

- P. O. Whimp and N. F. Curtis, *J. Chem. Soc. A*, 867 (1966).
- (11) S. C. Jackels, K. Farmery, E. K. Barefield, N. J. Rose, and D. H. Busch, *Inorg. Chem.*, **11**, 2893 (1972).
- (12) N. Sadasivan, J. A. Kernohan, and J. F. Endicott, *Inorg. Chem.*, **6**, 770 (1967).
- (13) D. P. Rillema, J. F. Endicott, and E. Papaconstantinou, *Inorg. Chem.*, **10**, 1739 (1971).
- (14) J. Vasilevskis and D. C. Olson, *Inorg. Chem.*, **10**, 1228 (1971).
- (15) F. V. Lovecchio, E. S. Gore, and D. H. Busch, *J. Am. Chem. Soc.*, **96**, 3109 (1974).
- (16) V. L. Goedken and D. H. Busch, *Inorg. Chem.*, **10**, 2697 (1971).
- (17) K. Farmery and D. H. Busch, manuscript in preparation.
- (18) V. L. Goedken, N. Kildahl, and D. H. Busch, manuscript in preparation.
- (19) L. G. Warner, Ph.D. Thesis, The Ohio State University, 1968.
- (20) K. M. Long and D. H. Busch, *Inorg. Chem.*, **9**, 505 (1970).
- (21) G. Dyer and D. W. Meek, *J. Am. Chem. Soc.*, **89**, 3983 (1967).
- (22) G. A. Barclay and R. S. Nyholm, *Chem. Ind. (N.Y.)*, 378 (1953).
- (23) M. J. Norgett, J. H. M. Thornley, and L. M. Venanzi, *Coord. Chem. Rev.*, **2**, 99 (1967).
- (24) Z. Dori and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 1394 (1966).
- (25) M. Ciampolini and P. Paoletti, *Inorg. Chem.*, **6**, 126 (1967).
- (26) L. Sacconi, M. Ciampolini, and G. P. Speroni, *Inorg. Chem.*, **4**, 1116 (1965).
- (27) L. Sacconi, I. Bertini, and R. Morassi, *Inorg. Chem.*, **6**, 1548 (1967).
- (28) E. Ochiai and D. H. Busch, *Inorg. Chem.*, **8**, 1474 (1969).
- (29) B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, **4**, 1102 (1965).
- (30) P. O. Whimp and N. F. Curtis, *J. Chem. Soc. A*, 867 (1966); 1827 (1966); 188 (1968).
- (31) N. F. Curtis, *J. Chem. Soc., Dalton Trans.*, 1212 (1973).
- (32) S. C. Cummings and D. H. Busch, *J. Am. Chem. Soc.*, **92**, 1924 (1970); *Inorg. Chem.*, **10**, 1220 (1971).
- (33) J. J. Christensen, D. J. Eatough, and R. M. Izatt, *Chem. Rev.*, **74**, 351 (1974).
- (34) N. F. Curtis, *J. Chem. Soc.*, 2644 (1964).
- (35) T. D. Dubois and D. W. Meek, *Inorg. Chem.*, **8**, 146 (1969).
- (36) W. J. Geary, *Coord. Chem. Rev.*, **7**, 81 (1971).
- (37) W. De W. Horrocks, G. R. Van Hecke, and D. D. W. Hall, *Inorg. Chem.*, **6**, 694 (1967).
- (38) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 338 (1959).
- (39) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Am. Chem. Soc.*, **86**, 4580 (1964).
- (40) S. Cockle, H. A. O. Hill, S. Ridsdale, and R. J. P. Williams, *J. Chem. Soc., Dalton Trans.*, 297 (1972).
- (41) G. N. Schrauzer and L. P. Lee, *J. Am. Chem. Soc.*, **90**, 6541 (1968).
- (42) S. Buffagni, L. M. Vallarino, and J. V. Quagliano, *Inorg. Chem.*, **3**, 671 (1964).
- (43) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds", Wiley, New York, N.Y., 1963.
- (44) N. F. Curtis, Y. M. Curtis, and H. K. J. Powell, *J. Chem. Soc. A*, 1015 (1966).
- (45) K. G. Caulton, *Inorg. Chem.*, **7**, 392 (1968).
- (46) R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).

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## Single Crystal Electronic Spectra and Ligand Field Parameters of Some Nickel(II) Amine–Isothiocyanato and Amine–Nitrito Complexes

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The single crystal linearly polarized electronic spectra of tetragonal  $\text{Ni(en)}_2(\text{NCS})_2$  and  $\text{Ni(en)}_2(\text{NO}_2)_2$  over the 8000–30000  $\text{cm}^{-1}$  range have been reported and assigned. Ligand field parameters,  $Dq$ ,  $Ds$ , and  $Dt$ , and angular overlap parameters,  $e\sigma'$  and  $e\pi'$  were derived from the assigned d–d spectra. These parameters have been compared with those of the respective tetragonal amine nickel complexes with known structure whose spectra were reliably assigned. The strong dependence of  $Dq$  on the metal–donor distance has been found for en and amine nickel complexes. The possibility of transferring the  $e\sigma'$  and  $e\pi'$  parameters of the donor atoms, corrected for the appropriate distance, is also discussed.

