The Polarised Single-crystal Electronic Spectra of Bisdi(2-aminoethyl)-aminenickel(II) Chloride Monohydrate

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The polarised single-crystal electronic spectra of bisdi(2-aminoethyl)aminenickel(II) chloride monohydrate has been measured and interpreted in D_{2h} symmetry by use of a vibronic mechanism. The small splitting of the octahedral T_{2g} and T_{1h} terms in D_{2h} symmetry is discussed in the light of the restricted tetragonal distortion of the complex.

THE electronic spectra of nickel(II) complexes have been extensively studied [1-3] and the ordering of the octahedral energy levels is well established. This work has been extended to investigate the assignment of tetragonal nickel(II) complexes.[4-6] However most of this work involved the use of solid diffuse reflectance techniques

FIGURE 1   Ni(den)$_2$Cl$_2$,H$_2$O; (A) the molecular structure; and (B) the crystal morphology

and as such any assignments can only be considered tentative. Hare and Ballhausen [7] have looked at the complex tetrakis(thiourea)nickel(II) chloride using a single-crystal method. In this case, the assignment in an axial symmetry was preferred but was not completely satisfactory. Hence, the need for reliable single-crystal data is apparent. This paper investigates the complex bisdi(2-aminoethyl)aminenickel(II) chloride monohydrate, hereafter referred to as Ni(den)$_2$Cl$_2$,H$_2$O.

EXPERIMENTAL

Preparation.—Crystals of Ni(den)$_2$Cl$_2$,H$_2$O were obtained by slow evaporation of an aqueous solution of diethylene-triamine and a slight excess of nickel(II) chloride.

Physical Measurements.—The polarised single-crystal electronic spectra were recorded on a Unicam SP 700 instrument modified as described elsewhere.[8] The crystal morphology was determined by Weissenberg techniques.

Crystallographic Data.—Ni(den)$_2$Cl$_2$,H$_2$O crystallises in the monoclinic [9] system (space-group $P2_1/c$) with cell dimensions $a = 13.50$, $b = 8.69$, $c = 14.01$ Å, $\beta = 102.5°$, and $Z = 4$. The complex has a compressed rhombic structure, with the two ligand molecules co-ordinated equatorially as found in Cu(den)$_2$Br$_2$,H$_2$O.[10] The com-

pression occurs along the Ni–N(sec) bond directions (2.06 Å) while the Ni–N(prim) bond lengths are 2.13 and 2.18 Å.

The molecular x, y, and z axes are defined as shown in Figure 1. In the space-group $P2_1/c$ the four molecules occur in two pairs, the z axes [defined as the Ni–N(sec) bond direction] of the two pairs being misaligned by at the most 12°. The x and y molecular axes being essentially contained by the ac-plane, will be aligned approximately parallel throughout the unit cell, with the y axis making an angle of *ca.* 25° with the c axis.

The crystal morphology is shown in Figure 1A; the purple diamond shaped plates have their (010) face well developed and the a and c axes lie along the short and long diagonals respectively.
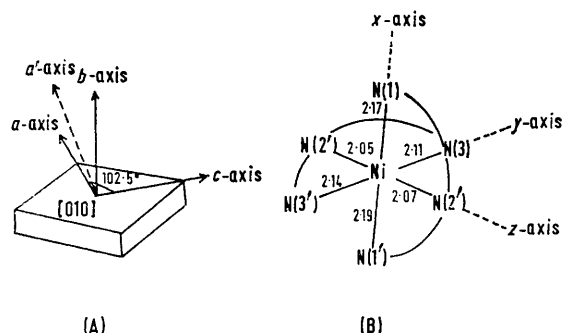
RESULTS

The electronic solid diffuse reflectance spectrum of Ni(den)$_2$Cl$_2$,H$_2$O shows three spin-allowed bands of medium intensity at 11.7, 18.6, and 28.8 kK; these absorptions corresponding to the transitions from the ground state ($^3A_{2g}$) to the states $^3T_{2g}(F)$, $^3T_{1g}(F)$, and $^3T_{1g}(P)$ manifolds of octahedral symmetry.

