The Vibronic Spectrum of Bis(diethyl dithiophosphato)nickel(II).
I. Band Assignments and Temperature Dependence[1a]

By J. D. LEBEDDA[1b] and R. A. PALMER*

The polarized electronic spectra of single crystals of bis(diethyl dithiophosphato)nickel(II) at ambient and cryogenic temperatures have been analyzed with respect to the polarizations and temperature dependence. Polarizations have been interpreted in terms of molecular orientations as seen from three orthogonal views of the monoclinic crystal. The temperature dependence of the band intensities has been used to estimate the energies of the allowing vibrational modes for the various bands. Fine structure in the spectrum at 4.2°K reveals at least six allowing modes followed by extensive symmetric mode progressions in quanta of 300 cm^{-1}. Assignments of the electronic energy levels are made in terms of the centrosymmetric space group D_{2h} and are in agreement with theoretical predictions.

Introduction

The esters of dithiophosphoric acid and certain of their metal complexes have long been known to possess numerous biologically significant properties. It is not surprising then that efforts to understand their structural and kinetic characteristics have been widespread. Among the metal complexes, those of diethyl dithiophosphate (dtp$^-$) have perhaps been most extensively investigated. The planar bis complexes of the d^8 transition metals with dtp$^-$ are of special interest because of their coordinatively unsaturated structure. In particular, the nickel(II) complex has attracted the attention of a wide range of investigators. Reports of the formation and nature of the base adducts of Ni(dtp)$_2$$^{2-5}$ include that of Livingstone and Mihkelson[2] in which the carcinostatic activity of Ni(dtp)$_2$ and its congeners is also described.

Our interest has been in the electronic structure of Ni(dtp)$_2$ and other dtp$^-$ complexes[6] and in the use of single-crystal polarized spectra in properly assigning the electronic energy levels. The electronic spectrum of Ni(dtp)$_2$ in solution has been explored in several places.[5,7–10] The interpretation of these data has in each case been in terms of the square-planar point group D_{4h}. This is also true of the recent analysis of the MCD solution spectrum.[8] Ideally the symmetry of the complex is D_{2h} and, as revealed by the three crystal structures reported,[11–13] the distortion of the coordination sphere to this geometry is pronounced and exact in the solid state. There is little reason to believe it is higher in solution and, in fact, there is indication that it may be lower. Tomlinson and Furlani[7] recently reported their polarized crystal spectra of Ni(dtp)$_2$.

Failing to observe any significant temperature dependence of the intensities, they chose to interpret their results in terms of an effective electronic symmetry of D_2. In light of the crystallographic requirement for a center of symmetry in crystalline Ni(dtp)$_2$, we have reinvestigated the single-crystal spectrum at ambient and cryogenic temperatures. We report here our analysis of the results of this investigation with respect to the polarizations and temperature dependence and offer a consistent interpretation of the electronic structure in terms of an effective electronic symmetry of D_{2h}. Extensive vibronic fine structure observed at temperatures below 70°K will be analyzed in the second paper of this series.

Experimental Section

Preparation and Crystal Growth.—The preparation of Ni(dtp)$_2$ was carried out as described by Jørgensen.[5] Diethyl dithiophosphate, technical grade, was obtained from Aldrich Chemical Co. and used without further purification as was Ni(NO$_3$)$_2$·6H$_2$O, reagent grade, obtained from Allied Chemical Corp. The product was washed twice with water and twice with cold methanol. It was then recrystallized three times from methanol. Crystals were grown from both methanol and 95% ethanol.

Instrumentation and Techniques of Measurement.—The equipment and techniques used have for the most part been described previously.[6,14] Spectra with light incident normal to the (100) face were measured using as-grown crystal plates of accurately known thickness. For spectra normal to the (010) and (001) planes, specimens had to be cut and polished to suitable thickness. In all cases the light was polarized along the extinction directions. Although the visible crystal spectra were measured at temperatures down to 5°K, the 26-kK region was measured only at ambient temperature owing to the high absorptivity and unavailability of a low-temperature microscope attachment for the spectrophotometer. The ambient-temperature microscope attachment, which uses achromatic reflecting optics, is described elsewhere.[15] Spectra were also measured in poly(methyl methacrylate) glasses.[6]

