1125. *Diamine Complexes of Nickel*(II). *Part II.*[1] *Complexes with* NN-*Dimethylethylenediamine.*

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Complexes of the type $Ni(R_2N{\cdot}[CH_2]_2{\cdot}NH_2)_2X_2$ (R = Me) and some corresponding hydrates have been prepared, and their magnetic, electrolytic-conductance, and electronic-spectral properties studied. When X = I, two diamagnetic isomers are formed. The position of the paramagnetic–diamagnetic change when R = Me differs from that when R = Et.[1] The reasons for this are discussed. A pronounced splitting of a band in the near-infrared region in the electronic spectra of the solid, paramagnetic complexes is reported, and a possible reason for this is suggested.

In a previous communication[1] we set out the reasons for our studies of the magnetic, electronic-spectral, and other physical properties of complexes of the type $Ni(diamine)_2X_2$ (X = an anion) and described the results for *NN*-diethylethylenediamine (represented below as a-dieen = *a*symmetrical-*die*thyl-*en*). We report here the results for *NN*-dimethylethylenediamine, $Me_2N{\cdot}[CH_2]_2{\cdot}NH_2$ (a-dimen).

The compounds we have isolated are listed in Table 1. Their stoicheiometry and general chemical behaviour resembles quite closely that of the a-dieen complexes. One striking difference, however, is the existence of two isomers of composition $Ni(a\text{-}dimen)_2I_2$. Dehydration of the blue dihydrate at room temperature gives an orange form, whereas a purple isomer is obtained by heating either the orange compound or the dihydrate to about 100°. Both isomers are very hygroscopic and rapidly revert to the dihydrate on exposure to the atmosphere. An unstable yellow compound was observed during the dehydration of the blue complex, $Ni(a\text{-}dimen)_2Br_2,2H_2O$, at room temperature, but conversion into the green anhydrous material occurred rapidly, and the yellow complex could not be isolated. The hygroscopic nature of both forms of the iodide $Ni(a\text{-}dimen)_2I_2$, and consequent formation of the dihydrate, contrasts with the behaviour of the a-dieen analogue, which forms no hydrate. Whereas the a-dieen complexes with the nickel halides are appreciably decomposed by water, the a-dimen complexes are much less labile (for example, the hydrated iodo-complex may be crystallised from water).

Table 1.

		Magnetic data			Λ_m ‡ (mho) in	
Complex	Colour	$10^6\chi_m$ * (c.g.s.u.)	Temp. (°K)	μ_{eff} † (B.M.)	$PhNO_2$	$MeNO_2$
$Ni(a\text{-}dimen)_2Cl_2$	Blue	4386	292	3·21	0·1	—
$Ni(a\text{-}dimen)_2Cl_2,H_2O$	Blue	3974	292	3·06	0·1	—
$Ni(a\text{-}dimen)_2Cl_2,4H_2O$	Blue	4448	290	3·23	0·1	—
$Ni(a\text{-}dimen)_2Br_2$	Green	4433	291	3·23	0·9	—
$Ni(a\text{-}dimen)_2Br_2,2H_2O$	Violet-blue	4329	291	3·19	0·9	—
$Ni(a\text{-}dimen)_2I_2$	Orange	Diamag.	289	—	§	78
$Ni(a\text{-}dimen)_2I_2$	Red-purple	Diamag.	285	—	§	75
$Ni(a\text{-}dimen)_2I_2,2H_2O$	Blue	4441	291	3·23	13·7	105
$Ni(a\text{-}dimen)_2(ClO_4)_2$	Orange	Diamag.	285	—	32·1	180
$Ni(a\text{-}dimen)_2(NO_3)_2$	Blue	4511	291	3·25	5·2	56
$Ni(a\text{-}dimen)_2(NCS)_2$	Violet	4286	291	3·17	0·2	5
$Ni(a\text{-}dimen)_2(CCl_3{\cdot}CO_2)_2$	Blue	4435	293	3·24	0·3	—
$Ni(a\text{-}dimen)_2(NO_2)_2$	Blue	4602	285	3·25	1·3	—

* Molar susceptibility corrected for diamagnetic contributions. † Calc. from $\mu_{eff} = 2{\cdot}84\,(\chi_m T)^{\frac{1}{2}}$.
‡ Molar electrolytic conductance at room temperature for 10^{-3}M-solns. § Insufficiently soluble.