The polarised single-crystal electronic spectra of Ni(den)$_2$Cl$_2$,H$_2$O have been recorded in the main face (010) (x and y) and the (100) face (z), which was obtained by cutting parallel to the c axis (long diagonal), and are shown in Figure 2. The spectra were recorded parallel to the
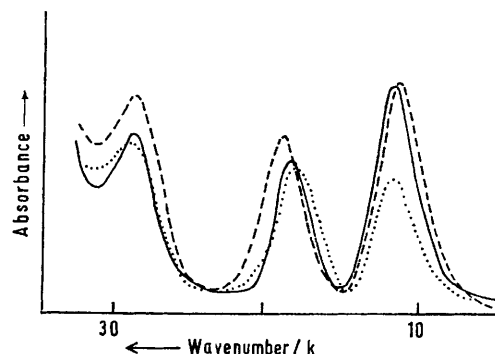

FIGURE 2   The polarised single-crystal electronic spectra of Ni(den)$_2$Cl$_2$,H$_2$O; Full line, z; dashed line, x; and dotted line, y

extinction directions in the crystal, the direction cosines of these being shown in Table 1, together with those of the molecular axes. The z-polarised spectrum was measured

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[10] F. S. Stephens, *J. Chem. Soc. (A)*, 1969, 2233.

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parallel to the b-crystallographic axis and is better than 95% pure despite a 12° misalignment within the unit cell. The extinction directions in the (010) face correspond reasonably well with the molecular x and y directions.

TABLE 1

Direction cosines of the molecular axes and the extinction directions

	a'	b	c
Ni–N(1)	+0·3497 (69°)	+0·0848 (85°)	+0·933 (21°)
Ni–N(2)	+0·0987 (84°)	+0·9947 (6°)	+0·0302 (88°)
Ni–N(3)	+0·9141 (24°)	+0·0892 (85°)	−0·3955 (66°)
x	+0·4226 (65°)	0·0000 (90°)	+0·9063 (25°)
z	0·0000 (90°)	+1·0000 (0°)	0·0000 (90°)
y	+0·9063 (25°)	0·0000 (90°)	−0·4226 (65°)

b And c are the crystallographic axes; a' axis perpendicular to b and c.

The x- and z-polarised spectra are of similar intensity and form, each having a one-absorption maxima in the three regions observed in the solid diffuse reflectance spectrum. The x polarisation absorbs at 11·2, 18·6, and 28·7 kK, while absorptions in z polarisation appear at 11·6, 18·3, and 28·7 kK. The y-polarised spectrum is less intense, but again has three bands at 11·6, 18·1, and 28·9 kK (Table 2).

TABLE 2

The assignment of the polarised single-crystal electronic spectra of Ni(den)$_2$Cl$_2$,H$_2$O

Energy/kK	Polarisation	Assignment	
11·2	x	$^3B_{3g} \longleftarrow {}^3B_{1g}$	
11·6	y	$^3B_{2g} \longleftarrow {}^3B_{1g}$	$\left.\right\} {}^3T_{2g}$
11·6	z	$^3B_{1g} \longleftarrow {}^3B_{1g}$	
18·1	y	$^3B_{2g} \longleftarrow {}^3B_{1g}$	
18·3	z	$^3B_{1g} \longleftarrow {}^3B_{1g}$	$\left.\right\} {}^3T_{1g}(F)$
18·6	x	$^3B_{3g} \longleftarrow {}^3B_{1g}$	
28·7	y	$^3B_{2g} \longleftarrow {}^3B_{1g}$	
28·7	z	$^3B_{1g} \longleftarrow {}^3B_{1g}$	$\left.\right\} {}^3T_{1g}(P)$
28·9	x	$^3B_{3g} \longleftarrow {}^3B_{1g}$	

DISCUSSION

The strict crystallographic site symmetry of Ni(den)$_2$Cl$_2$,H$_2$O is C_1. However, since this would show no polarisation properties, a higher ' effective symmetry ' of the electric field around the nickel(II) ion is indicated. If the conformation of the methylene groups in the ligand chain is ignored, the metal complex has approximately C_{2v} symmetry, while the approximate geometry of the NiN$_6$ chromophore (Figure 1) is clearly rhombic, as confirmed by the electronic spectra. The lack of a centre of symmetry in the molecule suggests an ' effective symmetry ' of C_{2v} or D_2. However, the polarised electronic spectra obtained experimentally clearly do not obey the selection rules demanded by these point-groups, D_2 symmetry requiring no absorption in the z polarisation, while under a C_{2v} symmetry only transitions to the $^3A_2$ component of $^3T_{1g}$ manifolds are allowed. (Figure 2 shows that this is not the case.) Hence, in spite of the lack of a formal centre of symmetry, the centrosymmetric point-group D_{2h} is preferred

[11] D. E. Billing and B. J. Hathaway, *J. Chem. Soc. (A)*, 1968, 1516.

in describing the symmetry of ligand field around the Ni^{II} ion.