### Introduction

The electronic spectra of tetragonal metal complexes have been extensively studied<sup>1</sup> largely because the number of ligand field parameters required by symmetry for the nonadditivity model corresponds to the number of independent mono-electronic d–d transitions,<sup>2</sup> as in the case of cubic complexes. Particular attention has been devoted to nickel(II) complexes, which have an orbitally nondegenerate ground state and show spectra with at least three spin-allowed d–d bands.<sup>3</sup> These spectra, however, often revealed small splittings of the transitions of the parent octahedral symmetry<sup>1,4</sup> thus providing the best justification for the rule of the average environment.<sup>5</sup> Even single crystal polarized electronic spectra often failed to show the tetragonal components well resolved.<sup>6–9</sup> For instance the spectra of  $\text{Ni}(\text{NH}_3)_4(\text{NCS})_2$  were practically unpolarized, while those of  $\text{Ni}(\text{NH}_3)_4(\text{NO}_2)_2$  did show some polarizations,<sup>9</sup> but the splittings were evaluated from the maxima of broad bands recorded at room temperature.

In the last few years there has been a revival of ligand field calculations for low-symmetry complexes,<sup>9–13</sup> and again tetragonal nickel complexes have been the subject of several studies in order to check the validity of ligand field parameterizations. In particular the possibility of transferring the ligand field parameters in the additivity scheme has been investigated.<sup>10</sup> In this scheme, the number of parameters required to fit the experimental data is larger than the number of independent d–d transitions so that significant values of the parameters cannot be obtained from the electronic spectra. The angular overlap model<sup>14</sup> (AOM), however, has been

shown<sup>10,15–17</sup> to be quite promising in overcoming this problem because it seems to have a more sound physical basis than conventional crystal field models and the values of some parameters can, in principle, be transferred from other similar complexes. It seems necessary therefore to study sets of closely related chromophores which can allow the determination of significant values of the AOM parameters in order to check the validity of the basic assumptions of the model.

With these considerations in mind we have looked for tetragonal nickel(II) amine complexes with the aim of determining the dependence of the best fitting angular overlap parameters on the metal–nitrogen distances. Such a dependence has been compared with that which can be calculated through the diatomic nickel–nitrogen overlap. The choice of amine ligands allows for the reasonable assumption<sup>1,15</sup> of the AOM– $\pi$  bonding parameter,  $e\pi'$ , equal to zero for  $\text{sp}^3$  nitrogen atoms. The complex  $\text{Ni(en)}_2(\text{NCS})_2$  (I), whose x-ray structure has been reported,<sup>18</sup> shows a large tetragonal splitting and appears to fit well the above requirements. We wish to report the single crystal electronic spectra of I, as well as those of  $\text{Ni(en)}_2(\text{NO}_2)_2$ <sup>18</sup> (II), for comparison purposes. Literature data on spectral assignments of complexes with known structure are also taken into consideration.

### Experimental Section

**Crystal Data.** The x-ray crystal structure of  $\text{Ni(en)}_2(\text{NCS})_2$  (I) has been determined by Brown and Lingafelter.<sup>18</sup> The compound is monoclinic, space group  $P2_1/a$ ,  $Z = 2$ ,  $a = 10.28 \text{ \AA}$ ,  $b = 8.26 \text{ \AA}$ ,  $c = 8.88 \text{ \AA}$ ,  $\beta = 121^\circ 3'$  with the nickel ion lying on a  $C_i$  site symmetry. The Ni–NCS distance is 2.15  $\text{ \AA}$ , whereas the Ni–N in-plane distances

**Table I.** The Squares of the Projections of the Molecular Axes along the Extinction Directions of  $\text{Ni(en)}_2(\text{NCS})_2$  and  $\text{Ni(en)}_2(\text{NO}_2)_2$ 

	<i>a</i>	<i>b</i>	<i>r</i>	<i>r'</i>
$\text{Ni(en)}_2(\text{NCS})_2$				
<i>z</i>	0.02	0.78	0.69	0.16
<i>x</i>	0.01	0.21	0.29	0.67
<i>y</i>	0.97	0.01	0.02	0.17
$\text{Ni(en)}_2(\text{NO}_2)_2^a$				
<i>z</i>	0.67	0.11		

<sup>a</sup> The projections of *x* and *y* are omitted in this case because they are not relevant to the discussion (see text).

are 2.09 and 2.11 Å. The isothiocyanate ion is bent, the Ni–N–C angle being 140°. Neglecting this, the overall symmetry of the chromophore is quite close to  $D_{2h}$ , the main distortion from tetragonal  $D_{4h}$  symmetry being the in-plane bond angles sensibly smaller than 90° (82 and 98°). Blue crystals were grown by slow evaporation of water solutions. Weissenberg techniques showed that the plates had the (001) face most highly developed, limited by lateral faces of the kind (110).

The x-ray crystal structure of  $\text{Ni(en)}_2(\text{NO}_2)_2$  (II) has been determined by Minacheva et al.<sup>19</sup> The compound is monoclinic, space group  $P2_1/a$ ,  $Z = 2$ ,  $a = 10.949$  Å,  $b = 6.744$  Å,  $c = 7.954$  Å,  $\beta = 105^\circ$ . The Ni–NO<sub>2</sub> distance is 2.13 Å, whereas the average Ni–N in-plane distance is 2.11 Å. Also in the present case the in-plane bond angles are 82 and 98°. Thin red crystals were grown by slow evaporation of methanol solutions. They were thin monoclinic plates parallel to the (001) face.

**Spectral Measurements.** The room and liquid nitrogen temperature spectra were recorded with the apparatus previously described.<sup>20</sup> The 4.2 K spectra were recorded on a Cary 14 spectrophotometer equipped with a cryogenic apparatus purchased from Oxford Instruments. A Glan-Thomson prism was used as a polarizer.

