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The Vibronic Spectrum of Bis(diethyl dithiophosphato)nickel(II). II. Temperature Dependence and Fine Structure Analysis[1a,b]

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The temperature dependence of the electronic spectrum of bis(diethyl dithiophosphato)nickel(II), Ni(dtp)$_2$, has been investigated, particularly in the temperature region below 80°K, and its band intensities have been found to conform well to the formula $I_T = I_0$ coth $(h\nu/2kT)$. Extensive vibronic fine structure on the first three d ← d bands at 70°K and below reveals at least six promoting modes followed by extensive symmetric mode progressions in quanta of 300 ± 2 cm^{-1}. The frequencies of the promoting (*ungerade*) modes have been compared to those of the ground state as revealed in the infrared and Raman spectra. The Raman spectrum shows clearly the totally symmetric stretching mode at 305 cm^{-1} corresponding to the excited-state mode responsible for the 300-cm^{-1} progressions in the vibronic spectrum.

Introduction

In the first paper of this series the band assignments and preliminary results of the temperature dependence of the vibronic spectrum of Ni(dtp)$_2$ (dtp$^-$ = diethyl dithiophosphate anion) were reported.[2] In this paper details of this temperature dependence are discussed, particularly those of the data collected below 80°K. In addition, the impressive array of fine structure, detectable only below 70°K, is analyzed. Previous work on the spectrum of Ni(dtp)$_2$ is reviewed in the first paper of the series, in which the assignments of the electronic transitions have been discussed.[2]

Experimental Section

Preparation and growth of single crystals of Ni(dtp)$_2$ have been described previously,[2] as have the crystal structure[3] and morphology[2,3] as well as the instrumentation[3] and electronic spectra techniques used.[2,4] Sample temperatures were measured with both a calibrated germanium resistor and a calibrated gallium arsenide diode. Far-infrared spectra were measured on a Hitachi Perkin-Elmer FIS-3 spectrophotometer. Infrared spectra above 250 cm^{-1} were measured with a Perkin-Elmer 621. Wavelength accuracy for the Cary 14R employed here is ±2 Å, which is better than ±5 cm^{-1} in the region investigated.

Raman spectra were run on a SPEX Industries Ramalog 4 laser Raman spectrometer equipped with a third monochromator, using the 4880-Å line of a Spectra Physics argon ion laser with 18 mW of power. To avoid sample destruction by the laser beam (the energy of which falls in a region of considerable absorption), the sample, as a pressed crystalline pellet, was rotated at 6000 rpm with the laser beam trained near the perimeter of the pellet disk.

Electronic band intensities were measured by cutting out and weighing the chart paper areas under the curves. Relative intensity measurements (on the same crystal at different temperatures) should be accurate to ±5%. Other intensities, which depend also on the measurement of crystal thickness, should be accurate to at least ±10%. Fine structure "intensity" is compared in terms of molar absorptivity (ϵ) measured from the individual maxima vertically to an extrapolation of the major band envelope curve.

The molecular coordinate system used defines the x axis as the Ni–P vector and the z axis as normal to the NiS$_4$P$_2$ plane. (See Figure 2.)

Results and Discussion

Temperature Dependence. The theory of the temperature dependence of the intensity of electronically forbidden, but vibronically allowed, transitions in centrosymmetric chromophores has been discussed at length by Ballhausen,[5] Holmes and McClure,[6] Englman,[7-9] and Satten and Wong[10] and more recently by McCaffery, *et al.*,[11] Lohr,[12,13] and Dickinson and Johnson.[14] Band intensity in such cases may be related to the absolute temperature by the expression $I_T = I_0$ coth $(h\nu/2kT)$ where I_0 is the intensity at 0°K and $h\nu$ is the energy of the promoting (*ungerade*) vibration. Below 80°K band intensity is expected to show little temperature dependence, since the population of the ground electronic state is expected to be concentrated in its zero vibrational level at 80° and below for most systems, unless the promoting vibration energy is unusually low ($h\nu <$ *ca.* 100 cm^{-1}). Perphaps because of this expectation little attention has been paid to temperature-dependence studies in this region. Data for Ni(dtp)$_2$ were collected at 300, 195, and 80°K and at ten temperatures between 3.0 and 70°K to ensure continuity in the low-temperature region. Results are shown graphically in Figure 1. Note the relative constancy of intensity below 80°K, conforming well to the theoretical prediction of intensity as a function of coth $(h\nu/2kT)$ and indicating that the promoting vibration (assuming that only one is involved) has an energy of approximately 150 cm^{-1}. It must be pointed out, however, that, it is unlikely that one and only one promoting vibration can account for band intensity in this system. Therefore, the coth formula as we use it is only a rough approximation.

