

The Assignment of the Electronic Spectra of Nickel(II) Complexes with Non-Conjugating Sulphur-Containing Ligands

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The polarised crystal, and solution, electronic spectra of some quadratic dithiocarbamate and related nickel(II) complexes have been measured. In the cases where alignments of the molecules are favourable, $\text{Ni}(\text{S}_2\text{P}(\text{OC}_2\text{H}_5)_2)_2$ and $\text{Ni}(\text{S}_2\text{CN}(n\text{-C}_3\text{H}_7)_2)_2$, a reasonable assignment of the bands occurring between 14 and 28 kK as being all due to « d-d » transitions, is possible. The separation of the four d-orbital energy levels is thus much greater than that in analogous oxygen and nitrogen containing complexes. Assignments in both D_{2h} and D_2 point groups are possible, and reasons are given for preferring the latter. Because the selection rules in both cases do not allow a distinction to be made between the $d_{xz} \rightarrow d_{xy}$ and $d_{x^2-y^2} \rightarrow d_{xy}$ transition, either order: $d_{xy} > d_{x^2-y^2} >$ or $< d_{xz} > d_{xz} > d_{yz}$, is possible. $\text{Ni}(\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2)_2$ gives an electronic spectrum also showing two bands between 26 kK and 28 kK which may be ascribed to the $d_{xz} \rightarrow d_{xy}$ and $d_{yz} \rightarrow d_{xy}$ transitions. This appears to be the first square planar nickel(II) complex to show four probably singlet-singlet bands in its electronic spectrum. These further bands are not easily identified in the other complexes because of the presence of nearby charge transfer absorption. The behaviour of the band energies on changes in the Ni-S distances is described and discussed.

Introduction

Much theoretical work on the relative ordering of the d orbitals in square planar transition metal complexes has been performed.¹ Since few crystal structures on these systems had been solved until recently, precise experimental studies using single crystals have been sparse. Furthermore, much of the work has relied heavily on the interpretation of the spectra of PtCl_4^{2-} ,² and related complexes.³ Consequently, the relative ordering in nickel(II) complexes has still not been satisfactorily settled, despite the fact that many square planar complexes are now known.⁴

The spectral work that has been done to date has been concerned mainly with « stacked » molecules

with the intention of identifying the bands arising from metal-metal interaction.⁵ The work on the polarised crystal spectra of $\text{Ni}(\text{CN})_4^{2-}$ is an exception,⁶ but in this case anomalous polarisation results were obtained, different from the solution spectra,⁷ which could be interpreted only by assuming a change in configuration, $D_{4h} \rightarrow D_{2d}$, in the excited state. Apart from this work the crystal spectra of some salicylal-diminenickel(II) and related complexes have been taken and interpreted in D_{2h} symmetry,⁸ although the assignment given was not complete.

Since this spectral work, attention has shifted towards square planar complexes with sulphur donor ligands.⁹ The crystal structure of several of these have been solved, especially those of dithiocarbamates. It has been found that the first absorption band in the electronic spectra of these complexes is very sensitive to changes in the in-plane bond lengths, and this was ascribed to π -antibonding effects, repulsion among non-bonding pairs or increases in the effective negative charge on the sulphur atom.¹⁰ However, this work was not complete, and no assignment for the bands observed was possible. Indeed, there is still doubt as whether several of the bands observed in solution are due to d-d or charge transfer transitions because of their relatively high intensity.⁹

Because of this measurements have been carried out of the single crystal spectra of a series of nickel(II) complexes containing sulphur-bonding ligands not attached to further groups which might cause extensive conjugation throughout the molecular framework. The intention is to identify the « d-d » transitions, attempt an assignment and evaluate the possible π -bonding effect of the sulphur atoms on the metal d-orbitals.

Experimental Section

All the complexes examined are by now well known and were prepared as in the literature (see individual crystal structure references). Crystals suitable for measurements were obtained by slow evaporation from

(1) See H. B. Gray, « Transition Metal Chemistry », Vol. I, p. 243, Dekker - New York, 1964.

(2) J. Chatt, G. A. Gamlen, and L. E. Orgel, *J. Chem. Soc.*, 1958, 486.

(3) P. Day, M. J. Smith, and R. J. P. Williams, *J. Chem. Soc. (A)*, 668 (1968).

(4) L. Sacconi, « Transition Metal Chemistry », Vol. 4, p. 199, Dekker, N. Y. 1968.

(5) e.g. B. G. Anex and K. Krist, *J. Amer. Chem. Soc.*, 89, 6114 (1967).

(6) C. J. Ballhausen, N. Bjerrum, R. Dingle, K. Eriks, and C. R. Hare, *Inorg. Chem.*, 4, 514 (1965).

(7) J. R. Perumareddi, A. D. Liehr, and A. W. Adamson, *J. Amer. Chem. Soc.*, 85, 249 (1963).

(8) J. Ferguson, *J. Chem. Phys.*, 34, 611 (1961).

(9) C. K. Jørgensen, *Inorg. Chim. Acta Revs.*, 2, 65 (1968).

