98. *Diamine Complexes of Nickel*(II). *Part I. Complexes with* NN-*Diethylethylenediamine.*

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The preparation and properties are described of 15 complexes of the type $Ni(Et_2N{\cdot}[CH_2]_2{\cdot}NH_2)_2X_2$ and of 4 similar corresponding dihydrates. Their magnetic, electrolytic-conductance, and electronic-spectral properties are reported. The results indicate that the ligand fields in these complexes are tetragonal. When X = BPh_4, BF_4, ClO_4, I, Br, or NO_3 the axial perturbation, due to X, of the planar ligand field generated by the diamine molecules is sufficiently weak to permit a singlet ground state for the nickel(II) ion. The other complexes are paramagnetic. Some infrared absorption data are given for the compounds where X = NCS, NO_2, and $\frac{1}{2}SO_4$, and for the compound $Ni[Et_2N{\cdot}(CH_2)_2{\cdot}NH_2],(NCS)_2$, for which a polymeric structure is suggested. The role of the water molecules in the hydrates is discussed.

NICKEL(II) forms with diamines numerous complexes of the type $Ni(diamine)_2X_2$, X = an anion, which either are diamagnetic or have magnetic moments of ~3 Bohr magnetons at room temperature. Changes from paramagnetism to diamagnetism and *vice versa* are often brought about by apparently trivial changes in the diamine or anion, and, in some cases, a paramagnetic and a diamagnetic form of the same compound can be isolated.[1]

Maki,[2] and Ballhausen and Liehr,[3] using the weak-field and the strong-field approach, respectively, have calculated the effect on the electronic energy levels of applying axial ligand-field perturbations to planar nickel(II) complexes. The relative energies of the lowest singlet and the lowest triplet state, and therefore the magnetic behaviour, are affected both by a change in the in-plane ligand field and by an axial perturbation of it. An increase in the axial component of the ligand field of a diamagnetic complex reduces the energy of the lowest triplet state relative to the singlet ground state, and eventually leads to the formation of a triplet ground state, with consequent paramagnetism. Such axial perturbations may be due to: (i) solvation, either in co-ordinating solvents,[4] or in solid disolvates; [5] (ii) polymerisation of apparently four-co-ordinate complexes, in the solid state [6] or in relatively non-co-ordinating solvents; [4] (iii) perturbation by the anions X in a complex of the type NiL_4X_2, where L_4 represents the planar field produced by four neutral, but not necessarily identical, ligands.

The magnetic behaviour of the diamine complexes $Ni(diamine)_2X_2$, referred to above, suggests that they are examples of class (iii) axial perturbation. Since these compounds may be obtained with a wide range of both nickel salts and diamines, we considered that a systematic study of their magnetic, electronic-spectral, and other physical properties would be of value in determining the factors influencing the formation of either a singlet or a triplet ground state in tetragonal nickel(II) complexes. We report here the results of such studies for *NN*-diethylethylenediamine, $Et_2N{\cdot}[CH_2]_2{\cdot}NH_2$, represented as Y below.

Nickel(II) complexes of this diamine were first reported by Mann,[7] who isolated violet-blue $NiY_2(NCS)_2$, apricot-coloured $NiY_2(PtCl_6)$, a pale blue (+)-camphor-β-sulphonate and (+)-α-bromocamphor-π-sulphonate and deep olive-green $NiY[(+)\text{-camphornitronate}]_2$. Mann found no evidence of geometrical or optical isomerism. Glaser and Pfeiffer [8] also obtained $NiY_2(NCS)_2$, as well as orange $NiY_2(ClO_4)_2$ and green $NiY(NCS)_2$.

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[1] (*a*) Lifschitz, Bos, and Dijkema, *Z. anorg. Chem.*, 1939, **242**, 97; (*b*) Lifschitz and Bos, *Rec. Trav. chim.*, 1940, **59**, 407; (*c*) Hein and Müller, *Z. anorg. Chem.*, 1956, **283**, 172.

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

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

[4] Clark, Macvicar, and O'Brien, *Canad. J. Chem.*, 1962, **40**, 822, and references cited therein.

[5] Basolo and Matoush, *J. Amer. Chem. Soc.*, 1953, **75**, 5663.

[6] Bullen, Mason, and Pauling, *Nature*, 1961, **189**, 291.

[7] Mann, *J.*, 1927, 2904.

[8] Glaser and Pfeiffer, *J. prakt. Chem.*, 1939, **153**, 300.

The compounds prepared during the present study are listed in Table 1. Attempts to prepare compounds of the type NiY_3X_2 were unsuccessful even when X was a relatively non-co-ordinating anion such as ClO_4^-. The complexes exhibit good general chemical stability, although some are decomposed by water. The isolation of a dihydrate, $NiY_2F_2,2H_2O$, is of interest since such complexes of nickel fluoride are not well known. Hydrates are obtained only with the sulphate and the halide complexes, and the ease with which they are formed varies with the anion concerned. The fluoro-complex exists only as the dihydrate, and attempted dehydration causes decomposition. The chloro-complex is obtained from the ethanolic reaction solution as the dihydrate, which is dehydrated at ~80°. The first product in the case of nickel bromide is the anhydrous compound, which, however, readily takes up water in air. The iodo-complex shows no tendency to form a hydrate. The complexes of nickel acetate and nickel dichloroacetate are monomeric in nitrobenzene. The other complexes are insufficiently soluble in suitable solvents for molecular-weight studies.

TABLE 1.

