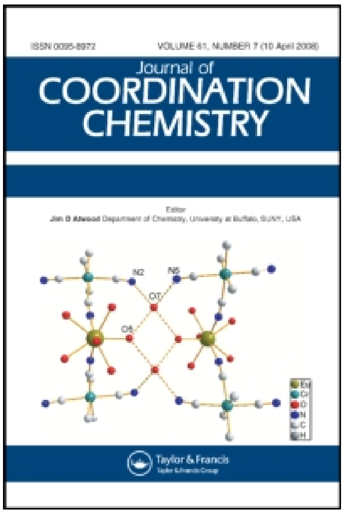

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NICKEL(II) COMPLEXES OF N,N'-DIBENZYLETHYLENE DIAMINE

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NICKEL(II) COMPLEXES OF N,N′-DIBENZYLETHYLENE DIAMINE

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Complexes formed by N,N′-dibenzylethylenediamine (DBEn) and nickel(II) salts exemplify a wide range of magnetic behavior and stereochemistry. $Ni(DBEn)_2Cl_2$, $Ni(DBEn)_2SO_4 \cdot H_2O$, $[Ni(DBEn)_2(H_2O)_2]Br_2 \cdot H_2O$, and $[Ni(DBEn)_2(H_2O)_2](ClO_4)_2$ or $(BF_4)_2$ are tetragonally-distorted octahedral complexes with essentially temperature-independent magnetic moments ($\mu_e \cong 3.1$ B.M.); $Ni(DBEn)_2(NO_3)_2$ contains *cis*-bidentate and ionic anions; and $Ni(DBEn)Cl_2$ and $Ni(DBEn)Br_2$ have polymeric six-coordinate structures in which weak ferromagnetic interaction occurs. Dehydration of the $[Ni(DBEn)_2(H_2O)_2]Br_2 \cdot H_2O$ gives an apparently five-coordinate compound $[Ni(DBEn)_2Br]Br$; dehydration of the perchlorate gives a variety of products according to the conditions of preparation of the perchlorate and of its dehydration. The products identified are blue $Ni(DBEn)_2(ClO_4)_2$, which has the spectral and magnetic properties of a tetragonally-distorted octahedral complex, yellow $Ni(DBEn)_2(ClO_4)_2 \cdot H_2O$, which from its magnetic moment ($\mu_e \simeq 2.0$ B.M., almost independent of temperature) and reflectance spectrum is a mixture of a diamagnetic species and the blue *dihydrate*; and pink $Ni(DBEn)_2(ClO_4)_2$ which appears to contain the diamagnetic species and the blue *anhydrate* in equilibrium as the magnetic moment and reflectance spectrum are temperature-dependent.

INTRODUCTION

Recently there has been much interest in the electronic spectra of transition-metal complexes in which tetragonal distortion is produced by ligands of unequal donor strengths;[1,2] in five coordination due to steric hindrance;[3] and in anomalous magnetic moments arising from equilibria between two spin states, magnetically non-equivalent sites in the unit cell, solute-solute or solute-solvent interactions, or configurational equilibria.[4] Many compounds of nickel(II) with N- and C-alkyl substituted ethylenediamines and higher polyamines are known to show these types of behavior. Some reports are available of nickel(II) complexes[5] with C-subtituted arylethylenediamines (phenylethylenediamine and stilbenediamine), but nothing is known of nickel(II) complexes with N-substituted arylkylethylenediamines. As an extension of our work[6a,c] on copper(II) complexes of DBEn, which were found to have varying stereochemistries, and on some pseudo-halide nickel(II) and cobalt(II) complexes,[6b] we report the preparation and properties of further new mono- and bis-DBEn complexes of nickel(II). N-benzylethylenediamine complexes of copper(II)[6d] and nickel(II)[6e] have also been investigated.

EXPERIMENTAL

Analar nickel(II) salts (B.D.H.) and DBEn (Aldrich Chemical Co.) were used without further purification. All the solvents used except dimethylformamide (DMF) were of AnalaR grade. DMF was purified as before.[6a] Physical measurements were carried out as before.[6a] The compounds below were dried in *vacuo* over calcium chloride unless otherwise stated.

1. Bis(N,N′-dibenzylethylenediamine)nickel(II) chloride

A warm ethanolic solution of $NiCl_2 \cdot 6H_2O$ (4.0 g, 50 ml) was treated with DBEn (8.1 g). After much shaking, the resulting blue solution gave a pale green solid which was filtered and washed with ethanol and acetone. Calcd. for $C_{32}H_{40}N_4Cl_2Ni$: C, 63.0; H, 6.6; N, 9.2. Found: C, 62.6; H, 6.7; N, 9.2.

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2. Diaquobis(N,N′-dibenzylethylenediamine)nickel(II) bromide monohydrate

A warm ethanolic solution of $NiBr_2 \cdot 3H_2O$ (4.0 g in 100 ml) was stirred with the ligand (7.1 g). On shaking, blue needles separated from the blue solution. These were then filtered and washed with ethanol and acetone. Calcd. for $C_{32}H_{46}N_4O_3Br_2Ni$: C, 51.1; H, 6.2; N, 7.4. Found: C, 51.4; H, 6.3; N, 7.0.

3. Bis(N,N′-dibenzylethylenediamine)nickel(II) bromide

On heating compound 2 at 135–140°, this pale green solid was obtained. Calcd. for $C_{32}N_{40}N_4Br_2Ni$: C, 54.95; H, 5.8; N, 8.0. Found: C, 54.6; H, 6.0; N, 8.5.