(10) P. Porta, A. Sgamellotti, and N. Vinciguerra, *Inorg. Chem.*, 7, 2625, (1968).

solutions in ethanol or toluene. In most cases only small crystals, typically about 2 mm², were obtained, which precluded low-temperature measurements on the microscope attachment used. However, the diethyl-dithiophosphate could be obtained from toluene as very large plates, up to 2 cm. in largest dimension, which allowed low-temperature measurements, using a crystal attachment with a Beckmann DK 1A spectrometer, to be taken. The spectrum obtained showed little significant change from that at room temperature.

The crystal spectra were obtained using a Shimadzu MPS 50L spectrophotometer equipped with a microscope attachment. The condensing lens system allowed measurement of surfaces on the crystal some 100 μ in diameter. The instrument operates with only one Glan-Thompson polariser, balancing of the two beams being first achieved using attenuation of the sample beam. To eliminate any possibility of spurious peaks appearing since there is no means of eliminating the optical characteristics of the polarizer using this system, the crystal spectra of several complexes already known in the literature¹¹ were first taken. Due attention was given to proper balancing and zeroing of the optical beams, before and after each run, important with this instrument, and the spectra obtained were all reproducible.

All the crystal examined are very strongly coloured, and had first to be ground down to a suitable thickness before sufficient light could be passed through them.

This was done by fastening the crystals to quartz plates using a polyester resin-which did not cause any detectable changes in the spectra-and grinding down to thin plates (10⁻¹-10⁻² mm). Grinding was done first with very fine glass paper and then with nujol-impregnated filter paper. Although the crystal faces so obtained were flat, as found under the microscope, they were not uniform in thickness. Consequently, intensity measurements were not attempted. Since there is little interference with the first two bands by other, weaker, bands under their envelopes, and no significant differences between solution and crystal spectra the intensities found from the solution spectra may be taken as being those relevant also for the solid state spectra. To ensure that absorption bands were not « lost » using this procedure, spectra of both thick and thin crystals were taken, (this also helped in deciding whether there were any effects due to stray and scattered light in the thin crystals). Spectra were taken with the polarizer parallel to the extinctions, which were first noted using a polarising microscope. The relation between extinction directions and crystallographic directions were then found using X-ray and optical interference methods.

Solution spectra were run on a Beckmann DK 1A spectrophotometer, using 1.0 and 0.1 cm cells with ethanol or toluene solutions thermostatted at 25 °C. The frequencies of the first band for all the complexes were found to be identical to those reported.¹⁰

Crystal Structures. Ni(S₂CNR₂)₂. 1) R=n-C₃H₇. Di-n-propyldithiocarbamatonicel(II) crystallises from

ethanol as thin green plates. The compound crystallises in the space group R $\bar{3}$.¹² a=25.20 Å; c=8.30 Å; z=9. Ni^{II} site symmetry C_{3i}, C₃ and C_i. The prominent face contains both the a and c axes. With the electric vector, (E), || to c the crystals are green in colour, becoming yellow when E || to a.

The molecules are aligned accurately with the out-of-plane molecular axis parallel to the c axis. The crystallographic projection on the X-Y plane shows a « propellor » type arrangement of the molecules in the in-plane molecular projection. Consequently, although convenient for in-plane and out-of-plane polarisation, which should be pure, the crystallographic alignment does not allow possible differences in in-plane (x- and y-polarisation to be observed.

2) R=C₂H₅. Long dark green monoclinic needles are given from chloroform solution crystallizing in the space group P2₁/c, a=6.189 Å; b=11.537 Å; c=11.693 Å; z=2; β =95°51'; Ni^{II} site symmetry C_i.¹³ The alignment of the molecules in the cell is not very convenient for interpretation of the crystal spectrum, the molecular z-axes being inclined at 85° to one another in the face, (100), examined. Despite this, dichroism in thin crystals was observed to be quite strong: green \leftrightarrow yellow, while in thicker crystals even stronger; red \leftrightarrow green, as reported previously.¹⁴ Little difficulty was found in finding crystals which were untwinned.

3) R=H and i-C₄H₉. As in the ethyl derivative, the unsubstituted and di-isobutyl substituted derivatives show gross misalignment of the molecular axes in the crystals. The dithiocarbamate grows from ethanol solution as black hexagonal plates developed on (100) which, on grinding down, show clear polarisation: yellow \leftrightarrow orange. In this face the molecular projection is mainly xy and z in a monoclinic cell, space group P2₁/c; a=8.96 Å; b=9.825 Å; c=11.28 Å; β =129°16'; z=4.¹⁵

Similarly, the isobutyl derivative gives black monoclinic prisms developed on the (100) face. Space group P2₁/c; a=11.785 Å, b=13.05 Å; x=16.64 Å; β =96°15'.¹⁶

Ni(S₂P(OC₂H₅)₂)₂. Two crystal structure determinations on bis(0,0'-diethyldithiophosphato) nickel(II) have been reported,¹⁷ both giving identical results, within experimental error. The crystals belong to the monoclinic system, space group P2₁/c; a=10.49 Å; b=10.31 Å; c=8.76 Å; β =102.6°; z=2; Ni^{II} site symmetry C_i. The (100) projection shows the molecule to be inclined at only a very small angle to the c-axis (5°). The spectrum of this face should be that of almost pure out-of-plane and in-plane polarisations. Similarly, the projection on the (001) face should give almost pure in-plane polarisation. The

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(17) J. F. Mc Conell and V. Kastalsky, *Acta Cryst.*, 22, 859 (1967).
Q. Fernando and C. F. Green, *J. Inorg. Nucl. Chem.*, 29, 747 (1967).

