The study of the complexation of 5-nitroorotic acid has been undertaken to gain further understanding of the important role played by metals in biochemical processes. In the present work we succeeded in isolating and determining the structure of a copper complex where both N(1) and N(3), as well as the carboxylate group, in a L^{3-} ligand are simultaneously involved as complexing sites. The UV study suggests that this complex exists also in solution. Consequently, the complexation site N(3) should not be neglected when biological processes are studied, as it might be stimulated either by the nature of the substituent on the pyrimidine ring or by the nature of the metal.

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Registry No. A, 85926-45-0; B, 85926-44-9; $Cu_3(NH_3)_6(C_5N_3O_6)_2$, 85955-86-8; 5-nitroorotic acid, 17687-24-0.

Supplementary Material Available: Listings of anisotropic thermal parameters for $Cu(NH_3)_2(C_5HN_3O_6)\cdot H_2O$ and $Cu_3(NH_3)_6(C_5N_3O_6)_2\cdot 5H_2O$ (Table IIS), least-squares planes equations (Table VI), and observed and calculated structure factor amplitudes and projections of unit-cell contents for A and B (25 pages). Ordering information is given on any current masthead page.

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Crystallographic and Spectroscopic Studies of Low-Symmetry Nickel(II) Complexes Possessing Long Nickel-Nitrogen Bonds

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The X-ray structure of bis(isothiocyanato)bis(*N*,*N*-diethylethylenediamine)nickel(II), $Ni[NH_2C_2H_4N(C_2H_5)_2]_2(NCS)_2$, is reported. The complex crystallizes in the triclinic space group $P\bar{1}$ with unit cell parameters a = 10.438 (10) Å, b = 8.073 (8) Å, c = 14.876 (14) Å, α = 87.2 (8)°, β = 109.6 (7)°, γ = 112.8 (8)°, and Z = 2. The nickel complexes are six-coordinate and all-trans. There is significant rhombic distortion due to bent NiNCS coordination, short $NiNH_2$ bonds, and long $NiN(C_2H_5)_2$ bonds. The single-crystal polarized spectrum of this crystal at 10 K is reported and analyzed in terms of rhombic symmetry. Single-crystal spectroscopic data for $[Ni[NH_2CH_2CH_2N(C_2H_5)_2]_2(H_2O)_2]^{2+}Cl^-{}_2$ and $Ni[(CH_3)_2NCH_2CH_2N(CH_3)_2]_2(NCS)_2$ at 10 K are also reported. The data are compared with a range of other nickel complexes of low symmetry where both X-ray and spectroscopic data are available. The angular overlap model (AOM) is used, and it is demonstrated that AOM parameters in this low symmetry parallel those previously encountered for higher symmetries. In particular the use of sterically hindered amines provides a data set in which the Ni-N bond varies from about 208 to 233 pm. The σ-N AOM parameter is shown to correlate with the nickel-nitrogen bond length.

Introduction

In recent years we have extensively studied the electronic spectra of low-symmetry metal complexes, especially those of nickel(II) and cobalt(II).[4-11] In general, we have utilized the angular overlap model (AOM)[12] and the normalized spherical harmonic Hamiltonian (NSH) approach;[13] the utilities of these two approaches have recently been compared and contrasted.[11] In this paper we ask the question: how do the angular overlap parameters, specifically those relating to σ-bonding, depend upon the length of the metal ligand bond? Clearly, since the magnitudes of the AOM parameters depend directly upon the metal-ligand overlap integral,[12] they are generally expected to decrease as the bond lengthens, but prior to this study there has been no extensive experimental test of this prediction. Such a correlation can ultimately lead to an experimentally defined analytical relationship between these quantities.

When an asymmetrically *N*,*N*-disubstituted ethylenediamine is used as a ligand, the steric hindrance by the dialkylamino group is expected to prevent the nitrogen atom from approaching the nickel atom to the optimum distance. Since the early work of Goodgame,[14,15] a fairly extensive series of complexes of nickel, cobalt, and copper containing asymmetrically disubstituted ethylenediamines has been reported, and X-ray structures are available for several of them (see Table VI for summary). Indeed such complexes generally display a "normal" $M-NH_2$ bond length and a lengthened $M-NR_2$ bond length.

We have already reported the single-crystal spectra, at 10 K, of several of these complexes, and of control complexes containing symmetrically disubstituted ethylenediamines, and

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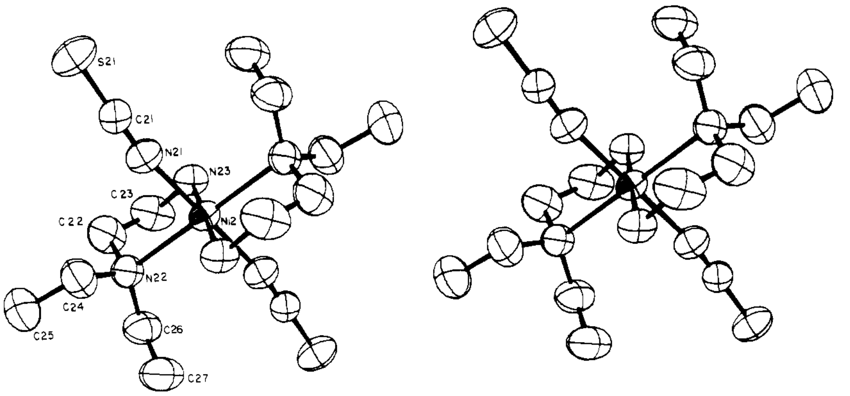

Figure 1. A stereoview of the molecular structure of Ni(*as*-$Et_2en)_2(NCS)_2$ (molecule 2).

report some additional data here. We also report the crystal structure of a further member of this series, bis(isothiocyanato)bis(*N,N*-diethylenediamine)nickel(II). This is shown to be an all-trans centrosymmetric species in which the Ni–N(Et_2) bond is significantly longer than the Ni–NH_2 bond.