Fine Structure Analysis. For a molecular complex, Ni(dtp)$_2$ is unusual in the impressive resolution of vibronic fine structure displayed by its crystal spectrum. The extent of the structure is illustrated in Figure 2,[15] along with the assignments of bands 1–4 as deduced in the first paper of this series.[2] This structure, which appears only in the

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[1] (a) Abstracted in part from the Ph.D. dissertation of J. D. Lebedda, Duke University, 1972. (b) Presented in part at the Southeast–Southwest Combined Regional Meeting of the American Chemical Society, New Orleans, La., Dec 1970. (c) NDEA Fellow, 1968–1971.

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Table I. Energies (E)[a] of Vibronic Maxima Associated with Band 1[b] in Ni(dtp)$_2$[c]

Assignment	v_1		v_2		v_3		v_4	
	E	ΔE	E	ΔE	E	ΔE	E	ΔE
$(1 \leftarrow 0)$	13,572	300	13,648	301	13,674	296	13,729	300
$(1 \leftarrow 0) + \alpha_g$	13,872	300	13,949	300	13,970	301	14,029	300
$+ 2\alpha_g$	14,172	302	14,249	300	14,271	293	14,329	297
$+ 3\alpha_g$	14,474	299	14,549	300	14,564	296	14,626	299
$+ 4\alpha_g$	14,773	301	14,849	302	14,860	295	14,925	298
$+ 5\alpha_g$	15,074	296	15,151		15,155		15,223	295
$+ 6\alpha_g$	15,370	294					15,518	292
$+ 7\alpha_g$	15,664	293					15,810	288
$+ 8\alpha_g$	15,957	293					16,098	285
$+ 9\alpha_g$	16,250	295					16,385	
$+ 10\alpha_g$	16,545							

Assignment	v_5		v_6		v_7		v_8	v_9	v_{10}
	E	ΔE	E	ΔE	E	ΔE	E	E	E
$(1 \leftarrow 0)$	13,806	302	13,818	304	13,605	295	13,749	14,763	14,002
$(1 \leftarrow 0) + \alpha_g$	14,108	301	14,122	304	13,900	292	(14,059)	(14,059)	
$+ 2\alpha_g$	14,409	296	14,426	295	14,192	294	14,347		
$+ 3\alpha_g$	14,705	295	14,721	290	14,486				
$+ 4\alpha_g$	15,000	295	15,011						
$+ 5\alpha_g$	15,295								

[a] Units of cm^{-1}. [b] $^1B_{1g} \leftarrow {}^1A_g; xy \leftarrow x^2 - y^2$.[2] [c] The progressions associated with each of the apparent promoting modes v_i are organized into columns, along with the intervals (ΔE) between successive maxima. The accuracy of the absolute energies (E) depends on the calibration of the spectrophotometer and is thought to be ±5 cm^{-1}. The precision of the measurements (comparing eight spectra) was ±1 cm^{-1} for the sharpest maxima and ±3 cm^{-1} for the broader ones, except for those indicated by parentheses, which are more uncertain. Owing to the high S/N ratio and relatively high resolution of the instrument (±(2–3) cm^{-1} in this region) the closely spaced peaks are easily observed and the trends toward (slight) anharmonicity observed are significant.

