994. *Spectral and Magnetic Studies of some Polymeric Complexes of Nickel Halides with Heterocyclic Ligands.*

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Reflectance spectra in the range 4000—28,000 cm.$^{-1}$, and magnetic susceptibilities from ~90 to 300°κ, are reported for the compounds L_2NiCl_2 (L = pyridine or quinoline), L_2NiBr_2 (L = pyridine), $LNiCl_2$ (L = pyridine, quinoline, or benzimidazole), $LNiBr_2$ (L = quinoline or benzimidazole), and $(Me_4N)NiCl_3$. The spectra of some of the compounds show marked deviations from O_h symmetry, and the bands have been assigned in D_{4h} or C_{4v} symmetry. All the complexes with heterocyclic ligands show ferromagnetic interactions.

A number of polymeric complexes of nickel(II) containing nitrogen-heterocyclic ligands and bridging halide ions have been reported. The magnetic moments at room temperature of several of these have been measured, and are rather higher than those normally found for octahedral or distorted octahedral complexes of nickel(II). For example, dichloro-dipyridinenickel(II) has a moment of 3·37 B.M.,[1] its bromo-analogue one of 3·30 B.M.,[2] and dichlorodiquinolinenickel(II) one of 3·41 B.M.,[3] compared with a " spin-only " value of 2·83 B.M.

In an octahedral complex, the nickel(II) ion has a $^3A_{2g}$ ground-state, for which no orbital contribution to the magnetic moment is expected. However, the ligand fields present in these complexes are expected to be rather weak, so that the " mixing-in " of the $^3T_{2g}$ first excited state by spin–orbit coupling may be appreciable, and, moreover, the contribution of temperature-independent paramagnetism to the susceptibility may not be negligible. The electronic spectral data previously reported for these compounds were insufficient to permit a reliable estimate to be made of the magnitude of these effects, and we have therefore made a detailed study of the magnetic and spectral properties of some complexes of this type with the general formulæ NiL_2X_2 and $NiLX_2$, where L is a nitrogen-heterocyclic ligand and X = Cl or Br (Table 1).

TABLE 1.

Electronic absorption spectra.

Compound	Absorption maxima (cm.$^{-1}$)
$Ni(C_5H_5N)_2Cl_2$	24,100, ~22,200(sh), 13,900, ~12,200(sh), 8400, 6000
$Ni(C_5H_5N)_2Br_2$	23,350, ~21,400(sh), ~19,800(sh), 13,700, ~11,600(sh), 8000, 5800
$Ni(C_9H_7N)_2Cl_2$ (yellow form)	22,700, ~19,200(sh), 13,150, 12,000, 7550, ~6000(sh)
$Ni(C_5H_5N)Cl_2$	22,400, ~18,900(sh), 13,100, ~12,200(sh), 7800, ~6500(sh)
$Ni(C_9H_7N)Cl_2$	21,100, ~18,500(sh), 11,100, ~10,200(sh), 6400
$Ni(C_9H_7N)Br_2$	20,000, ~17,500(sh), ~14,500(sh), 10,800, ~9500(sh), 6250
$Ni(C_7H_6N_2)Cl_2$	21,700, ~18,500(sh), ~16,000(sh), 13,000, 11,800, 7450, ~6100(sh)
$Ni(C_7H_6N_2)Br_2$	20,900, ~17,900(sh), 12,200, ~11,100(sh), 7200, ~6100(sh)
$(Me_4N)NiCl_3$	21,200, ~18,200(sh), ~14,300(sh), ~12,800(sh), 11,200, 6600

The complexes dichloro- and dibromo-(benzimidazole)nickel(II), which have not been previously described, can be prepared directly by mixing ethanolic solutions of benzimidazole and nickel halide in 1 : 1 molar ratio. With pyridine and quinoline, however, this method gives only 2 : 1 complexes which decompose to the 1 : 1 compounds when heated. We have been unable to prepare the red, diamagnetic isomers of dichloro- and dibromo-diquinolinenickel(II) briefly mentioned by Downs and Ongley.[4] When the paramagnetic isomers were heated to 120° in an open bottle, loss of quinoline occurred, with the quantitative formation of the pinkish-red dichloro(quinoline)nickel(II),[5] or its bromo-analogue.