			Magnetic data				Λ_m in $PhNO_2$ §	
Complex	Colour	M. p.	$10^6\chi_m$ (c.g.s.u.)	10^6D † (c.g.s.u.)	Temp. (°K)	μ ‡ (B.M.)	10^{-3}M	4×10^{-4}M
$[NiY_2](ClO_4)_2$	Orange	~265° *	—	—	291°	Diamag.	(*c*)	63
$[NiY_2](BF_4)_2$	Orange	~265 *	—	—	292	Diamag.	(*c*)	62
$[NiY_2](BPh_4)_2$	Orange	~150 *	—	—	294	Diamag.	46·4	53
$[NiY_2](NO_3)_2$	Orange	188—189	—	—	294	Diamag.	8·0	12·4
$[NiY_2F_2],2H_2O$	Blue	86	(*b*)	(*b*)	(*b*)	(*b*)	1·6	(*b*)
$[NiY_2Cl_2],2H_2O$	Blue	(*a*)	4534	274	292	3·27	2·3	(*b*)
$[NiY_2Cl_2]$	Green	186—191 *	4588	248	292	3·29	2·2	(*b*)
$[NiY_2Br_2],2H_2O$	Blue	(*a*)	4486	296	292	3·25	(*c*)	12·4
$[NiY_2Br_2]$	Orange	~216 *	—	—	293·5	Diamag.	(*c*)	11·0
$[NiY_2I_2]$	Red	~225	—	—	293·5	Diamag.	(*c*)	26·0 (*d*)
$[NiY_2(CH_3{\cdot}CO_2)_2]$ ...	Blue	106	4273	263	292	3·18	1·0	(*b*)
$[NiY_2(CHCl_2{\cdot}CO_2)_2]$ ...	Blue	164—165	4279	319	292	3·18	1·4	(*b*)
$[NiY_2(CCl_3{\cdot}CO_2)_2]$ ...	Blue	126—127 *	4607	347	292	3·29	2·1	(*c*)
$[NiY_2(CF_3{\cdot}CO_2)_2]$	Blue	207—208	4191	271	292	3·14	1·9	(*b*)
$[NiY_2(CBr_3{\cdot}CO_2)_2]$ ...	Blue	103—104 *	(*b*)	(*b*)	(*b*)	(*b*)	2·8	(*b*)
$[NiY_2(CHPh_2{\cdot}CO_2)_2]$	Blue	154	4409	449	293	3·23	0·3	(*b*)
$[NiY_2(NO_2)_2]$	Blue	131—132	4337	217	292	3·20	2·2	(*b*)
$[NiY_2(NCS)_2]$	Violet	206—207	4373	263	291	3·20	1·9	(*b*)
$NiY(NCS)_2$	Green	222	4399	169	292	3·22	(*c*)	(*b*)
$NiY_2(SO_4),2H_2O$	Blue	~220 *	3937	267	292·5	3·04	1·3	(*b*)

(*a*) Loses water at ~80° and is converted into the corresponding anhydrous compound. (*b*) Not measured. (*c*) Insufficiently sol. (*d*) Concn. $2·5 \times 10^{-4}$M.

* With decomp. † D = diamagnetic correction. ‡ Calc. from $\mu = 2·84(\chi_m T)^{\frac{1}{2}}$. § Molar electrolytic conductance (mho) at room temperature.

Magnetic Measurements.—The magnetic data for the complexes are shown in Table 1. Complexes with anions of negligible or low co-ordinating ability are diamagnetic, while those with anions of medium to good co-ordinating power have, with the exception of the nickel sulphate complex, room temperature magnetic moments of 3·2 ± 0·1 B.M., which is the usual range for octahedral or weakly tetragonal nickel(II) complexes.

On either side of a singlet–triplet ground state " cross-over " point the energy separation between the lowest singlet and the lowest triplet state would have, over a small range, values comparable with thermal energies, in which case magnetic moments of 0—~3 B.M. might be obtained. While planar inner-complexes of nickel(II) often yield solutions with magnetic moments of 0—~3 B.M.,[4] this type of behaviour can be attributed to solvation and/or polymerisation rather than to the thermal regulation of singlet–triplet distribution. It appears that, so far, no unambiguous example of anomalous magnetism due to thermal population of closely separated singlet and triplet states has been observed for solid nickel(II) complexes. Harris, Lenzer, and Martin[9] recently isolated forms of di-(2-hydroxyacetophenone imine)nickel(II), its *N*-methyl analogue, and di-(2-hydroxyacetophenone oxime)nickel(II), with magnetic moments from 1·3—1·6 B.M. at ~80°K to 2·5—3·0 B.M. at 350°K. However, they concluded that their results indicated the presence of tetrahedral nickel(II) species rather than tetragonal complexes with small energy separations between the lowest singlet and the lowest triplet level, although the latter possibility was not excluded. The lack of this type of anomalous magnetism for solid nickel(II) complexes is not surprising since the critical singlet–triplet separation is quite small ($kT = 205$ cm.$^{-1}$ at 295°K). However, thermal equilibrium between doublet and quartet states has been proposed to account for the variation with temperature of the magnetic moment of di-(2,6-diformylpyridine dihydrazone)cobalt(II) iodide.[10] No " intermediate " magnetic moments at room temperature were observed for the nickel(II) complexes with our diamine. The magnetic cross-over occurs, apparently quite abruptly, between NiY_2Cl_2, $\mu = 3{\cdot}29$ B.M., and diamagnetic NiY_2Br_2. Thus, with the chloro-complex the triplet ground state lies too far below the lowest singlet state for thermal population of the latter to occur at room temperature, whereas the apparently small change of replacing chloride by bromide ions weakens the axial component of the ligand field sufficiently to bring the singlet ground state well below the lowest triplet level. In this respect, there is interest in the comparatively small differences between the values of the ligand field parameter Δ (or $10Dq$) for nickel(II) octahedrally co-ordinated by chloride, $\Delta \approx 7100$ cm.$^{-1}$, and by bromide, $\Delta \approx 6900$ cm.$^{-1}$.[11] However, direct comparison of the Δ values of the anions is instructive only if the in-plane field remains constant. It is possible that the formation of a vacant 3*d*-orbital ($d_{x^2-y^2}$) on passing from a paramagnetic to a diamagnetic complex will enhance the in-plane field in the diamagnetic case compared with the paramagnetic case to an extent such that a Boltzmann distribution between singlet levels and triplet levels is precluded.

The magnetic data thus merely divide the complexes into two groups, those with singlet ground states, and those with triplet ground states, but provide no measure of the relative ligand field tetragonality of complexes within each of these two main classifications.

Electrolytic Conductance Measurements.—Solvents which are sufficiently polar to act as ionising media, *e.g.*, nitrobenzene or nitromethane, possess some co-ordinating power, and solutions in these solvents of tetragonal complexes with labile metal–anion bonds will exhibit equilibria of the type:

$$[NiL_4X_2] + 2S \rightleftharpoons [NiL_4S_2]^{2+} + 2X^- \quad \text{(where S = solvent)}$$

The results of the electrolytic conductance measurements in nitrobenzene (Table 1) may be compared with the well-established values[12] of 20—30 mho for uni-univalent electrolytes and 40—60 mho for bi-univalent electrolytes under similar conditions. On the basis of these results, the complexes may be divided into three main classes: (*a*) the paramagnetic complexes have molar conductances of ~2 mho and may therefore be classed as " non-electrolytes," with the solvation equilibria lying well to the left-hand side; (*b*) the diamagnetic complexes with anions of negligible co-ordinating ability, ClO_4^-, BF_4^-, and BPh_4^-, are virtually completely dissociated as bi-univalent electrolytes under these conditions; (*c*) the diamagnetic complexes with Br^-, I^-, and NO_3^-, where $\Lambda_m = 8$—26 mho, may be termed " intermediate electrolytes." The last series is, therefore, almost certainly tetragonal rather than planar in the solid state, *i.e.*, better represented as $[NiL_4X_2]$ than as $[NiL_4]X_2$, but with quite labile Ni–X bonds, with the order of lability $I^- > Br^- \sim NO_3^-$.

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[9] Harris, Lenzer, and Martin, *Austral. J. Chem.*, 1961, **14**, 420.