The electronic spectroscopic data and the X-ray data are correlated, using the angular overlap method, to show that there is a clear experimental relationship between nickel–nitrogen bond distance and the corresponding σ-bonding AOM parameter.

Experimental Section

Preparation of the Crystals. The thiocyanato complexes were prepared by established techniques.[14-16] Crystals of a quality suitable for spectroscopy were obtained by slow deposition from acetonitrile solution. Analyses for nickel were excellent in all cases. Ni(*as*-$Et_2en)_2Cl_2$ (see footnote to Table IV for abbreviations used in this paper) crystallizes as a blue dihydrate when hydrated nickel(II) chloride is treated with an excess of *N,N*-diethylethylenediamine in methanol. The complex can be dehydrated at 76 °C in vacuo (weight loss: found 9.95; calcd 9.74%).

Recording and Analysis of Spectra. Electronic spectra were obtained in the ultraviolet, visible, and near-infrared regions on a Cary 14 spectrophotometer. Low temperatures were provided by a Displex cryogenic refrigerator. Polarization of the spectra was obtained by passing plane-polarized light along orthogonal extinction axes of the crystal.

The d^8 matrices were solved in D_{2h} symmetry on a Commodore Model 8032 microcomputer and plotted on an Epson MX-80 printer.

X-ray Data for Bis(isothiocyanato)bis(*N,N*-diethylethylenediamine)nickel(II). Purple single crystals suitable for precession photography and intensity data collection were obtained by evaporation from an acetonitrile solution of the complex. Preliminary measurements indicated triclinic symmetry, and successful refinement of the structure in the space group $P\bar{1}$ confirmed it as the correct choice. A parallelepiped-shaped crystal was mounted on a Syntex $P2_1$ automatic diffractometer equipped with scintillation counter and graphite monochromator. Unit cell dimensions were determined by a least-squares fit of the setting angles of 15 reflections well distributed in reciprocal space. Crystal data information is given in Table I. The data were collected as previously described.[16] The intensities of three standard reflections (1$\bar{1}$1; 3$\bar{1}\bar{2}$; 1$\bar{1}$3) were measured every 97 reflections and showed a root-mean-square deviation of 1.7% for which no correction was made. Five reflections (100; 0$\bar{1}$1; $\bar{1}$13; $\bar{1}$11; $\bar{1}$00) with intensities too large for accurate coincident correction were measured again at lower tube power. Intensity data were converted to structure factors through the application of the Lorentz–polarization factor. No absorption or extinction corrections were made.

Structure Determination and Refinement. The structure was solved by the heavy atom method. The positions of the nickel atoms were determined from a Patterson map at 0,0,0 and and 0,$^1/_2$,$^1/_2$ by considering the condition imposed by the density measurements of two molecules per cell. The structure was refined by a full-matrix least-squares procedure that minimized the function $\Sigma w(|F_o| - |F_c|)^2$. The weight, *w*, was chosen to be $1/\sigma_F{}^2 = 4L_pI/(\sigma'_I)^2$ with $(\sigma'_I)^2 = (\sigma_I)^2 + (0.02I)^2$. After anisotropic refinement of the non-hydrogen atoms, all hydrogen atoms could be located on a difference electron density map. The final discrepancy factors for 3751 observed reflections, after refinement of postional and anisotropic thermal parameters for non-hydrogen atoms and positional parameters for all hydrogen atoms with fixed isotropic temperature factors, are $R = (\Sigma||F_o| - |F_c||)/\Sigma|F_o| = 0.024$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.042$. Isotropic temperature factors for hydrogen atoms were set 50% greater than those of the atoms to which they were attached.

Table I. Crystal Data for Ni(*as*-$Et_2en)_2(NCS)_2$ (I)

formula	$NiC_{14}H_{32}N_6S_2$
M_r	407.29
cell parameters	
a, Å	10.438 (10)
b, Å	8.073 (8)
c, Å	14.876 (14)
α, deg	87.2 (8)
β, deg	109.6 (7)
γ, deg	112.8 (8)
V, Å^3	1083 (2)
Z	2
ρ(calcd), g cm^{-3}	1.25
ρ(obsd) (flotation, C_6H_{12}/CCl_4), g cm^{-3}	1.22 (1)
space group	$P\bar{1}$
cryst dimens, mm	0.4 × 0.3 × 0.2
temp, °C	25
radiation	Mo Kα
μ, cm^{-1}	10.8
2θ range, deg	4.4–60.0
scan rate, min^{-1}	4.0–29.0
no. of independent reflections	6357
no. with $I > 3\sigma(I)$	3751
final R_w	0.042
final *R*	0.024

Results and Discussion

Structure of Ni(*as*–$Et_2en)_2(NCS)_2$. The nickel atoms from two independent molecules are located at the corners of the cell (arbitrarily designated molecule 1) and at the center of the $\overline{bc}$ faces (designated molecule 2). The molecules at the corners are not related to molecules at the face centers by crystallographic symmetry. The structure and atom numbering for molecule 2 are shown in stereoview in Figure 1. A packing diagram for the unit cell is available as supplementary material. Table II contains atomic coordinates; parts a and b of Table III contain bond lengths and angles. For a list of other materials available, see the supplementary material statement at the end of this article.

The overall geometry about the nickel atom is approximately octahedral, as expected. In both molecules the nickel atom and the four nitrogen atoms of the chelating ligands are constrained to be planar by crystallographic symmetry. Also the two thiocyanate groups are N-bonded to the nickel at the axial sites in the two molecules.