4. Bis(N,N′-dibenzylethylenediamine)nickel(II) sulfate monohydrate

To an aqueous solution of $NiSO_4 \cdot 6H_2O$ (5.2 g in 20 ml), the ligand in methanol (9.6 g in 50 ml) was added very slowly with stirring. The resulting blue solid was filtered and washed with methanol. Calcd. for $C_{32}H_{42}N_4O_5SNi$: C, 58.8; H, 6.5; N, 8.6. Found: C, 58.2; H, 6.5; N, 8.4.

5. Bis(N,N′-dibenzylethylenediamine)nickel(II) nitrate

An ethanolic solution of $Ni(NO_3)_2 \cdot 6H_2O$ (2.9 g in 25 ml) was treated with ethanolic ligand (4.8 g in 20 ml). The dark blue complex which soon separated was filtered and washed with ethanol. Calcd. for $C_{32}H_{40}N_6O_6Ni$: C, 57.9; H, 6.1; N, 12.7. Found: C, 57.6; H, 6.3; N, 12.8.

6. Diaquobis(N,N′-dibenzylethylenediamine)nickel(II) tetrafluoroborate

$Ni(BF_4)_2 \cdot 6H_2O$ (0.010 mole) was dissolved in cold 2,2-diethoxypropane, and treated with the ligand (0.020 mole) in the same solvent. After much shaking, a pale blue solid separated. This was filtered, washed with ethanol, and dried over P_4O_{10} *in vacuo*. Attempts to dehydrate this compound at 120° to see if it behaved similarly to the dehydrated perchlorates led to decomposition. Calcd. for $C_{32}H_{44}N_4O_2B_2F_8Ni$: C, 51.3; H, 5.9; N, 7.5. Found: C, 50.6; H, 6.0; N, 8.0.

7. Diaquobis(N,N′-dibenzylethylenediamine)nickel(II) perchlorate

To a solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (4.0 g) in cold, 2,2-diethoxypropane (50 ml) was added an excess of the ligand (12 g) in the same solvent. The pale blue crystals, which separated after the addition of 25–30 ml of absolute ethanol and much shaking, were filtered, washed with absolute ethanol and dried *in vacuo* over P_4O_{10} without the change in color which occurred with the compound prepared in 96% ethanol (see 8 and 9). Compound 7 could also be prepared in absolute ethanol. The use of an excess of ligand did not produce a tris(amine) compound, presumably because of steric effects. Calcd. for $C_{32}H_{44}N_4O_{10}Cl_2Ni$: C, 49.6; H, 5.7, N, 7.2. Found: C, 49.3; H, 5.7; N, 7.8.

8. Diaquobis(N,N′-dibenzylethylenediamine)nickel(II) perchlorate

A 96% ethanolic solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (4.65 g in 40 ml) was treated with ligand (4.8 g). The light blue complex which soon separated was filtered, washed first with 96% ethanol and then with a small amount of ether, and air-dried. Calcd. for $C_{32}H_{44}N_4O_{10}Cl_2Ni$: C, 49.6; H, 5.7; N, 7.2. Found: C, 49.4; H, 5.8; N, 7.9.

9. Bis(N,N′-dibenzylethylenediamine)nickel(II) perchlorate monohydrate

On drying *in vacuo* over P_4O_{10}, the blue compound 8 gave this yellow compound which reverted rapidly to the blue compound in air. The yellow compound was sealed *in vacuo* in Pyrex tubes to prevent rehydration. Even five days drying over P_4O_{10} did not remove the remaining water. This compound is extremely hygroscopic. Calcd. for $C_{32}H_{42}N_4O_9Cl_2Ni$: C, 50.8; H, 5.6; N, 7.4. Found: C, 49.7; H, 6.1; N, 7.5.

10. Bis(N,N′-dibenzylethylenediamine)nickel(II) perchlorate

When compound 8 was heated at 120° under vacuum, it became orange and then pink. The orange material could not be isolated. The pink compound was preserved in sealed tubes since it also reverted to compound 8 in air. The pink compound could also be prepared by heating cmpound,7 at *ca.* 140° under vacuum. This compound is extremely hygroscopic. Calcd. for $C_{32}H_{40}N_4O_8Cl_2Ni$: C, 52.0; H, 5.6; N, 7.6; Ni, 8.0. Found: C, 49.9; H, 5.9; N, 7.6; Ni, 7.8.

11. Bis(N,N'-dibenzylethylenediamine)nickel(II) perchlorate

This blue anhydrous compound was obtained on drying compound 8 in a stream of nitrogen at 120°. Calcd. for $C_{32}H_{40}N_4O_8Cl_2Ni$: C, 52.0; H, 5.6; N, 7.6. Found: C, 50.6; H, 5.4; N, 7.7.†

12. Mono(N,N'-dibenzylethylenediamine)nickel(II) chloride

An ethanolic solution of $NiCl_2 \cdot 6H_2O$ (4.0 g in 50 ml) was treated with the ligand in ethanol (4.05 g in 10 ml). From the resulting green solution, yellowish-green crystals separated after long shaking. These were filtered and washed with ethanol. Calcd. for $C_{16}H_{20}N_2Cl_2Ni$: C, 51.9; H, 5.45; N, 7.6. Found: C, 53.1; H, 5.9; N, 7.5.