[1] Gill, Nyholm, Barclay, Christie, and Pauling, *J. Inorg. Nuclear Chem.*, 1961, **18**, 88.
[2] King, Körös, and Nelson, *J.*, 1963, 5449.
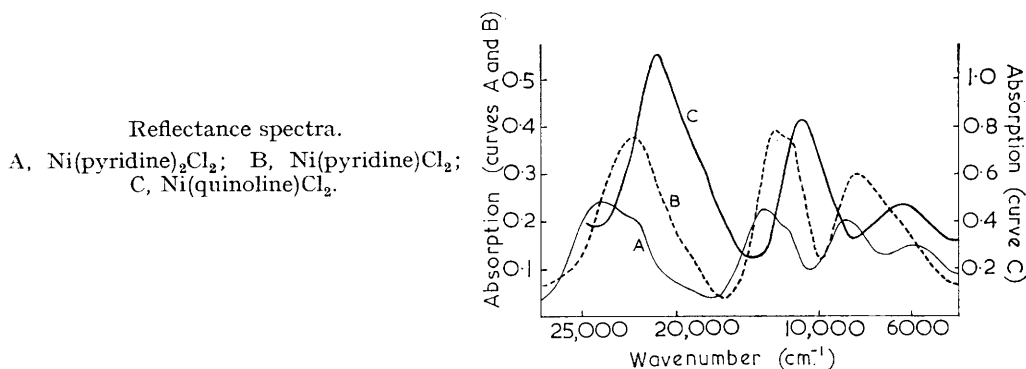[3] Goodgame and Goodgame, *J.*, 1963, 207.
[4] Downs and Ongley, *Chem. and Ind.*, 1963, 493.
[5] Pomilio, *Rend. Accad. Sci. fis. mat. (Napoli)*, 1911, Ser. 3, **17**, 342 (*Chem. Abs.*, 1912, **6**, 1289).

When six-co-ordinate dichlorodiquinolinenickel(II) was heated at 120° in a sealed ampoule, partial formation of the mono-quinoline complex occurred, and the remaining 2 : 1 complex changed from yellow to the blue, tetrahedral isomer, this change being reversed on cooling.

No compound of stoicheiometry $Ni(benzimidazole)_2Cl_2$ was obtained, all attempts to prepare one resulting in a mixture of the 1 : 1 and 4 : 1 compounds, and attempts to prepare di-iodo(quinoline)nickel(II) were also unsuccessful. Brown, Nuttall, and Sharp,[6] who first described dichloro(pyridine)nickel(II), were unable to prepare the corresponding bromo- or iodo-compounds.

Electronic Spectra.——The electronic spectra of the compounds were measured by the reflectance technique in the range 4000—28,000 cm.$^{-1}$ (Table 1). The compound $(Me_4N)NiCl_3$ has an essentially octahedral arrangement of chloride ions surrounding each nickel ion. Its spectrum may therefore be assigned in O_h symmetry as: $^3A_{2g} \longrightarrow {}^3T_{2g}$ at 6600 cm.$^{-1}$; $^3A_{2g} \longrightarrow {}^3T_{1g}(^3F)$ at 11,200; $^3A_{2g} \longrightarrow {}^1E_g(^1D)$ at ~12,800; $^3A_{2g} \longrightarrow {}^1T_{2g}(^1D)$ at ~18,200; $^3A_{2g} \longrightarrow {}^3T_{1g}(^3P)$ at 21,200. From this, Δ, the ligand-field parameter, is

Reflectance spectra.
A, $Ni(pyridine)_2Cl_2$; B, $Ni(pyridine)Cl_2$; C, $Ni(quinoline)Cl_2$.

