral NiL₂Cl₂ occurs, and, in view of the high molar extinction coefficients observed, that this process also is probably virtually complete.

There are very few systems for nickel(II) where, with the same anion and neutral ligand, octahedral NiL₄X₂

and tetrahedral NiL₂X₂ can be prepared. When L = benzimidazole and X = Br, not only these but also diamagnetic, planar [NiL₄]Br₂ are known.¹ The structural chemistry of the system is also very dependent on the presence of solvent molecules, even when these are not co-ordinated to the metal ion.¹ It therefore appeared worthwhile, in spite of the approximations necessary (see Experimental section) to attempt a study of the equilibrium between the 2:1 and the 4:1 complexes in solution, in order to throw some light on the factors influencing the structure adopted.

TABLE 4

Equilibrium constants and some thermodynamic parameters for reaction (1)

X	Solvent	K (20°)	$-\Delta H^\circ$ (kcal./mole)	$-\Delta S^\circ$ (cal./°C/mole)
Cl	Acetone	$2.2 (\pm 0.2) \times 10^2$	—	—
	Acetone	$5.3 (\pm 0.4) \times 10^2$	—	—
I	MeNO ₂	$1.25 (\pm 0.15) \times 10^4$	10 ± 1	15.5 ± 3
	Acetone	$15.5 (\pm 1) \times 10^2$	15 ± 1.5	36.5 ± 4.5
	MeNO ₂	$19 (\pm 2) \times 10^4$	22 ± 2	50 ± 5

The overall standard free-energy changes (Table 4) favour the formation of the octahedral species, the more so on passing from chloride to iodide. A much greater change occurs on passing from acetone to nitromethane solutions, emphasising the importance of the solvent in the chemistry of these complexes.

EXPERIMENTAL

Dibromobisbenzimidazolenickel(II).—A solution of benzimidazole (2.4 g.) and nickel bromide hexahydrate (3.5 g.) in ethanol (5 ml.) was evaporated to dryness. The resulting solid was dissolved in acetone (8 ml.), filtered, and the solution heated to boiling. Hot carbon tetrachloride (15 ml.) was added, and the solvent decanted, leaving a deep blue oil. This was triturated with successive portions of hot carbon tetrachloride until it solidified, when it was filtered off and dried *in vacuo* at 100° (yield 59%). The very hygroscopic complex melted at 254° (Found: Br, 35.4; Ni, 12.9. C₁₄H₁₂Br₂N₄Ni requires Br, 35.1; Ni, 12.9%).

Di-iodobisbenzimidazolenickel(II).—A solution of Ni(NO₃)₂·6H₂O (3.2 g.) in acetone (5 ml.) was added to a solution of sodium iodide (3.3 g.) in acetone (20 ml.), chilled, and dried over molecular sieves for several hours, then filtered into a solution of benzimidazole (2.36 g.) in acetone (25 ml.). The deep green solution was evaporated to dryness, and the resultant solid dried at 120°. It was then extracted with 20 ml. of acetone, the filtered extract was heated to boiling, and the solid precipitated by addition of hot carbon tetrachloride (50 ml.). The hygroscopic solid was washed by decantation with hot carbon tetrachloride and dried *in vacuo* (yield 76%), m. p. 218° (decomp.) (Found: C, 30.6; H, 2.25; Ni, 10.8. C₁₄H₁₂I₂N₄Ni requires C, 30.6; H, 2.2; Ni, 10.7%).