Crystal Structure and Morphology.[11–13]—Bis(diethyl dithiophosphato)nickel(II) is monoclinic, space group $P2_1/c$, with two molecules per unit cell. The cell dimensions are $a = 10.493 \pm 0.005$ Å, $b = 10.300 \pm 0.003$ Å, $c = 8.76 \pm 0.01$ Å, $\beta = 102.59 \pm 0.05$.[12] The site symmetry of the metal atom is C_i and the molecular symmetry is D_{2h} within experimental error. The x molecular axis is represented by the Ni–P vector and the z molecular axis is normal to the NiS$_4$ plane. In the (001) and (100) crystal planes the molecular axes are symmetrically disposed about the extinction directions. In the (010) crystal plane the molecular axes are either aligned with or symmetrically disposed about the extinction directions.

Crystals of appreciable size are easily grown from methanol

(1) (a) Presented in part at the Southeast–Southwest Combined Regional Meeting of the American Chemical Society, Dec 1970, and abstracted from the Ph.D. thesis of J. D. Lebedda, Duke University, 1972. (b) NDEA Fellow, 1968–1971.

(2) S. E. Livingstone and A. E. Mihkelson, *Inorg. Chem.*, **9**, 2545 (1970).

(3) (a) R. L. Carlin, J. S. Dubnoff, and W. F. Huntress, *Proc. Chem. Soc., London*, 229 (1964); (b) A. Sgamellotti, C. Furlani, and F. Magrini, *J. Inorg. Nucl. Chem.*, **30**, 2655 (1968).

(4) S. Ooi and Q. Fernando, *Inorg. Chem.*, **6**, 1558 (1967).

(5) C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **24**, 1572 (1962).

(6) J. D. Lebedda and R. A. Palmer, *Inorg. Chem.*, **10**, 2704 (1971).

(7) A. A. G. Tomlinson and C. Furlani, *Inorg. Chim. Acta*, **3**, 487 (1969).

(8) Q. Looney and B. E. Douglas, *Inorg. Chem.*, **9**, 1955 (1970).

(9) R. Ripan and C. Mirel, *Rev. Roum. Chim.*, **9**, 567 (1964).

(10) R. Ripan, C. Mirel, and D. Lupu, *ibid.*, **11**, 701 (1966).

(11) E. A. Glinskaya and M. A. Porai-Koshits, *Kristallografiya*, **4**, 241 (1959).

(12) J. F. McConnell and V. Kastalsky, *Acta Crystallogr.*, **22**, 853 (1967).

(13) Q. Fernando and C. D. Green, *J. Ing. Nocurl. Chem.*, **29**, 647 (1967).

(14) P. L. Meredith and R. A. Palmer, *Inorg. Chem.*, **10**, 1049 (1971).

(15) R. A. Palmer, to be submitted for publication.

solution. They grow on the surface of the solution as pseudo-hexagonal plates and on the bottom of the beaker as polyhedra with the pseudohexagonal face most prominent. The pseudohexagonal face of thin plates invariably contains the (100) crystal plane. The plates are usually elongated along the c axis. Some confusion seems to have arisen in previous accounts of the crystal spectra[7] as to the correct orientation of the crystal and molecular axes. We have carefully verified the positions of the axes in our crystals by X-ray diffraction and have used the data of McConnell and Kastalsky[12] in calculating the relationships between the crystal and molecular axes.[6,14]

Results and Discussion

Assignments.—Although several reports have appeared concerning the electronic structure of Ni-(dtp)$_2$,[5,7-10] the actual assignment of the ligand field bands has not been convincingly made. In excellent agreement with previously reported solution data,[5] we find four bands which can be assigned to the ligand field spectrum, as follows: ν_1, 14.6 kK (ϵ 72); ν_2, 16.3 kK (ϵ 15); ν_3, 19.1 kK (ϵ 92); ν_4, 26.1 kK (ϵ 840). The band designated as ν_2 was first noticed by Tomlinson and Furlani.[7] Ripan, *et al.*,[10] have assigned ν_1 to the spin-forbidden band $^3A_{2g} \leftarrow {}^1A_{1g}$ (in D_{4h}), an assignment which we find highly questionable in light of the high molar absorptivity. They have assigned ν_3 to $^1A_{2g} \leftarrow {}^1A_{1g}$ and ν_4 to a charge-transfer band. It is then said[10] that the charge-transfer bands mask the remaining d $\leftarrow$ d transitions. Jørgensen,[5] also using D_{4h}, assigned ν_1 to $^1A_{2g} \leftarrow {}^1A_{1g}$, ν_3 to $^1E_g \leftarrow {}^1A_{1g}$, and ν_4 to $^1B_{1g} \leftarrow {}^1A_{1g}$, assuming all d $\leftarrow$ d bands are observed before charge-transfer sets in. The MCD results have been interpreted as indicating a degenerate excited state for ν_1.[8] Assignment in D_{4h} symmetry seems incompatible with the polarized crystal spectral data presented here and elsewhere.[7] On the other hand, assignment in D_2 symmetry (ν_1, $^1B_1 \leftarrow {}^1A_1$; ν_2, $^3B_1 \leftarrow {}^1A_1$; ν_3, $^1B_1 \leftarrow {}^1A_1$; ν_4, $^1B_2 + {}^1B_3 \leftarrow {}^1A_1$)[7] is not justifiable in light of the crystal symmetry and observed temperature dependence.