Table I.

Compound	Crystal spectrum		Solution	
	Polarisation Direction		ν_{\max}	E_{\max}
$\text{Ni}(\text{S}_2\text{CNR}_2)_2$ R = H	xy	z	16.08	70
	15.1 (+z) 20.33 (+z)	16.95 (+xy)	21.20 ? 24.0 sh 26.32 31.43 40.5	160 1400 3700 29,000 16000
$-\text{C}_2\text{H}_5$	16.03 (+z) 21.4 (+z)	16.75 (+xy) 18.8	16.00 21.50 sh ? 24.20 sh	100 220 1600
			25.80 30.8	5500 30,000
$-\text{n}-\text{C}_3\text{H}_7$	16.05 20.66 sh 21.50 sh 24.50	17.15 23.4 sh 25.6 27.6	16.26 22.10 sh ? 24.30 sh	80 520 1900
			26.20 26.75	5050 5300
$-\text{i}-\text{C}_4\text{H}_9$	16.13 (+z) 21.5 (+z)	17.0 sh (+xy)	16.10 21.0 sh ? 23.3 sh	95 230 1650
			25.32 sh 25.90 30.9	6400 6800 40,000
$\text{Ni}(\text{S}_2\text{P}(\text{OC}_2\text{H}_5)_2)_2$	x	y	14.3	76
	(001): 14.9 face 19.2 25.5	15.2 19.0 25.5	19.0 26.1 sh C.T.— 32.0	96 1650 1580
	xy	z		
	(100): 14.9 face 19.8 25.8	— 17.2 26.5		
$\text{Ni}(\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2)_2$	xy	z	14.0	74
	(001): 14.0 face 18.3 26.2 27.8	17.0 26.1 —	17.9 25.60 27.60	98 1600 2115
	x	y		
	(100): 13.9 face 18.2 26.2 sh 27.8	13.9 18.2 26.2 sh 27.8		

(001) face, that most developed when crystals are grown from ethanol solution, shows little dichroism. The (100) face was obtained by carefully grinding a crystal at right angles to the well developed face, and shows strong dichroism: purple \leftrightarrow yellow.

$\text{Ni}(\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2)_2$. This dithiophosphinate derivative crystallizes in space group $\text{C}2/c$, $a = 13.28 \text{ \AA}$; $b = 11.55 \text{ \AA}$; $c = 17.00 \text{ \AA}$; $\beta = 103^\circ 43'$; $z = 4$. The nickel(II) site symmetry is C_i and the molecular axes in both the required projections are grossly misaligned¹⁰ (see Figure 3). The small prismatic purple needles developed on the (100) face show little dichroism in this face. The (001) face, however shows strong dichroism ($E 51^\circ$ to b-deep purple; $E 39^\circ$ to b-pale blue).

Results

The crystal spectra obtained, together with the projection of each face examined, are shown in Figures 1 to 4 Table I gives the relevant energies of the bands, while Figure 5 shows the solution spectra of the dithiophosphinate and unsubstituted dithiocarbamate complexes.

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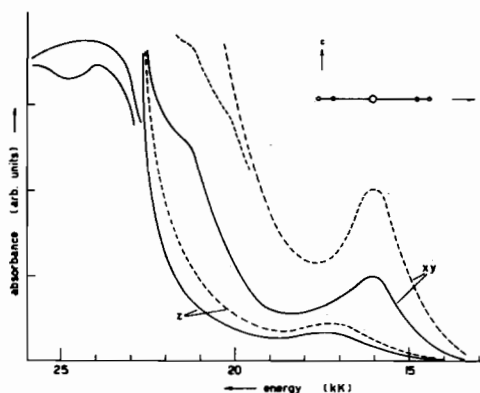


Figure 1. The polarised crystal spectrum of $\text{Ni}(\text{S}_2\text{CN}(-\text{C}_2\text{H}_5)_2)_2$; --- thick crystal; — thin crystal.