about 6600 cm.$^{-1}$, and B', the interelectronic repulsion parameter, about 840 cm.$^{-1}$. For this calculation, the energy of the $^3A_{2g} \longrightarrow {}^3T_{2g}$ band was taken as the value of Δ, and B' was found from the relationship [7]

$$15B' = \text{Energy } {}^3T_{1g}(^3F) + \text{Energy } {}^3T_{1g}(^3P) - 3\Delta.$$

This method appears to give slightly lower values of Δ, and higher values of B', than does the use of the two higher-energy bands only, in the interaction matrix given by Tanabe and Sugano.[7] Our figures differ somewhat from those of Asmussen and Bostrup,[8] who, from observations of the higher-energy bands, calculated the values $\Delta = 7000$—7200 and $B' = 770$—795 cm.$^{-1}$ for the rubidium, cæsium, and pyridinium salts of the $[NiCl_3]^-$ anion. Whilst this assignment seems to be the most reasonable one, it does not account for the weak shoulder at ~14,300 cm.$^{-1}$, which appears to be due to a spin-forbidden transition. It is possible that the ligand field in this complex is distorted from true octahedral symmetry, and that the low-symmetry component (probably trigonal) splits the $^3A_{2g} \longrightarrow {}^3T_{1g}(^3F)$ transition, giving spin-allowed bands at 11,200 and 12,800 cm.$^{-1}$, and $^3A_{2g} \longrightarrow {}^1E_g(^1D)$ at 14,300 cm.$^{-1}$.

Dichlorodipyridinenickel(II) has a distorted octahedral structure, with each nickel ion surrounded by two nitrogen atoms and four chloride ions.[1] Its electronic spectrum cannot be interpreted on an octahedral model, owing to the considerable splitting of the bands, especially the one at lowest energy, which consists of two quite distinct components, a weaker one at 6000 and a stronger one at 8400 cm.$^{-1}$ (see Figure). These may be assigned as the $^3B_{1g} \longrightarrow {}^3B_{2g}$ and $^3B_{1g} \longrightarrow {}^3E_g$ transitions, respectively, in D_{4h} symmetry. The

[6] Brown, Nuttall, and Sharp, *J. Inorg. Nuclear Chem.*, 1963, **25**, 1067.
[7] Tanabe and Sugano, *J. Phys. Soc. Japan*, 1954, **9**, 753.
[8] Asmussen and Bostrup, *Acta Chem. Scand.*, 1957, **11**, 745.

remaining bands are then assigned as: $^3B_{1g} \longrightarrow {}^3A_{2g}$ at 12,300 cm.$^{-1}$; $^3B_{1g} \longrightarrow {}^3E_g$ at 13,900; $^3B_{1g} \longrightarrow {}^3A_{2g}(^3P)$ at $\sim$22,400; $^3B_{1g} \longrightarrow {}^3E_g(^3P)$ at 24,100. The D_{4h} component of the field splits the two $^3T_{1g}$ upper states of O_h symmetry to approximately the same extent (1700 and 1900 cm.$^{-1}$), but the $^3T_{2g}$ upper state shows a somewhat larger splitting (2400 cm.$^{-1}$). According to the theory of McClure,[9] this implies that the pyridine ligands are stronger σ-donors and weaker π-donors than the chloride ions, a conclusion well in accord with expectation. The values of Δ and B' (Table 2) were calculated by using the weighted mean of the two components of a split band as a measure of the energy of the unsplit band. It was assumed that the more intense component represented the transition to the orbital doublet.

If Ni(pyridine)Cl$_2$ has a distorted octahedral structure, with one nitrogen atom and four chloride ions surrounding the nickel ion (C_{4v} symmetry), it should have a spectrum intermediate between those of the two foregoing compounds, as far as band energies are concerned; this is the case (see Figure). The band splittings [$\sim$1300 cm.$^{-1}$ for the $^3T_{2g}$ state and $\sim$900 for the $^3T_{1g}(^3F)$ state] are about half those for dichlorodipyridinenickel(II). No splitting of the $^3T_{1g}(^3P)$ upper state was observed, but splittings of less than 1000 cm.$^{-1}$ would not be resolved in this region.