A closely related structure, *trans*-bis(ethylenediamine)bis(isothiocyanato)nickel(II), has been determined by two-di-

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Table II. Fractional Atomic Coordinates and Isotropic Thermal Parameters for Non-hydrogen Atoms[a] for Ni(*as*-$Et_2en)_2(NCS)_2$ (I)

atom	10^4x	10^4y	10^4z
Ni(1)	0	0	0
S(11)	1595 (1)	5376 (1)	2059 (1)
C(11)	811 (3)	3572 (4)	1299 (2)
N(11)	295 (3)	2291 (3)	763 (2)
N(12)	2300 (3)	1413 (3)	−145 (2)
N(13)	1198 (3)	−709 (4)	1277 (2)
C(12)	3130 (4)	452 (5)	549 (3)
C(13)	2823 (4)	271 (5)	1490 (3)
C(14)	3093 (4)	3405 (4)	188 (3)
C(15)	2442 (5)	4581 (5)	−474 (3)
C(16)	2222 (4)	1050 (6)	−1145 (3)
C(17)	3718 (5)	1624 (7)	−1293 (4)
Ni(2)	0	5000	5000
S(21)	1601 (1)	10674 (1)	3593 (1)
C(21)	932 (4)	8723 (5)	4009 (2)
N(21)	481 (3)	7357 (4)	4315 (2)
N(22)	−2486 (3)	4120 (4)	4053 (2)
N(23)	27 (3)	3612 (4)	3869 (2)
C(22)	−2430 (5)	3665 (7)	3113 (3)
C(23)	−1510 (5)	2577 (7)	3210 (3)
C(24)	−2967 (5)	5682 (7)	3965 (3)
C(25)	−4555 (6)	5316 (9)	3273 (4)
C(26)	−3573 (5)	2472 (6)	4315 (3)
C(27)	−3804 (5)	2816 (8)	5239 (4)

[a] Estimated standard deviations referred to the least significant digit are given in parentheses in this and subsequent tables.

Table III. Bond Lengths and Bond Angles for Ni(*as*-$Et_2en)_2(NCS)_2$ (I)

a. Bond Lengths (Å)

Ni(1)-N(11)	2.081 (2)	Ni(2)-N(21)	2.079 (4)
Ni(1)-N(12)	2.304 (3)	Ni(2)-N(22)	2.331 (3)
Ni(1)-N(13)	2.086 (3)	Ni(2)-N(23)	2.080 (3)
N(11)-C(11)	1.164 (4)	N(21)-C(21)	1.157 (3)
C(11)-S(11)	1.637 (4)	C(21)-S(21)	1.641 (2)
N(12)-C(12)	1.503 (4)	N(22)-C(22)	1.488 (5)
N(12)-C(14)	1.512 (4)	N(22)-C(24)	1.514 (3)
N(12)-C(16)	1.499 (4)	N(22)-C(26)	1.511 (5)
C(12)-C(13)	1.525 (5)	C(22)-C(23)	1.506 (7)
C(13)-N(13)	1.491 (4)	C(23)-N(23)	1.488 (5)
C(14)-C(15)	1.515 (5)	C(24)-C(25)	1.548 (5)
C(16)-C(17)	1.537 (6)	C(26)-C(27)	1.528 (6)

b. Bond Angles (deg)

N(11)-Ni(1)-N(12)	91.3 (1)	N(21)-Ni(2)-N(22)	88.9 (1)
N(11)-Ni(1)-N(13)	88.4 (1)	N(21)-Ni(2)-N(23)	90.2 (1)
N(12)-Ni(1)-N(13)	83.0 (1)	N(22)-Ni(2)-N(23)	82.3 (1)
Ni(1)-N(11)-C(11)	162.8 (3)	Ni(2)-N(21)-C(21)	171.3 (3)
N(11)-C(11)-S(11)	178.0 (2)	N(21)-C(21)-S(21)	178.9 (2)
Ni(1)-N(12)-C(12)	100.1 (2)	Ni(2)-N(22)-C(22)	100.1 (2)
Ni(1)-N(12)-C(14)	115.8 (2)	Ni(2)-N(22)-C(24)	111.4 (1)
Ni(1)-N(12)-C(16)	110.6 (2)	Ni(2)-N(22)-C(26)	116.4 (2)
C(12)-N(12)-C(14)	107.4 (2)	C(22)-N(22)-C(24)	108.8 (3)
C(12)-N(12)-C(16)	110.9 (2)	C(22)-N(22)-C(26)	108.5 (3)
C(14)-N(12)-C(16)	111.4 (2)	C(24)-N(22)-C(26)	110.9 (2)
N(12)-C(12)-C(13)	112.5 (3)	N(22)-C(22)-C(23)	112.0 (4)
C(12)-C(13)-N(13)	108.8 (3)	C(22)-C(23)-N(23)	109.7 (4)
C(13)-N(13)-Ni(1)	110.9 (2)	C(23)-N(23)-Ni(2)	110.3 (3)
N(12)-C(14)-C(15)	113.8 (3)	N(22)-C(24)-C(25)	116.3 (1)
N(12)-C(16)-C(17)	115.7 (3)	N(22)-C(26)-C(27)	113.2 (4)

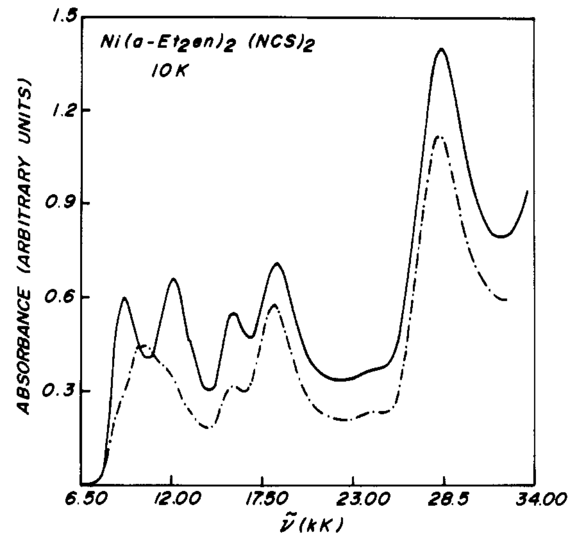

Figure 2. Crystal spectrum at 10 K of Ni(*as*-$Et_2en)_2(NCS)_2$ in two orthogonal polarizations.