[10] Stoufer, Busch, and Hadley, *J. Amer. Chem. Soc.*, 1961, **83**, 3732.

[11] Asmussen and Bostrup, *Acta Chem. Scand.*, 1957, **11**, 745.

[12] Nyholm and his co-workers, *J.*, 1951, 38; 1956, 4375; 1959, 3997; Foss and Gibson, *J.*, 1949, 3063.

The conductances of the paramagnetic complexes are too small to provide a reliable assessment of their relative labilities, though they are all less labile than the diamagnetic compounds. This behaviour appears to parallel quite closely the extent of the tetragonality of the ligand fields indicated by the magnetic and spectral studies.

The electrolytic conductances of complexes from each of classes (*a*), (*b*), and (*c*) above were also determined in nitromethane and acetonitrile. Increasing donor capacity of the solvent should facilitate ionisation of the anionic ligands. Complexes which are weak electrolytes in nitrobenzene should give, in solvents of greater donor capacity, conductances which come nearer to those of full bi-univalent electrolytes. The results, some of which are given in Table 2, are in agreement with this, and suggest that the order of co-ordinating power of these solvents is $PhNO_2 < MeNO_2 < MeCN$.

Electronic Absorption Spectra.—The electronic absorption spectra of the complexes were studied in the visible and the near-infrared region, in solution and in the solid state (the ranges of study are listed in the Experimental section). The numerical results are shown in Table 3 and a selection of typical spectra in Figs. 1—3.

The spectra of the paramagnetic complexes will be considered first. All were studied

TABLE 2.

Values of molar conductance, Λ_m (mho), for 10^{-3}M-solutions.

	$PhNO_2$	$MeNO_2$	MeCN
$[NiY_2][BPh_4]_2$	46·4	140	234
$[NiY_2(NO_3)_2]$	8·0	75·6	179
$[NiY_2(CHCl_2{\cdot}CO_2)_2]$	1·4	21·1	60·5

TABLE 3.

Electronic absorption spectra of $Ni^{II}Y_2$ complexes.

Complex	State *	Absorption max. (cm.$^{-1}$) (ε_{molar} for solutions)
$[NiY_2](ClO_4)_2$	Solid, C_4Cl_6 mull	21,400
	$CH_3{\cdot}NO_2$ (0·02M)	21,400(66·5)
$[NiY_2](BF_4)_2$	Solid, C_4Cl_6 mull	21,300
	$CH_3{\cdot}NO_2$ (0·02M)	21,400(69·5)
$[NiY_2](BPh_4)_2$	Solid, C_4Cl_6 mull	20,700
$[NiY_2(NO_3)_2]$	Solid, C_4Cl_6 mull	21,400
$[NiY_2F_2],2H_2O$	Solid, reflectance	26,500, 15,900, $\sim$13,500sh
	$CH_3{\cdot}OH$ (0·01M)	26,000(17·1), 15,040(6·1), $\sim$13,500sh, 9654(4·9)
$[NiY_2Cl_2],2H_2O$	Solid, reflectance	26,880, 16,340
	$CH_3{\cdot}OH$ (0·01M)	25,060(24·0), $\sim$20,800sh, 14,790(9·1), 9524(5·1)
$[NiY_2Cl_2]$	Solid, reflectance	25,500, $\sim$23,500sh, 15,040, $\sim$13,200sh
	$CH_3{\cdot}OH$ (0·01M)	25,060(21·5), $\sim$20,800sh, 14,770(8·4), 9804(4·0)
$[NiY_2Br_2],2H_2O$	Solid, reflectance	26,320, 15,550
	$CH_3{\cdot}OH$ (0·006M)	24,400sh, 21,100(43·0), 14,810(7·4), 9090(4·8)
$[NiY_2Br_2]$	Solid, C_4Cl_6 mull	21,500
$[NiY_2I_2]$	Solid, C_4Cl_6 mull	21,200
$NiY_2SO_4,2H_2O$	Solid, reflectance	26,810, $\sim$21,700sh, 16,000, 13,330
	$CH_3{\cdot}OH$ (0·01M)	25,640(20·5), 15,270(9·1), 9240(7·4)
$[NiY_2(NCS)_2]$	Solid, reflectance	27,550, 17,480, $\sim$15,000sh
	CH_2Cl_2 (0·01M)	27,400(22·7), 17,180(8·5), 11,000(8·1), $\sim$9100sh
$NiY(NCS)_2$	Solid, reflectance	15,870
$[NiY_2(NO_2)_2]$	Solid, reflectance	$\sim$20,400sh, 16,890, $\sim$14,800sh
	CH_2Cl_2 (0·01M)	17,040(9·5), 9800(6·6)
$[NiY_2(CH_3{\cdot}CO_2)_2]$	Solid, reflectance	26,670, 16,340, $\sim$14,100sh
	CH_2Cl_2 (0·01M)	25,770(25·2), 15,430(11·2), 9090(9·2)
$[NiY_2(CHCl_2{\cdot}CO_2)_2]$	Solid, reflectance	26,740, 16,400, $\sim$15,000sh
	CH_2Cl_2 (0·01M)	26,670(10·0), 16,420(4·7), 10,000(5·1)
$[NiY_2(CCl_3{\cdot}CO_2)_2]$	Solid, reflectance	27,000, 16,260
	CH_2Cl_2 (0·01M)	26,670(12·8), 16,260(6·1), 9865(5·1)
$[NiY_2(CF_3{\cdot}CO_2)_2]$	Solid, reflectance	27,000, 16,250
	CH_2Cl_2 (0·01M)	26,810(10·7), 16,390(5·6), 10,000(4·9)
$[NiY_2(CHPh_2{\cdot}CO_2)_2]$	Solid, reflectance	26,810, 16,390, $\sim$14,600sh
	$CH_3{\cdot}OH$ (0·01M)	25,910(23·5), 15,400(8·6), 9260(8·3)
	CH_2Cl_2 (0·01M)	26,390(22·4), 16,000(11·1), 9590(7·9)

* C_4Cl_6 = Hexachlorobutadiene.

in the solid state by reflectance. Attempts were made to obtain transmission spectra of Nujol mulls, but the intensities of the absorption bands were generally too low for reliable determination of band positions. Dichloromethane was used as solvent wherever possible to minimise the likelihood of solvation. However, the nickel sulphate and the nickel halide complexes were only slightly soluble in this solvent and methanol was used for these. The compound $NiY(NCS)_2$ is insoluble in common organic solvents and its spectrum could be obtained only for the solid state.