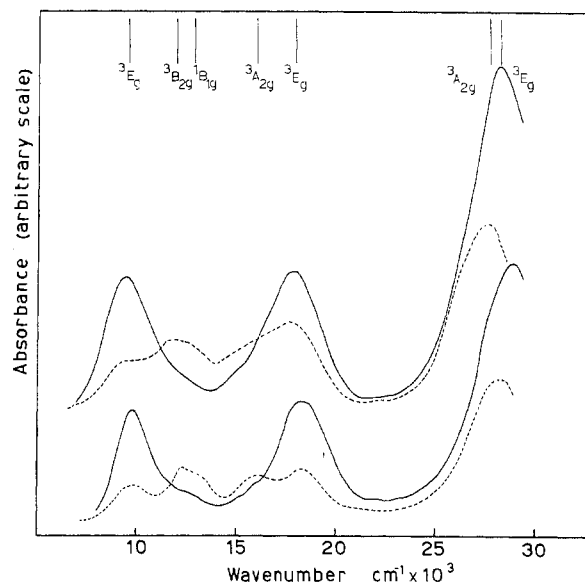
Polarized spectra of I were recorded both on the (001) face (with the electric vector of incident radiation parallel to *a* and *b*, respectively) and on the (110) face. In the latter case the spectra were recorded along the extinction directions, *r* and *r'*, making an angle of 45° with the *c* axis. The squares of the components of the molecular axes (*z* is parallel to the Ni–NCS direction; *x* is parallel to the shorter in-plane bond direction) along the *a*, *b*, *r*, and *r'* directions are reported in Table I. Polarized spectra of II were recorded on the (001) face. The components of the *z* direction, chosen as for I, on the *a* and *b* directions are also reported in Table I.

## Results

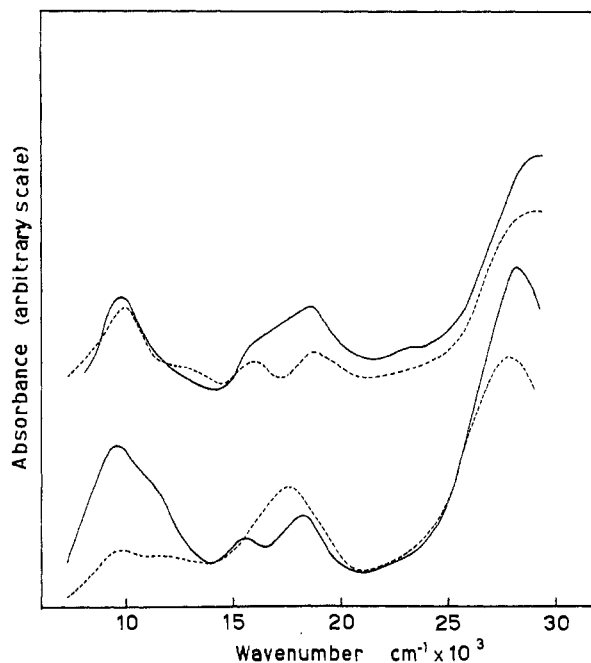
The electronic spectra of I, recorded on the (001) and (110) faces, are reported in Figures 1 and 2, respectively. Both the series of spectra show well-developed polarization properties in agreement with the figures of Table I. These spectra are dramatically different from the spectra of the analogous complex  $\text{Ni}(\text{NH}_3)_4(\text{NCS})_2$  in which the parent octahedral transitions were practically unsplit.<sup>9</sup> The spectra recorded parallel to *a* and *r'*, which should be quite different if there were significant in-plane anisotropy (see Table I), do not show any substantial shift of the maxima (see below), suggesting that the *x* and *y* molecular axes are practically equivalent in the present chromophore.<sup>21</sup>

In the spectrum recorded parallel to *b* three maxima are observed at 9.6, 17.9, and 28.3 kK at room temperature which shift to 9.8, 18.3, and 28.9 kK at liquid nitrogen temperature. The blue shift of the transitions lowering the temperature is accompanied by a decrease of the integrated band intensities, suggesting that the transitions are allowed by the usual vibronic coupling mechanism.<sup>22</sup> The room-temperature spectra parallel to *a* and *r'* show a shoulder at ~10 kK, a maximum at 12.0, shoulders at 13 and ~15–16, and maxima at 17.8 and 27.7 kK. These bands in the *a* spectrum also shift to higher frequencies on cooling, decreasing in integrated intensities in accord with a vibronic mechanism. In both the spectra some low-intensity absorptions can be found at 22–23 kK.

In Figure 3 are reported the spectra recorded on the (001)



**Figure 1.** Single crystal polarized electronic spectra of  $\text{Ni(en)}_2(\text{NCS})_2$  recorded on the (001) face: upper, room temperature; lower, liquid nitrogen temperature; (—) electric vector parallel to *b*; (---) electric vector parallel to *a*.



**Figure 2.** Single crystal polarized electronic spectra of  $\text{Ni(en)}_2(\text{NCS})_2$  recorded on the (001) face: lower, room temperature; upper, liquid nitrogen temperature; (—) electric vector parallel to *r*; (---) electric vector parallel to *r'*.

face at 4.2 K. The overall appearance of the spectra is similar to that of the high-temperature spectra, apart from a marked sharpening which in the case of the *a* spectrum allows a clear resolution of the maxima in the envelopes of the 12–13 and 16–18 kK bands. The former absorption is resolved into two distinct maxima at 12.5 and 13.5 kK, while in the latter envelope a maximum can be located at 16.4 kK. In the *a* spectrum a small maximum can be detected at 22.6 kK.