Our assignments assuming D_{2h} symmetry (as indicated by our observation of pronounced decrease in intensity with temperature) are shown in Table I and are

TABLE I
BAND MAXIMA OF Ni(dtp)$_2$ CRYSTAL SPECTRA[a] (kK)

Temp, °K	ν_3 $^1B_{1g} \leftarrow {}^1A_g$	ν_2 $^1B_{3g} \leftarrow {}^1A_g$[b]	ν_1 $^1B_{1g} \leftarrow {}^1A_g$
300	19.2	16.8	14.5
195	19.4	17.0	14.7
80	19.7	17.2	14.9
4	19.8	17.3	15.1

[a] ν_4 ($^1B_{2g} \leftarrow {}^1A_{1g}$) appears at 300° as a shoulder principally in the $\|c$ polarization at *ca.* 26.5 kK. [b] Taken only from the (010) view.

also defined by the low-temperature glass spectrum shown in Figure 1. Note in this spectrum the intensity of ν_2 and the sharpness of ν_4, both of which will be discussed later.

Our assignments agree very well in most respects with those made by Gray, *et al.*,[16] for the bis(maleonitriledithiolate) complex of nickel(II). Their assignments, which correlate with the results of molecular orbital calculations, differ from ours only in the positions of the ligand (π) charge-transfer bands and of the yz levels. These differences might possibly be explained by the somewhat larger intrachelate angle of the maleo-
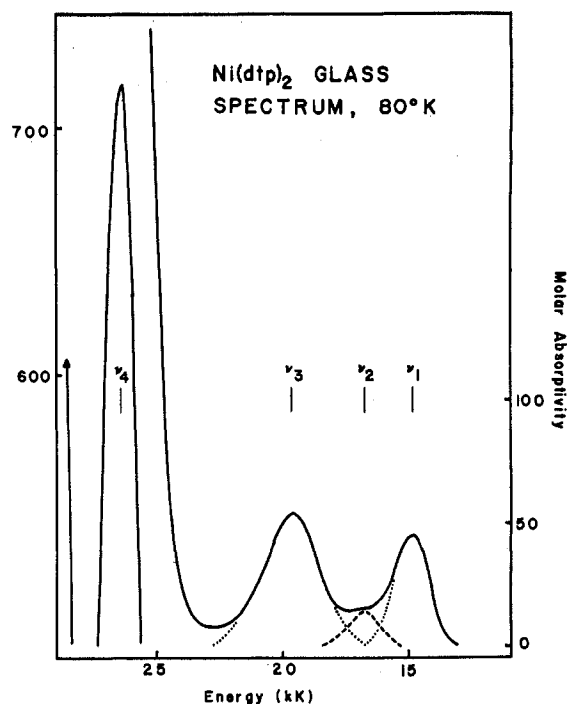
(16) S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. S. Gray, *J. Amer. Chem. Soc.*, **66**, 4594 (1964).