The solution spectra of the chloro- and the hydrated bromo-complexes are discussed below. The spectra of these two compounds in the solid state and those of the other paramagnetic compounds, both as solids and in solution, show three main bands, one in each of the regions: 28,000—25,000 cm.$^{-1}$ (band I); 17,500—15,000 cm.$^{-1}$ (band II); and 11,000—9,000 cm.$^{-1}$ (band III) (see Figs.). Band I was obscured by charge-transfer absorption in the spectra of $NiY_2(NO_2)_2$ and $NiY(NCS)_2$. Band II usually shows, in the spectra of the solid compounds, either a shoulder or pronounced asymmetry towards lower energy. In the spectrum of the solid sulphato-complex a small band is clearly resolved on the low-energy side of band II. The spectra of the solid sulphato- and nitro-complexes each contain a shoulder between bands I and II. The presence of these weak bands is barely observable in the solution spectra, apart from a slight asymmetry of band II towards lower energy in some cases. However, the relative optical densities of bands in reflectance spectra are usually related only qualitatively to the true extinction coefficients of the bands in solution spectra, the normal effect being an apparent enhancement of the strengths of weak bands in the spectra of the solids. Band III was not observed completely in the reflectance spectra. Some asymmetry was often found for this band in the solution spectra, this being especially noticeable for $NiY_2(NCS)_2$. Apart from the disappearance of the weak bands or shoulders mentioned above, there were only small differences in band positions between the spectra of dichloromethane solutions and of the solid compounds. Somewhat larger changes were observed with methanol as solvent, but, except for the bromo- and the chloro-complexes, the main features of the spectra remained the same.

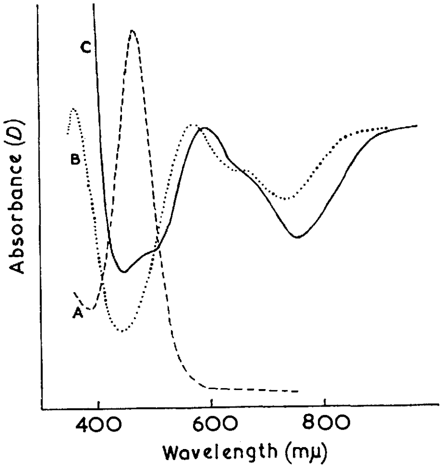

FIG. 1. Spectra of some solid nickel(II) complexes. A, $NiY_2(NO_3)_2$, C_4Cl_6 mull; B, $NiY_2(NCS)_2$, reflectance; C, $NiY_2(NO_2)_2$, reflectance.

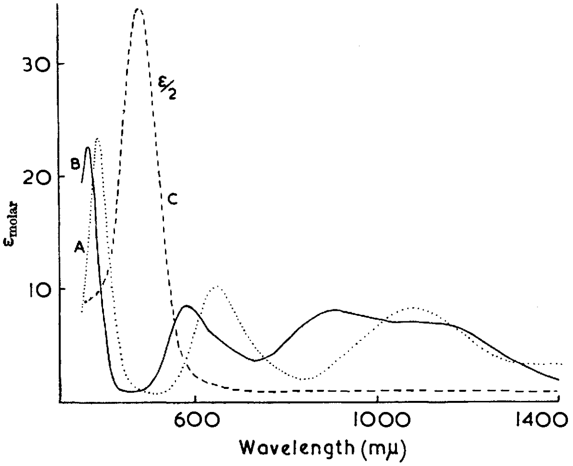

FIG. 2. Solution spectra. A, $NiY_2(CHPh_2{\cdot}CO_2)_2$, 0·01M in MeOH; B, $NiY_2(NCS)_2$, 0·01M in CH_2Cl_2; C, $NiY_2(BF_4)_2$, 0·02M in $MeNO_2$ (note change in ε_{molar} scale).

The theoretical work of Maki [2] has been used to interpret the spectra. Since our diamine has a tertiary and a primary amino-group, the in-plane field may be either *cis*

(C_{2v}) or *trans* (D_{2h}). It is to be expected that the *trans*-arrangement would be preferred, especially because of the steric requirements of the tertiary amino-groups. Although the in-plane field would thus be formally of D_{2h} symmetry, there is probably little difference between the ligand-field strengths of the two types of amino-groups and the spectra of these amine complexes might resemble those of similar complexes of D_{4h} symmetry. In accord with this, there is good agreement between the spectrum of dichlorodi-(*NN'*-diphenylethylenediamine)nickel(II) [2] and those of the complexes of our unsymmetrical diamine.

On the basis of D_{2h} symmetry, bands I, II, and III are assigned as the spin-allowed transitions ${}^3B_{3g} \longrightarrow {}^3B_{2g}$, ${}^3B_{3g} \longrightarrow {}^3B_{2g}$, and ${}^3B_{3g} \longrightarrow {}^3B_{1g}$, respectively. The weak band or shoulder on the low-energy side of band II and the asymmetry observed for band III probably correspond to spin-forbidden transitions from the ${}^3B_{3g}$ ground state to levels of ${}^1G$ and ${}^1D$ free-ion origin, which gain intensity by interaction, *via* spin-orbit coupling, with triplet states. If the symmetry of the in-plane field is effectively D_{4h} then the assignments become: I, ${}^3B_{2g} \longrightarrow {}^3A_{2g}$; II, ${}^3B_{2g} \longrightarrow {}^3E_g$; III, probably a composite band due to ${}^3B_{2g} \longrightarrow {}^3B_{1g}$ and ${}^3B_{2g} \longrightarrow {}^3A_{2g}$.

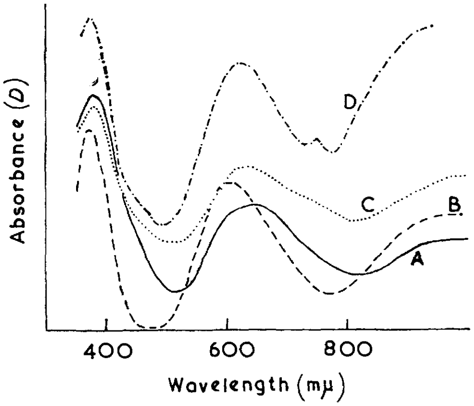

FIG. 3. Reflectance spectra of the hydrates. A. $NiY_2Br_2,2H_2O$; B, $NiY_2Cl_2,2H_2O$; C, $NiY_2F_2,2H_2O$; D, $NiY_2SO_4,2H_2O$.

A measure of the ligand-field tetragonality of $Ni(diamine)_2X_2$ may be obtained from the relative positions of X and the diamine in the spectrochemical series.[13] Since $[NiY_3]^{2+}$ could not be prepared, direct determination of the Δ value of the diamine could not be made, but it is probably close to that of ethylenediamine. The infrared spectra (see below) of $NiY_2(NCS)_2$ and $NiY_2(NO_2)_2$ indicate that the anions are co-ordinated through nitrogen. Of those anions studied in the present work, *N*-bonded thiocyanate and nitrite groups lie closest to the diamine in the spectrochemical series. It is, therefore, of interest to consider how well assignments of the electronic absorption spectra of these two compounds can be made on the basis of the calculations of Liehr and Ballhausen [14] for nickel(II) complexes of O_h symmetry.