The spectra of II recorded at room and liquid nitrogen temperature are reported in Figure 4. In this case large shifts of the maxima with the polarization directions are not observed, and the spectra closely resemble the ones reported by Ballhausen and Hare<sup>9</sup> for  $\text{Ni}(\text{NH}_3)_4(\text{NO}_2)_2$ . The spectrum recorded parallel to *a* shows at room temperature a shoulder

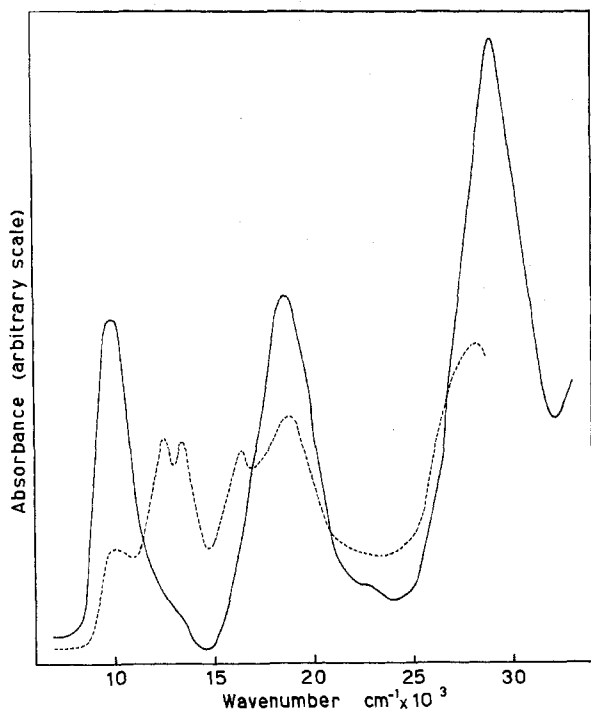


Figure 3. Single crystal polarized electronic spectra of  $\text{Ni}(\text{en})_2(\text{NCS})_2$  recorded on the (001) face at 4.2 K: (—) electric vector parallel to  $b$ ; (---) electric vector parallel to  $a$ .

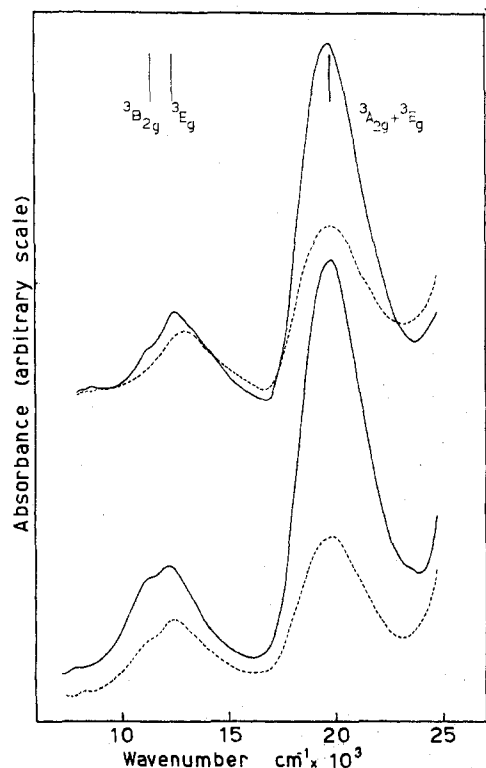


Figure 4. Single crystal polarized electronic spectra of  $\text{Ni}(\text{en})_2(\text{NO}_2)_2$  recorded on the (001) face: lower, room temperature; upper, liquid nitrogen temperature; (—) electric vector parallel to  $a$ ; (---) electric vector parallel to  $b$ .

at 11.4 kK, a maximum at 12.2 kK (with another shoulder at 13.5 kK), and an intense maximum at 19.8 kK. The spectrum recorded parallel to  $b$  shows shoulders at 11.4 and 13.6 and maxima at 12.4 and 19.8 kK. The  $b$  spectrum is less intense than the  $a$  spectrum. The spectra above 23 kK are obscured by an intense charge transfer or ligand absorption.

Table II. The Assignment of the Absorption Maxima to the Electronic Transitions of  $\text{Ni}(\text{en})_2(\text{NCS})_2$  and  $\text{Ni}(\text{en})_2(\text{NO}_2)_2$  ( $D_{4h}$  Symmetry)<sup>a</sup>

	$\text{Ni}(\text{en})_2(\text{NCS})_2$ Obsd	$\text{Ni}(\text{en})_2(\text{NO}_2)_2$ Calcd <sup>b</sup>	$\text{Ni}(\text{en})_2(\text{NO}_2)_2$ Obsd
${}^3\text{B}_{1g} \rightarrow {}^3\text{E}_g({}^3\text{T}_{2g})$	9.6	9.5	12.2
${}^3\text{B}_{2g}({}^3\text{T}_{2g})$	12.0	12.0	11.4
${}^1\text{A}_{1g}$ } ( ${}^1\text{E}_g$ )	13.2	12.2	
${}^1\text{B}_{1g}$ }		13.4	
${}^3\text{A}_{2g}({}^3\text{T}_{1g}, \text{F})$	16.0	15.9	19.8
${}^3\text{E}_g({}^3\text{T}_{1g}, \text{F})$	17.9	17.8	19.8
${}^1\text{E}_g({}^1\text{E}_g)$	22	22.6	
${}^3\text{A}_{2g}({}^3\text{T}_{1g}, \text{P})$	27.7	27.6	
${}^3\text{E}_g({}^3\text{T}_{1g}, \text{P})$	28.3	28.4	

<sup>a</sup> All the values are expressed in kK. <sup>b</sup>  $Dq = 1203 \pm 16 \text{ cm}^{-1}$ ;  $Ds = 656 \pm 73 \text{ cm}^{-1}$ ;  $Dt = 230 \pm 26 \text{ cm}^{-1}$ ;  $B = 883 \pm 18 \text{ cm}^{-1}$ ;  $C = 3353 \pm 72 \text{ cm}^{-1}$ .