13. Mono(N,N'-dibenzylethylenediamine)nickel(II) bromide

A warm ethanolic solution of $NiBr_2 \cdot 3H_2O$ (5.0 g in 100 ml) was treated with a solution of the ligand in ethanol (4.4 g in 15 m.). From the resulting green solution, a green solid soon separated. It was filtered and washed with ethanol. Calcd. for $C_{16}H_{20}N_2Br_2Ni$: C, 41.9; H, 4.4; N, 6.1. Found: C, 41.6; H, 4.5; N, 6.1.

All compounds except the sulfate are soluble in DMF. The hydrated compounds had water absorptions in their i.r. spectra which were absent from the spectra of the remainder.

RESULTS AND DISCUSSION

Magnetically Normal Compounds

Magnetic measurements from 300°K down to liquid nitrogen temperature (Table I) show that all compounds except 4, 9, 10, 12 and 13, are magnetically-normal. They obey the Curie law or the Curie–Weiss law with small Curie–Weiss constants, $\theta < 6°$, and their magnetic moments are in the range 3.0–3.2 B.M. and independent of temperature. These results are typical of octahedral nickel(II) complexes which generally have temperature-independent magnetic moments within the range 2.9–3.3 B.M. at 300°K. Octahedral structures are confirmed by the reflectance spectra except for $Ni(DBEn)_2Br_2$ (see below).

Magnetically Anomalous Compounds

The complex $Ni(DBEn)_2SO_4 \cdot H_2O$ obeys the Curie–Weiss law ($\theta = 16°$). The small variation in magnetic moment with temperature can be ascribed to weak antiferromagnetic interaction in a polymeric octahedral structure with bridging anions (see below).

The magnetic moments of $Ni(DBEn)Cl_2$ and $Ni(DBEn)Br_2$ are temperature-dependent, higher than generally observed for octahedral nickel(II) complexes. θ values of −21° and −28°, respectively, are observed (Table III). The appreciably large and negative values of θ indicate some ferromagnetic interaction as found[7] for other polymeric nickel(II) complexes.

The magnetic results of compounds 9 and 10 are discussed with their spectral properties below.

Dehydration of the Two Forms of $Ni(DBEn)_2(ClO)_2 \cdot 2H_2O$

It was noted by Curtis and Curtis[8] that the removal of water molecules from *trans*-$[Ni(en)_2(H_2O)_2](NO_3)_2$ gives the paramagnetic compound *trans*-$[Ni(en)_2(ONO_2)_2]$. (en = ethylenediamine.) Farago and James[9] have prepared the orange diamagnetic compound $[Ni(en)_2](ClO_4)_2$ by dehydration of $[Ni(en)_2(H_2O)_2](ClO_4)_2$, but found it impossible to remove the water from $[Ni(en)_2(H_2O)_2](Ph_4B)_2$ by heating *in vacuo.* This behavior was considered due to the presence of intramolecular hydrogen bonding between the two *cis*-coordinated water molecules in the tetraphenylborate complex but hydrogen bonding between *trans*-coordinated water molecules and perchlorate ions in the perchlorate complex. However, Nelson and Ragsdale[10] were able to dehydrate the tetraphenylborate complex simply by leaving the complex on a watch glass open to the air or in a desiccator over H_2SO_4. Hence, they have criticized the work of Farago and James, and they consider that the loss of water from a tetraphenylborate complex should be easy because of the inability of the tetraphenylborate ion to form

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†Thermal analysis of this compound in a stream of nitrogen at 120° gave a loss in weight of 4.6%. Calcd. for $2H_2O$: 4.65%.

TABLE I

Effective magnetic moments (B.M.); atom susceptibilities (c.g.s.) at 300 K and 90 K; Curie–Weiss constants, θ, and diamagnetic corrections of nickel(II) complexes.

Complex	$10^6 \chi_{Ni}$ 300 K	$10^6 \chi_{Ni}$ 90 K	$\mu_{eff}{}^a$ 300 K	$\mu_{eff}{}^a$ 90 K	θ K°	10^6 Diam. corrn.
1. $Ni(DBEn)_2Cl_2$	3950	13520	3.12	3.12	0	−182
2. $[Ni(DBEn)_2(H_2O)_2]Br_2 \cdot H_2O$	4066	13190	3.14	3.09	3	−242
3. $Ni(DBEn)_2Br_2$	3953	13700	3.09	3.10	0	−203
4. $Ni(DBEn)_2SO_4 \cdot H_2O$	3892	11630	3.07	2.90	16	−185
5. $Ni(DBEn)_2(NO_3)_2$	3928	13560	3.08	3.10	0	−170
6. $[Ni(DBEn)_2(H_2O)_2](BF_4)_2$	3984	13330	3.10	3.12	0	−240
7. $[Ni(DBEn)_2(H_2O)_2](ClO_4)_2$	4062	13070	3.16	3.06	5	−224
8. $[Ni(DBEn)_2(H_2O)_2](ClO_4)_2{}^b$	3971	13460	3.12	3.12	0	−224
9. $Ni(DBEn)_2(ClO_4)_2 \cdot H_2O^c$	1704	6098	2.02	2.06	−7	−211
10. $Ni(DBEn)_2(ClO_4)_2{}^d$	3046	6825	2.72	2.22	–	−198
11. $Ni(DBEn)_2(ClO_4)_2{}^e$	4030	12850	3.12	3.02	6	−198
12. $Ni(DBEn)Cl_2$	4400	17800	3.26	3.57	−21	−113
13. $Ni(DBEn)Br_2$	4475	19750	3.31	3.75	−28	−136

[a] Curie–Weiss law taken as $\chi_{Ni} \propto 1/T + \theta$. Corrections have not been made for the minor effects of temperature-independent paramagnetism. Measurements of compounds 9, 10, 11 were carried out on samples in pyrex tubes sealed under vacuum.