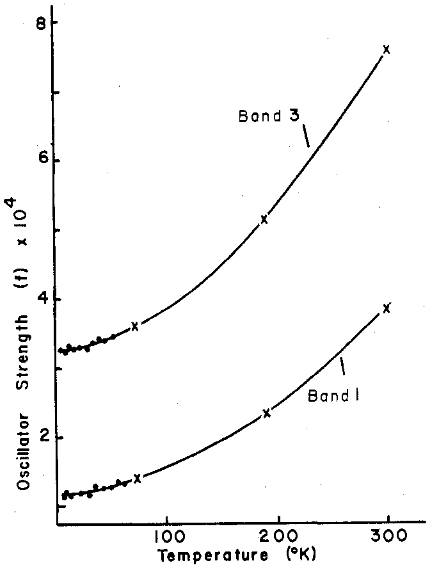

Figure 1. Temperature dependence of spectral band intensity in Ni(dtp)$_2$.

crystal spectra below 75°K and is completely absent in the spectrum of the poly(methyl methacrylate) glass, covers virtually the entire envelopes of the first three electronic bands. Perhaps because of the strongly allowed charge-transfer tail which encroaches on band 4 or perhaps because of the intermolecular coupling intensity,[2] vibronic structure is absent in this region. Since the structure is best resolved on band 1, these components, in their well-defined progressions, are listed in Table I. Table II lists the weaker, less well-resolved fine structure which appears on bands 2 and 3. The progressions are all apparently in quanta of 300 ± 2 cm^{-1} in the initial members and show minimal anharmonicity throughout. The energies of the fine structure peaks show no significant dependence on temperature between 3.0 and 70°K. The structure begins to broaden noticeably at around 50°K and at 70°K appears only as shoulders on the low-energy side of band 1. Structure on

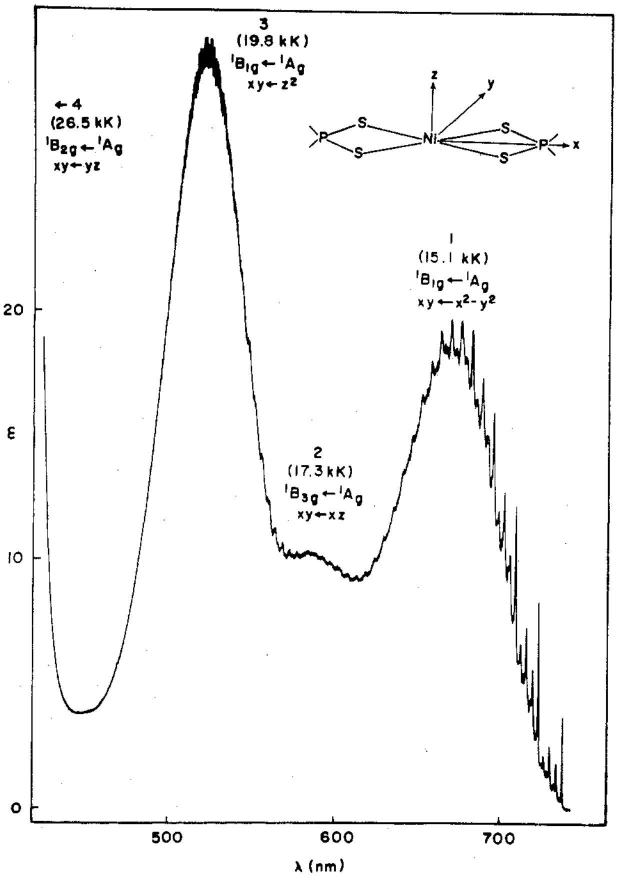

Figure 2. Crystal spectrum (‖c (100 face)) of Ni(dtp)$_2$ at 4.0°K (photograph of recorder trace). Band assignments given as deduced previously[2] using axis system shown. (See discussion of axis systems and orbital symmetries in the review by Hush and Hobbs.[15]) Numerical data were derived from spectra recorded with 10-fold wavelength scale expansion.