At liquid nitrogen temperature in both the polarizations the apparent intensity of the low-frequency maximum increases as compared to the 11.4 kK shoulder, and a high-frequency shift is also observed. The band in the  $a$  polarization shows a maximum at 12.7 kK while in the  $b$  spectrum the maximum is at 12.9 kK.

## Discussion

**Assignment of the Spectra.** Notwithstanding the actual low symmetry of the chromophores, the electronic spectra do not show any appearance of symmetry components lower than tetragonal and the assignment will be attempted in  $D_{4h}$  symmetry. Also for similar copper complexes the polarized electronic spectra were assigned in  $D_{4h}$  symmetry.<sup>23</sup> On this basis the assignment of I is straightforward, with the bands which appear in parallel polarization assigned as  ${}^3\text{B}_{1g} \rightarrow {}^3\text{E}_g$  in accord with an  $e_u$  vibration mostly effective in giving intensity to the transition.<sup>9</sup> The bands which are mostly  $\perp$  are to be assigned to transitions to orbitally nondegenerate triplets as shown in Table II. The band with a maximum at 13.2 kK can be assigned to transitions to either  ${}^1\text{A}_{1g}({}^1\text{D})$  or  ${}^1\text{B}_{1g}({}^1\text{D})$  levels or both. The absorptions in the region of 22 kK can also be assigned to spin-forbidden transitions arising from  ${}^1\text{D}$ .

The two systems of bands centered at 12 and 20 kK, respectively, in the spectrum of II must be attributed to the transitions originating from  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$  and  ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$  of octahedral symmetry, respectively. In the high-frequency band no shift of the maxima is observed, although the overall intensity of the absorption changes in the two polarization directions. In  $D_{4h}$  symmetry the  ${}^3\text{B}_{1g} \rightarrow {}^3\text{A}_{2g}({}^3\text{T}_{1g})$  and  $\rightarrow {}^3\text{E}_g({}^3\text{T}_{1g})$  transitions therefore are assigned to the band at 19.8 kK. Under the envelope of the low-frequency band at least two spin-allowed transitions must be contained as shown by the presence of a maximum and a shoulder. The shape of the absorption does not markedly change with the polarization directions nor with the temperature. This pattern is in contrast with a simple tetragonal vibronic mechanism, and the operation of other vibrating normal modes as well as a magnetic dipole mechanism<sup>7</sup> cannot be excluded. The broad nature of the band does not allow a deeper insight into the vibronic mechanism. A detailed assignment cannot be attempted, and we suggest, on the grounds of the lower position of en as compared to  $\text{NO}_2$  in the spectrochemical series, that the 11.4 kK band is assigned as  ${}^3\text{B}_{1g} \rightarrow {}^3\text{B}_{2g}({}^3\text{T}_{2g})$  and the 12.2 kK maximum as  ${}^3\text{B}_{1g} \rightarrow {}^3\text{E}_g({}^3\text{T}_{2g})$ . A similar scheme was used for the assignment of the complex  $\text{Ni}(\text{NH}_3)_4(\text{NO}_2)_2$ .<sup>9</sup> However, the suggested energy level order was contrary to that expected on the basis of the assignment, and we suggest that also in that case  ${}^3\text{B}_{2g}$  is lower in energy than  ${}^3\text{E}_g$ . In the present assignment the ligand field parameters for  $\text{Ni}(\text{NH}_3)_4(\text{NO}_2)_2$  can be estimated by band splitting as  $Dq = 1120 \text{ cm}^{-1}$ ,  $Ds = -100 \text{ cm}^{-1}$ , and  $Dt = -91 \text{ cm}^{-1}$ .

**Table III.** The Relation between the Different Ligand Field and Angular Overlap Schemes for Tetragonal Complexes with Equatorial Amine Donors

$$\begin{aligned}
 I_2^{\parallel} &= \frac{10}{3}Dq - \frac{7}{2}Ds & e_{\sigma}^{\parallel} &= \frac{10}{3}Dq - 2Ds - \frac{5}{2}Dt \\
 Dq^{\parallel} &= \frac{1}{6}I_2^{\parallel} = Dq - \frac{7}{4}Dt & e_{\pi}^{\parallel} &= -\frac{3}{2}Ds + \frac{10}{4}Dt \\
 I_2^{\perp} &= 0.55Dq & e_{\sigma}^{\perp} &= \frac{10}{3}Dq \\
 Dq^{\perp} &= Dq & e_{\pi}^{\perp} &= 0
 \end{aligned}$$

**Ligand Field Parameters.** The complete assignment of the spin-allowed transitions of I allows the calculation of the ligand field parameters  $Dq$ ,  $Ds$ ,  $Dt$ , and  $B$ . The matrices reported by Lever,<sup>24</sup> including of course CI, were used and the values of the parameters were calculated through a least-squares analysis. The values are reported in Table II together with the estimated standard deviations and the observed and calculated energies of the transitions. The observed spin-forbidden transitions were not used to fit the experimental spectra though their energies were satisfactorily reproduced using the values of the parameters obtained as described previously and reducing  $C$  from the free ion value of the same amount as  $B$ . An attempt was also made to take into account also the actual low symmetry of the complex by relaxing the in-plane bond angles from  $90^\circ$  to the experimental values, the overall symmetry of the chromophore reducing to  $D_{2h}$ . The expected splitting of the  ${}^3E_g$  transition in this case should be about  $1000\text{ cm}^{-1}$ , hardly consistent with the appearance of the electronic spectra. It cannot be excluded that an accidental balance of  $D_{2h}$  and lower symmetry components can simulate tetragonal symmetry.