With the isothiocyanato-complex the presence of two components for band III, at 11,000 and ~9,100 cm.$^{-1}$, indicates deviation from O_h symmetry. A splitting of about 2000 cm.$^{-1}$ for ${}^3A_{2g} \longrightarrow {}^3T_{2g}(F)$ is not satisfactorily accounted for by spin-orbit coupling, for the energy spread of the ${}^3T_{2g}$ multiplet is only 500—600 cm.$^{-1}$.[14] Moreover, the weaker component of band III, the shoulder at ~9100 cm.$^{-1}$, is not due to the spin-forbidden transition ${}^3A_{2g} \longrightarrow {}^1E_g(D)$ since, for ${}^3A_{2g} \longrightarrow {}^3T_{2g}$ of 11,000 cm.$^{-1}$, this should occur at higher energy (~12,500 cm.$^{-1}$) rather than at lower energy. The shoulder at ~15,000 cm.$^{-1}$ in the spectrum of the solid compound cannot be assigned satisfactorily for O_h symmetry if the band at 17,480 cm.$^{-1}$ is due to ${}^3A_{2g} \longrightarrow {}^3T_{1g}(F)$.

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[13] " Modern Co-ordination Chemistry," eds. Lewis and Wilkins, Interscience Publ., Inc., New York, 1960, p. 266.

[14] Liehr and Ballhausen, *Ann. Phys.*, 1959, **6**, 134.

In Table 4 the experimental data for the nitro-complex are compared with those calculated for O_h symmetry, with $\Delta = 10{,}000$ cm.$^{-1}$. There is reasonable agreement for the two spin-allowed bands of lowest energy but no confirmation could be made by means of the third [$^3A_{2g} \longrightarrow {}^3T_{1g}(P)$], and there is very poor agreement for the lowest spin-forbidden transition. Moreover, a Δ value of 10,000 cm.$^{-1}$ would be unexpected, in view of the values of 11,000 cm.$^{-1}$ for $[Ni(NH_3)_6]^{2+}$ and ~11,500 cm.$^{-1}$ for $[Ni\,en_3]^{2+}$. Thus the tetragonality of the ligand field is sufficiently pronounced to be apparent in the electronic absorption spectra when the anion is NCS^- or NO_2^-, as well as with anions which lie towards the weaker end of the spectrochemical series.

TABLE 4.

Comparison of observed energies of absorption bands of $[NiY_2(NO_2)_2]$ with the theoretical values for O_h symmetry with $\Delta = 10{,}000$ cm.$^{-1}$.

Transition	Theoretical *	Observed	Transition	Theoretical *	Observed
$^3A_{2g} \longrightarrow {}^3T_{2g}$	9750—10,250	9800 †	$^3A_{2g} \longrightarrow {}^1A_{1g}(G)$	21,000	~20,400 ‡
$^3A_{2g} \longrightarrow {}^1E_g(D)$	12,800	~14,800 ‡	$^3A_{2g} \longrightarrow {}^1T_{2g}(D)$	22,000	—
$^3A_{2g} \longrightarrow {}^3T_{1g}(F)$	15,500—16,500	16,890 ‡	$^3A_{2g} \longrightarrow {}^3T_{1g}(P)$	26,500	§

* From ref. 14. † From solution spectrum. ‡ From reflectance spectrum. § Region hidden by absorption edge.

Transmission absorption spectra of the solid diamagnetic complexes, as hexachlorobutadiene mulls, showed one band at 20,700—21,500 cm.$^{-1}$, which may be assigned as $^1A_g \longrightarrow {}^1B_{3g}$ for D_{2h} symmetry, or $^1A_{1g} \longrightarrow {}^1A_{2g}$ for D_{4h} symmetry. Intense absorption at higher energy prevented detection of other singlet–singlet transitions expected in this region. The band energies for the solid diamagnetic complexes are not identical, although the differences cover a range of only 800 cm.$^{-1}$. This indicates that the electronic energy levels concerned are influenced by changes in the anion, and points to differing nickel-anion interactions in the solid compounds. For Br^-, I^-, and NO_3^-, weak co-ordination is indicated by the electrolytic conductance data. The perchlorate ion can co-ordinate although its ability to do so is very small.[15] However, the infrared spectrum of $NiY_2(ClO_4)_2$ contains no bands indicative of co-ordinated perchlorate.[15] It appears, therefore, that any nickel-anion interactions in our diamine complexes with ClO_4^-, BF_4^-, and BPh_4^- are of an electrostatic nature.

Studies of solution spectra of the diamagnetic complexes were limited by solubility to the perchlorate and tetrafluoroborate, which gave yellow solutions in nitromethane, with spectra characteristic of nickel(II) with singlet ground state. These results, and the electrolytic conductance data, indicate that $[NiY_2(MeNO_2)_2]^{2+}$ ions are probably present, with the axial perturbation due to the solvent molecules insufficient to cause the formation of a triplet ground state.

The bromo- and the chloro-complexes in methanol show spectral bands characteristic both of paramagnetic and of diamagnetic nickel(II). This has been observed with some other diamine complexes of nickel(II), and is being studied further.

Infrared Absorption Spectra.—We shall discuss here the spectra of only the sulphate, thiocyanate, and nitrite complexes. Further results will be reported later, with the results for nickel(II) complexes with other diamines.

The main relevant feature of the spectrum of $NiY_2SO_4,2H_2O$ is a broad, very strong band at 1000—1175 cm.$^{-1}$, which probably consists of at least two, and probably three, strong components. This indicates that the sulphate groups are co-ordinated,[16] in agreement with the electrolytic conductance data. However, the breadth and the lack of resolution of the absorption, which are doubtless caused by hydrogen bonding between

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[15] Hathaway and Underhill, *J.*, 1961, 3091; Barker, Harris, and McKenzie, *Proc. Chem. Soc.*, 1961, 335.

[16] Nakamoto, Fujita, Tanaka, and Kobayashi, *J. Amer. Chem. Soc.*, 1957, **79**, 4904.

the sulphate groups and the water molecules, preclude a more detailed interpretation of the spectrum. Attempts to dehydrate the complex caused decomposition.

Thiocyanate ion has three infrared-active fundamental modes: the C–N stretch ν_1, the NCS bend ν_2, and the C–S stretch ν_3. Co-ordinated thiocyanate can be attached to the metal by either nitrogen (isothiocyanato) or sulphur (thiocyanato), or can function as a bridging group. Infrared studies of " thiocyanate " complexes have shown that the frequencies of ν_3,[17-19] ν_2 [18] and its first overtone,[18] and also, to some extent, ν_1 [17,18,20] may be used to determine the way in which the " thiocyanate " groups are co-ordinated.