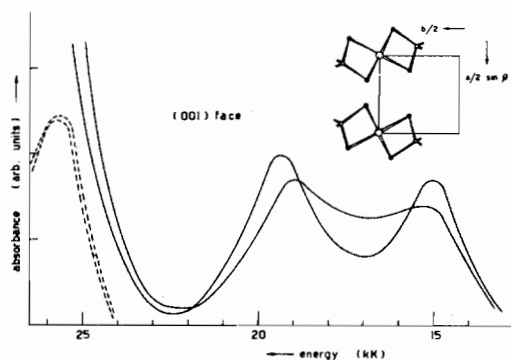
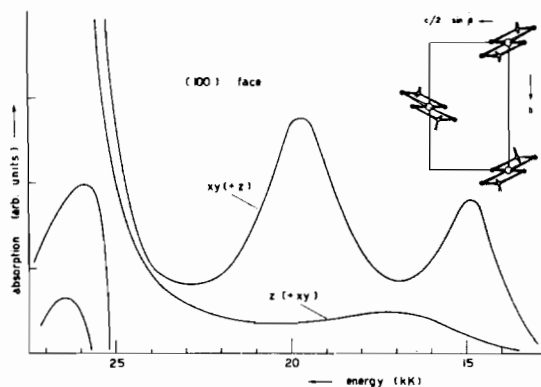


Figure 2. Crystal spectra of (100) and (001) faces of $\text{Ni}(\text{S}_2\text{P}(\text{OC}_2\text{H}_5)_2)_2$. --- thin crystal.

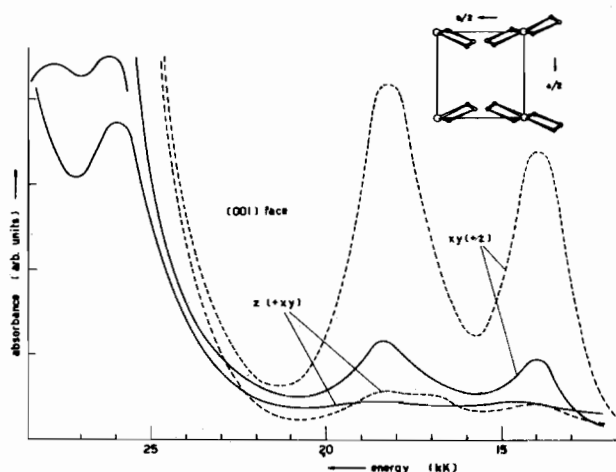
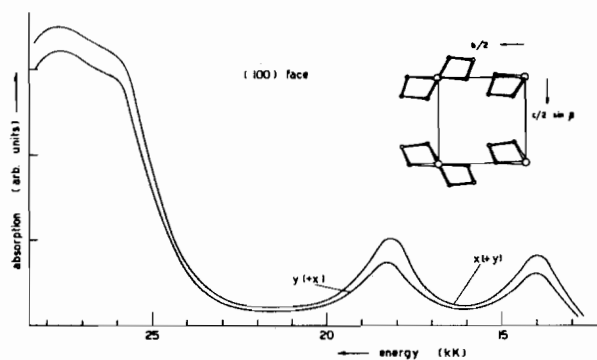


Figure 3. Crystal spectra of (100) and (001) faces of $\text{Ni}(\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2)_2$. --- thick crystal.

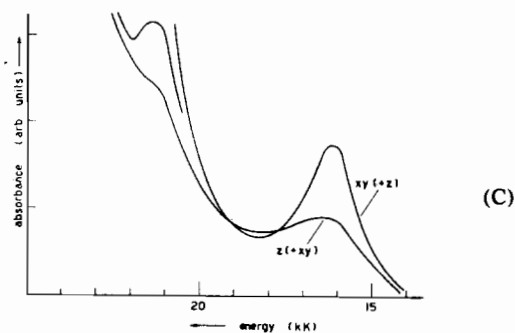
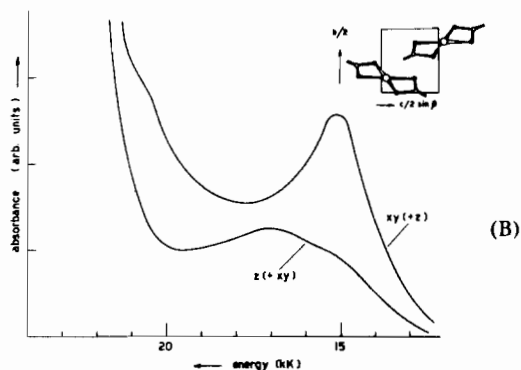
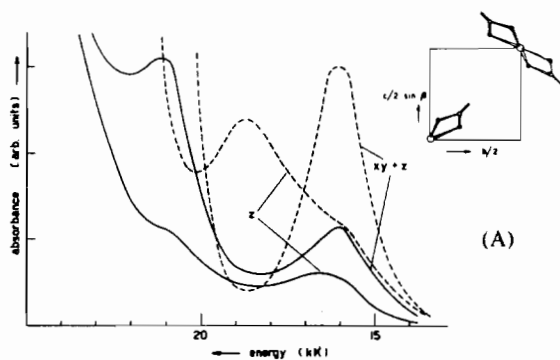


Figure 4. Crystal spectra of $\text{Ni}(\text{S}_2\text{CNR}_2)_2$ projections containing mainly xy and z- molecular projections; (A) $\text{R}=\text{C}_2\text{H}_5$; (B) $\text{R}=\text{H}$; (C) $\text{R}=\text{i-C}_4\text{H}_9$.