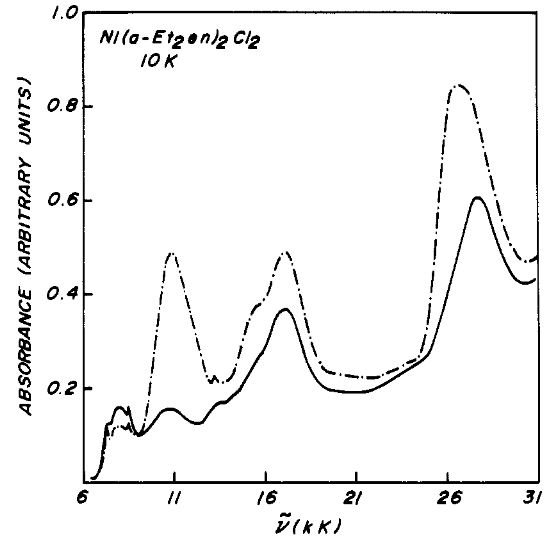

Figure 3. Crystal spectrum at 10 K of $[Ni(as\text{-}Et_2en)_2(H_2O)_2]^{2+}Cl^-_2$ in two orthogonal polarizations.

mensional projections by Brown and Lingafelter.[17] The molecule crystallizes in the space group $P2_1/a$ and, as in the Et_2en structure, is centrosymmetric as required by the observed two molecules per cell. Unlike this ethylenediamine structure the in-plane coordination about the Ni atom is highly unsymmetrical in Ni(*as*-$Et_2en)_2(NCS)_2$. The two Ni–N bonds are 2.086 (3) and 2.304 (3) Å in the molecule at the origin and 2.080 (3) and 2.331 (3) Å for the other symmetry-unrelated molecule. The longer distance is associated with the tertiary amine. The shorter Ni–N bonds are typical of octahedrally coordinated Ni(II) and agree well with the two relatively symmetrical Ni–N bonds of 2.09 and 2.11 Å observed for $Ni(en)_2(NCS)_2$. The configuration of the chelate rings in both complexes is gauche. Carbon atoms C(12) and C(13) lie on opposite sides of the plane determined by the nickel and chelate nitrogens by 0.47 and 0.13 Å, respectively. The corresponding distances for C(22) and C(23) are 0.45 and 0.26 Å, respectively. Brown and Ligafelter found found the carbon atoms symmetrically above and below the plane by 0.34 Å in $Ni(en)_2(NCS)_2$.[17]

For both compounds the ambidentate SCN− group is nitrogen bonded to nickel with comparable Ni–N bond distances. The (Ni(1)–N(11)–C(11) and Ni(2)–N(21)–C(21) angles in Ni(*as*-$Et_2en)_2(NCS)_2$ are 162.8 (2)° and 171.3 (3)°, respectively. An explanation for the almost 10° difference in the two molecules is not apparent. The corresponding angle for $Ni(en)_2(NCS)_2$ is 140°.[17] As noted by Brown and Ligafelter, the valence bond angle at the nitrogen in isothiocyanato bonding is quite variable in the various compounds that have been investigated.[17]

Crystal Electronic Absorption Spectra. Experimental data are shown in Figures 2–4 and listed in Table IV. As expected for six-coordinate nickel(II), all our spectra show three regions of d–d absorption, the lowest of which, associated with the T_{2g} level in O_h, shows the best resolved low-symmetry splitting.

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Table IV. Comparison of Observed and Calculated Electronic Spectra (Data in Wavenumbers)[a]

complex I		complex II		complex IV		complex V	
obsd	calcd[b]	obsd[d]	calcd[b]	obsd	calcd[b]	obsd	calcd[b]
9 140	8 910 (3)	7 770	7 725 (3)	9 400	9 495 (B_2)	9 200	9 185 (3)
10 420	10 355 (1)	10 610	10 565 (2)	9 600	9 670 (E)	11 200	11 140 (1)
12 120	12 350 (2)	10 770	10 645 (1)	9 600	9 670 (E)	11 520	11 190 (2)
15 770	15 720 (2)	15 450	15 560 (2)	14 570	14 550 (A_2)	16 150	16 185 (1)
18 350	18 010 (1)		16 200 (1)	16 380	16 105 (E)	17 425	17 310 (2)
18 350	18 065 (3)	17 080	17 170 (3)	16 380	16 105 (E)	18 040	18 395 (3)
28 310	27 545 (2)	26 520	26 515 (2)	26 250	26 135 (A_2)	*c*	27 345 (2)
28 310	28 310 (1)	26 520	26 600 (1)	26 250	26 245 (E)	*c*	27 495 (1)
28 310	28 640 (3)	27 760	27 745 (3)	26 250	26 245 (E)	*c*	28 260 (3)

[a] Complexes: I, Ni(*as*-Et$_2$en)$_2$(NCS)$_2$; II, Ni(*as*-Et$_2$en)$_2$(H$_2$O)$_2$$^{2+}$]Cl$^-_2$; IV, Ni(TMen)$_2(NCS)_2$; V, Ni(*as*-Me$_2$en)$_2(ONO)_2$. Abbreviations: *as*-Et$_2$en, *N,N*-diethylethylenediamine; *as*-Me$_2$en, *N,N*-dimethylethylenediamine; *s*-Et$_2$en, *N,N'*-diethylethylenediamine; TMen = *N,N,N',N'*-tetramethylethylenediamine. All data (calculated and observed) are rounded to the nearest 5 wavenumbers. [b] The numerals (1), (2), and (3) refer to assignment ot B_{1g}, B_{2g}, and B_{3g}, respectively. However the assignment of labels is arbitrary and may be permuted (see text). Nevertheless all transitions with a common number, such as (1), will belong to the same symmetry designation. Complex (IV) is labeled in tetragonal symmetry. [c] Obscured by nitrito absorption. [d] Weak, sharp absorptions to either side of the band at 7770 cm^{-1} are the NH stretch overtones usually seen in this region. In addition, weak spin-forbidden features are seen around 13 100 cm^{-1}.