Figure 1.—Poly(methyl methacrylate) glass spectrum of Ni(dtp)$_2$ at 80°K.

nitriledithiolate ligand (97°) when compared to that of the diethyl dithiophosphate (88°). Gray's assignments and those of Tomlinson and Furlani[7] are compared to ours in Figure 2.
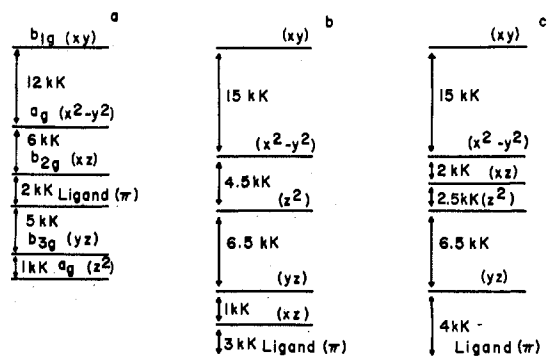

Figure 2.—Band assignments in (NiS$_4$) coordination clusters of D_{2h} symmetry: a, Ni(mnt)$_2$; b, Ni(dtp)$_2$;[7] c, Ni(dtp)$_2$ (this work).

Another interesting comparison is with the work of Ferguson, who has analyzed the electronic structure of Cu(acac)$_2$, using the crystal spectra,[17] in terms of D_{2h} symmetry. The order of the one-electron orbital levels indicated by his assignments corresponds exactly to that deduced from our assignment of the Ni(dtp)$_2$ spectrum. The energy spacings are also similar. Further, the work of Cotton, *et al.*,[18] on the bis(β-keto enolate)-nickel(II) complexes also lends support to our conclusions. Cotton found, as did Ferguson,[17] that all four spin-allowed d $\leftarrow$ d bands in these systems appear within a relatively small energy range—especially the

(17) J. Ferguson, *J. Chem. Phys.*, **34**, 1609 (1961).
(18) F. A. Cotton, C. B. Harris, and J. J. Wise, *Inorg. Chem.*, **6**, 909 (1967).

first three—with the $^1B_{2g} \leftarrow {}^1A_g$ band occurring at a somewhat higher energy.[19]

As mentioned previously, we find the assignment of ν_1 to a spin-forbidden band as done by Ripan, *et al.*,[10] unlikely considering the intensity of the band. For the same reason, Tomlinson and Furlani's assignment of ν_2 as being the spin-forbidden counterpart of ν_3 is not the most likely of several possibilities. The molar absorptivity of ν_2 is fully one-sixth that of ν_3 (Figure 1). Other work indicates that most spin-forbidden bands appear only very weakly in diethyl dithiophosphate complexes.[6] In the bis(maleonitriledithiolate) complex of nickel(II) spin-forbidden bands were not observed at all and the spin-allowed bands had molar absorptivities approximately the same as those of nickel diethyl dithiophosphate.[16] Even in the bis(maleonitriledithiolate) complex of platinum(II), where spin–orbit coupling should be very significant, the spin-forbidden bands had molar absorptivities estimated at about $^1/_{20}$th of the spin-allowed bands.[16] There are innumerable examples in the literature of diamagnetic nickel(II) complexes which do not exhibit spin-forbidden bands, due apparently to their extremely weak intensity. For those which do (for example, $Ni(CN)_4{}^{2-}$) the spin-forbidden bands are 100 times weaker than the spin-allowed bands.[20] Tomlinson and Furlani reported the band at 26 kK (ν_4) to be broad and hence deduced that it must contain two components.[7] Our evidence is to the contrary. The ν_4 band appears very sharp and shows no evidence of splitting even at low temperatures, as can be seen in Figure 1.

Polarization data also support our assignment. The molecular components of the crystal polarizations are shown in Table II.[6,14] Vibronic selection rules for

TABLE II
CALCULATED MOLECULAR COMPONENTS OF THE CRYSTAL SPECTRA OF Ni(dtp)$_2$

Face		x^a	y	z^a
(001)	$\|a$	0.867	0.092	0.039
	$\|b$	0.045	0.814	0.140
(100)	$\|b$	0.045	0.814	0.140
	$\|c$	0.088	0.093	0.821
(010)^b	60°	0.432	0.173	0.394
	30°	0.044	0.173	0.787

^{a} x axis coincident with Ni–P vector; z axis normal to NiS$_4$ plane. ^{b} Polarizations given in degrees from c axis here and in the text.