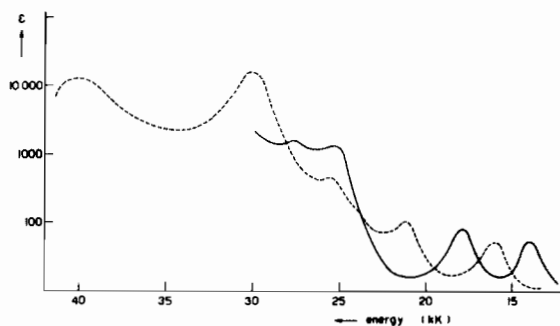


Figure 5. Solution spectra. (A) $\text{Ni}(\text{S}_2\text{CN}(\text{H}_2)_2)$; (B) $\text{Ni}(\text{S}_2\text{P}(\text{C}_6\text{H}_5)_2)_2$ both in toluene at 25°C .

The first point to emerge from the data is that the crystal spectra show several extra bands in the visible region while solution spectra normally show

only two bands together with a higher intensity, higher energy shoulder. In neither case were bands at energy lower than 13 kK observed.

Because of the favourable alignment in the crystals, the *n*-propyldithiocarbamate and the dithiophosphate may be considered first. The former shows two strong bands, at ~ 16.0 and 21.5 kK when \vec{E} is \parallel to *c*, *i.e.* \parallel to the molecular plane. When \vec{E} is rotated by 90° , *i.e.* $\vec{E} \perp$ to the molecular plane, both of these bands are completely absent and a very broad, low intensity band centred at ~ 17.1 kK appears. The slight assymetry of the 16.0 kK band in in-plane polarisation indicates that this broad band may be present in both directions. Although further bands appeared in the range 26.0 - 28 kK they appeared to show effects due to stray and scattered light and their polarisation properties may not be genuine; this is indicated by the very different intensities which these bands show in solution. A thicker crystal gave identical results but for the appearance of a further shoulder on the 21.5 kK band in in-plane polarisation, which disappeared completely in the other direction.

Similarly, the dithiophosphate shows two intense bands, in the (100) face, with \vec{E} parallel to the plane of the molecule, which are absent when \vec{E} is 90° to the plane, uncovering a broad band at 17.3 kK. There is a further, higher intensity band at ~ 258 kK in (mainly) *xy*-polarisation which shifts, sensibly, ~ 0.6 kK, to higher energy in (mainly) *z*-polarisation. These bands did not appear to be very affected by extraneous light effects. In the (001) face there is no shift in this band, in both directions it appears at ~ 25.8 kK, this difference from the other face also indicates that it is probably genuine. In this face the two bands at lower energy are present in both orientations. The band shape shows that the slight changes in energy of the first band in going from the (100) face -14.9 kK to the (001) face -15.2 kK are possibly caused by the presence of a weak broad band, corresponding to that present at 17.3 kK in the (100) face, under the envelope.

Such net polarisation effects as observed in these cases are not, of course, shown by the other complexes, although they all follow the same pattern. The phosphinate spectrum is very like that of the phosphate, apart from the behaviour of the highest energy band. This band, at 26.0 kK, is clearly resolved and is obviously more intense in *xy* polarisation than in *z*-, while a further band is present, at 27.8 kK more intense in the *xy*-direction. Both bands are present in the in-plane directions, *i.e.* the (100) face (figure 3), the higher energy one being slightly more intense.

The diethyldithiocarbamate derivative shows an extra band at 18.85 kK in a thick crystal, which appears to be of similar intensity to that of the band at 16.0 kK. No sign of the band is seen in a thin crystal, nor in solution. The crystal structure shows that the nickel(II) atom has 2 carbon atoms, above and below the plane, from neighbouring

molecules in the cell. Although these are at very long distances it appears that their perturbation exerts some influence on the intensity of this, presumably spin-forbidden, transition (see below), making it comparable to that of a spin allowed one.

Turning to the solution spectra, it is seen that, where the second band occurs only as a shoulder on a rapidly rising background, its intensity is considerably greater than when it is removed. Thus, in the diethyldithiocarbamate $\epsilon = 500$ - 160 , compared with a first-band intensity of $\epsilon = 50$ - 100 , while in the dithiophosphate $\epsilon_1 = 74$ as compared to $\epsilon_2 = 98$. It is more difficult to compare the intensity of the band at ~ 26 kK since in no case is it sufficiently removed from the rapidly rising ultra-violet absorption.

However, the 27.6 kK shoulder in the solution spectrum of the dithiophosphate is much higher in intensity than the band at 25.6 kK, whereas in the crystal spectra, in which this shoulder is resolved better, the two bands are of comparable intensity. Consequently, it appears reasonable to assume that the shoulders at 24 - 26 kK are borrowing much intensity from the charge-transfer band, with ϵ $20,000$ - $30,000$, at 30 - 32 kK.