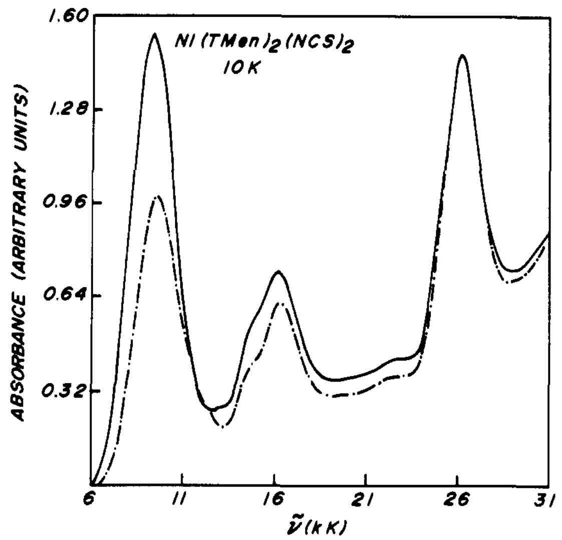

Figure 4. Crystal spectrum at 10 K of Ni(TMen)$_2$(NCS)$_2$ in two orthogonal polarizations.

Comparison of spectra recorded at 300 K with the spectra recorded at 10 K reveals that the absorption bands generally shrink in area with cooling of the crystal, as expected for centrosymmetric complexes exhibiting vibronically activated absorption. Each species will be dealt with in turn.

Ni(*as*-Et$_2$en)$_2$(NCS)$_2$ (I). The spectrum of this species (Figure 2) shows clear evidence of rhombic symmetry since in the region of the first orbital triplet (in O_h) are seen three peaks all of which, from their intensity and bandwidth, are probably spin allowed. The X-ray structure discussed above indeed shows the rhombic character with a short Ni–NH$_2$ bond, a bent Ni–NCS bond, and a long Ni–NEt$_2$ bond (see Table III). As anticipated from previous experience[7] the higher orbital triplets (in O_h) show less resolution, although there are clearly at least two components to the $^3T_{1g}$(F) (in O_h) multiplet near 17 500 cm^{-1}. The species has two independent molecules in the unit cell, which differ primarily in the Ni–NCS bend angle, and the molecule with the more bent thiocyanate bond is expected to exhibit a greater degree of rhombicity than the other. Consideration of the region of the first orbital triplet (near 10 000 cm^{-1}) does indeed suggest two pairs of overlapping triplets associated with the two different molecules. Since individual components cannot readily be assigned to individual molecules, we choose, at this level of analysis, to utilize the average component energies for purposes of calculation.

The crystal spectrum of the related complex Ni(*as*-Me$_2$en)$_2$(NCS)$_2$ has also been considered. There is no well-resolved splitting of the first d–d band, only a barely perceptible shoulder at low energy. This complex is clearly much closer to cubic symmetry than the *as*-Et$_2$en analogue, and no detailed analysis is attempted.

[Ni(*as*-Et$_2$en)$_2$(H$_2$O)$_2$]$^{2+}$Cl$^-_2$ (II). When freshly prepared from dry solvents, this species is green and probably contains coordinated chloride ions. However in concert with other species of this type, the crystals are very hygroscopic and will turn blue as they pick up water. The hydrate is readily obtained by crystallization from slightly wet alcohol. Indeed it has proved impossible to grow crystals of the anhydrous complex suitable for spectroscopy. In Figure 3 the spectrum of the hydrated species shows behavior closer to tetragonal rather than rhombic symmetry. If chloride ion were coordinated a rhombic spectrum would be anticipated since the e_σ value for Cl$^-$ is expected to be low (about 1700 cm^{-1}). The observation of a tetragonal spectrum is consistent with water coordination since the field for water and for the long Ni–NEt$_2$ bond should be quite similar, leading to tetragonal rather than rhombic distortion. Although the crystal structure of this complex is not known, it is likely to possess an all-trans centrosymmetric structure since the crystal electronic absorption intensities markedly decrease with temperature, indicative of vibronic coupling. Note that the relative intensities of the absorption in the hatched polarization in Figure 3 are greater than those in the solid line polarization and therefore probably reflect the similar Cartesian vectors (e.g., x, y), while the weaker polarization (z) is dominated by the third.

Ni(*as*-Me$_2$en)$_2$(Cl$_3$CCOO)$_2$ (III). The spectrum of this species has been previously discussed,[7] but due to an error[18] in a matrix element in Table VIII of ref 13, the relationship between the AOM and normalized spherical harmonic Hamiltonian (NSH) parameters as given in ref 7 also contains an error. The corrected mapping between the AOM and NSH models has been reported,[11] and the corrected AOM parameters (which differ only slightly from those presented previously) are shown in Table V.

Ni(TMen)$_2$(NCS)$_2$ (IV). The polarized spectra of this species are shown in Figure 4. This complex, like complex I, possesses an NiN$_6$ chromophore but is clearly not octahedral, but rather has a tetragonal spectrum which is better discussed in D_{4h}. The spectra are unusual in that the intensity of the lowest band appears to be almost insensitive to cooling; possibly

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(18) Element $\langle E_gO{:}V''{:}E_g\epsilon\rangle$ in Table VIII, ref 13, is incorrect. It should be replaced with the value $-(2/7)DU + (5/7)(1/15^{1/2})DV$.

the activating vibrational frequency is exceptionally high.[21] It is also unusual that neither the $^3T_{2g}$ nor the $^3T_{1g}(P)$ levels (in O_h) are split, yet the $^3T_{1g}(F)$ terms shows definite structure. The relative intensities in the $^3T_{1g}(F)$ band region suggest that, in D_{4h} symmetry, $E(^3A_{2g}) < E(^3E_g)$.

The infrared spectrum shows only one CN stretching frequency consistent with a *trans*-diisothiocyanate though it should be admitted that the absorption is somewhat broader than usually encountered.

Ni(*as*-Me$_2$en)$_2$(ONO)$_2$ (V). The spectrum of this complex has been discussed previously but with emphasis on the nitrito group.[8] The complex is centrosymmetric[19] with an all-trans nitrito-bound rhombic arrangement. The electronic spectrum (Figure 1, ref 8) is clearly rhombic in character, with the initial orbital triplet (in O_h) split into three components. In this case the $^3T_{1g}(P)$ components are obscured by nitrite absorption, but their absence is of little importance since they are rarely resolved.