The spectrum of Ni(benzimidazole)Cl$_2$ is very similar to that of Ni(pyridine)Cl$_2$, though with all the bands at slightly lower energies. It seems, therefore, that they have similar structures, and it is unlikely that the benzimidazole acts as a bridging ligand in this compound.

The six-co-ordinate form of Ni(quinoline)$_2$Cl$_2$ has a spectrum similar to that of Ni(pyridine)$_2$Cl$_2$. It is noticeable, however, that quinoline produces a weaker ligand-field than pyridine, all the spectral bands appearing at lower energies for the quinoline compound. This may be due either to the weaker basicity of quinoline or to the steric hindrance, caused by the benzene ring, forcing either the nitrogen atom or the chloride ions to form longer bonds to the nickel ion. The band splittings for this compound are also smaller than for Ni(pyridine)$_2$Cl$_2$, and were not clearly resolved. An estimate of the positions of the components suggests that the splittings of the $^3T_{1g}$ and $^3T_{2g}$ states are each reduced by about one third.

The spectrum of Ni(quinoline)Cl$_2$ is not intermediate between those of Ni(quinoline)$_2$Cl$_2$ and (Me$_4$N)NiCl$_3$. Whilst the spectrum suggests an essentially octahedral environment for the nickel ion, there being very little splitting of the spectral bands by a component of lower symmetry, the Δ value (6400 cm.$^{-1}$) is lower than that for (Me$_4$N)NiCl$_3$. One possible explanation is that the nickel ion is five-co-ordinate, with one nitrogen atom and four chloride ions co-ordinated. This seems improbable in an infinite lattice such as is likely to exist in this compound, and we therefore suggest that there may be a sixth, longer bond to a chloride ion opposite the quinoline, making a weak contribution to the ligand field. The total ligand-field along this axis, due to the quinoline plus the distant chloride ion, is then slightly weaker than that, due to two chloride ions, on each of the other two axes, giving the reduced Δ value, and very little splitting of the spectral bands. In this situation, however, the centre of symmetry of the molecule is destroyed more effectively than in the Ni(pyridine)Cl$_2$ structure, and the intensities of the bands are affected in two ways. First, the whole spectrum becomes more intense, and, secondly, the relative strengths of the first two bands are strikingly altered. In the centrosymmetric complexes, the first two bands ($^3A_{2g} \longrightarrow {}^3T_{2g}$, and $^3A_{2g} \longrightarrow {}^3T_{1g}$ in O_h symmetry; $^3B_{1g} \longrightarrow {}^3B_{2g} + {}^3E_g$, and $^3B_{1g} \longrightarrow {}^3A_{2g} + {}^3E_g$ in D_{4h} symmetry) have roughly equal intensities. In Ni(quinoline)Cl$_2$, the first band has a much lower intensity than the second (see Figure).

The spectra of the bromo-complexes are very similar to those of the corresponding chloro-compounds, except that the bands are moved to lower energies, reflecting the decreased ligand-field strength, and the band splittings are slightly greater.

[9] McClure, *Proc. 6th Internat. Conf. Co-ordination Chem.*, 1961, 498.

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TABLE 2.

Some spectral and magnetic parameters.