Discussion

For most of the complexes the Ni atom occupies a site of symmetry C_i , consequently all d-orbitals must belong to the same representation A_g , and the only ungerade vibrations must be α_u . Since each Cartesian coordinate in this symmetry belongs to α_u no transition is strictly forbidden in any polarisation. Complete polarization of some bands can then only be explained by detailed calculation of intensities or by « fitting » the results to an approximate symmetry rather than by applying rigorous « yes-no » selection rules based on the site symmetry.¹⁸

Ignoring the differences in site symmetry and the differences of orientation of the side chains attached to the phosphorus or nitrogen atoms, the molecular unit present may be considered that of Figure 5, with varying « rectangular » angles γ and varying Ni-S distances. The coordinate system shown is that which makes the d_{xy} orbital the highest energy one. (Since the molecular unit is rectangular the *x*- and *y*-axes cannot be elements of symmetry if they go through the sulphur nuclei).

Ignoring all but the chromophore $Ni^{II}S_4$ leaves us with an approximately D_{4h} symmetry, for which the well-known vibronic selection rules¹⁹ would be expected to hold. All three singlet-singlet transitions: ${}^1A_{2g} \leftarrow {}^1A_{1g}$, ${}^1B_{1g} \leftarrow {}^1A_{1g}$ and ${}^1E_g \leftarrow {}^1A_{1g}$ would be present in in-plane (*xy*) polarisation. In out of plane (*z*) polarisation the second transition is expected to be strongly polarised since the α_{1u} mode which activates it is not a normal vibration of the chromophore. The strong *z*-polarisation of the first two bands, and the possible existence of two further bands in *xy*-pola-

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Table II. Breakdown of D_{4h} Selection Rules in D_{2h} and D_2 Symmetry

D_{4h}	D_{2h}		D_2		Assignment
			Electronically allowed	Vibronically allowed	
${}^1A_{1g} \rightarrow {}^1A_{2g}$	$\left. \begin{array}{l} {}^1B_{1g} \\ {}^3B_{1g} \end{array} \right\}$	$\left. \begin{array}{l} \alpha_u(z) \\ \beta_{2u}(x) \\ \beta_{3u}(y) \end{array} \right\}$	$\left. \begin{array}{l} {}^1B_1 \\ {}^3B_1 \end{array} \right\} x$	$\left. \begin{array}{l} \beta_2, \beta_3(y, z) \\ \alpha(x) \end{array} \right\}$	14.0 16.13 *
$\rightarrow {}^1B_{1g}$	$\left. \begin{array}{l} {}^1B_{1g} \\ {}^3B_{1g} \end{array} \right\}$	$\left. \begin{array}{l} \alpha_u(z) \\ \beta_{2u}(x) \\ \beta_{3u}(y) \end{array} \right\}$	$\left. \begin{array}{l} {}^1B_1 \\ {}^3B_1 \end{array} \right\} x$	$\left. \begin{array}{l} \beta_2, \beta_3(y, z) \\ \alpha(x) \end{array} \right\}$	18.2-21.5 16.75-17.15
$\rightarrow {}^1E_g$	$\left. \begin{array}{l} {}^1B_{2g} \\ {}^3B_{2g} \end{array} \right\}$	$\left. \begin{array}{l} \beta_{1u}(x) \\ \alpha_u(y) \\ \beta_{3u}(z) \end{array} \right\}$	$\left. \begin{array}{l} {}^1B_2 \\ {}^3B_2 \end{array} \right\} z$	$\left. \begin{array}{l} \beta_1, \beta_3(x, z) \\ \alpha(z) \end{array} \right\}$	25.8-26.2 **
	$\left. \begin{array}{l} {}^1B_{3g} \\ {}^3B_{3g} \end{array} \right\}$	$\left. \begin{array}{l} \alpha_u(x) \\ \beta_{1u}(y) \\ \beta_{2u}(z) \end{array} \right\}$	$\left. \begin{array}{l} {}^1B_3 \\ {}^3B_3 \end{array} \right\} y$	$\left. \begin{array}{l} \beta_1, \beta_2(x, z) \\ \alpha(y) \end{array} \right\}$	26.5-27.2 **

* Presumably unobserved in z polarisation because of « weak » vibration, not seen in xy and x or y due to masking by more intense singlet-singlet. ** The shoulder in $Ni(S_2CN(n-C_3H_7)_2)_2$ at 20.66 kK is probably due to a singlet-triplet of either the 1B_2 or 3B_3 state.

risation with different characteristics, in the dithiophosphate and dithiophosphinate complexes, show that this point group does not explain the spectra. Even if the polarisation were rationalized on the basis of D_{4h} symmetry the chelate rings would prevent the vibrations being considered as if the group were D_{4h} . Turning to D_{2h} symmetry, four transitions are expected, of which the first two are transitions to states of the same symmetry, which are then expected to be identical in properties. According to the selection rules, the u-type modes of vibration are all present, consequently they allow all vibronic d-d transitions in all directions. An assignment of the transitions cannot, then, be made a priori. This problem is responsible for much of the uncertainty in the assignments of analogous nickel(II) complexes of the same symmetry. It may be handled in two ways, the first by taking low temperature measurements assuming that the temperature effect on an electronic transition induced by vibrational mode k is given by $\coth(h\nu_k/kT)$ and that there is only a single frequency (or narrow range) promoting the transition. On performing this on $Cuacac_2$, which is similar in point group and vibrational modes present, it was postulated that only the bending modes are important (or, at least, those modes at $190-250\text{ cm}^{-1}$).²⁰ The second consists in first calculating the level order using a Hückel m.o. method and then extrapolating to a known crystal spectrum. In this way from the crystal spectrum of bisdipivaloylmethanidonickel(II) it was found that the β_{3u} mode is ineffectual, the α_u mode nearly so, with the β_{1u} and β_{2u} modes being the potent ones.²¹