[b] Prepared in 96% ethanol.

[c,d,e] Yellow, pink and blue compounds respectively.

hydrogen bonds. In the present study two forms of $[Ni(DBEn)_2(H_2O)_2](ClO_4)_2$ have been isolated: compound 8, which on dehydration loses water readily, and compound 7, which does not.

Thus, it is possible that both previous groups of workers are correct, because we have isolated two hydrates of the same formula which behave differently on dehydration, presumably due to solid state effects such as hydrogen bonding. This conclusion is supported by the fact that one form of $[Ni(DBEn)_2(H_2O)_2](ClO_4)_2$ can be converted into the other by dissolving (recrystallizing) one in the solvent from which the other was prepared.

DMF solutions of both compounds 7 and 8 have three bands at almost the same positions, as shown below. The extinction coefficients for the highest and the lowest energy bands differ markedly.

Compound 7 $\nu_{max}\, cm^{-1}$	*Compound 8* $\nu_{max}\, cm^{-1}$
26,700 (17.93)	26,600 (14.80)
16,100 (6.33)	16,300 (6.96)
9,800 (7.38)	9,800 (8.23)

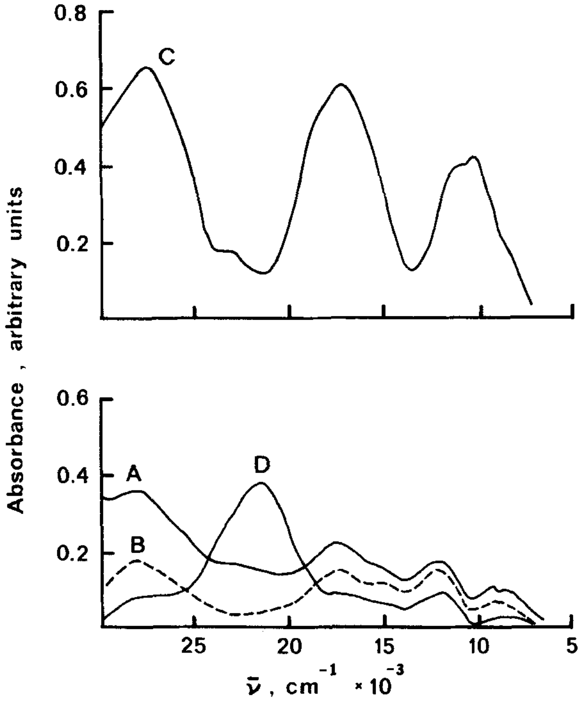


FIGURE 1 Reflectance spectra at liquid nitrogen temperature of A, $[Ni(DBEn)_2(H_2O)_2](ClO_4)_2$ obtained from 2,2-diethoxypropane; B, $[Ni(DBEn)_2(H_2O)_2](ClO_4)_2$ obtained from 96% ethanol; C, $[Ni(DBEn)_2(NO_3)]NO_3$; and D yellow $Ni(DBEn)_2(ClO_4) \cdot H_2O$.

Reflectance Spectra

The considerable splitting of the ν_1 band ($^3A_{2g} \rightarrow {}^3T_2$ transition in O_h symmetry) in the diffuse reflectance spectra (Table II, Figure 1) of the

TABLE II
Diffuse reflectance spectra at room and liquid nitrogen temperature

No.	Compound	Temp ($^\circ$K)	ν_{max}(cm^{-1} x 10^{-3})								
				ν_3			ν_2			ν_1	
1.	Ni(DBEn)$_2$Cl$_2$	295		25.2s	20.0vwsh		15.2s		12.0msh		7.8
	blue	80		25.5s	20.0vwsh		15.6s		11.8m	10.6wsh	8.0
2.	[Ni(DBEn)$_2$(H$_2$O)$_2$]Br$_2$ · H$_2$O	295	27.5s	25.5wsh	22.0vwsh	17.0s	15.4vwsh		12.0m		9.0
	blue-violet	80	28.0s	25.8wsh	21.0wsh	17.5s	15.3sh	13.0sh	12.1m	9.3m	8.6
3.	Ni(DBEn)$_2$Br$_2$	295		25.2s	20.0wsh		15.7sbr		12.1msh		7.6
	pale green	80		25.5s	20.0wsh		16.0sbr		12.1m		8.0
4.	Ni(DBEn)$_2$SO$_4$ · H$_2$O	295	26.8s				16.4s		12.0m		8.4
	blue	80	27.4s				16.7s	13.0sh	12.0m		9.0
5.	Ni(DBEn)$_2$(NO$_3$)$_2$	295	27.2vs		22.4vwsh		17.0vs		10.2s		
	blue	80	27.5vs		23.2wsh		17.3vs	11.2sh	10.45s		8.6
6.	[Ni(DBEn)$_2$(H$_2$O)$_2$](BF$_4$)$_2$	295	27.6s	25.7wsh		17.0s	15.0vwsh		12.1m		8.6
	pale blue	80	28.0s	26.0wsh	21.5wsh	17.4s	15.3wsh		12.1m	9.3m	8.8
7.	[Ni(DBEn)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$	295	27.6s		22.0vwsh	17.0m	15.0vwsh		12.0m		8.6
	pale blue	80	28.1s		22.6wsh	17.6m	15.1wsh		12.1m	9.2m	8.7
8.	[Ni(DBEn)$_2$(H$_2$O)$_2$](ClO$_4$)$_2$	295	27.6s	25.9wsh		17.0s			12.1m		8.6
	pale blue	80	28.0s	25.8wsh		17.5s	15.1wsh		12.1m	9.1m	8.7
9.	Ni(DBEn)$_2$(ClO$_4$)$_2$H$_2$O	295	27.0wsh		21.1vs	16.6vwsh			12.1m		8.6
	yellow	80	27.6wsh		21.4vs	17.3vw			12.0m		8.6
10.	Ni(DBEn)$_2$(ClO$_4$)$_2$	295	27.3m		20.4vs	16.8wsh		13.2w	12.1w†		
	pink	90	27.6m		20.8vs	17.5wsh		13.4w	12.2w		
11.	Ni(DBEn)$_2$(ClO$_4$)$_2$	295	27.2	24.8vwsh	20.0vwsh	16.8m		13.2m	12.2m		7.3
	blue	90	27.7s	25.0vwsh	20.6w	17.4m		13.2m	12.2m		7.5
12.	Ni(DBEn)Cl$_2$	295	24.3s		20.0vwsh	14.4m	12.4wsh		9.3s		7.8
	yellow green	90	24.4s	23.0vwsh	20.0vw	14.7s	12.9vw	11.9w	9.6s		7.9
13.	Ni(DBEn)Br$_2$	295	23.2s	19.0wsh		13.9	12.2msh	11.4vwsh	8.8s		7.2
	green	90	23.4s	19.0w		14.3s	12.5msh	11.4wsh	9.2s		7.4