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Compound	Δ (cm.$^{-1}$)	B' (cm.$^{-1}$)	Diamag. corrn. $\times 10^6$ (c.g.s.u.)	TIP $\times 10^6$ (c.g.s.u.)	θ (°K)	μ * (B.M.)	$-\lambda'$ (cm.$^{-1}$)
$Ni(C_5H_5N)_2Cl_2$	7600	980	165	272	19 ± 2	3.17 ± 0.03	230 ± 20
$Ni(C_5H_5N)_2Br_2$	7250	970	180	288	13	3.14	200
$Ni(C_9H_7N)_2Cl_2$	7050	940	213	297	19	3.22	240
$Ni(C_5H_5N)Cl_2$	7000	950	110	299	34	3.31	300
$Ni(C_9H_7N)Cl_2$	6400	850	135	327	18	3.22	220
$Ni(C_9H_7N)Br_2$	6250	810	160	336	5	3.24	230
$Ni(C_7H_6N_2)Cl_2$	7000	860	125	299	30	3.31	300
$Ni(C_7H_6N_2)Br_2$	6800	820	150	307	20	3.17	210
$(Me_4N)NiCl_3$	6600	840	213	318	0	3.20	220

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* Corrected for θ and TIP.

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Magnetic Properties.—The magnetic properties of all these compounds have been studied over the temperature range ~90—300°K (Table 2). Replicate determinations were made, in most cases on separately prepared samples of the complexes. The resultant susceptibilities were corrected for diamagnetism and for temperature-independent para-magnetism (TIP) calculated from the relationship

$$TIP = 8N\beta^2/\Delta \approx 2.09/\Delta \text{ c.g.s.u.,}$$

where Δ is the energy of the level ($^3T_{2g}$) being mixed into the ground-state. For these compounds, which have comparatively small values of Δ, the TIP amounts to about 300×10^{-6} c.g.s.u., or about 7% of the room-temperature susceptibility. Graphs of $1/\chi$ (χ = susceptibility corrected in this way) against temperature gave straight lines for all the compounds studied (at least eight different temperatures were used for each compound). The compounds Ni(pyridine)$_2$Cl$_2$, Ni(pyridine)$_2$Br$_2$, Ni(pyridine)Cl$_2$, Ni(quinoline)$_2$Cl$_2$ (yellow form), Ni(quinoline)Cl$_2$, Ni(quinoline)Br$_2$, Ni(benzimidazole)Cl$_2$, and Ni(benzimidazole)Br$_2$ all give positive values of θ in the relationship corresponding to

$$\mu = 2.84[\chi(T - \theta)]^{\frac{1}{2}},$$

ferromagnetic interaction between the metal ions, with values of θ ranging from 5 to 34°K. No dependence of the susceptibility on field-strength was observed, for fields between about 2400 and 6700 gauss, except for one sample of Ni(benzimidazole)Br$_2$, which showed a slight field-dependence at all temperatures. This sample had good analyses and an electronic spectrum indistinguishable from those of other samples of the compound which showed no field-dependence. Moreover, graphs of susceptibility against the reciprocal of the field strength gave straight lines at all temperatures, and the susceptibilities at infinite field, obtained by extrapolation, agreed well with the normal susceptibilities of the other samples of the compound. This behaviour indicates the presence of ferromagnetic impurity in this sample.

For the chloro-complexes, the magnitude of the θ value appears to depend on the number of heterocyclic ligands present, being very similar for Ni(pyridine)$_2$Cl$_2$ and Ni(quinoline)$_2$Cl$_2$, and for Ni(pyridine)Cl$_2$ and Ni(benzimidazole)Cl$_2$. The θ value increases as the number of chloride-ion bridges in the compound increases, being about 19° for L$_2$NiCl$_2$, about 32° for LNiCl$_2$, and 68° for NiCl$_2$,[10] in which the ferromagnetic intralayer interactions are considered to occur through the chloride bridges.[11] The compound Ni(quinoline)Cl$_2$, however, has a lower θ value than would be expected from this correlation, which supports the deduction from the spectral data that the co-ordination polyhedron in this compound may be rather unusual.

[10] Starr, Bitter, and Kaufman, *Phys. Rev.*, 1940, **58**, 977.
[11] Kanamori, *J. Phys. and Chem. Solids*, 1959, **10**, 87.