D_{2h} symmetry and the observed polarizations appear in Table III. Note from Table II that the $\|a$ polarization yields principally x intensity, $\|b$, principally y, and $\|c$, principally z. In the (010) crystal plane the

TABLE III
VIBRONIC SELECTION RULES FOR D_{2h}, Ni(dtp)$_2$

Transition	Electronic excited state	Predicted polarizn (allowing vibration)				Obsd polarizn
		(α_u)	(β_{1u})	(β_{2u})	(β_{3u})	
$xy \leftarrow x^2 - y^2$ $xy \leftarrow z^2$	B_{1g}	z	...	x	y	x, y
$xy \leftarrow yz$	B_{2g}	y	x	...	z	z
$xy \leftarrow xz$	B_{3g}	x	y	z	...	z

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

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

60° polarization is principally xz and the 30° polarization is mainly z.

The ambient-temperature crystal spectra are shown in Figure 3. In the crystal spectrum the data in the

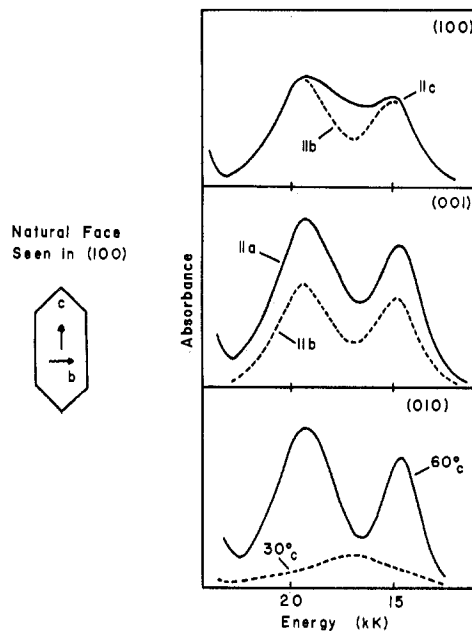Figure 3.—Polarized crystal spectra of Ni(dtp)$_2$ normal to three orthogonal planes at 300°K. The drawings are approximately to the same scale, although exact measurement of the thickness of the polished (001) and (010) plates was not possible.

region between 24 and 28 kK collected with the microscope attachment reveal the $\|c$ polarization of ν_4, though resolution of the band is not as distinct as in the glass or solution. Since this indicates polarization $\|z$ (Table II), the assignment to the $^1B_{2g} \leftarrow {}^1A_g$ ($yz \rightarrow xy$) transition is logical. The fact that ν_1 and ν_3 show the same polarization behavior (allowed most strongly $\|b$ ($\|y$)) indicates that they have the same symmetry and are thus assigned to transitions from the $x^2 - y^2$ and z^2 orbitals, respectively. The observation of two bands with identical polarization is the key empirical factor in rejecting D_{4h} as the effective symmetry of this complex. In this aspect we agree with the previous treatment.[7]

We depart from the earlier analysis, however, in that assumption of a vibronic mechanism seems an inescapable conclusion from the temperature-dependence data (Table IV). The odd normal modes of vibration for a MS$_4$ group having D_{2h} symmetry are two M–S stretches of β_{2u} and β_{3u} symmetry, two M–S in-plane bends (β_{2u} and β_{3u}), and two out-of-plane bending modes (α_u and β_{1u}). The temperature-dependence data shown in Table IV and discussed later suggest that the bending modes are the most important. Cotton and Wise came to similar conclusions in their work on the bis(β-keto enolate) complexes.[19] Comparing Tables II and III with the observed spectra shown in Figure 3 and assuming that our assignments are correct, the effective modes appear to be β_{2u} and, to a lesser extent, β_{3u}, both in-plane bends, with α_u and β_{1u} contributing to a much lesser extent. This satisfactorily explains why ν_2 ($^1B_{3g} \leftarrow {}^1A_g$) is such a weak transition compared to ν_1 and ν_3 ($^1B_{1g} \leftarrow {}^1A_g$); *i.e.*, for ν_2 the electric dipole is z oriented, whereas the most effective vibrations are in

Table IV
Temperature Dependence of Intensities in the Electronic Spectrum of Ni(dtp)₂ in Crystals and Glasses

Crystal Spectra

| Temp, °K | Integrated band intensity (I),[a] ϵ units | | | |
| | ν_1 | | ν_3 | |
	‖b	‖c	‖b	‖c
300	4.0	3.7	7.3	8.1
195	2.7	2.5	5.9	6.0
80	1.4	1.3	3.8	3.8
0	1.1[b]	0.9[b]	3.4[b]	3.6[b]
	65% decrease		53% decrease	