† A weak band at about 7500 cm^{-1} seems to be obscured by vibrational absorptions (Figure 2).

two forms of the dihydrated perchlorate at room and liquid nitrogen temperature is consistent with tetragonal structures. The reflectance bands 8600 and 12,100 cm^{-1} can be assigned to the transitions arising from the splitting of the $^3T_{2g}$ term in tetragonal (D_{4h}) symmetry, i.e. to the $^3B_{1g} \rightarrow {}^3E_g$ and $^3B_{1g} \rightarrow {}^3B_{2g}$ transitions, respectively. The transition to the $^3B_{2g}$ level is dependent only on the in-plane field strength 10Dq for the DBEn. The transition to the ^3E_g state is predominantly a function of 10Dq for the amine and of the distortion parameter Dt. The breadth of the 8600 cm^{-1} band indicates that the actual symmetry is less than D_{4h}. Low temperature spectra show about 500 cm^{-1} splitting of this band. Also the breadth and high intensity of the 12,000 cm^{-1} band indicate some intermixing with other bands, possibly with the spin-forbidden transitions to the ^1D state ($^3B_{1g} \rightarrow {}^1A_{1g}$ and $^3B_{1g} \rightarrow {}^1B_{1g}$).

The splitting of the ν_1 band due to the tetragonality of the complexes varies considerably. The splitting is given by: $(35/4)Dt = (5Dq^{xy} - Dq^z)$ where Dq^{xy} and Dq^z are the crystal field splitting parameters for the planar and axial ligands respectively.[11] Hence if the axial field remains approximately constant, the splitting of ν_1 should increase with the strength of the planar amine ligand field. Since N-substituted en ligands are more basic than en itself, the splitting of ν_1 would be expected to be more in the DBEn complexes than in the corresponding en complexes. The observed lower splitting for DBEn complexes (~3500 cm^{-1} for the compounds containing the cation $[Ni(DBEn)_2(H_2O)_2]^{2+}$ compared with 3900 cm^{-1} for $[Ni(en)_2(H_2O)_2]^{2+}$) can be ascribed to the weaker ligand field arising from steric hindrance more than counter-balances the increased basicity. Recent kinetic studies[12] have shown that steric effects are important in the formation of nickel(II)-DBEn complexes.

The broad, asymmetric room temperature reflectance band at 17,000 cm^{-1} can be assigned to the transition to the $^3T_{1g}(F)$ level (ν_2). At liquid nitrogen temperature a shoulder develops on the low energy side near 15,100 cm^{-1} and the main band moves about 500 cm^{-1} to higher energy. The shoulder can be assigned to the $^3B_{1g} \rightarrow {}^3A_{2g}(F)$ transition, and the broad band near 17,500 cm^{-1} to the doubly degenerate $^3B_{1g} \rightarrow {}^3E_g(F)$ transition. This indicates splitting of about 2500 cm^{-1} of the $^3T_{1g}(F)$ level. Rowley and Drago[13] have calculated splittings for this level of 2300 cm^{-1} for $Ni(py)_4Br_2$ and ~1800 cm^{-1} for $Ni(py)_4Cl_2$ (py = pyridine). The very weak, broad shoulder near 21,000–22,000 cm^{-1} can be assigned to the transitions to ^1D and ^1G states. The room temperature reflectance band near 27,500 cm^{-1} can be assigned to transitions to the $^3T_{1g}(P)$ level (ν_3). On cooling this band moves about 300–600 cm^{-1} towards higher energy, and a shoulder develops near 25,800 cm^{-1}. The band and the shoulder can be assigned to the $^3B_{1g} \rightarrow {}^3E_g(P)$ and $^3B_{1g} \rightarrow {}^3A_2(P)$ transitions, respectively.