The bromo-complexes all have smaller θ values than have the corresponding chloro-compounds, though the differences are less than that between nickel chloride and nickel bromide.[12]

The magnetic moments, corrected for the ferromagnetism, were used to calculate the values of the spin–orbit coupling constants (λ') for the nickel ion in these complexes, from the relationship

$$\mu = 2 \cdot 83(1 - 4\lambda'/\Delta).$$

Whilst no great accuracy may be claimed for these values (Table 2), and any comparison of the figures for different compounds would be of doubtful value, they show that reasonable values of λ' are sufficient to account for the magnetic moments of these complexes. They also show that λ' is reduced to an average of about 75% of the free-ion value.

The magnetic properties of $(Me_4N)NiCl_3$ differ considerably from those of the salts of this anion measured by Asmussen and Soling [13] who observed strong antiferromagnetism, with θ values becoming less negative as the size of the univalent cation was increased. The cæsium salt has a structure consisting of close-packed layers of chloride plus cæsium ions, with nickel ions in those octahedral holes completely surrounded by chloride ions.[14] Each nickel ion therefore has three chloride ions in common with each of two other nickel ions, and magnetic interactions are expected to be strong. With cations much larger than cæsium, the close-packed layers would probably be pushed further apart, thus reducing the magnetic coupling. In the case of the tetramethylammonium compound, the disparity in size between the cations and the chloride ions has evidently either reduced the magnetic coupling to zero or made a different structure more stable. A correlation between the magnetic results of Asmussen and Soling [13] and the spectral data given by Asmussen and Bostrup [8] shows that the lowest values of θ occur with the lowest values of Δ and the highest values of B'. Our measurements fit quite well into this series (Table 3). However,

TABLE 3.

Magnetic and spectral parameters for salts of $[NiCl_3]^-$.

Salt	θ (°K)	Δ (cm.$^{-1}$)	B' (cm.$^{-1}$)
$RbNiCl_3$	-112	7200	780
$CsNiCl_3$	-76	7100	770
$C_5H_5NHNiCl_3$	-36	7000	795
$(Me_4N)NiCl_3$	0	6600	840

Asmussen and Bostrup do not state how their calculations of Δ and B' were carried out, and their spectral data for the pyridinium salt are rather similar to our observations on the tetramethylammonium compound. It is therefore difficult to draw firm conclusions from the trend in the figures.

Discussion.—The magnetic moment of a nickel ion in an octahedral environment is expected to be independent of temperature provided the compound is magnetically dilute. Even in tetragonally distorted complexes, where the spin degeneracy of the ground-state is raised by spin–orbit coupling,[15] temperature-dependence of the magnetic moment is expected only at temperatures comparable with δ (cm.$^{-1}$), the splitting of the ground state. For dichlorodipyridinenickel(II), δ would be about 9 cm.$^{-1}$, and the other compounds we have studied should have smaller splittings. No change in the magnetic moment should therefore be observable with temperature in the range of our measurements. This system is therefore well suited to studies of magnetic coupling between the metal ions. It seems probable that related compounds containing other metal ions such as cobalt(II) would also show magnetic interactions, though, where the metal ion has an orbital triplet ground-state,

[12] Tsubokawa, *J. Phys. Soc. Japan*, 1960, **15**, 2109.
[13] Asmussen and Soling, *Z. anorg. Chem.*, 1956, **283**, 3.
[14] Wells, " Structural Inorganic Chemistry," Oxford University Press, London, 1962, p. 376.
[15] Figgis, *Trans. Faraday Soc.*, 1960, **56**, 1553.

these would be difficult to observe. There is also no reason to suppose that they would always be of a ferromagnetic nature, since the sign of the interaction will depend on the number of d-electrons. In particular, in manganese(II), where the $^6A_{1g}$ ground-state should permit detection of magnetic coupling, it is likely to be antiferromagnetic.[16]

Both the magnetic and the spectral studies indicate that benzimidazole is very similar to pyridine as a ligand, suggesting that it co-ordinates through its tertiary nitrogen atom in these compounds. The Δ values for analogous pyridine and benzimidazole complexes are very similar, whilst the quinoline compounds have lower values. On the other hand, the values of the Racah interelectronic repulsion parameter (B') are lowest for the benzimidazole complexes, suggesting that these have the most covalent character in the ligand–metal bonding.