Results of Physical Measurements.—Our previous studies[1] have shown that the electronic ground state, and thence the magnetic and electronic-spectral properties, of a complex $Ni(a\text{-}dieen)_2X_2$ depends upon the nature of the anion X. As may be seen from the magnetic

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[1] Part I, Goodgame and Venanzi, *J.*, 1963, 616.

TABLE 2.

Electronic absorption spectra of NiD_2X_2 (D = a-dimen).

Complex	State *	Absorption max. (cm.$^{-1}$) (ε_{molar} for solutions)
NiD_2Cl_2	Solid	26,100, $\sim$22,200sh, 16,000, 12,500, 9710
	$CH_3{\cdot}OH$	25,850 (13·8), 15,750 (7·5), 12,300 (1·8), 9390 (11·4)
NiD_2Cl_2,H_2O ...	Solid †	27,450‡, 16,950, $\sim$13,250sh, $\sim$11,400br
$NiD_2Cl_2,4H_2O$ ...	Solid	27,200, $\sim$25,300sh, 16,900, $\sim$13,250sh, 11,100, $\sim$8640sh
NiD_2Br_2	Solid †	24,800, $\sim$20,850sh, $\sim$19,600sh, 15,050, 11,950
	$CH_3{\cdot}OH$	25,600 (15·8), $\sim$21,750sh, $\sim$20,400sh, 15,550 (7·9), $\sim$12,100sh, 9260 (11·8)
$NiD_2Br_2,2H_2O$	Solid	27,550, $\sim$21,050sh, 17,200, 11450, $\sim$8570sh
NiD_2I_2, orange	Solid †	21,150
NiD_2I_2, purple	Solid †	20,100
	$CH_3{\cdot}OH$	$\sim$27,000sh, 21,050 (11·3), 16,000 (8·0), 9390 (10·2)
$NiD_2I_2,2H_2O$ ...	Solid †	27,050, 16,350, $\sim$12,650sh
$NiD_2(ClO_4)_2$ ...	Solid †	21,750
	$CH_3{\cdot}NO_2$ (*a*)	21,100 (41·1)
$NiD_2(NO_3)_2$	Solid	27,450‡, 16,950, 11,850, 7840
	CH_3NO_2	§, 16,600 (14·8), 10,000 (7·7)
$NiD_2(NCS)_2$ ...	Solid	27,450, $\sim$22,200sh, 17,250, $\sim$12,600sh, 10,400
$NiD_2(CCl_3{\cdot}CO_2)_2$	Solid	27,600‡, 16,650, 11,000, $\sim$8600sh
	$CHCl_3$	27,250 (7·9), 16,800 (5·1), $\sim$12,650sh, 9860 (6·9)br
$NiD_2(NO_2)_2$	Solid	27,250, 17,300, 10,950, $\sim$8740sh
	$CHCl_3$	(*b*), 20,300 (9·5), $\sim$17,250sh, 10,750 (6·8)
	$CH_3{\cdot}OH$	(*b*), $\sim$22,500sh, 16,400 (14·0), 11,000 (8·3)

* Solids by reflectance; solutions 0·01M. † Not measured $<$10,000 cm.$^{-1}$. ‡ Band asymmetric to low-energy side. § Region obscured by cut-off of solvent in the ultraviolet region. (*a*) 0·015M. (*b*) Region obscured by charge-transfer absorption.

data (Table 1) and the spectral data (Table 2), the a-dimen series behaves similarly. With both diamines, the chloro-complex and complexes with anions lying above the chloride ion in the spectrochemical series have room-temperature magnetic moments of $\sim$3·2 B.M. and electronic spectra characteristic of the nickel(II) ion with a spin-triplet ground state, whereas compounds with anions of negligible, or very low, co-ordinating ability, such as the perchlorate ion, are diamagnetic. However, the paramagnetic-diamagnetic cross-over points for the two series differ. With a-dieen, diamagnetic complexes are formed when X = I, Br, or NO_3, but with a-dimen the bromo- and nitrato-complexes are paramagnetic. The change in magnetism with change in anion is abrupt, and no anomalous magnetic behaviour in the solid state has been observed.