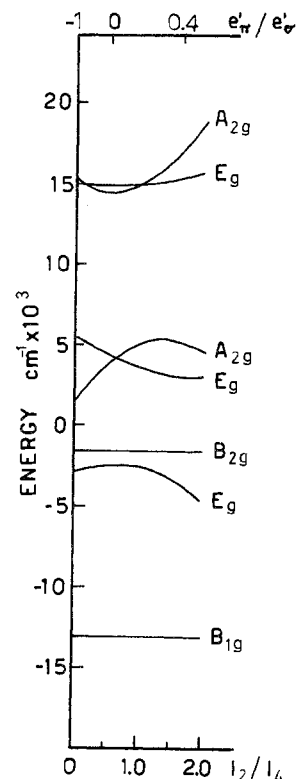
In the case of II the number of observed transitions is not sufficient to obtain a reasonable least-squares fit. Therefore  $Dq$  was calculated as  $1140\text{ cm}^{-1}$  from the energy of the  ${}^3B_{1g} \rightarrow {}^3B_{2g}$  transition, and rough guesses of  $Ds$  and  $Dt$  were obtained through the splitting of the  ${}^3T_{2g}$  and  ${}^3T_{1g}$  levels as  $-68$  and  $14\text{ cm}^{-1}$ , respectively.

If all the ligands are considered as linearly ligating<sup>25</sup> and  $e_{\pi}{}^{14}$  for the equatorial nitrogen atoms is assumed as zero,<sup>15</sup> a one-to-one correspondence can be drawn between the ligand field and the angular overlap model<sup>1,26</sup> as shown in Table III. In the additivity scheme of the ligand field, the  $e_{\pi}{}^{\perp} = 0$  condition corresponds to setting the radial integral ratio,  $I_2/I_4$ ,<sup>16</sup> for the equatorial nitrogen atom as 0.55. On this basis a one-to-one correspondence can be drawn also between the additivity and the nonadditivity<sup>26</sup> ligand field parameters (Table III). With the above expressions the values of the parameters for I and II can be calculated as shown in Table IV. The parameters for  $\text{Ni}(\text{NH}_3)_4(\text{NCS})_2$  and  $\text{Ni}(\text{NH}_3)_4(\text{NO}_2)_2$  are also reported for comparison purposes. The estimated errors in the parameters of I were evaluated through error propagation techniques.<sup>27</sup> The  $Dq$  value for the isothiocyanate ion is in the present case exceptionally low if compared with the position of isothiocyanate in the spectrochemical series<sup>28</sup> and the value found in  $\text{Ni}(\text{NH}_3)_4(\text{NCS})_2$  for instance. This low value accounts for the observed large

**Table IV.** The Values of the Ligand Field (Additivity Scheme) and Angular Overlap Parameters for the Donor Atoms in  $\text{Ni}(\text{en})_2(\text{NCS})_2$ ,  $\text{Ni}(\text{en})_2(\text{NO}_2)_2$ ,  $\text{Ni}(\text{NH}_3)_4(\text{NCS})_2$ , and  $\text{Ni}(\text{NH}_3)_4(\text{NO}_2)_2$ <sup>a</sup>

	$\text{Ni}(\text{en})_2(\text{NCS})_2$ <sup>b</sup>		$\text{Ni}(\text{en})_2(\text{NO}_2)_2$ <sup>c</sup>		$\text{Ni}(\text{NH}_3)_4(\text{NCS})_2$ <sup>c,d</sup>		$\text{Ni}(\text{NH}_3)_4(\text{NO}_2)_2$ <sup>c,e</sup>	
	N	NCS	N	$\text{NO}_2$	N	NCS	N	$\text{NO}_2$
$Dq$	1203 (16)	800 (21)	1140	1260	1075	1103	1120	1280
$I_2$	4006 (50)	1714 (267)	3800	3775	3583	3968	3733	3090
$e_{\sigma}^{\parallel}$	4010 (53)	2123 (100)	3800	3942	3583	3843	3733	4165
$e_{\pi}^{\parallel}$	0	-409 (146)	0	-191	0	125	0	-75

<sup>a</sup> All the values are expressed in  $\text{cm}^{-1}$ . <sup>b</sup> Estimated standard deviations in parentheses. <sup>c</sup> No safe estimation of the error was possible for these complexes.  $Dq$  value of N must be affected by an error comparable to that of ( $I$ ), while the other parameters may be affected by an error at best equal to that of ( $I$ ). <sup>d</sup> See ref 9. <sup>e</sup> See ref 9 and present work.

**Figure 5.** Energy level diagram for the triplet states of a tetragonal nickel(II) complex as a function of the  $I_2/I_4$  and  $e_{\pi}^{\parallel}/e_{\sigma}^{\parallel}$  ratios for the axial ligands.

splitting of the parent octahedral levels in I in contrast with the spectra of  $\text{Ni}(\text{NH}_3)_4(\text{NCS})_2$  which closely resemble those of purely octahedral symmetry. The low  $Dq$  value may be due either to the large Ni-NCS distance (it is  $2.15\text{ \AA}$  in I while it is  $2.07$  for the ammonia analogue<sup>9</sup>) and/or the small Ni-N-C angle which may possibly reduce the extent of the  $\sigma$  overlap for the ligand. Indeed the  $e_{\sigma}^{\parallel}$  parameter is much lower than the corresponding one for the equatorial nitrogen ligands and  $e_{\pi}^{\parallel}$  is probably negative, whereas it is small and positive for the complex  $\text{Ni}(\text{NH}_3)_4(\text{NCS})_2$ .<sup>1</sup> Actually the  $e_{\pi}^{\parallel}$  value of I is affected by a large error (see Table IV), and since the values are estimated through energy values obtained from the maxima of broad bands, sample calculations were performed using for the transition energy different values varying within the half-width of the bands. The corresponding  $e_{\pi}^{\parallel}$  values are found to vary between  $0$  and  $-400\text{ cm}^{-1}$ . It appears therefore that a small and negative value of  $e_{\pi}^{\parallel}$  is consistent with the spectral data. The energy level dependence on the  $e_{\pi}^{\parallel}/e_{\sigma}^{\parallel}$  (or  $I_2/I_4$ ) ratio, at constant  $Dq$ , of the apical positions is shown in Figure 5.