The spectrum, but not the X-ray structure, of the related complex Ni(*as*-Et$_2$en)$_2$(ONO)$_2$ has also been reported.[8] From the appearance of three well-resolved peaks in the first d–d band, it is also rhombic. However in view of the complexity of nitrito-bound species[20] no analysis of the spectrum will be attempted until structural data are available.

Analysis of Data. Although polarized spectra are obtained by aligning the electric vector of the polarized light with a crystal extinction axis, these data do not provide unequivocal assignments in such low-symmetry species, though they clearly aid in the identification of components in the spectra. The philosophy is developed of comparing and contrasting data obtained from as large a series of related complexes as possible, and the veracity of the analysis for individual complexes is not argued in exclusion of other data.

In tetragonal complexes, the axial and equatorial AOM parameters are uniquely assignable to specific ligands once assignment to orbital singlet and orbital doublet states has been made. This is not the case in rhombic complexes, where it is immaterial which ligand is assigned to lie on the x axis, which on y, and which on z. Thus in solving a rhombic spectrum, one may deduce a set of e_σ (x), e_σ (y), and e_σ (z) values, but there may be no unambiguous way to determine which AOM parameter is associated with which ligand. The problem can be resolved in certain space groups by full analysis of the orientation of the crystal vectors with the electric field, but this is not generally true in compounds of such low symmetry where polarization may even be frequency dependent. In fitting the observed spectrum our computer program generates values for the AOM parameters along the x, y, and z axes and will provide identical energies (but not assignments) if the x, y, and z values are permuted. All the excited states are orbital singlets and the symmetry labels are arbitrary since they depend upon one's choice of x, y, and z. The sequence of energies is fitted without recourse to the symmetry labels of the transitions concerned. All the systems studied here exhibit vibronic spectra, and there is little value at this level of analysis in trying to determine whether any states may be vibronically forbidden.

Having identified a set of AOM parameters that correctly predicts the sequence of observed energies to within reasonable error (e.g., ±300 cm^{-1}) we may then use chemical knowledge to identify which AOM vector should be assigned to which ligand. Thus previous experience[4,8] requires that e_σ(N) values of 4000–4800 cm^{-1} are associated with the Ni–NH$_2$ bond vector. Oxygen ligands such as water, trichloroacetate, and nitrite, generally yield e_σ(O) values in the region 2500–3000 cm^{-1}, while nickel–halogen σ values fall below 2000 cm^{-1}. The NEt$_2$ bond is more sterically hindering than NMe$_2$ and therefore $e_\sigma(\text{NEt}_2) < e_\sigma(\text{NMe}_2) < e_\sigma(\text{NH}_2)$ should be observed. However caution should be exercised in using this criterion since, at least for the complex Ni(TMen)(NO$_2$)$_2$, the Ni–NMe$_2$ distance is not elongated.[22]

The isothiocyanate ion has previously been shown to yield e_σ(NCS) values near 4000 and near 2000 cm^{-1}. This variation is evidently associated with the Ni–NCS bond angle.[23] Thus normal Ni–N values near 4000 cm^{-1} are seen when the Ni–NCS bond is essentially linear, but lower values occur when it is bent.

The maximum number of independent AOM parameters that can be derived from the electronic spectrum of a rhombic complex is four for d^1 species but in excess of four for d^2 species.[24] Curiously, in D_{2h} symmetry, it is impossible to determine more than the sum of the $e_\sigma(x)$ and $e_\sigma(y)$ values from the spectra of rhombic d^1 ions. In rhombic d^2 (d^3, d^7, and d^8), however, all three σ AOM parameters can be uniquely derived because of the additional information inherent in these spectra.[24]

It is generally assumed that the π parameter for a saturated amine is zero, leaving only four AOM parameters, plus the Racah parameter B, to predict nine observed transitions. Experimentally no more than six are observed, the remainder being obscured by other bands.

The splitting of the first band (T_{2g} in O_h) is essentially defined by the three values Dq_x, Dq_y, and Dq_z, while the splitting of the second band is more sensitive to the π parameters. In general it is possible to find a fit with a fairly small value of $e_\pi(z)$ (with $e_\pi(x)$, $e_\pi(y) = 0$) and also to find a comparable fit to the transition energies with a small value of $e_\pi(y)$ (with $e_\pi(x)$, $e_\pi(z) = 0$) of opposite sign to that previously identified for $e_\pi(z)$. These two fits (necessarily) have identical $e_\sigma(x)$ values that, because of their magnitudes, are clearly associated with the $e_\sigma(\text{NH}_2)$ vector but have markedly different sets of $e_\sigma(y)$ and $e_\sigma(z)$ values. In all cases a distinction between these two fits could be drawn on the basis of chemical experience as outlined above; a comparison between observed and calculated data is shown in Table IV, and the AOM data sets are shown in Table V, together with some previously published data for several other complexes. We decline to argue that these AOM data sets are unequivocally correct but believe that they represent the best conclusions within the constraints and errors of the study.

The parameters, as assigned, all fall within the regions outlined above for the various ligands. The tetragonal Ni(TMen)$_2$(NCS)$_2$ complex deserves some special comment. The axial and equatorial fields are almost identical, in keeping with the quasi-cubic nature of the spectrum, but this is achieved by widely different values of the σ and π parameters. The very low value for e_σ(NCS) associated with a high negative e_π(NCS) value is strongly reminiscent of Ni(en)$_2$(NCS)$_2$ (Table V) where the Ni–NCS bond angle is 140°;[17] similar bending is therefore predicted in the TMen complex.[25]

Unfortunately it is the Ni(*as*-Et$_2$en)$_2$(NCS)$_2$ species (I) that is the least satisfying, probably because there are two independent molecules in the unit cell and their orientation clearly leads to overlapping features in the electronic spectrum. Although both e_σ(NCS) and e_π(NCS) are slightly higher than

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(25) The X-ray structure of Ni(TMen)$_2$(NCS)$_2$ is under investigation, but its solution is being impeded by problems of crystal disorder (K. B. Mertes and R. Sheldon, work in progress).