The electrolytic-conductance data for the a-dimen complexes (Table 1) follow the pattern previously found for the a-dieen series. The paramagnetic complexes, except for the nitrate, are virtually non-electrolytes in nitrobenzene. The perchlorate complex is a bi-univalent electrolyte in nitromethane, but there is some evidence for ion-pairing in nitrobenzene (10^{-3}M), since the value of $\Lambda_m = 32$ mhos is below the range normally found for fully dissociated complexes $M^{2+}2X^-$ under these conditions. Moreover, the dissociation increases on dilution, a more usual value of Λ_m being then found. In both nitrobenzene and nitromethane the iodo-complexes display " intermediate-electrolyte " behaviour similar to that found for the iodo-, bromo-, and nitrato-complexes with a-dieen.[1] Although the bromide $Ni(a\text{-dimen})_2Br_2$, which appears to be just on the paramagnetic side of the magnetic cross-over point, is essentially a non-electrolyte, the corresponding nitrato-complex, which is also paramagnetic, evidently contains fairly labile metal–anion bonds since nitrobenzene and nitromethane solutions show definite conductivity.

The electronic absorption spectra of the a-dimen complexes are generally similar to those of the a-dieen complexes. Since we have discussed the latter in some detail,[1] we shall mention here only those features which are new. The reflectance spectra of the isomers of the iodide $Ni(a\text{-dimen})_2I_2$ consist, in each case, of one band in the visible region (${}^1A_{1g} \longrightarrow {}^1A_{2g}$ in D_{4h} symmetry, ${}^1A_g \longrightarrow {}^1B_{3g}$ in D_{2h} symmetry [2]). The band for the purple

[2] Maki, *J. Chem. Phys.*, 1958, **28**, 651.

isomer (at 20,100 cm.$^{-1}$) lies ~1000 cm.$^{-1}$ lower in energy than that for the orange form (at 21,150 cm.$^{-1}$). Although quantitative comparison of the intensities of bands in reflectance spectra must be interpreted with caution, it may be mentioned that the optical density of the band for the purple isomer is almost twice that for the orange form. Both isomers are either insoluble in, or are decomposed by, most solvents. A solution may be obtained in methanol, but the spectrum (Table 2) contains bands characteristic of a mixture of paramagnetic and diamagnetic nickel(II). Similar behaviour is observed for the bromo-complex (Table 2), as well as for nickel(II) complexes with other diamines.[1,3] The paramagnetic components of methanol solutions of Ni(a-dimen)$_2$X$_2$, where X = Cl, Br, or I, have the following orders of band energies: visible band, I > Cl > Br; near-infrared band, I ~ Cl > Br. Were the paramagnetic component in each case of the type [Ni(a-dimen)$_2$X$_2$], the order expected would be Cl > Br > I. The observed order suggests that the paramagnetic component for the solution of the iodo-complex is [Ni(a-dimen)$_2$(MeOH)$_2$]$^{2+}$, since neutral oxygen donor atom ligands lie somewhat above the chloride ion in the spectrochemical series.[4] This is consistent both with the fact that in the solid state the bromo- and chloro-complexes are paramagnetic whereas the iodo-complex is diamagnetic, and with the results of the electrolytic-conductance studies.

The blue nitro-complex gives a reddish-purple solution in chloroform and a green-blue solution in methanol. The spectra of these solutions differ from the reflectance spectrum of the solid. The difference is more pronounced with the chloroform solution, the spectrum of which contains a band at 20,300 cm.$^{-1}$ not observed for the solid state. The spectrum of the methanol solution also contains an additional band, which appears as a shoulder (at ~22,500 cm.$^{-1}$) on the edge of a strong charge-transfer absorption in the ultraviolet region. In methanol there is also a shift in the position of the main visible band from 17,300 cm.$^{-1}$ in the solid to 16,400 cm.$^{-1}$ in solution. Analogous shifts were observed for the visible bands of the a-dieen–nickel(II) complexes in methanol as compared with the solid state or with dichloromethane solutions.[1] However, the compound Ni(a-dieen)$_2$(NO$_2$)$_2$ in dichloromethane showed no anomalous effects.