The compounds $Ni(DBEn)_2Br_2 \cdot 3H_2O$ and $Ni(DBEn)_2(BF_4)_2 \cdot 2H_2O$ have similar colors and reflectance spectra to the perchlorate dihydrates, and the spectra are similarly assigned. These complexes therefore contain the same cation *trans*-$[Ni(DBEn)_2(H_2O)_2]^{2+}$. In confirmation, the perchlorates have a broad infrared band in the range 1020–1150 cm^{-1}, characteristic of uncoordinated perchlorate.[14]

The compound $Ni(DBEn)_2SO_4 \cdot H_2O$ has a reflectance spectrum characteristic of a *trans*-nickel(II) complex, and similar assignments can be made. The i.r. spectrum of the sulfate has three bands near both 1100 and 600 cm^{-1} as expected if the anions act as bridging groups in a *trans* chain[6a] polymer. The three bands in the reflectance spectrum of $Ni(DBEn)_2(NO_3)_2$ obtained at room temperature can be assigned on the basis of O_h symmetry (Table 3), and there is good agreement between observed values

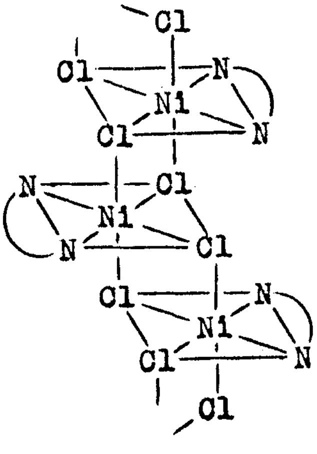
TABLE III
Atomic susceptibilities (c.g.s.) and magnetic moments (B.M.) of compounds showing appreciable variation with temperature or anomalous behavior.

				$Ni(DBEn)Cl_2$				
T (°K)	299.0	272.3	240.0	196.5	169.4	139.6	108.2	85.7
$10^6\chi_A$	4396	4904	5642	7008	8309	10390	13990	18630
μ_e(B.M.)	3.26	3.28	3.31	3.33	3.37	3.42	3.49	3.59
				$Ni(DBEn)Br_2$				
T (°K)	302.3	274.5	243.7	199.5	171.0	140.3	111.5	89.0
$10^6\chi_A$	4482	5012	5687	7238	8670	10920	14500	19760
μ_e(B.M.)	3.31	3.33	3.34	3.41	3.46	3.51	3.60	3.77

of ν_2 and ν_3 and those calculated[15] on this basis. Unlike the above *trans*-complexes, its ν_1 band is unsplit, and since *trans*-complexes are expected[16] to show double the splitting of *cis*-compounds with the order of levels inverted, this complex can be assigned the structure *cis*-$[\mathrm{Ni(DBEn)_2(NO_3)}]\mathrm{NO_3}$. At liquid nitrogen temperature three absorptions appear (Figure 1) at 8600sh, 10,450 and 11,200sh $\mathrm{cm^{-1}}$ in place of the ν_1 band (10,200 $\mathrm{cm^{-1}}$). These presumably represent transitions to the three components of the $^3T_{2g}$ term in C_{2v} symmetry, and the overall splitting is about half that of the *trans*-complexes. Comparison of the intensities of reflectance spectra can only be qualitative, but the bands of this compound are much more intense than those of the previous compounds in support of the *cis*-assignment. In confirmation it was found that the i.r. absorptions of the nitrate groups occur at 1497s, 1364s, 1275s, 833w, 808m, 741m, 700s, and 695s, close to values found for other compounds[8] containing ionic and bidentate nitrate groups. In addition, the reflectance spectrum is very like that of *cis*-$[\mathrm{Ni(en)_2NO_3}]\mathrm{ClO_4}$, but not that of *trans*-$\mathrm{Ni(en)_2(NO_3)_2}$.[8] The value of 15B (13,600 $\mathrm{cm^{-1}}$) for this complex derived from[15] the expression $15B = \nu_3 + \nu_2 - 3\nu_1$ is also comparable to the values obtained for other nickel(II) complexes of *cis*-octahedral structures, e.g. for $[\mathrm{Ni(en)_2NO_3}]\mathrm{ClO_4}$, $[\mathrm{Ni(en)_2NO_3}]\mathrm{BF_4}$, $[\mathrm{Ni(en)_2NO_3}]\mathrm{I}$, and $[\mathrm{Ni(tmd)_2NO_3}]\mathrm{ClO_4}$, (tmd = N,N,N',N'-tetramethylethylenediamine), 15B is 13,000, 13,200, 13,100 and 12,800 $\mathrm{cm^{-1}}$, respectively. The weak shoulder at 22,400 $\mathrm{cm^{-1}}$ is assigned to spin-forbidden transitions to the ^1D and ^1G states.

The room temperature spectrum of $\mathrm{Ni(DBEn)_2Cl_2}$ is typical of a *trans*-octahedral complex; the considerable splitting of the ν_1 band (Table 2) eliminates the possibility of a *cis*-structure like that of $[\mathrm{Ni(en)_2Cl_2}]_2$. The spectrum [27,000 $\mathrm{cm^{-1}}$ ($\epsilon = 29.8$), 16,900 $\mathrm{cm^{-1}}$ (14.0), 10,200 $\mathrm{cm^{-1}}$ (10.8)] of this compound in DMF was almost identical with its reflectance spectrum, and the extinction coefficients were almost double those of other compounds. These, except for the sulfate which was insoluble, were extensively solvolysed since their reflectance spectra differed from the solution spectra. The molar conductance of the nitrate in DMF was somewhat greater than expected for a 1:1 electrolyte so that a little solvolysis must have occurred.