The drawback of the first method is that both the u-type in-plane bends and stretches are of the same symmetry, which still does not allow an independent assignment. The second conclusion has the disadvantage that it allows no independent check

of the calculations; it also appear to be based on some rather ambiguous polarisation results in which the bands were not well separated²¹ and the polarisation very unclear.

Despite this, the spectra may be interpreted consistently assuming the second set of conclusions. Since, in z-polarisation the first two transitions are allowed only by the almost ineffectual α_u vibration they are expected to be absent, as observed. Turning to the higher energy bands, in the (001) face of the dithiophosphinate the band at $\sim 26\text{ kK}$ may be assigned as the $d_{yz} \rightarrow d_{xy}$ transition, being more intense in xy- than in z-polarisation (see Table II). Since the β_{3u} mode is responsible for activating the $d_{xz} \rightarrow d_{xy}$ transition in z-polarisation, the band at 27.8 kK may be assigned to this transition because it loses much intensity in this direction. In the (100) face both bands are present with relative intensities consistent with the vibrational « power » assumed. The higher energy bands in the phosphate are not as clear but may similarly be assigned. The splitting of the band is not as marked as in the phosphinate, $\sim 0.5\text{ kK}$, but this may be due to the fact that the higher energy component is partly masked by that at lower energy. That there is a splitting is seen by comparison with the (100) face, where the band envelope does not shift markedly in position. For reasons mentioned previously these bands are not easily observed in the other complexes, although one, or both, of the bands at 24 kK and 26 kK in the propyl dithiocarbamate may also be due to the same transitions.

Although this assignment rationalizes the observed spectra it is unsatisfactory for two reasons. Firstly, the α_u mode is an out-of-plane bending mode like the β_{1u} and would be expected to be equally effective since both could give effective d-p mixing. Secondly, the intensities of all the bands, especially those of the higher energy ones, are somewhat high. This is even allowing for the apparent increase in intensity of bands which occur only as shoulders on steeply-rising charge transfer absorptions.

(20) J. Ferguson, R. L. Belford, and T. S. Piper, *J. Chem. Phys.*, **37**, 1569 (1962).

(21) F. A. Cotton and J. J. Wise, *Inorg. Chem.*, **6**, 917 (1967).

Consequently a D_2 symmetry, including a greater « power » of out-plane bands as compared to other vibrations-as has been found in many other cases,¹¹ seems preferable. Also, the use of the D_2 symmetry has the additional advantage that it rationalizes the smaller contribution of magnetic dipole absorption. The magnetic dipole operator components transform as rotations, from which the d_{z^2} and $d_{x^2-y^2}$ d_{xy} should be absent in z-polarisation, as observed. The 26.0 kK band in the phosphinate may then be assigned as the ${}^1B_3 \leftarrow {}^1A$ transition electronically and, vibronically, (β_{2u} mode) allowed in xy-polarisation and only vibronically allowed, but by a strong vibration (β_{1u} mode) in z. Similarly for the ${}^1B_2 \leftarrow {}^1A$ transition. Both of these transitions are electronically allowed in both x- and y-directions, which satisfactorily accounts for the spectrum of the (100) face of the phosphinate. The assignment arrived at is shown in Table II.

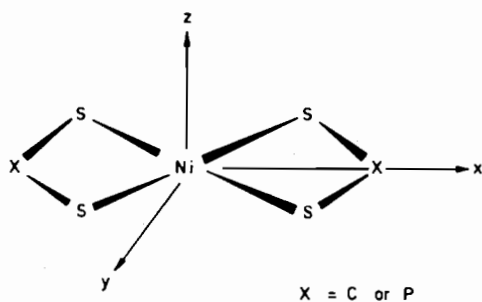


Figure 6. Molecular axis system used.

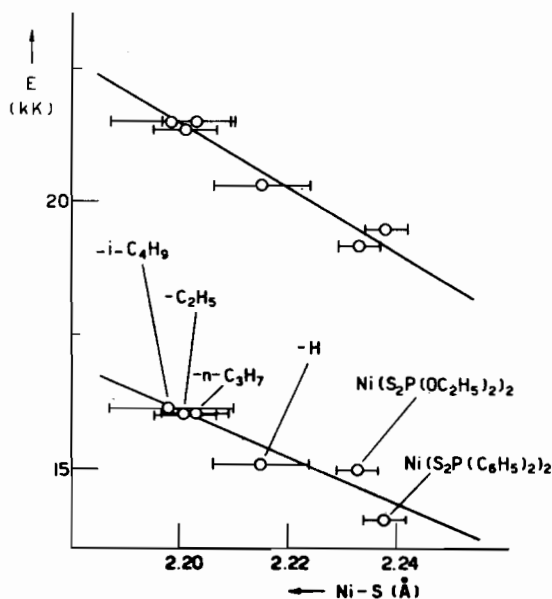


Figure 7. Change in energy of bands due to $d_{x^2-y^2}$ and $d_{z^2} \rightarrow d_{xy}$ with Ni-S bond length.