The spectra of the solid a-dimen and a-dieen complexes have been measured by the reflectance technique in the near-infrared region, down to 4000 cm.$^{-1}$. A selection of the experimental traces in this region is given in Figs. 1 and 2. Numerical data for bands considered to be due to *d–d* transitions are given in Tables 2 and 3. Bands due to overtones of vibrational modes were identified by comparison of the spectra of the paramagnetic complexes with the reflectance spectra of the diamagnetic compounds, and also with the transmission spectra of the pure diamines (1 mm. path-length). Nearly all the solution spectra show only one near-infrared *d–d* band, but in the majority of the reflectance spectra this band is split into two components. This will be further discussed below.

TABLE 3.

Reflectance spectra of some Ni^{II}(a-dieen)$_2$ complexes in the near-infrared region.

Complex	Absorption max. (cm.$^{-1}$) *	Complex	Absorption max. (cm.$^{-1}$) *
Ni(a-dieen)$_2$Cl$_2$	8700	Ni(a-dieen)$_2$(CHCl$_2$·CO$_3$)$_2$	10,100, ~7750sh
Ni(a-dieen)$_2$Cl$_2$,2H$_2$O	10,450, 7520	Ni(a-dieen)$_2$(CCl$_3$·CO$_2$)$_2$	9890, ~7550sh
Ni(a-dieen)$_2$(NO$_2$)$_2$	10,350, ~7870sh	Ni(a-dieen)$_2$(CF$_3$·CO$_2$)$_2$	10,150, ~7550sh
Ni(a-dieen)$_2$(NCS)$_2$	~11,350sh, 8910	Ni(a-dieen)$_2$(CHPh$_2$·CO$_2$)$_2$	10,150, ~7870sh
Ni(a-dieen)(NCS)$_2$	9130 †	Ni(a-dieen)$_2$SO$_4$,2H$_2$O	10,200

* Bands due to i.r. overtones omitted (see text). † Assymetric on low-energy side.

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[3] Furlani, *Gazetta*, 1958, **88**, 279; Sone and Kato, *Z. anorg. Chem.*, 1959, **301**, 277; Atkinson, Goodgame, Twycross, and Venanzi, unpublished observations.

[4] Jørgensen, " Absorption Spectra and Chemical Bonding in Complexes," Pergamon Press, Oxford, 1962, Ch. 7.

The spectra of the solid hydrates show a marked increase in absorption at ~5000 cm.$^{-1}$ compared with those of the anhydrous compounds. Both water and primary amino-groups have bands in this region,[5] and interaction due to hydrogen bonding might be expected.

Discussion.—The spin-multiplicity of the electronic ground state of nickel(II) in a tetragonal ligand field of D_{4h} symmetry depends upon the degree of tetragonality of this field.[2,6] When the in-plane field is formed by two unsymmetrical ligands such as $R_2N\cdot[CH_2]_2\cdot NH_2$, assumed on steric grounds to chelate in *trans*-positions, the symmetry becomes D_{2h}, although, in quantitative terms, departure from D_{4h} symmetry may not be appreciable. In D_{2h} symmetry the formation of a spin-triplet ground state for *trans*-$Ni(R_2N\cdot[CH_2]_2\cdot NH_2)_2X_2$ becomes increasingly favoured as (i) the difference between the in-plane and the axial ligand field decreases, and (ii) the rhombic component of the in-plane field increases.[2] Thus, changes in the magnetic behaviour of complexes of this type should depend upon the relative ligand-field strengths of $-NR_2$, $-NH_2$, and X^-, provided that there are no appreciable steric interactions between the $-NR_2$ groups and the anions.

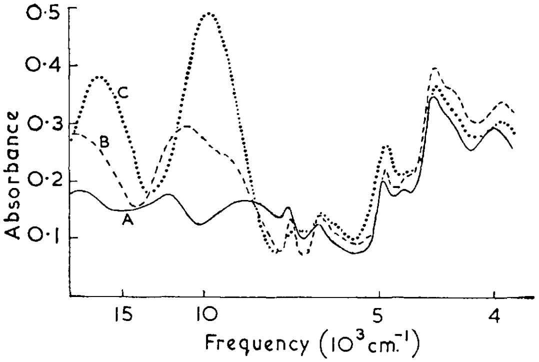

FIG. 1. Reflectance spectra of some $Ni(a\text{-dimen})_2X_2$ complexes.
A, X = NO_3; B, X = NO_2; C, X = Cl.