$\mathrm{Ni(DBEn)Cl_2}$ and $\mathrm{Ni(DBEn)Br_2}$ could have tetrahedral, planar, or *cis*-polymeric octahedral structures. Gill and Nyholm[17] have shown that tetrahedral complexes of nickel(II) are usually produced when steric and electronic requirements of the ligands make a planar or an octahedral configuration unfavorable. Most alkylenediamines and N- and C- substituted alkylenediamines give 1:3 or 1:2 nickel(II) complexes with octahedral structures, and 1:1 complexes with tetrahedral or polymeric octahedral structures. On the other hand, the more bulky C-substituted diamines, e.g. 2,3-butylene diamine,[18] 2-phenylethylene-diamine, and stilbenediamine, give planar, diamagnetic compounds. The reflectance spectra of the mono(DBEn) complexes (Table 2) resemble those of other polymeric octahedral nickel(II) complexes[19] and are different from those of tetrahedral[19] or planar[10] nickel(II) complexes. This and the magnetic interactions indicate polymeric structures (I). The reflectance spectra show considerable splitting of the ν_1 and ν_2 bands unlike that of *cis*-$[\mathrm{Ni(DBEn)_2NO_3}]\mathrm{NO_3}$. This is ascribed to the greater difference in ligand field strengths between N and Cl than between N and O.



(I)

Dehydration of $\mathrm{Ni(DBEn)_2Br_2 \cdot 3H_2O}$ at 135–140° gave the anhydrous compound $\mathrm{Ni(DBEn)_2Br_2}$. This process caused the ν_1, ν_2, and ν_3 relectance bands to move to lower energies and to increase in intensity; the fine structure was removed and a weak shoulder developed at 20,000 $\mathrm{cm^{-1}}$. This spectrum is not that of octahedral, tetrahedral, or planar nickel (II)i) ions, but resembles the spectrum of the five coordinate nickel(II) complex $[\mathrm{Ni(trenMe)Cl}]\mathrm{Cl}$[3] (Figure 2). Both the hydrated and

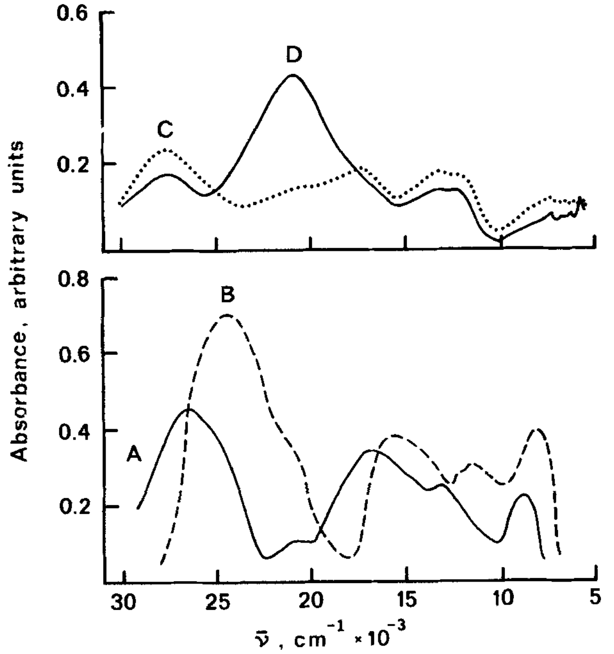


FIGURE 2 Reflectance spectra at liquid nitrogen temperature of A, $Ni(DBEn)_2Br_2$; B, $[Ni(trenMe)Cl]Cl$; C, blue $Ni(DBEn)_2(ClO_4)_2$ and D, pink $Ni(DBEn)_2(ClO_4)_2$

the anhydrous compounds are 1:1 electrolytes in DMF. Five coordination with nickel(II) in such complexes is usually due to steric interaction preventing a sixth group from bonding. However, the copper(II) complex, $Cu(DBEn)_2Br_2$, exists[6ac] in five and six coordinate forms which can be obtained by different preparative procedures. This fact indicates that steric interaction is not the only factor determining the formation of a five coordinate complex.

Dehydration of $[Ni(DBEn)_2(H_2O)_2](ClO_4)_2$, compound 8, under vacuum for several days over P_4O_{10} gave the yellow $Ni(DBEn)_2(ClO_4)_2 \cdot H_2O$, compound 9. The magnetic behavior of this compound is interesting. The plot of reciprocal susceptibility against temperature is a straight line giving a Curie–Weiss constant θ of $-7°$. The magnetic moment of *ca.* 2 B.M. is almost independent of temperature between 90° and 300°K, but is anomalously low (Figure 3).

This result is believed to be due to the presence of diamagnetic and paramagnetic nickel(II) species within the same lattice, i.e., planar (or highly tetragonally distorted octahedral) and octahedral species. The presence of planar and tetrahedral species, as with $Ni[P(CH_2 \cdot Ph)Ph_2]_2Br_2$,[20] or tetrahedral and octahedral species as with the brown form of Ni(quinoxaline)Br_2,[21] can be excluded since no bands assignable to tetrahedral nickel(II) are present in the reflectance spectra which are comparatively weak;