Glass Spectra

| Temp, °K | Integrated band intensity (I), arbitrary units | |
	ν_1	ν_3
300	1.00	1.00
195	0.75	0.89
80	0.50	0.62
5	0.47	0.50
	53% decrease	50% decrease

[a] I for ν_2 also decreases *ca.* 60% in the crystal, but its overlap with ν_1 and ν_3 makes accurate area measurement difficult. Data taken from (001) (natural) face spectra on crystals of known thickness. [b] Calculated.

the *xy* plane. Cotton concluded that the β_{1u} and β_{2u} modes are most effective while the β_{3u} and α_u modes are ineffectual.[19]

Further qualitative correlation between the results illustrated in Figure 3 and the analyses in Tables II and III, *particularly as regards the dominant influence of the β_{2u} mode*, is observed in (1) the polarization of ν_2 in the (100) spectrum (‖b, 14% *z*; ‖c, 82% *z*; allowed in the *z* polarization by β_{2u}), (2) the polarization of ν_1 and ν_3 in the (010) spectrum (60°, 43% *x*; 30°, 4% *x*; allowed in the *x* polarization by β_{2u}), and (3) the persistence of substantial intensity in ν_1 and ν_3 in the ‖c spectra despite low percentage of *x* polarization. The influence of the β_{3u} mode is seen in the comparison of the ‖b and 30° polarizations; in the 30° polarization *both x* and *y* components are very small and the $^1B_{1g} \leftarrow {}^1A_{1g}$ bands (ν_1 and ν_3) are correspondingly weak.

Temperature Dependence.—That the effective electronic symmetry is D_{2h} and that the transitions gain intensity *via* a vibronic mechanism is confirmed by a careful study of the temperature dependence of the band intensities. The theory of the enhancement of transition intensity in centrosymmetric chromophores has been discussed at length by Ballhausen,[21] Holmes and McClure,[22] and Englman[23-25] and more recently by McCaffery, *et al.*,[26] and Lohr.[27,28] Band intensity in such cases may be related to the absolute temperature by the expression

$$I_T = I_0 \coth \frac{h\nu}{2kT}$$

where I_0 is the intensity at 0°K and $h\nu$ is the energy of the allowing vibration. The temperature dependence of the intensities of the electronic bands ν_1, ν_2, and ν_3 is

(21) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962.
(22) O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957).
(23) R. Englman, *Mol. Phys.*, **3**, 24 (1960).
(24) R. Englman, *ibid.*, **3**, 48 (1960).
(25) R. Englman, *ibid.*, **4**, 183 (1961).
(26) A. J. McCaffery, J. R. Dickinson, and P. N. Schatz, *Inorg. Chem.*, **9**, 1563 (1970).
(27) L. L. Lohr, Jr., *J. Chem. Phys.*, **50**, 4596 (1969).
(28) L. L. Lohr and D. S. McClure, *ibid.*, **49**, 3516 (1968).

illustrated in Table IV. Using these data the frequency of the allowing vibrations can be estimated: for ν_1, 110 cm⁻¹; for ν_2, 160 cm⁻¹; for ν_3, 200 cm⁻¹. However, it has been noted by Lohr that, if more than one vibration is active, then I_T is given by a sum of coth terms.[27] This implies that the allowing frequency, $h\nu$, obtained from a calculation of this nature will be an average value. In fact, in this example, where some vibrations are more effective than others, the calculation will yield a weighted average. Our data then indicate that the most important allowing vibrations occur somewhere around 150 cm⁻¹. The temperature dependence of ν_1 and ν_3 in the crystal is graphically revealed in Figure 4. This compares well with data on other sys-
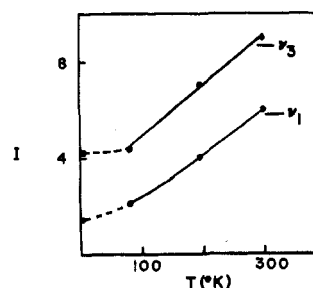

Figure 4.—Temperature dependence of band intensities of ν_1 and ν_3 in Ni(dtp)₂ crystal spectra.

tems.[22] A more extensive study of the details of the temperature dependence will be published in the second part of this series. Accurate data for ν_4 at cryogenic temperatures were not obtainable because of equipment limitations and the high absorptivity in this region. A temperature-dependence study was also done in the poly(methyl methacrylate) glass. The results for ν_1 and ν_3 are shown in Table IV. It can be seen that these bands are significantly less temperature dependent in the glass than in the crystal. This implies that a lattice mode may be at least partly responsible for the intensity enhancement. Cotton suggested for the bis(β-keto enolate) complexes of copper(II) and nickel(II) that bending modes are responsible for the vibronic intensity.[19] Our data suggest that it is a combination of lattice modes and bending modes.