Table V. Angular Overlap Model (AOM) Parameter Sets[a] (Data in Wavenumbers)

		NH_2	NMe_2	NHEt	NEt_2	NCS	oxygen
Ni(*as*-Et_2en)$_2$(NCS)$_2$ ($B = 869$, $DQ = 29\,512$; this work)	e_σ	4650			2485	4305	
	e_π	0			0	530	
	Dq	13 950			7350	10 795	
Ni(*as*-Et_2en)$_2$(H_2O)$^{2+}$ ($B = 880$, $DQ = 27\,294$; this work)	e_σ	4770			2640		3050
	e_π	0			0		400
	Dq	14 310			7920		7550
Ni(*as*-Me_2en)$_2$(ONO)$_2$ ($B = 820$, $DQ = 29\,695$; ref 8)	e_σ	4665	3005				2450
	e_π	0	0				−510
	Dq	13 995	9015				9390
Ni(TMen)$_2$(NCS)$_2$ ($B = 848$, $DQ = 26\,593$; this work)	e_σ		3165			2115	
	e_π		0			−920	
	Dq		9495			10 025	
Ni(*as*-Me_2en)$_2$(TCA)$_2$ ($B = 875$, $DQ = 28\,504$; ref 7)	e_σ	4545	3555				2800
	e_π	0	0				400
	Dq	13 635	10 665				6800
Ni(*s*-Et_2en)$_2$(ONO)$_2$ ($B = 850$, $DQ = 28\,424$; ref 10, 11)	e_σ			4490			2550
	e_π			0			530
	Dq			13 470			5530
Ni(en)$_2$(NCS)$_2$ ($B = 883$, $DQ = 29\,388$; ref 23)	e_σ	4010				2123	
	e_π	0				−409	
	Dq	12 030				8005	
Ni(NH_3)$_4$(NCS)$_2$ ($B = 900$, $DQ = 29\,811$; ref 23, 26)	e_σ	3583				3843	
	e_π	0				125	
	Dq	10 749				11 029	
Ni(NH_3)$_6$$^{2+}$ ($B = 910$, $DQ = 30\,248$; ref 23)	e_σ	3667					
	e_π	0					
	Dq	11 000					
Ni(en)$_2$(NO_2)$_2$ (ref 23)	e_σ	3800					
	e_π	0					
	Dq	11 400					
Ni(NH_3)$_4$(NO_2)$_2$ (ref 23, 26)	e_σ	4000					
	e_π	0					
	Dq	12 000					

[a] See Table IV for comparison of calculated and observed data.

anticipated, it is noteworthy that the overall Dq (NCS) is identical, in fact, with the value in the nickel tetrammine analogue (Table V). There is probably greater uncertainty in the relative values of σ-and π-NCS contributing to Dq (recall that $Dq(\mathrm{L}) = 3e_\sigma(\mathrm{L}) - 4e_\pi(\mathrm{L})$).

The two oxygen-bound nitrito complexes have widely different π parameters but similar σ parameters. In the *as*-Me_2en complex where the nitrito groups are terminal Ni—O—N—O, the nitrito group behaves as a very weak π-acceptor, while in the *cis*-*s*-Et_2en complex with bidentate nitrite Ni(O_2N), the positive e_π value infers π donation. More data are needed to see whether there is any justification in such a conclusion. However it does seem that, on the basis of both the nitrito and thiocyanato evidence, the relative insensitivity of ligand Dq values from one complex to another may hide quite wide variations in σ- and π-bonding with change in ligand binding geometry. Note also that the presence of a weak Ni-N bond strengthens the other Ni-N bond presumably to meet the requirements of the Pauling electroneutrality principle. Table V also includes values for the global DQ values (NSH approach[13]), which are a measure of the average field experienced by the metal ion. Four of the six NiN_6 chromophores in Table V have essentially identical DQ values; evidently, in a global sense, the weakness of one pair of bonds is compensated by the strengthening of the others. An exception is the TMen complex where all the bonds are weak and where, perhaps, steric effects prevent the molecule from adjusting appropriately.

Given the above assignments it is now possible to relate AOM parameters with bond lengths. Tables V and VI include a collection of data for which both X-ray and spectroscopic information are available, while Figure 5 shows a plot of the AOM e_σ values for the Ni–N bond against the Ni–N bond lengths, determined from X-ray studies. This plot is a greatly extended version of one first introduced by Bertini and coworkers.[23] In this latter work, the species $Ni(NH_3)_4(NO_2)_2$ was also included but was poorly behaved, lying significantly off an otherwise good linear relationship. In fact these workers inadvertently interchanged the assignment[26] for this species. With the correct assignment, the species fits the correlation well. Note that in the nitro complexes included here, it is possible to obtain unambiguous AOM parameters from only the lowest energy crystal field band. This is due to the overlap of the second and third crystal field bands with charge transfer bands associated with the nitro group.[27] We thus report only

Table VI. Summary of Relevant X-ray Structural Data (Angstroms)

Ni(*as*-Et_2en)$_2$(NCS)$_2$[a]	r(Ni–NH_2) = 2.09–2.09, r(Ni–NEt_2) = 2.30–2.33 r(Ni–NCS) = 2.08, ∠Ni–NC = 162°, 171°
Ni(*as*-Me_2en)$_2$(ONO)$_2$[b]	r(Ni–NH_2) = 2.08, r(Ni–NMe_2) = 2.22
Ni(*s*-Et_2en)$_2$(ONO)$_2$[c]	r(Ni–NHEt) = 2.12
Ni(en)$_2$(NCS)$_2$[d]	r(Ni–NH_2) = 2.09–2.11 r(Ni–NCS) = 2.15, ∠Ni–NC = 140°
Ni(NH_3)$_4$(NCS)$_2$[e]	r(Ni–NH_3) = 2.15 r(Ni–NCS) = 2.07, ∠Ni–NC = 180°
Ni(NH_3)$_6$$^{2+}$[f]	r(Ni–NH_3) = 2.15
Ni(en)$_2$(NO_2)$_2$[g]	r(Ni–NH_2) = 2.09–2.10, r(Ni–NO_2) = 2.13
Ni(NH_3)$_4$(NO_2)$_2$[e]	r(Ni–NH_3) = 2.07, r(Ni–NO_2) = 2.23

[a] This work. [b] Reference 19. [c] Reference 29. [d] Reference 17. [e] Reference 30. [f] Reference 23, 21. [g] Reference 32. The symbol ∠NiNC refers to the bond angle between nickel and thiocyanate ligand in all cases.