The infrared spectrum of $NiY_2(NCS)_2$ indicates that isothiocyanate groups are present. The strong band at 2092 cm.$^{-1}$ (see Table 5) is in the usual range for the C–N stretching frequencies of isothiocyanates. The shoulder at 2050 cm.$^{-1}$ in the mull spectrum may be attributed to crystal effects, since it is absent in the solution spectrum. The C–S stretching frequency could not be distinguished with certainty from bands due to the diamine Y. A weak band at 784 cm.$^{-1}$ for the chloro-complex is replaced by a medium-strong one at 787 cm.$^{-1}$, with a shoulder at 791 cm.$^{-1}$, when the anion is NCS^-. It is probable that the band due to the C–S stretch, which is usually quite weak,[18] is hidden by a diamine band. However, a C–S stretching frequency of ~790 cm.$^{-1}$ is in agreement with *N*-bonding. The first overtone of the NCS bending mode was observed as a medium-weak, broad band at 960 cm.$^{-1}$, with a very weak band at 945 cm.$^{-1}$. Two bands in this region have been reported for complexes containing ionic thiocyanate,[17b] but, except for $K_3Mo(NCS)_6,CH_3{\cdot}CO_2H,H_2O$, the overtone of the NCS bending mode in isothiocyanates has been observed only as a single, broad band.[18] Sulphur-bonded thiocyanate groups usually show more than two bands, and these at lower frequencies.[18] Attempts to examine the low-energy isothiocyanate bands in solution were unsuccessful, because of the limited solubility of the compound in suitable solvents.

TABLE 5.

Infrared data.

Complex	State *	Bands (cm.$^{-1}$) due to anions
$NiY_2(NCS)_2$	M	2092s, 2050sh, 960mw,br, 945vw, 790ms †
	S	2087s
$NiY(NCS)_2$	M	2136sh, 2125s, 2096s, 2077s, 968w, 948w, 807w, 750sh
$NiY_2(NO_2)_2$	M	1364s, 1170sh, 1161s, 824s,sp

* M = Mull; S = solution. † Band possibly due to the diamine (see text).

The formation of a complex $NiY(NCS)_2$, observed by Glaser and Pfeiffer,[8] has been confirmed. The magnetic and visible spectral data show that the compound has a distorted octahedral structure. Polymerisation to give this arrangement is in accord with the insolubility of the compound in all common organic solvents. Thiocyanate bridges are indicated by the infrared spectrum of the solid, with three bands and a pronounced shoulder in the C–N stretching region, and two weak bands in the region of the NCS bending overtone. A weak, sharp band at 807 cm.$^{-1}$ and a pronounced shoulder at 750 cm.$^{-1}$ do not appear in the spectrum of $[NiY_2Cl_2]$, and may be assigned as C–S stretching frequencies. This suggests that both terminal and bridging " thiocyanate " groups are present; however, crystal effects could not be checked.

The very sharp, strong band at 824 cm.$^{-1}$ in the spectrum of $[NiY_2(NO_2)_2]$ may be assigned as ν_2, the symmetric NO_2 bend, and shows that the compound contains nitro-, rather than nitrito-groups.[21] Since but one strong band is observed in this region the

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[17] (*a*) Chamberlain and Bailar, *J. Amer. Chem. Soc.*, 1959, **81**, 6412; (*b*) Baldwin, *J.*, 1961, 471.

[18] Lewis, Nyholm, and Smith, *J.*, 1961, 4590.

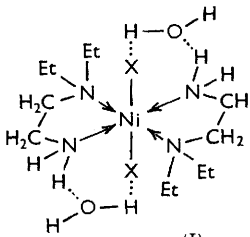
[19] Cotton, Goodgame, Goodgame, and Sacco, *J. Amer. Chem. Soc.*, 1961, **83**, 4157.

[20] Chatt and Duncanson, *Nature*, 1956, **178**, 997; Fujita, Nakamoto, and Kobayashi, *J. Amer. Chem. Soc.*, 1956, **78**, 3296; Mitchell and Williams, *J.*, 1960, 1912.

[21] Penland, Lane, and Quagliano, *J. Amer. Chem. Soc.*, 1956, **78**, 887.

anions are in *trans*-positions.[22] The remaining infrared-active vibrations of the co-ordinated nitro-groups, *viz.*, the antisymmetric and the symmetric N–O stretches (ν_3 and ν_1, respectively), should be observed,[22] as strong bands, in the following regions: ν_3, 1419 ± 16; ν_1, 1334 ± 14 and 1312 ± 7 cm.$^{-1}$. All bands in these regions in the spectrum of $NiY_2(NO_2)_2$ were also present in the spectrum of the chloro-complex. However, strong bands were found at 1364 and 1161 cm.$^{-1}$, with a shoulder at 1170 cm.$^{-1}$. Further studies of the infrared spectra of complexes of the type $[Ni(diamine)_2(NO_2)_2]$ are being undertaken.

Hydrates.—During the present investigation four hydrates, $[NiY_2X_2],2H_2O$, were obtained (see Table 1). These can be formulated as (A) $[NiY_2(H_2O)_2]X_2$ or (B) $[NiY_2X_2],2H_2O$. The complexes of type A contain the same complex cation irrespective of the anionic ligand X. However, measurements of the electronic absorption spectra of these complexes in the solid state in the region 350—1000 mμ show that the bands due to *d–d* transitions are shifted by a change of the anion X (see Fig. 3). Moreover, conductance measurements in nitrobenzene show that the fluoro-, chloro-, and sulphato-complexes are non-electrolytes, while the bromo-complex shows only a low molar conductance. These facts indicate that the complexes are of type B. On this assumption it is most likely that the water molecules are hydrogen-bonded as shown in (I). This formulation gives a satisfactory account of the following features: (1) in all cases two molecules of water of crystallisation are held; (2) the ease of dehydration increases in the order $F \sim SO_4 < Cl < Br$, and the iodo-derivative is anhydrous; (3) the infrared spectra all show a very broad region of absorption at 3100—3600 cm.$^{-1}$, as would be expected from the overlap of bands due to O–H and N–H, both free and hydrogen-bonded.



(I)

If the structural formula (I) is correct, the change in magnetic susceptibility observed on hydration of $[NiY_2Br_2]$ can be explained as follows: The formation of a six-membered ring by hydrogen bonding could result in an increase in the axial perturbation of the ligand field, with the formation of a triplet ground state. Dichlorobis-(*NN*-diethylethylenediamine)nickel(II) is paramagnetic; therefore any changes in the axial ligand field on hydration have no pronounced effect on the magnetic properties, although the electronic absorption spectra of the hydrated and the anhydrous forms show some differences (see Table 3). Conversely, both $Ni(1,2\text{-diphenylethylenediamine})_2Cl_2$ and its dihydrate are diamagnetic;[1a] evidently, with these two compounds an increase in the axial component of the ligand field by hydrogen bonding is insufficient to change the spin multiplicity of the ground state of the nickel(II) ion.

EXPERIMENTAL

Nickel salts which are not commercially available were prepared as follows.