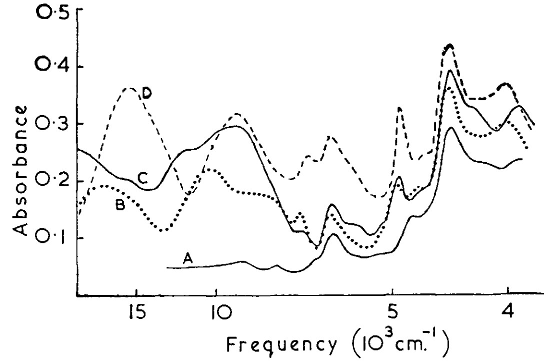

FIG. 2. Reflectance spectra of some $Ni(a\text{-dieen})_2X_2$ complexes.
A, X = I; B, X = $CF_3\cdot CO_2$; C, X = -NCS; D, X = Cl.

The magnetic results for the complexes where R = Me or Et give the following positions for the paramagnetic–diamagnetic change:

	Diamagnetic	Paramagnetic
R = Me, X =	I	Br, Cl, NO_3
R = Et, X =	I, Br, NO_3	Cl

Since the nitrate ion is polyatomic, a rigorous comparison is probably best achieved only for the halogeno-complexes.

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[5] Goddu and Delker, *Analyt. Chem.*, 1960, **32**, 140.
[6] Ballhausen and Liehr, *J. Amer. Chem. Soc.*, 1959, **81**, 538.

Now it is known[7] that the formation constants of nickel(II) complexes with *N*-substituted ethylenediamines are smaller than are those for ethylenediamine. These decreases, which were attributed to steric factors,[7] are greater with increasing alkyl substitution. Leussing has discussed[8] the complex-forming abilities of *C*- and *N*-substituted ethylenediamines with nickel(II) in terms of the E_r and δH_{Ni} parameters of George and McClure.[9] *N*-Substitution was found to decrease the δH_{Ni} values for $Ni(diamine)^{2+}$, although there was but little change in E_r. This weakening of the ligand-field strength on *N*-substitution was again attributed to steric effects. Electronic-spectral data[8] also suggested that the Δ values for ethylenediamines were slightly decreased on *N*-substitution.

Therefore, the order of Δ values concerned appears to be: $I < Br < Cl \ll -NR_2 < -NH_2$. With this order, the effect of varying R on the Δ value of the $-NR_2$ group will be such that factors (i) and (ii) above will work in conjunction (if we assume that the Δ value of the $-NH_2$ group is essentially independent of the changes in substituents at the $-NR_2$ group). Thus, if a change in R decreases the Δ value for $-NR_2$, then the tetragonal component of the field will be decreased and the rhombic component of the in-plane field increased, both effects increasing the probability that a paramagnetic complex will be formed. On this basis, the magnetic data for the bromo-complexes indicate that the $-NMe_2$ group is more weakly co-ordinating than $-NEt_2$, on the assumption that the nickel–bromide ion interactions are the same in each case. However, available evidence suggests that $-NEt_2$ forms a weaker bond to nickel(II) than does $-NMe_2$. The formation constants for mono-*N*-alkyl-substituted and *NN'*-disubstituted ethylenediamines with nickel(II) and for *NN*-disubstituted ethylenediamines with copper(II) decrease in the order Me $>$ Et.[7] Moreover, the δH_{Ni} values for *NN'*-dialkylethylenediamines are also in the above order.[8]

The energies of the near-infrared *d–d* bands for paramagnetic tetragonal nickel(II) complexes also provide a measure of changes in total ligand-field strengths for related compounds.[10] The splitting observed for this band in the spectra of most of the solid a-dimen and a-dieen complexes renders a direct comparison of this nature open to some uncertainty. However, the bands for the a-dimen complexes are at higher energies than are those for the a-dieen analogues. Moreover, this is observed for the anhydrous chloro-complexes, for which the bands are not split. It appears, therefore, that the changes in the position of the magnetic cross-over point on replacement of Me by Et in $R_2N\cdot[CH_2]_2\cdot NH_2$ are primarily concerned, not with the variation in the total strength of the in-plane ligand field, nor with its rhombic component, but with the steric interaction with the anions. The $-NMe_2$ group evidently permits the bromide ion, though not the iodide ion, to approach close enough to the nickel ion to provide an axial perturbation of the planar field sufficient to give a spin-triplet ground state, but with the more bulky $-NEt_2$ group this is precluded.