Table II. Energies of Vibronic Maxima Associated with Bands 2[a] and 3[a] in Ni(dtp)$_2$[b]

16,708	17,819	18,605	19,689
16,872	17,976	18,755	19,814
17,021	18,123	18,911	19,952
17,167	18,152	19,080	20,101
17,316	18,278	19,231	20,227
17,467	18,318	19,395	20,408
17,643	18,437	19,516	

[a] Band 2: $^1B_{2g} \leftarrow {}^1A_g$; $xy \leftarrow xz$. Band 3: $^1B_{1g} \leftarrow {}^1A_g$; $xy \leftarrow z^2$.[2]
[b] Fine structure in this region is broad and each "maximum" undoubtedly contains several components. Thus, no attempt is made to organize the maxima into progressions. However, intervals of *ca.* 300 cm^{-1} are evident between many maxima.

Table III. Polarization Ratios of Peaks in Vibronic Progressions on Band 1 in Ni(dtp)$_2$[a]

n	v_1	v_2	v_3	v_4	v_5
0	0.38	0.46	0.50	0.29	0.44
1	0.31	0.41	0.20	0.27	0.53
2	0.39	0.39		0.48	0.75
3	0.54	0.45	0.47	0.82	1.00
4	0.90	0.54	0.50	1.30	1.40
5	0.94			1.30	
6	1.11			2.75	
7	3.00				

[a] For each of the first five progressions listed in Table I the ratio of molar absorptivity measured as illustrated in Figure 3 is given for the individual maxima.

bands 2 and 3 (barely visible at 50°K) is not observed at all at 70°K. No structure whatsoever (on any of the electronic bands) could be observed at 80°K.

Referring to Table I and Figure 2, the first progression (associated with mode v_1) appears relatively sharp and intense ($\epsilon \simeq 1$-4; $\Delta\nu_{1/2} = 22$ cm^{-1}) and reveals little anharmonicity until after the sixth member. The progressions associated with v_2 and v_3 appear as a closely spaced doublet. Each contains six members, and neither can be detected beyond the electronic maximum. The fourth progression, based on v_4, is characteristically sharp and almost as intense as that based on v_1. Both the v_4 and v_1 progressions are the only ones which can be seen on the high-energy side of band 1. Finally the v_5 and v_6 progressions appear as a doublet which merges close to the electronic band maximum. They are broad and weak, and their intensities (especially that of v_6) diminish rapidly. Table I also includes the progressions v_7, v_8, v_9, and one other maximum (v_{10}) all of whose members are *extremely* weak and whose vibrations are probably not associated with the NiS$_4$ moiety, but rather with superposed lattice modes or molecular vibrations in other parts of the molecule. This fine structure, as well as that on bands 2 and 3, is observed in both polarizations in the (100) plane as well as in both polarizations in the (010) plane. (The spectrum normal to the (001) plane was not measured at cryogenic temperatures, owing to difficulties in cutting and polishing crystals of suitable thickness and keeping them intact at lower temperatures.)

Although the energies of the fine structure components show no significant polarization dependence, the intensities are considerably polarized. This is illustrated in Figure 3 along with polarization ratios of the maxima of the more prominent progressions on band 1 (see also Table III). Molar absorptivities of the individual maxima are listed in Table IV. Although the fine structure does get slightly broader in the later members of the progressions, the peaks generally have half-widths of 20-25 cm^{-1} in all progressions. As can be seen from Table IV, maximum intensity for the peaks in the ∥c (100) polarization is attained between the second and third members of each progression, whereas in the ∥b (100) polarization it is the third or fourth member that is most intense. Note also that the intensities of each progression follow a similar pattern, increasing by a factor of 2.5-3 and then decreasing to intensities equivalent to or less than that of the 1 ← 0 component. The general harmonicity of the progressions and the large number of members in each indicate deep potential wells with many distinct levels before the continua are reached. The relatively large intensities of the (1 ← 0) components with respect to the intensities of the strongest members of each progression are characteristic of transitions to potential wells whose maxima are at only slightly greater values of the normal coordinate than that of the ground state.