Nickel Iodide.—Commercial nickel iodide was found to be practically insoluble in ethanol. Accordingly, solutions of nickel nitrate and sodium iodide in ethanol were mixed in 1 : 2 molar ratio, and the sodium nitrate was filtered off.

Nickel Thiocyanate and Tetraphenylborate.—These salts were prepared as was the iodide. The method was not completely satisfactory for nickel tetraphenylborate as this is only sparingly soluble in cold alcohol.

Nickel Nitrite.—This was prepared as was the iodide, but from methanolic solutions, cooled in acetone–solid carbon dioxide before filtration.

Nickel Salts with Chloro- and Fluoro-substituted Acetic Acids.—These were prepared by the action of nickel carbonate on an aqueous solution of the acid.

Nickel Tribromoacetate.—Attempts to prepare nickel tribromoacetate by the method described for the fluoro- and chloro-substituted acetic acids resulted in the formation of insoluble, basic products. Sodium tribromoacetate was therefore prepared by mixing equimolar

[22] Chatt, Duncanson, Gatehouse, Lewis, Nyholm, Tobe, Todd, and Venanzi, *J.*, 1959, 4073.

quantities of sodium hydroxide and tribromoacetic acid in ethanol. An ethanolic solution of the calculated quantity of nickel nitrate was added and the precipitated sodium nitrate filtered off.

Nickel Diphenylacetate.—This salt was prepared by the method described above for the tribromoacetate. The mixture was filtered hot; nickel diphenylacetate is practically insoluble in cold ethanol.

The preparation and some properties of the complexes are given below. M.p.s are given in Table 1.

Difluorobis-(NN*-diethylethylenediamine*)*nickel*(II) *Dihydrate.*—Finely powdered nickel fluoride (0·48 g.) and *NN*-diethylethylenediamine (0·96 g.) in ethanol (30 c.c.) were shaken for a week. The unchanged nickel fluoride was filtered off and the solution evaporated. The residue was extracted with hot ethyl acetate which, on cooling, yielded a blue solid. This was filtered off and dried *in vacuo* (yield, 0·15 g.). The *compound* is decomposed by water (Found: Ni, 15·9. $C_{12}H_{36}F_2N_4NiO_2$ requires Ni, 16·1%). Attempts to dehydrate the complex led to decomposition.

Dichlorobis-(NN*-diethylethylenediamine*)*nickel*(II) *Dihydrate.*—The diamine (3·84 g.) was added to a solution of nickel chloride (4·76 g.) in ethanol. The blue solid which immediately separated was recrystallised from butan-1-ol and air-dried (yield, 56%). The *compound* is decomposed by water (Found: Ni, 14·6; Cl, 17·6. $C_{12}H_{36}Cl_2N_4NiO_2$ requires Ni, 14·7; Cl, 17·8%).

Dichlorobis-(NN*-diethylethylenediamine*)*nickel*(II).—This was prepared by recrystallising the previous complex from ethanol and drying the product *in vacuo* over sulphuric acid for several days. The green anhydrous *compound* is reconverted into the blue dihydrate when kept in the atmosphere (Found: N, 15·75; Ni, 16·3; Cl, 19·4. $C_{12}H_{32}Cl_2N_4Ni$ requires N, 15·5; Ni, 16·2; Cl, 19·6%).

Dibromobis-(NN*-diethylethylenediamine*)*nickel*(II).—The diamine (1·68 g.) was added to a solution of nickel bromide (1·37 g.) in ethanol. An orange solid was immediately formed, which was filtered off, washed with ethanol, and dried *in vacuo* over sulphuric acid. During the filtration, the surface layer of product absorbed moisture from the atmosphere, becoming blue. However, after storage in the desiccator for several days, the *compound* was entirely orange (Found: Ni, 13·0; Br, 35·4. $C_{12}H_{32}Br_2N_4Ni$ requires Ni, 13·0; Br, 35·4%). The yield was practically quantitative. When the compound is heated, its colour deepens to red, this colour change being reversible. In the atmosphere it readily absorbed moisture and was converted into the blue dihydrate.

Dibromobis-(NN*-diethylethylenediamine*)*nickel*(II) *Dihydrate.*—This was prepared by placing a finely powdered sample of the anhydrous compound on a watch-glass over a beaker of water, for 2 days; there was then complete conversion into the blue form (Found: N, 11·3; Ni, 12·1; Br, 33·0. $C_{12}H_{36}Br_2N_4NiO_2$ requires N, 11·5; Ni, 12·05; Br, 32·8%). When heated, the *compound* loses water and is converted into the orange anhydrous complex. This was carried out quantitatively: Loss in weight: Found, 7·3. Calc. for loss of $2H_2O$, 7·4%.

Di-iodobis-(NN*-diethylethylenediamine*)*nickel*(II).—The diamine (3·36 g.) was added to an ethanolic solution of nickel iodide (3·12 g.), a red precipitate being formed which was filtered off and dried *in vacuo* (yield, 88%). The compound showed no tendency to absorb water from the atmosphere and no blue form was observed. The crude compound was recrystallised from tetrahydrofurfuryl alcohol (recovery 15%). When the compound was cooled in acetone/solid carbon dioxide the colour changed to pale yellow, but it reverted to red at room temperature. The *compound* is decomposed by water and when heated with ethyl methyl ketone or di-n-butyl ether (Found: N, 10·0; Ni, 10·8; I, 46·4. $C_{12}H_{32}I_2N_4Ni$ requires N, 10·3; Ni, 10·8; I, 46·6%).

Dinitratobis-(NN*-diethylethylenediamine*)*nickel*(II).—The diamine (1·92 g.) was added to a solution of nickel nitrate (2·91 g. in ethanol). A dark green solution was formed, which, overnight, yielded the orange crystalline *complex* (74%) (Found: C, 35·1; H, 7·5; Ni, 14·15. $C_{12}H_{32}N_6NiO_6$ requires C, 34·7; H, 7·8; Ni, 14·1%).

Bis-(NN*-diethylethylenediamine*)*nickel*(II) *Perchlorate.*—This was obtained in 74% yield analogously to the preceding complex. The orange solid was precipitated as soon as the diamine was added to the nickel perchlorate solution. The crude *compound* was recrystallised from nitromethane (recovery, 37%) (Found: C, 29·5; H, 6·6; Ni, 11·85. $C_{12}H_{32}Cl_2N_4NiO_8$ requires C, 29·4; H, 6·6; Ni, 12·0%). The compound becomes pale yellow on cooling, and red on heating. It is decomposed by water.

Bis-(NN-*diethylethylenediamine*)*nickel*(II) *Tetrafluoroborate*.—This was obtained in 68% yield by the method used for the corresponding complex of nickel perchlorate. The crude orange *compound* was recrystallised from nitromethane (recovery, 13%). It also becomes pale yellow on cooling and red on heating (Found: N, 12·1; Ni, 12·5. $C_{12}H_{32}B_2F_8N_4Ni$ requires N, 12·1; Ni, 12·6%).