Anomalous magnetic behaviour in the solid state due to a Maxwell–Boltzmann distribution between the lowest spin-singlet and spin-triplet states[6,11] might be expected for small variations in the fields due to the axial ligands X^- in series NiL_4X_2. With both a-dimen and a-dieen as in-plane ligands, the magnetic cross-over point occurs when X^- is a halide ion. However, although the differences in the Δ values between the individual halide ions are very small,[4] in both series of complexes the magnetic change is complete and abrupt. We suggested previously[1] that the reason for this lies in the increase in the in-plane field, due to the pairing of electrons in the d_{z^2} orbital, leaving the $d_{x^2-y^2}$ orbital vacant. Discontinuities might therefore be expected in the variation of both the strength of the in-plane field and in the degree of tetragonal perturbation, in the region of the

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[7] Basolo and Murmann, *J. Amer. Chem. Soc.*, 1952, **74**, 5243; 1954, **76**, 211; Irving and Griffiths, *J.*, 1954, 213.

[8] Leussing, *Inorg. Chem.*, 1963, **2**, 77.

[9] George, *Rec. Trav. chim.*, 1956, **75**, 671; George and McClure, *Progr. Inorg. Chem.*, 1959, **1**, 381.

[10] Bostrup and Jørgensen, *Acta Chem. Scand.*, 1957, **11**, 1223.

[11] Maki, *J. Chem. Phys.*, 1958, **29**, 1129.

change in the spin-multiplicity of the ground state. A similar suggestion has since been made by Leussing.[8] *X*-Ray studies by Nyburg and Wood [12] of the diamagnetic and the paramagnetic form of $Ni(H_2N\cdot[CHPh]_2\cdot NH_2)_2(CHCl_2\cdot CO_2)_2$ are in agreement with this. In the paramagnetic form, the nickel–nitrogen distances are 2·05 Å, but in the diamagnetic isomer they are decreased to 1·90 Å. However, since the major factor responsible for the magnetic changes with the a-dimen and a-dieen complexes appears to be steric interaction involving the anions, the changes in the tetragonal component of the ligand field due to variation of X^- would, in any case, be much larger than the normal Δ values for these ions would indicate.

Both isomers of the iodide $Ni(a\text{-dimen})_2I_2$ are diamagnetic, in contrast to the magnetic behaviour of the isomers often found with complexes with *C*-substituted ethylenediamines.[13] With the latter, the high-temperature forms are paramagnetic, *e.g.*, yellow, diamagnetic $Ni(H_2N\cdot CHPh\cdot CH_2\cdot NH_2)_2(NO_3)_2 \xrightarrow{120^\circ}$ the blue, paramagnetic isomer. The electronic absorption spectra of the a-dimen nickel iodide complexes indicate that the planar field is weaker in the purple than in the orange isomer. Single-crystal *X*-ray studies of these compounds are in progress.[14]

The splitting of the near-infrared *d–d* band in the reflectance spectra of most of the paramagnetic complexes merits some discussion. First, there is the question whether both of the components listed in Tables 2 and 3 are in fact *d–d* bands, or whether one of them is a vibrational overtone. Our reasons for the assignment we make are: (*a*) the two or three bands which occur in the 12,500—6500 $cm.^{-1}$ region in the reflectance spectra of the diamagnetic complexes or in the transmission spectra of the pure diamines are very weak (see Fig. 2, curve A) and are sharp; (*b*) the spectra of the anhydrous chloro-complexes do not show this splitting; (*c*) no splitting is observed in the solution spectra, except for $Ni(a\text{-dieen})_2(NCS)_2$. Moreover, the bands in the solution spectra do not correspond to either of the components observed for the solids, but have energies intermediate between these. For the thiocyanate $Ni(a\text{-dieen})_2(NCS)_2$ the solid and solution spectra are very similar.