Tetraethylammonium Benzimidazoletribromonickelate(II).—A solution of benzimidazole (1.18 g.) and tetraethylammonium bromide (2.10 g.) in *n*-butanol (10 ml.) was added to one of NiBr₂·3H₂O (2.73 g.) in *n*-butanol (30 ml.). Benz-

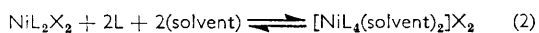
⁴ P. Pauling, *Inorg. Chem.*, 1966, **5**, 1498.⁵ G. Garton, D. E. Henn, H. M. Powell, and L. M. Venanzi, *J. Chem. Soc.*, 1963, 3625.

ene (10 ml.) was added, and the solution was slowly evaporated to about 20 ml., whereupon a blue oil began to form. It was left to cool, whereupon the oil crystallised. The solvent was decanted, and the crystals were washed with benzene and dried *in vacuo*. The very hygroscopic compound melted at 140° (Found: C, 33.0; H, 5.1; N, 7.45. $C_{15}H_{28}Br_3N_3Ni$ requires C, 32.95; H, 4.8; N, 7.7%).

The complexes of stoichiometry of NiL_4X_2 have been described.¹

Physical Measurements.—Solution spectra were obtained with Perkin-Elmer 4000 and 350 and Unicam SP 500, and reflectance spectra with Unicam SP 500 and Beckman DK 2 spectrometers. Infrared spectra were obtained with a Grubb-Parsons Spectromaster spectrometer. Magnetic susceptibilities were measured with the Gouy balance described previously⁶ and electrolytic conductances with a Philips PR 9500 conductance bridge and a conventional cell.

Measurements of Equilibrium Constants.—The decrease in intensity of the electronic spectral bands due to NiL_2X_2 were measured as known amounts of benzimidazole were added to the solutions of the 2 : 1 complexes (initial concentration *ca.* 0.0025M). Two equilibria involving conversion of 2 : 1 into 4 : 1 complexes were considered likely:



Equilibria involving the formation of NiX_4^{2-} , $NiLX_3^-$, NiL_6^{2+} , or NiL_4^{2+} were ruled out as no spectral bands attributable to these species were observed. For the chloro- and bromo-complexes the electrolytic conductances remained low throughout the addition of L, indicating that for these systems equilibrium (1) predominates. However, the conductances of solutions of NiL_2I_2 increased on addition of L, and the molar conductances of the 4 : 1 component of the equilibrium approximated to that of a 1 : 1 electrolyte. In this case, therefore, solvation of the 4 : 1 product probably occurs, so that the equilibrium con-

stant determined from the reduction in the concentration of the 2 : 1 compound concerns the conversion of this into a mixture of the 4 : 1 species.

The spectra of the pure 4 : 1 species in solution could not be determined as addition of a large excess of L resulted in the precipitation of solid 4 : 1 compounds. No direct measure was therefore available of the concentration of the 4 : 1 species, so the equilibrium constants were calculated from the relation (3), where *a* = initial concentration of 2 : 1

$$K = [a - b]/[b][c - 2(a - b)]^2 \quad (3)$$

complex, *b* = equilibrium concentration of 2 : 1 complex, and *c* = concentration of ligand added. A small absorption due to the 4 : 1 complex would be expected at the wavelength used for the concentration measurement (the maximum of the visible absorption band of the 2 : 1 complex). This was estimated by using the band-shape and intensity found for $NiL_4(NCS)_2$ with the band maxima shifted to the positions found for some typical paramagnetic 4 : 1 complexes, *e.g.*, $NiL_4X_2(\text{acetone})_n$ (*X* = Cl, Br, or I).^{1,7} This is expected to be accurate to within about 10%, which would make little difference to the equilibrium constants observed.

For all three halide systems the equilibrium constant at a given temperature remained steady, supporting the assumption that the equilibrium involved the addition of 2 mol. of L to the 2 : 1 complex. The variation of equilibrium constant with temperature was measured for the bromo- and iodo-complexes in nitromethane, and for the iodo-complex in acetone, over a temperature range of 32°.

We thank the S.R.C. for a Studentship (to M. J. W.) and for a grant for the construction of the Gouy balance.

[7/605 Received, May 17th, 1967]

⁶ D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 1964, 2790.

⁷ M. J. Weeks, Ph.D. Thesis, London University, 1966.