The  $Dq$  value for  $\text{NO}_2$  of II appears quite reasonable and in good agreement with the value observed for  $\text{Ni}(\text{NH}_3)_4(\text{NO}_2)_2$ .<sup>9</sup> In both the complexes the  $e_{\sigma}^{\parallel}$  and  $e_{\pi}^{\parallel}$  values are quite similar, the Ni- $\text{NO}_2$  distances being  $2.13$  and  $2.15\text{ \AA}$ , respectively. Again,  $e_{\pi}^{\parallel}$  values are found to be negative

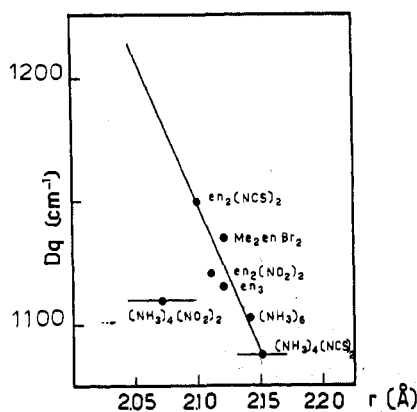


Figure 6. The dependence of  $Dq$  on the nickel–nitrogen distance for amine complexes. The symbols have the meaning used throughout the text. References:  $\text{Me}_2\text{en}$ ,<sup>30</sup>  $\text{en}_2(\text{NCS})_2$ ,<sup>18</sup>  $\text{en}_2(\text{NO}_2)_2$ ,<sup>19</sup>  $\text{en}_3$ ,<sup>31,32</sup>  $(\text{NH}_3)_6$ ,<sup>33,31</sup>  $(\text{NH}_3)_4(\text{NCS})_2$ ,<sup>34</sup>  $(\text{NH}_3)_4(\text{NO}_2)_2$ ,<sup>34</sup>

according to the current view on the coordination bond in this ligand.

**The Relationship between  $Dq$  and the Nickel–Nitrogen Distance.** The values of the ligand field parameters calculated for I and II for the equatorial nitrogen donor atoms and the values of similar donor atoms found in the literature are reported in Figure 6 against the experimental nickel–nitrogen distance. The number of experimental points is unfortunately low, but they appear to follow a rather regular pattern.  $Dq$  (or  $e_{\sigma'}$ ) decreases smoothly with the distance with the possible exception of  $\text{Ni}(\text{NH}_3)_4(\text{NO}_2)_2$ , whose structural parameters as well as those of  $\text{Ni}(\text{NH}_3)_4(\text{NCS})_2$  are affected by a large error.<sup>19</sup> The line of Figure 6 has been calculated as to minimize the error sum through the relation

$$Dq = \frac{3}{10} e_{\sigma'} = K S_{\sigma}^2$$

where  $S_{\sigma}^2$ , the diatomic nickel–nitrogen  $\sigma$  overlap, was evaluated using Clementi nickel 3d and nitrogen 3p functions.<sup>29</sup> Using  $sp^3$  orbitals does not affect the dependence of the overlap on the distance, in the range of interest, while it only changes the value of  $K$ . The results reported are referred to nitrogen 3p for the sake of simplicity. The charge distribution was assumed in every case as corresponding to  $\text{Ni}^0\text{--N}^0$ . The value of  $K$  obtained is 239 (3) kK. The average distance of the points of the curve from the experimental points is in general small, again with the exception of  $\text{Ni}(\text{NH}_3)_4(\text{NO}_2)_2$ ,<sup>34</sup> giving an idea of the order of magnitude of the error in transferring the ligand field parameters from one chromophore to the other. The dependence of  $Dq$  on the distance is a rather steep one showing how caution must be used in the assumption of the values of ligand field parameters for complexes of unknown crystal structure. The suggested value of  $K$  cannot be considered very satisfactory due to the small number of points used to evaluate it and to the uncertainty associated with some of the distance values.

It should be noted furthermore that the present model is an extremely simplified and rough one since (i) no differentiation has been introduced among primary, secondary, and tertiary nitrogens, (ii) the charge distribution has been assumed as a constant throughout the series of chromophores, and (iii) the calculated diatomic overlap has not included all the orbitals which by symmetry can be mixed. Despite these severe limitations the results appear to be encouraging and suggest that the AOM can provide some useful first approximation guesses of the values of the parameters to be used to assign

the d–d spectra. As an example of the use which can be made of the values of Figure 6 we have taken into consideration the spectra of  $\text{Ni}(\text{cyclam})\text{Cl}_2$ <sup>35</sup> (cyclam is the macrocyclic ligand 1,4,8,11-tetraazacyclotetradecane). They show four maxima at 8.4, 14.9, 19, and 28 kK. The envelope of the 14.9 kK absorption is unsymmetrical toward the low-frequency edge. These spectra were assigned using the  $Dq$  of 1420  $\text{cm}^{-1}$  for the equatorial ligand<sup>4</sup> which is a very high value. The structure of the complex has been reported,<sup>36</sup> the average in-plane Ni–N distance being 2.06 Å. Using the data of Figure 6,  $Dq$  is estimated as 1300  $\text{cm}^{-1}$  for this ligand which would require the transition  ${}^3\text{B}_{1g} \rightarrow {}^3\text{B}_{2g}$  ( $=10Dq$ ) at 13000  $\text{cm}^{-1}$ . This band might be contained under the envelope of the 14.9 kK absorption. As a matter of fact a band at this frequency is clearly resolved in the corresponding bromo derivative, suggesting that 1300  $\text{cm}^{-1}$  is a reasonable value for the equatorial  $Dq$ .