Neither interpretation can account for the sensibly higher intensity of the second singlet-singlet band, nor can it distinguish between the $d_{x^2-y^2}$, and $d_{z^2} \rightarrow d_{xy}$ transitions. Presumably, the first is caused by the presence of very close weak, spin-forbidden bands.

The other, weak bands present may be assigned to singlet-triplet transitions. For no single compound were all the bands expected observed, consequently the transitions assigned (see Table II) are tentative.

Since the $d_{x^2-y^2}$ and d_{z^2} level order cannot be determined from the experimental results, alone it is necessary to resort to a brief survey of the present theoretical position.

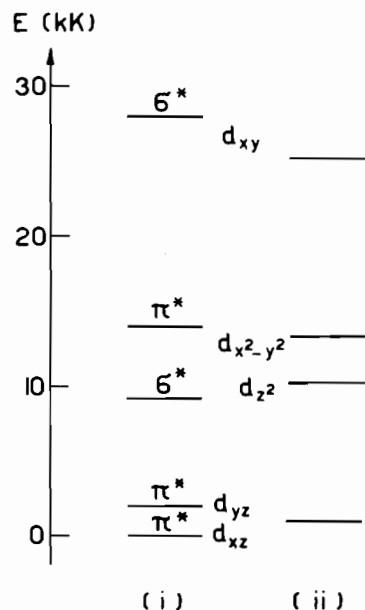


Figure 8. Suggested energy level order for $Ni(S_2P(C_6H_5)_2)_2$, applicable to all complexes (i) found; (ii) corrected for inter-electronic repulsion assuming $F_2 = 10F_4 = 700 \text{ cm}^{-1}$ as in ref. 1, and degeneracy of 1B_g and 3B_g states.

The m.o. calculations of Cotton²² performed on a compound containing oxygen ligands, indicated that the σ -antibonding orbital was some 0.4 kK to lower energy than the π -antibonding orbital. However, this order could not be verified from e.s.r. measurements on the copper(II)-doped nickel(II) complex examined²³ and the overlap parameters used in the calculation are not applicable to the sulphur ligand case. Other, stronger arguments have been put for the opposite order of these two levels based, apart from m.o. calculations and other considerations, upon the similarity of the $10 Dq$ values for the square planar and analogous octahedral cases and on calculations of the energy levels from the triplet-singlet separation. The great change in Ni-S bond length in going from the square planar e.g. $Ni(S_2P(C_6H_5)_2)_2$, and $Ni = 2.238 \text{ \AA}$ to the analogous octahedral compound, e.g. $Ni(S_2P(C_6H_5)_2)_2-2py$ which has Ni-S avge = 2.50 \AA ; with $10 Dq = 790 \text{ cm}^{-1}$,²⁴ means that this analogy is not easy to apply. However, on this basis the assignment with d_{xy} highest in energy would appear more reasonable since a $10 Dq$ value of $\sim 20 \text{ kK}$ seems to be rather large. Since all the spin-forbidden transitions were not observed, the

(22) F. A. Cotton and J. J. Wise, *Inorg. Chem.*, 6, 919 (1967).
(23) F. A. Cotton and J. J. Wise, *ibid.*, 6, 915 (1967).

second mentioned calculation cannot be performed. One possible way of distinguishing between these two levels would be to observe the displacement of the two bands with decrease in Ni-S bond length together with speculations as to the relative dependence of σ and π bonding. It might be expected that closer approach of the sulphur atoms to the metal would result in a greater destabilisation of the π^* orbital with respect to the σ^* orbital. Figure 6 shows, however, that this is not the case, both bands increasing in energy by about the same amount throughout the series, (allowing for the errors in bond lengths). This illustrates the importance of the out-of-plane sulphur lone pairs in contributing, also, to π -bonding in the plane. The almost exactly similar behaviour of the two bands is also indirect evidence that ligand-orbital metal-orbital admixture is important in both σ and π bonding. However, it still provides no clue as to the relative order of these two levels, and that shown in Figure 8 follows the work of Gray.¹

Conclusions

The polarisation properties of these non conjugating NiS₄ systems show that the bands occurring between 14 kK and 28 kK are probably all due to (predominantly) d-d transitions and not charge-transfer transitions.

However, despite the net polarisation results obtained, it is not possible, experimentally, to unambiguously assign the spectra because of the nature of the selection rules in D_{2h} and D₂ symmetry. Unless it is possible to find some square planar nickel(II) system with D_{4h} symmetry, where the $d_{x^2-y^2} \rightarrow d_{xy}$ and $d_z^2 \rightarrow d_{xy}$ transitions may be distinguished, an assignment for nickel(II) in a square planar environment cannot be made.

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