The $^3T_{2g}$ level in O_h symmetry is split by tetragonal distortions (D_{4h} symmetry) into two levels, ^3E_g and $^3B_{1g}$. However, the expected splitting of the near-infrared band is rarely observed; [10,15,16] examples are $Ni(C_5H_5N)_4Cl_2$ [10,16] and Ni(*NN'*-diphenylethylenediamine)$_2$Cl$_2$ [15] (although Maki [15] assigned the two band-components for the latter compound as $^3B_{2g} \longrightarrow {}^3A_{2g}$ and $^3B_{2g} \longrightarrow {}^3B_{1g}$). For a series of compounds NiL_4X_2, with a constant in-plane field due to L_4 and with no steric interaction between the ligands L and the anions X, the splitting of the near-infrared band should, to a first approximation, depend upon the relative Δ values of L and X. Since we are dealing with comparatively large differences in Δ, in considering the a-dimen and a-dieen complexes we shall assume the effective planar field to have D_{4h} symmetry, and that the diamines occupy a position close to ethylenediamine in the spectrochemical series, which, for the ligands concerned, is: $Cl^- < R\cdot CO_2^- < {}^-NCS^- < en < {}^-NO_2^-$.[4] On this basis, the splitting of the near-infrared *d–d* band should be smallest for the nitro- and isothiocyanato-complexes and greatest for the chloro-complex. The experimental results do not support this. The chloro-complexes and $Ni(a\text{-dimen})_2(NCS)_2$ show no splitting of this band, whereas with $Ni(a\text{-dieen})_2(NCS)_2$, the hydrated chloro-complexes, and the nitro-, carboxylato-, and paramagnetic nitrato-complexes in the solid state the band is split.

In the absence of structural data for any of the compounds showing this effect, any explanation is necessarily speculative. However, the splitting could possibly arise from asymmetric geometrical distortions of the ligand field, due to steric interactions between

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[12] Nyburg and Wood, personal communication.

[13] Lifschitz, Bos, and Dijkema, *Z. anorg. Chem.*, 1939, **242**, 97; Lifschitz and Bos, *Rec. Trav. chim.*, 1940, **59**, 407; Hein and Müller, *Z. anorg. Chem.*, 1956, **283**, 172.

[14] Dr. J. R. Chadwick, Northampton College of Advanced Technology, London.

[15] Maki, *J. Chem. Phys.*, 1958, **29**, 162.

[16] Ref. 4, pp. 296—297.

the $-NR_2$ groups and the polyatomic anions in the solid state. Such interactions might well be less effective in solution. Further studies of the spectra of nickel(II) complexes with other diamines are in progress.

EXPERIMENTAL

Preparation of the Complexes.—The following general method of preparation was used. The diamine was added, directly or in ethanol, to an aqueous or ethanolic solution of the nickel salt, the diamine : nickel salt molar ratio being 2 : 1. The solid complexes usually separated either immediately or after periods of up to 2 days. They were filtered off, dried *in vacuo* over sulphuric acid, and, where possible, recrystallised. Further details for individual compounds are given below.

Dichlorobis-(NN-*dimethylethylenediamine*)*nickel*(II) *monohydrate*, pale blue needles from ethanol (60% yield) (Found: Cl, 21·9; Ni, 18·1. $C_8H_{26}Cl_2N_4NiO$ requires Cl, 21·9; Ni, 18·1%). The compound loses water at ~100°, becomes green at ~150°, and decomposes at 250—255°.

Dichlorobis-(NN-*dimethylethylenediamine*)*nickel*(II) *tetrahydrate*, deep blue, formed on storage of the mother-liquor from the preparation of the previous complex, crystals were washed with ethanol, and air-dried (Found: Cl, 18·8; Ni, 15·6. $C_8H_{32}Cl_2N_4NiO_4$ requires Cl, 18·8; Ni, 15·5%).

Dichlorobis-(NN-*dimethylethylenediamine*)*nickel*(II), pale blue, obtained by heating the monohydrate to ~70° *in vacuo* over phosphorus pentoxide (Found: Cl, 23·2; Ni, 19·2. $C_8H_{24}Cl_2N_4Ni$ requires Cl, 23·2; Ni, 19·2%).

Dibromobis-(NN-*dimethylethylenediamine*)*nickel*(II) *dihydrate*, hexagonal, violet-blue plates from 90% aqueous ethanol (air-dried, 25% yield) (Found: Br, 37·2; Ni, 13·7. $C_8H_{28}Br_2N_4NiO_2$ requires Br, 37·1; Ni, 13·7%). The compound evolves water at ~100°, discolours at ~250°, and melts with frothing and decomposition at 278°.