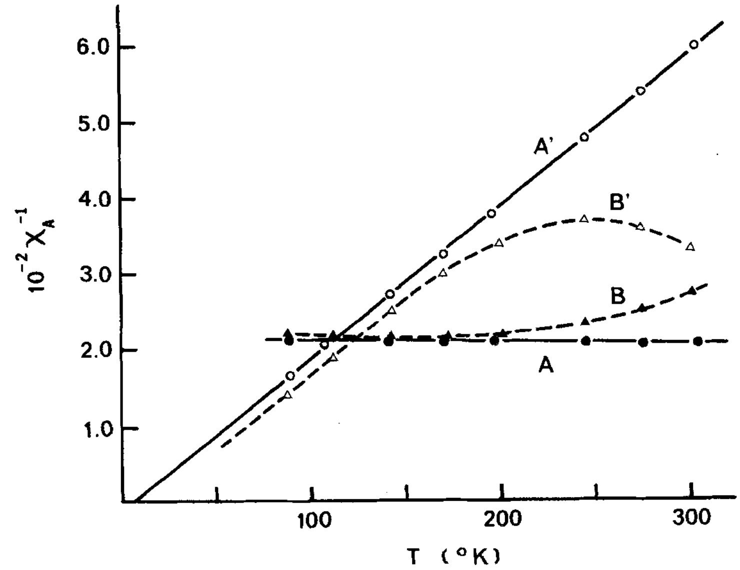


FIGURE 3 Variation with temperature of effective magnetic moments, μ_e, of yellow $Ni(DBEn)_2(ClO_4)_2 \cdot H_2O$, curve A, and of pink $Ni(DBEn)_2(ClO_4)_2$, curve B, Curves A A′ and B′ show the variation of the corresponding reciprocal atom susceptibilities $10^{-2}\chi_A^{-1}$ with temperature.

any tetrahedral component would be expected to lead to some temperature-dependence of the magnetic moment; and co-existence of tetrahedral and octahedral species would produce a moment much greater than 2 BM. The behavior is analogous to that of bis-(*meso*-stilbenediamine)-nickel(II) dichloroacetate, $\frac{2}{3}CH_3OH \cdot \frac{4}{3}H_2O$.[5] From the susceptibility of the hydrated compound 8, it is possible to estimate that about 50% of the nickel(II) ions are present as the paramagnetic, presumably octahedral form, and 50% as the diamagnetic form.

It is difficult to compare intensities of reflectance spectra of different compounds, but this compound has reflectance bands characteristic of compound 8, considerably reduced in intensity; and an additional, comparatively intense band at 21,000 cm^{-1} which can be assigned to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition of a planar, diamagnetic species. There was no change in the relative intensities of the 21,000 cm^{-1} band and the other bands on cooling to liquid nitrogen temperature (Figure 1) (compare compound 10 below). This compound is so hygroscopic that it is difficult to record the i.r. spectrum, but bands near 3500 cm^{-1} and 1600 cm^{-1} indicate the presence of water, and a broad band between 1000–1150 cm^{-1} indicates the presence of ionic perchlorate.[14] This compound is believed to contain paramagnetic $[Ni(DBEn)_2(H_2O)_2](ClO_4)_2$ and diamagnetic $[Ni(DBEn)_2](ClO_4)_2$ species in 1:1 proportions.

Thermal analysis of compound 8 in a stream of nitrogen at 120° caused formation of the blue, anhydrous compound 11 with the expected loss in weight. This compound is not hygroscopic. Larger quantities were obtained by heating compound 8 under nitrogen at 120°. It has a magnetic moment of 3.12 B.M. which does not vary with temperature. Its reflectance spectrum (Figure 2) is that of a tetragonally distorted octahedral complex; and its i.r. spectrum shows the absence of water and the presence of coordinated perchlorate groups.[14] It is therefore assigned the structure $[Ni(DBEn)_2(ClO_4)_2]$. On the other hand, when compound 8 was heated under continuous vacuum at 120° it gave a highly hygroscopic, anhydrous, pink compound 10. Compound 10 has a reflectance spectrum (Figure 2) almost identical with that of the octahedral anhydrous compound 11 except for an extra broad and intense band at 20,200 cm^{-1}. On cooling to liquid nitrogen temperature, this band moved to 20,800 cm^{-1} and increased in intensity relative to the other bands in the spectrum which also are less intense than in the room temperature spectrum. The magnetic moment also diminishes as the temperature is lowered, and the plot of reciprocal susceptibility against absolute temperature (Figure 3) shows a maximum at 244°K typical of a system[21] in which a spin equilibrium is present. However, the moment curve is not asymptotic to 0 B.M. at low temperatures as it should be for an equilibrium between a diamagnetic and single paramagnetic form. It appears that there are two paramagnetic forms present: about 50% compound 11, and about 50% another form in equilibrium with a diamagnetic substance at room temperature, but converted predominantly into the diamagnetic form at liquid nitrogen temperature. The i.r. spectrum indicates the absence of water and the presence of both ionic and coordinated perchlorate groups at room temperature; on exposure to moist air the compound soon became blue and there were marked changes in the 1100 cm^{-1} region.

Although it is conceivable that the magnetic behavior of compound 9 could be due to the presence of a mechanical mixture of paramagnetic and diamagnetic compounds, this would not be so for the pink compound 10 because a mixture would not give this marked variation of magnetic moment with temperature. Whatever the detailed explanation of the magnetic behavior the existence of paramagnetic and diamagnetic forms of these compounds seems established. The orange compound which could not be isolated (see preparation of compound 10) could be a mixture of yellow and pink substances or the fully diamagnetic form. The latter is more likely since nickel(II) perchlorate complexes of tmd and N,N,N′,N′-tetramethylethylenediamine (ted) show[23] somewhat analogous behavior in that $[Ni(tmd)_2](ClO_4)_2$ is orange and diamagnetic with ionic perchlorate groups while $[Ni(ted)_2(ClO_4)_2]$ is blue and paramagnetic with monodentate perchlorate. Also the orange compound[9] $[Ni(en)_2](ClO_4)_2$ is diamagnetic.

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