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**Registry No.**  $\text{Ni}(\text{en})_2(\text{NCS})_2$ , 15602-85-4;  $\text{Ni}(\text{en})_2(\text{NO}_2)_2$ , 17835-68-6.

## References and Notes

- (1) A. B. P. Lever, *Coord. Chem. Rev.*, **3**, 119 (1968).
- (2) J. S. Griffith, "The Theory of Transition-Metal Ions", University Press Cambridge, London, 1961.
- (3) L. Sacconi, *Transition Met. Chem.*, **4**, 199 (1968).
- (4) D. A. Rowley and R. S. Drago, *Inorg. Chem.*, **6**, 1092 (1967).
- (5) C. K. Jorgensen, "Absorption Spectra and Chemical Bonding in Complexes", Pergamon Press, New York, N.Y., 1961.
- (6) N. S. Hush and R. J. M. Hobbs, *Prog. Inorg. Chem.*, **10**, 259 (1968).
- (7) J. Ferguson, *Prog. Inorg. Chem.*, **12**, 159 (1970).
- (8) C. W. Reimann, *J. Phys. Chem.*, **74**, 561 (1970).
- (9) C. R. Hare and C. J. Ballhausen, *J. Chem. Phys.*, **40**, 792 (1964).
- (10) H. A. Hitchmann, *Inorg. Chem.*, **11**, 2386 (1972).
- (11) A. F. Schreiner and D. J. Hamm, *Inorg. Chem.*, **12**, 2041 (1973).
- (12) J. C. Donini, B. R. Hollebene, G. London, A. B. P. Lever, and J. C. Hempel, *Inorg. Chem.*, **14**, 455 (1975).
- (13) D. W. Smith, *Struct. Bonding (Berlin)*, **12**, 49 (1972).
- (14) C. E. Schaffer and C. K. Jorgensen, *Mol. Phys.*, **9**, 401 (1965).
- (15) J. Glerup, O. Monsted, and C. E. Schaffer, "Proceedings of the 16th International Conference on Coordination Chemistry," Dublin, 1974, p 2.14a.
- (16) I. Bertini, D. Gatteschi, and A. Scozzafava, *Inorg. Chem.*, **14**, 812 (1975).
- (17) I. Bertini, P. Dapporto, D. Gatteschi, and A. Scozzafava, *Inorg. Chem.*, **14**, 1639 (1975).
- (18) B. W. Brown and E. C. Lingafelter, *Acta Crystallogr.*, **16**, 753 (1963).
- (19) L. K. Minacheva, M. A. Porai-Koshits, and A. S. Antsyshkina, *J. Struct. Chem. (Engl. Transl.)*, **10**, 72 (1969).
- (20) I. Bertini, M. Ciampolini, and L. Sacconi, *J. Coord. Chem.*, **1**, 73 (1971).
- (21) The possibility that the in-plane axes were located in different positions was also taken into account. If the axes are chosen so that  $x'$  bisects the small in-plane angle the components along  $a$  are 0.37 for  $x'$  and 0.61 for  $y'$  and along  $r'$  0.76 for  $x'$  and 0.09 for  $y'$ . The conclusions regarding the in-plane anisotropy are independent of the in-plane axis choice.
- (22) C. J. Ballhausen, "Introduction to Ligand Field Theory", McGraw-Hill, New York, N.Y., 1962.
- (23) B. J. Hathaway, D. E. Billing, P. Nicholls, and I. M. Procter, *J. Chem. Soc. A*, 319 (1969).
- (24) A. B. P. Lever, "Inorganic Electronic Spectroscopy", Elsevier, Lausanne, 1968.
- (25) C. K. Jorgensen, "Modern Aspects of Ligand Field Theory", North-Holland Publishing Co., Amsterdam, 1971.
- (26) C. E. Schaffer, *Struct. Bonding (Berlin)*, **14**, 69 (1973).
- (27) W. C. Hamilton, "Statistics in Physical Science", Ronald Press, New York, N.Y., 1964.
- (28) C. K. Jorgensen, "Oxidation Numbers and Oxidation States", Springer-Verlag, Berlin, 1969.
- (29) E. Clementi, *IBM J. Res. Dev.*, **9**, 2 (1965).
- (30) R. Nasanen, L. Lemmetti, U. Lamminivu, and H. Abdalla, *Suom. Kemistil. B*, **41**, 1 (1966).
- (31) L. N. Swink and M. Atoji, *Acta Crystallogr.*, **13**, 639 (1960).
- (32) R. Dingle and R. A. Palmer, *Theor. Chim. Acta*, **6**, 249 (1965).
- (33) A. Bianchi and P. L. Orioli, unpublished results.
- (34) M. A. Porai-Koshits and M. L. Dikareva, *Kristallografiya*, **4**, 650 (1959).
- (35) B. Bosnich, M. L. Tobe, and G. A. Webb, *Inorg. Chem.*, **4**, 1109 (1965).
- (36) B. Bosnich, R. Mason, P. J. Pauling, G. B. Robertson, and M. L. Tobe, *Chem. Commun.*, 97 (1965).