EXPERIMENTAL

The preparations of dichlorodiquinolinenickel(II) [3] and tetramethylammoniumtrichloro-nickelate(II) [17] have been described previously. Where several samples of a compound were prepared, the analyses quoted are for one sample only. The other samples had comparable analyses.

Physical measurements were carried out as described previously.[18]

Dichlorodipyridinenickel(II).—A solution of pyridine (1·2 g.) in ethanol (5 ml.) was added to a solution of nickel chloride hexahydrate (3·55 g.) in ethanol (20 ml.) The heavy, pale yellow-green precipitate, which formed with evolution of heat, was filtered off, washed with ethanol containing a small amount of pyridine, and dried *in vacuo*; yield 60% (Found: C, 41·6; H, 3·6; Cl, 24·4; Ni, 20·2. Calc. for $C_{10}H_{10}Cl_2N_2Ni$: C, 41·9; H, 3·5; Cl, 24·4; Ni, 20·4%).

Dibromodipyridinenickel(II).—This was prepared as described by King, Körös, and Nelson [2] (Found: C, 31·5; H, 2·8; Br, 42·1; Ni, 15·3. Calc. for $C_{10}H_{10}Br_2N_2Ni$: C, 31·9; H, 2·7; Br, 42·4; Ni, 15·6%).

Dichloro(pyridine)nickel(II).—Dichlorodipyridinenickel(II) was heated at 120° to constant weight (weight loss, 27·5; calc., 27·5%) (Found: C, 28·6; H, 2·4; Ni, 28·2. Calc. for $C_5H_5Cl_2NNi$: C, 28·8; H, 2·4; Ni, 28·2%).

Dichloro(quinoline)nickel(II).—Dichlorodiquinolinenickel(II) was heated at 120° to constant weight (weight loss, 33·1; calc., 33·4%) (Found: C, 42·0; H, 2·6; Ni, 22·7. Calc. for $C_9H_7Cl_2NNi$: C, 41·75; H, 2·7; Ni, 22·7%).

Dibromo(quinoline)nickel(II).—Dibromodiquinolinenickel(II) was heated at 100° to constant weight (weight loss, 27·1; calc., 27·1%), to give the *product* (Found: C, 31·0; H, 2·1; Br, 46·05; Ni, 16·9. $C_9H_7Br_2NNi$ requires C, 31·1; H, 2·0; Br, 46·0; Ni, 16·9%).

Dichloro(benzimidazole)nickel(II).—A solution of nickel chloride hexahydrate (4·75 g.) and benzimidazole (2·35 g.) in ethanol (15 ml.) was evaporated to dryness. The yellow *solid* was thoroughly washed with ethanol and acetone, and dried at 120°; yield 69% (Found: C, 34·45; H, 2·4; Cl, 28·5; Ni, 23·6. $C_7H_6Cl_2N_2Ni$ requires C, 34·0; H, 2·5; Cl, 28·7; Ni, 23·7%).

Dibromo(benzimidazole)nickel(II).—This was prepared by a method analogous to that used for dichloro(benzimidazole)nickel(II). The pinkish orange *solid* was obtained in 65% yield (Found: C, 24·7; H, 1·9; Br, 47·7; Ni, 17·4. $C_7H_6Br_2N_2Ni$ requires C, 25·0; H, 1·8; Br, 47·45; Ni, 17·4%).

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[16] Goodenough, " Magnetism and the Chemical Bond," Interscience, New York, 1963, p. 180.
[17] Cotton, Faut, and Goodgame, *J. Amer. Chem. Soc.*, 1961, **83**, 344.
[18] Forster and Goodgame, *J.*, 1964, 2790.