Dibromobis-(NN-*dimethylethylenediamine*)*nickel*(II), green, obtained by drying the dihydrate *in vacuo* over phosphorus pentoxide (wt. loss: found 8·3; theor., 8·35%) (Found: Br, 40·3; Ni, 14·85. $C_8H_{24}Br_2N_4Ni$ requires Br, 40·5; Ni, 14·9%). The compound is hygroscopic, and reverts to the dihydrate on exposure to the atmosphere.

Di-iodobis-(NN-*dimethylethylenediamine*)*nickel*(II) *dihydrate*. An ethanolic solution of the diamine and nickel iodide was evaporated to dryness. The solid residue was dissolved in the minimum quantity of cold water, and the solution allowed to evaporate *in vacuo* over sulphuric acid. Blue crystals were formed, which were filtered off, washed with a small amount of water, and air-dried (52% yield) (Found: I, 48·0; Ni, 11·3. $C_8H_{28}I_2N_4NiO_2$ requires I, 48·4; Ni, 11·2%).

Di-iodobis-(NN-*dimethylethylenediamine*)*nickel*(II). (i) Orange isomer. This complex was obtained by drying the dihydrate *in vacuo* over phosphorus pentoxide at room temperature for several hours (wt. loss: found, 6·9; theor., 6·9%) (Found: N, 11·2; Ni, 11·9. $C_8H_{24}I_2N_4Ni$ requires N, 11·5; Ni, 12·0%). It is converted into the red-purple isomer at ~100°.

(ii) Red-purple isomer. This compound was prepared by drying the dihydrate as above, but at ~100° for several hours and then at ~135° (wt. loss: found 6·9; theor., 6·9%) (Found: N, 11·2; Ni, 11·9%), m. p. ~255° (decomp.). Both isomers are hygroscopic and revert to the dihydrate on exposure to the atmosphere.

Bis-(NN-*dimethylethylenediamine*)*nickel*(II) *perchlorate*. An ethanolic solution of the diamine and nickel perchlorate was evaporated to dryness. Recrystallisation of the solid residue from 1 : 1 methanol–ethanol gave a 12% yield of orange needles (Found: C, 22·7; H, 5·6; Ni, 13·5. $C_8H_{24}Cl_2N_4NiO_8$ requires C, 22·1; H, 5·6; Ni, 13·5%). When heated, the compound gradually becomes very dark red and melts with decomposition and frothing at 260°.

Dinitratobis-(NN-*dimethylethylenediamine*)*nickel*(II), blue crystals on recrystallisation from methanol (35% yield; m. p. 228°) (Found: N, 23·1; Ni, 16·4. $C_8H_{24}N_6NiO_6$ requires N, 23·4; Ni, 16·35%).

Di-isothiocyanatobis-(NN-*dimethylethylenediamine*)*nickel*(II), blue plates on recrystallisation from butan-1-ol (68% yield; m. p. 272° with decomp.) (Found: Ni, 16·8; NCS, 33·1. $C_{10}H_{24}N_6NiS_2$ requires Ni, 16·7; NCS, 33·1%).

Bistrichloroacetatobis-(NN-*dimethylethylenediamine*)*nickel*(II), blue needles on recrystallisation from butan-1-ol (65% yield) (Found: N, 9·7; Ni, 10·6. $C_{12}H_{24}Cl_6N_4NiO_4$ requires N, 10·0; Ni, 10·5%). The compound discolours at ~142° and decomposes at 210—215°.

Dinitrobis-(NN-*dimethylethylenediamine*)*nickel*(II). A methanolic solution of the diamine and nickel nitrite was evaporated to dryness. Recrystallisation of the solid residue, first, from butan-1-ol and then from nitromethane gave a 24% yield of blue crystals, m. p. 212° (decomp.) (Found: N, 25·4; Ni, 17·7. $C_8H_{24}N_6NiO_4$ requires N, 25·7; Ni, 17·95%).

Physical Measurements.—Most of the reflectance spectra were obtained with a Beckman DK2 recording spectrophotometer. The magnetic susceptibilities of some of the compounds were measured with a Gouy balance of the conventional type. The other physical measurements were carried out as previously described.[1]

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