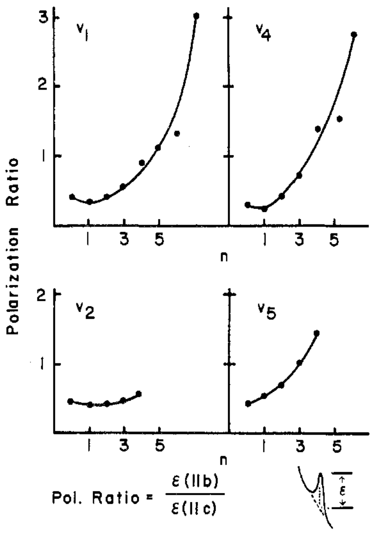

Figure 3. Polarization ratios of peaks in vibronic progressions on band 1 in Ni(dtp)$_2$. The index n refers to the number of quanta of the α_g mode involved (see Table I).

Table IV. Molar Absorptivities of Fine Structure Peaks in Vibronic Progressions on Band 1 in Ni(dtp)$_2$[a]

n	v_1	v_2	v_3	v_4	v_5	v_6
			∥c			
0	1.5	0.8	0.4	1.1	0.6	0.2
1	3.6	1.9	1.0	2.4	1.1	0.3
2	4.2	2.0		2.7	1.0	0.5
3	3.5	1.4	1.1	2.1	0.6	
4	2.0	0.8	0.8	1.3	0.3	
5	1.1	0.3	0.4	0.6		
6	0.6			0.3		
7	0.2					
			∥b			
0	0.6	0.4	0.2	0.3	0.3	0.1
1	1.1	0.8	0.2	0.6	0.6	
2	1.6	0.8		1.3	0.8	
3	1.9	0.6	0.5	1.7	0.6	
4	1.8	0.5	0.4	1.7	0.5	
5	1.0			0.8		
6	0.6			0.7		
7	0.6					

[a] For spectra measured with the light beam normal to the (100) face and polarized as indicated, the molar absorptivities of the members of each of the first six progressions listed in Table I, measured as illustrated in Figure 3, are given.

The successful analysis of the electronic spectrum of Ni(dtp)$_2$ in terms of D_{2h} symmetry[2] requires that the interpretation of the vibronic structure should also be compatible with this choice of effective point group. Considering

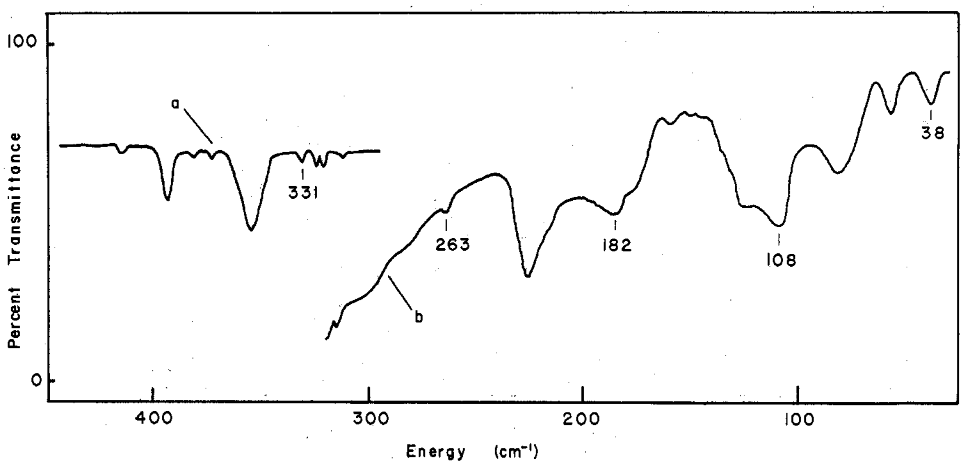

Figure 4. Far-infrared spectrum of Ni(dtp)$_2$: a, in KBr disk; b, in Nujol mull.

only the NiS$_4$ core (exact D_{2h} symmetry) there are nine vibrations expected. Of these, six are *ungerade*: β_{1u} (out-of-plane bend), α_u (out-of-plane bend), two β_{2u} modes (in plane; one bend, one stretch), and two β_{3u} modes (in plane; one bend, one stretch). Since the fine structure is most distinct and best resolved on band 1 ($^1B_{1g} \leftarrow {}^1A_g; xy \leftarrow x^2-y^2$), it is perhaps best to assign the peaks employing the data collected from this band.