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(28) The data reported here differ slightly from those previously published because of the error reported above (ref 18).

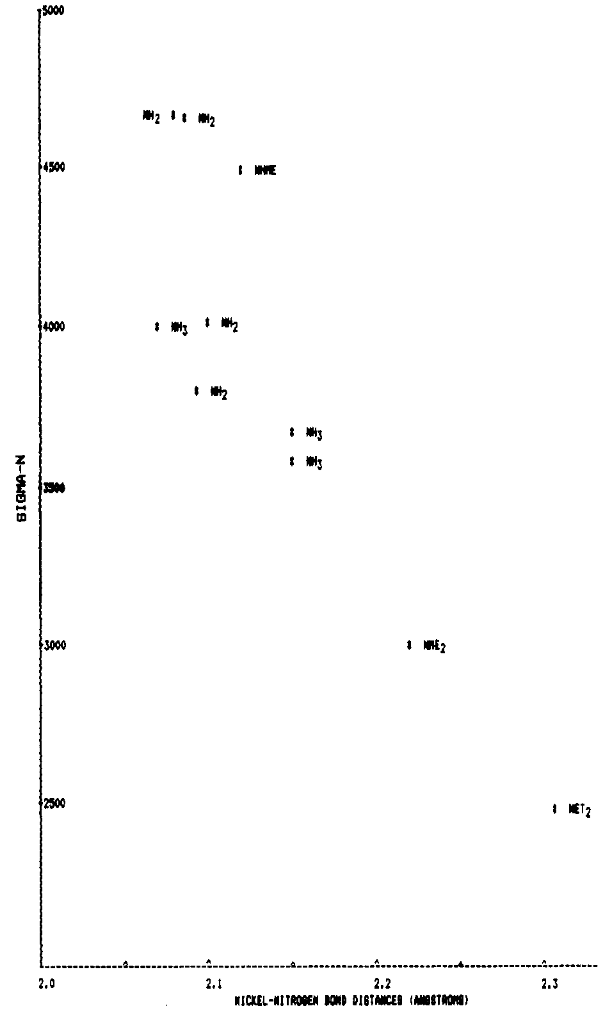

Figure 5. A plot of $e_\sigma(\mathrm{N})$ values (see Table V) vs. Ni–N lengths (see Table VI).

the $e_\sigma(\mathrm{NH_2})$ parameter in Table V. No reliable estimate of the AOM parameters for the nitro group in these complexes appears possible at present.

Clearly the correlation indicates that the AOM $e_\sigma(\mathrm{N})$ parameter decreases with increasing bond length in a regular, but not necessarily linear, manner as overlap decreases. Although the AOM method is couched in terms of orbital overlap, it is likely that the bonding in these nickel complexes is rather ionic and the AOM parameters probably reflect primarily ionic destabilization of the nickel d orbitals of σ symmetry. The reduction in σ value may then follow a power of the metal ligand distance in parallel with crystal field theory. Further data should clarify such a relationship, which may also shed light on the nature of the metal–ligand bond.

These data indicate that the AOM procedure may be utilized to analyze the spectra of low-symmetry nickel(II) complexes with numerical values for the AOM parameters that agree well with those found for higher symmetry species; i.e., the notion of transferability is justified here. However the $e_\sigma(\mathrm{N})$ data lead to the conclusion that where bond length extension occurs σ AOM parameter values are very significantly reduced.

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Appendix

The one-electron d-orbital matrix elements in a field of D_{2h} symmetry are as follows:

$$\langle z^2|V|z^2\rangle = (1/2)[e_\sigma(x) + e_\sigma(y)] + 2e_\sigma(z)$$

$$\langle yz|V|yz\rangle = 2e_\pi(y) + 2e_\pi(z)$$

$$\langle xz|V|xz\rangle = 2e_\pi(x) + 2e_\pi(z)$$

$$\langle xy|V|xy\rangle = 2e_\pi(x) + 2e_\pi(y)$$

$$\langle x^2 - y^2|V|x^2 - y^2\rangle = (3/2)[e_\sigma(x) + e_\sigma(y)]$$

$$\langle z^2|V|x^2 - y^2\rangle = (3^{1/2}/2)[e_\sigma(y) - e_\sigma(x)]$$

These were used as a basis to calculate the energies of d^2 Slater determinants to which were added the necessary interelectronic repulsion terms in the Racah parameter B. This generated a linear equation of symmetry A_g and three 3 × 3 determinants of symmetry B_{1g}, B_{2g}, and B_{3g}. The AOM parameters were multiplied by −1 to provide the solutions for d^8 and the secular determinants diagonalized by standard methods. This procedure generated the transition energies for d^8 in a rhombic field as a function of the AOM parameters input. A simple iteration routine was used to fit these to the observed spectra.

Registry No. I, 42534-31-6; II, 42490-14-2; III, 73426-90-1; IV, 73503-67-0; V, 58893-98-4.

Supplementary Material Available: Tables of observed and calculated structure factors, anisotropic thermal parameters, fractional coordinates, and isotropic thermal parameters for hydrogen atoms for $\mathrm{Ni[NH_2CH_2CH_2N(C_2H_5)_2]_2(NCS)_2}$ and a stereoview of the unit cell (21 pages). Ordering information is given on any current masthead page.

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