Bis-(NN-*diethylethylenediamine*)*nickel*(II) *Tetraphenylborate*.—This orange *compound* was prepared, analogously to the previous complex, in 22% yield (Found: N, 6·1; Ni, 6·3. $C_{60}H_{72}B_2N_4Ni$ requires N, 6·0; Ni, 6·3%).

Sulphatobis-(NN-*diethylethylenediamine*)*nickel*(II) *Dihydrate*.—The diamine (3·36 g.) was added to a methanolic solution of nickel sulphate (2·63 g.). A blue-green solution was formed from which a blue solid gradually separated. The product was filtered off and dried *in vacuo* (yield, 87%). The *compound* is very labile and is readily decomposed by most solvents on heating (Found: Ni, 13·7. $C_{12}H_{36}N_4NiO_6S$ requires Ni, 13·9%).

Dinitrobis-(NN-*diethylethylenediamine*)*nickel*(II).—The diamine (1·92 g.) was added to a methanolic solution of nickel nitrite (1·03 g.). After a day, the deep blue-green solution was evaporated to dryness at the water-pump. The residual *complex* recrystallised from ethyl acetate as blue crystals in practically quantitative yield (Found: C, 37·8; H, 8·4; Ni, 15·3. $C_{12}H_{32}N_6NiO_4$ requires C, 37·6; H, 8·4; Ni, 15·3%).

Dithiocyanatobis-(NN-*diethylethylenediamine*)*nickel*(II).—This compound, which was first described by Mann,[7] was prepared as follows: the diamine (1·92 g.) was added to an ethanolic solution of nickel thiocyanate (1·75 g.). The violet solid, which was immediately precipitated, was filtered off and recrystallised from methanol as violet needles (Found: Ni, 14·4; SCN, 28·4. Calc. for $C_{14}H_{32}N_6NiS_2$: Ni, 14·4; SCN, 28·5%).

Dithiocyanato-NN-*diethylethylenediaminenickel*(II).—This green compound was prepared by the method of Glaser and Pfeiffer [8] (Found: Ni, 20·2; SCN, 39·9. Calc. for $C_8H_{16}N_4NiS_2$: Ni, 20·2; SCN, 39·9%).

Diacetatobis-(NN-*diethylethylenediamine*)*nickel*(II).—This was prepared analogously to the complex with nickel nitrite. The blue *compound* was recrystallised from ethyl acetate (yield, 51%). When finely powdered the compound is deliquescent (Found: N, 13·3; Ni, 14·2. $C_{16}H_{38}N_4NiO_4$ requires N, 13·7; Ni, 14·3%).

Bisdichloroacetatobis-(NN-*diethylethylenediamine*)*nickel*(II). —The diamine (1·92 g.) was added to an aqueous solution of nickel dichloroacetate (4·23 g.). The solid *complex* formed was filtered off, washed with water, dried *in vacuo*, and recrystallised from ethyl acetate as blue needles in 30% yield (Found: C, 35·6; H, 6·3; Ni, 10·6. $C_{16}H_{34}Cl_4N_4NiO_4$ requires C, 35·1; H, 6·3; Ni, 10·7%).

Bistrichloroacetatobis-(NN-*diethylethylenediamine*)*nickel*(II).—This was obtained in practically quantitative yield as for the previous complex. The crude solid was recrystallised from butan-1-ol, the recovery of the blue *compound* being 37% (Found: N, 8·7; Ni, 9·5. $C_{16}H_{32}Cl_6N_4NiO_4$ requires N, 9·1; Ni, 9·5%).

Bistrifluoroacetatobis-(NN-*diethylethylenediamine*)*nickel*(II) was also prepared by the method described above, forming blue needles (42%) from ethanol (Found: C, 37·7; H, 6·3; Ni, 11·3. $C_{16}H_{32}F_6N_4NiO_4$ requires C, 37·2; H, 6·2; Ni, 11·35%).

Bistribromoacetatobis-(NN-*diethylethylenediamine*)*nickel*(II).—The diamine (0·48 g.) was added to an ethanolic solution of nickel tribromoacetate (1·63 g.). A pale blue solid *complex* was immediately formed, which was filtered off, washed with a little ethanol, and dried *in vacuo* (yield quantitative) (Found: Ni, 6·7. $C_{16}H_{32}Br_6N_4NiO_4$ requires Ni, 6·65%).

Bisdiphenylacetatobis-(NN-*diethylethylenediamine*)*nickel*(II).—The diamine (2·88 g.) was added to a hot solution of nickel diphenylacetate (4·82 g.) in ethanol (75 c.c.). The blue-green solution was cooled in ice overnight; blue needles of the *complex* were formed. These were filtered off and dried *in vacuo* (yield, 71%) (Found: Ni, 8·15. $C_{40}H_{54}N_4NiO_4$ requires Ni, 8·2%).

Magnetic Susceptibility Measurements.—These were carried out at room temperature with a magnetic susceptibility balance of the Faraday type, similar to that described by Milligan and Whitehurst.[23] The measurements were carried out over a range of field strengths to test for ferromagnetic impurities. Diamagnetic corrections were calculated from Pascal's constants.[24]

Molecular-weight Determinations.—These were carried out cryoscopically in nitrobenzene

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[23] Milligan and Whitehurst, *Rev. Sci. Instr.*, 1952, **23**, 618.

[24] Ref. 13, p. 403.

by the standard Beckmann method: Found for $[NiY_2(CH_3{\cdot}CO_2)_2]$, *M*, 389 (calc., 409) (concn. 0·48%); Found for $[NiY_2(CHCl_2{\cdot}CO_2)_2]$, *M*, 563 (calc., 547) (concn. 0·737%).

Electrolytic Conductance.—These measurements were made with a conventional cell, previously calibrated with aqueous potassium chloride.

Electronic Absorption Spectra.—Solution spectra and mull spectra were obtained by using a Perkin-Elmer model 4000 recording spectrophotometer. Reflectance spectra were measured with a Unicam S.P. 500 spectrophotometer fitted with the standard reflectance accessory and with magnesium carbonate as a standard. The ranges of study were: Solid, by reflectance, 350—1000 mμ; solid, hexachlorobutadiene mull, 300—2300 mμ; nitromethane solutions, 370—2100 mμ; dichloromethane solutions, 350—2100 mμ.

Infrared Absorption Spectra.—These were recorded on a Perkin-Elmer 21 spectrophotometer, with calcium fluoride and sodium chloride prisms in the usual ranges. The relevant results are shown in Table 5.

We thank Miss C. E. Atkinson for the reflectance spectrum of one of the complexes. One of us (D. M. L. G.) thanks the Department of Scientific and Industrial Research for a Research Studentship at the University of Oxford, where most of the work was carried out.

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