Six distinct progressions have been characterized on band 1 (*vide supra*), which are probably associated with *primary* vibrations (those which might be expected to have the greatest effect and hence be first-order perturbations). The most intense vibronic progressions are v_1 and v_4. Because of this and since their intensities and polarization ratios are very similar, it is not unreasonable to assign them to vibrations of the same symmetry. Since β_{2u} has been shown to be the most effective mode in promoting intensity in band 1,[2] this is a reasonable assignment. Since the bending modes are expected at lower energy than the stretches, v_1 is assigned to the β_{2u} bend and v_4 to the β_{2u} stretch. In the β-keto enolates, Cotton and Wise suggested that bending modes are more effective than stretches;[16] this also seems to be the case in Ni(dtp)$_2$ since the progression based on v_1 is more intense than that based on v_4. Similarly, v_2 is assigned to the β_{3u} bend (the next most effective vibration) and v_5 to the β_{3u} stretch. Finally v_3 is probably associated with the α_u mode and v_6 (the weakest progression to the β_{1u} mode, which (according to the selection rules) is not expected to contribute intensity to the $^1B_{1g} \leftarrow {}^1A_g$ ($xy \leftarrow x^2-y^2$) transition). Although these assignments appear to be most reasonable, they are, by no means, unambiguous or unique. They are also complicated by the fact that, as evident from the low energy of the allowing modes deduced from temperature dependence, lattice modes may, at least in part, be responsible for the intensity.

Correlation with Vibrational Spectra. The four most intense progressions on band 1 are separated by energies of 79, 76, and 70 ± 3 cm^{-1}. These presumably represent the separations between the energies of the *ungerade* promoting modes of the excited state, upon which the progressions are based. If it is true that the promoting modes in the ground state (the depopulation of which is the reason for the decrease in band intensity with temperature) are the same as those associated with the false origins in the excited state ((1 ← 0) members in Table I) and that among these promoting modes the influence of one (β_{2u}) predominates, then a group of infrared transitions with an average energy of about 150 cm^{-1} [2] and with spacings of approximately 70-80 cm^{-1} should be found in the vibrational spectrum.

Figure 4 shows the far-infrared spectrum of crystalline Ni(dtp)$_2$ in a Nujol mull and in a KBr disk. The spectrum reveals at least two possible sets of four bands which have the proper energy separations and average energy to be associated with the allowing modes for v_1, the v_2-v_3 doublet, v_4, and the v_5-v_6 doublet: 38, 108, 182, and 263 cm^{-1} or 108, 182, 263, and 331 cm^{-1}. Arbitrarily assuming that all the allowing vibrations are molecular modes (as opposed to lattice modes), then the latter choice is more likely. If this is the case, then based strictly on their apparent effectiveness in promoting intensity in the electronic spectrum (as noted above), the assignments of the four bands would be as follows: 108 cm^{-1}, β_{2u} bend; 182 cm^{-1}, β_{3u} bend; 263 cm^{-1}, β_{2u} stretch; 331 cm^{-1}, β_{3u} stretch and β_{1u} bend. One obvious discrepancy in these assignments is that the assigned energy of the β_{1u} bending mode is too high. However, as noted above, the β_{1u} mode should not contribute to the vibronic intensity, and thus its assignment is uncertain in the first place. Another problem with these assignments is that both of the β_{2u} modes are assigned energies greater than the average promoting mode energy calculated from the crude coth formula. It should also be noted that the energy differences from the infrared do not necessarily have to coincide exactly with those from the fine structure analysis, since the infrared data are for the ground electronic state, whereas the vibronic fine structure is associated with the excited electronic state. Small energy differences are readily explainable in terms of different shapes for ground- and excited-state potential wells, a resonable condition for states of different symmetry.