The vibronic selection rules in D_{2h} symmetry are shown in Table 3. It is also assumed that the b_{1u} mode of vibration is the most effective in giving rise to the intensity. In D_{2h} symmetry, the b_{1u} mode corresponds to an out-of-plane bending mode, and the particular efficiency of this mode of vibration has been observed previously in the assignment of metal complexes.[11,12]

In the z polarisation, the b_{1u} mode allows the $^3B_{1g} \longleftarrow {}^3B_{1g}$ transitions and may be assigned to the
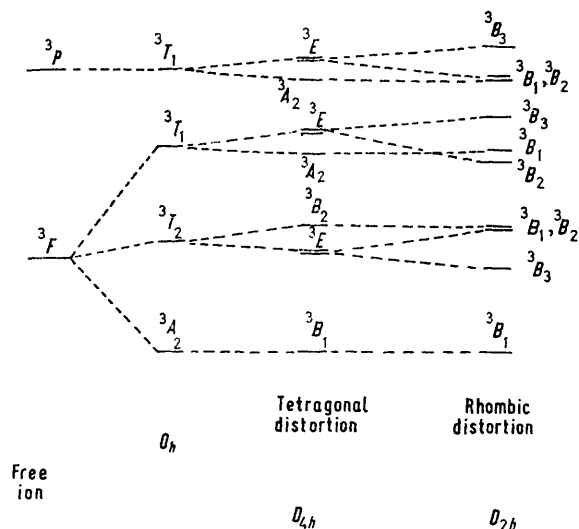

FIGURE 3 Energy levels of the nickel(II) ion in the complex Ni(den)$_2$Cl$_2$,H$_2$O in D_{2h} symmetry; the subscript g has been omitted from all terms

bands appearing at 11·6, 18·3, and 28·7 kK. In the x and y polarisations, the b_{1u} mode activates the $^3B_{3g} \longleftarrow {}^3B_{1g}$ and $^3B_{2g} \longleftarrow {}^3B_{1g}$ transitions respectively and leads to the complete assignment recorded in Table 3. The

TABLE 3

Vibronic selection rules in D_{2h} symmetry with a $^3B_{1g}$ ground state

Transition	Polarisation		
	$z(B_{1u})$	$x(B_{3u})$	$y(B_{2u})$
$^3B_{1g} \longleftarrow {}^3B_{1g}$	b_{1u}	b_{3u}	b_{2u}
$^3B_{2g} \longleftarrow {}^3B_{1g}$	b_{2u}	a_u	b_{1u}
$^3B_{3g} \longleftarrow {}^3B_{1g}$	b_{3u}	b_{1u}	a_u

assignment in D_{2h} symmetry of a molecule lacking a centre of symmetry has also been observed for the complex tetrakis(thiourea)nickel(II) chloride.[7]

The above assignment establishes the sequence of energy levels shown in Figure 3. The observed splitting of the octahedral manifolds is extremely small compared with the splitting encountered in other tetragonal nickel–nitrogen systems such as Ni(py)$_4$Cl$_2$, where the separation is 2000 cm^{-1} as compared with 500 cm^{-1} in the Ni(den)$_2$Cl$_2$,H$_2$O complex.

[12] B. J. Hathaway, D. E. Billing, P. Nicholls, and I. M. Procter, *J. Chem. Soc. (A)*, 1969, 319.

The relatively small splitting of these levels may be attributed to the small rhombic distortions of the molecule, brought about by the chelating effect of the diethylenetriamine ligand which prevents the N-atoms occupying the normal tetragonal positions. The small magnitude of these splittings also indicates that the complexes may be considered as essentially octahedral with a small rhombic component. This being the case, it is possible to calculate the ' octahedral ' parameters Dq and B with reasonable accuracy for $Ni(den)_2Cl_2,H_2O$. From an analysis of the spectra using these assignments and the relevant Tanabe–Sugano diagram, we obtain $Dq = 1176$ and $B = 784$ cm^{-1}. A comparison of these values with those obtained for other nitrogen co-ordinating complexes, e.g., $[Ni(NH_3)_6]^{2+}$ ($Dq = 1100$, $B = 846$ cm^{-1}) and $Ni(en)_3(NO_3)_2$[13] ($Dq = 1185$ and $B = 790$ cm^{-1}) indicates that there is very little variation of Dq or B with the mode of co-ordination of the nitrogen ligands. This suggests that the effect of the chelate rings, although influencing the molecular geometry of the complex, has little effect on the value of the ligand-field parameters and the effective symmetry, which are determined almost entirely by the $Ni-N_6$ co-ordination sphere.

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