Finally, we must consider assignment of the mode responsible for the lengthy progressions built on the above promoting modes. The vibronic progressions, because of their regularity and length, are most likely associated with a totally symmetric mode—probably the symmetric Ni-S stretch. Turning to the Raman spectrum in Figure 5, we note first that the prediction (based on the D_{2h} symmetry of the Ni-S$_4$ cluster) of three symmetric modes is exactly fulfilled (with the exception of the additional small bands at 245 and 315 cm^{-1}). Of course, this may be fortuitous to some extent since lattice modes may also contribute to the Raman spectrum. However, if the bands are all due to molecular modes, then the two low-energy bands should be assigned to the β_{1g} stretching and α_g bending modes, respectively, and the band at 305 cm^{-1} is obviously the predicted to-

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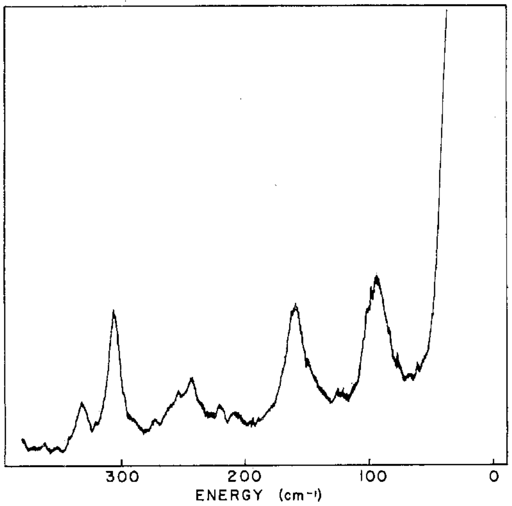

Figure 5. Raman spectrum of microcrystalline $Ni(dtp)_2$.

tally symmetric stretching mode (α_g). The slightly higher energy of the ground-state symmetric stretch thus revealed in the Raman spectrum, with respect to the symmetric stretch observed in the vibronic progressions, is again in keeping with expectation, although, even with the evidence of extensive 0-0 overlap between the ground- and excited-state potential wells, one might have expected to find the α_g fundamental at somewhat higher energy in the Raman spectrum.

These correlations, though reasonably self-consistent, are not unique, and further investigation, particularly of the Raman spectrum, is planned in order to make more certain assignments. The present data call into question the assignments by previous workers of the infrared band at 351 cm^{-1} [17,18] or 327 cm^{-1} [19] to the *unsymmetric* Ni-S stretching mode since the symmetric mode would be expected at higher energy than the unsymmetric. However the intensity of the 305-cm^{-1} band coupled with its exclusion from the ir spectrum makes it the most likely choice for the totally symmetric mode. Further, no other transition of comparable intensity appears in the Raman spectrum at higher energy.

Summary

The salient features of this work are now summarized.

1. Careful temperature-dependence studies, particularly below 80°K, of electronic band intensities of the polarized single-crystal spectral of $Ni(dtp)_2$ reveal compliance with the theoretically predicted relationship $I = I_0 \coth (h\nu/2kT)$ and indicate an approximate promoting mode frequency of 150 cm^{-1}.
2. Vibronic fine structure analysis of the crystal spectra below 75°K reveals at least six allowing noncentric modes separated by about 70-80 cm^{-1} and progressions in a totally symmetric mode of 300 ± 2 cm^{-1} based on these modes and containing as many as eleven members.
3. Exceptionally good correlation of the vibronic structure analysis with the vibrational data obtained from the far-infrared and laser Raman spectra is found. Tentative assignments of the bands in both vibrational spectra have been made. The totally symmetric mode is observed in the Raman spectrum at 305-cm^{-1} correlating excellently with the 300-cm^{-1} progression mode in the vibronic spectrum.

Registry No. $Ni(dtp)_2$, 16743-23-0; $Ni(dtp)_2$, 3911-05-5.

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