Another surprising observation obtained from the glass spectra was that, as far as could be discerned, ν_4 shows little if any temperature dependence. This, coupled with the fact that the temperature-dependent intensity calculations reveal slightly different average allowing vibrations for ν_1 and ν_3 (which are of the same symmetry), led us to presume that perhaps another intensity-stealing mechanism (in addition to vibronic coupling) was operative. One possibility for the other intensity-stealing mechanism is intermolecular coupling. Lohr and McClure have discussed the process in detail.[28] The intensification is an indication of the extent of metal–metal interaction. According to Lohr and McClure, the cooperative mechanism does not give rise to a temperature dependence of the type anticipated for vibronic coupling and may intensify some crystal field bands more than others; this is totally consistent with our observations.

The specific nature of the intermolecular coupling possible in Ni(dtp)₂ can be seen from an examination of the packing of the molecular units within the crystal

lattice.[12] The d_{yz} orbitals from neighboring nickel atoms, which are unobstructed by the ligands, should interact significantly. Since ν_4 is associated with the electronic transition from the d_{yz} orbital, the molecular perturbation (along with the proximity of ν_4 to charge transfer) can be used to explain its intensity.[29] The other three spin-allowed bands steal intensity princi-

(29) It has been suggested by one reviewer that the agreement between the polarization of ν_4 and the selection rule prediction for the $^1B_{2g} \leftarrow ^1A_g$ transition may in fact be fortuitous and that the band might be an allowed charge-transfer transition with a small matrix element. Although we have given reasons for its assignment to a d–d transition, the charge-transfer possibility cannot be conclusively ruled out.

pally by a vibronic mechanism with only a small amount of intermolecular coupling involved, hence their temperature dependence. The enhanced absorptivity of the bands in the solution spectrum as compared to the crystal spectrum quite possibly indicates a distortion from centrosymmetry in solution.

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 first three bands contain as many as six distinct progressions containing up to ten members each. The analysis of this vibronic structure will be published in part II of this series.

The Kinetics of Substitution Reactions of Poly(ethylenamine)nickel(II) Complexes

BY WILLIAM S. MELVIN,[1a] DAVID P. RABLEN,[1b] AND GILBERT GORDON*

The rates of the ligand-substitution reactions of a series of nickel(II) complexes in aqueous solution have been measured by using the stopped-flow technique. The effects which nonlabile ligands have on subsequent substitution processes were examined. The complexes used in the study include hexaaquonickel(II), mono(ethylenediamine)nickel(II), mono(diethylenetriamine)nickel(II), and bis(ethylenediamine)nickel(II). The substituting ligands used were 1,10-phenanthroline, 2,2'-bipyridine, and 2,2',2''-terpyridine. In that the actual rate of water exchange on each specific nickel(II) complex is reported in the literature, a direct comparison between ligand-substitution rates and water-exchange rates could be made. These experiments provide a test of the generally accepted mechanism for complex formation.

Introduction

Interest in the relationship between substitution rates and water-exchange rates on transition metal ions has been widespread.[2] For the substitution of monodentate ligands on the aquated nickel(II) ion, a direct relationship apparently exists between these two processes.[3] In the absence of specific information to the contrary, this observation has been applied[4–6] to account for the increased reactivities which were observed when nonlabile ligands were coordinated to nickel(II). Although the extension of this simple relationship is appealing, it has been shown that a marked increase in the ligand-substitution rate[7] is not necessarily accompanied by a significant change in the water-exchange rate[8] in the metal ion complex.

The need for more specific experiments to examine the relationship between ligand-substitution rates and water-exchange rates is apparent and is the basis of the experiments reported here.

The nickel(II) complexes used to examine the effects which nonlabile ligands have on subsequent substitu-

tion processes are hexaaquonickel(II), mono(ethylenediamine)nickel(II), mono(diethylenetriamine)nickel-(II), and bis(ethylenediamine)nickel(II). These complexes were chosen in that they allow direct rate comparisons without imposing severe changes on the basic nature of the complex. Since the number of coordinated water molecules on the nickel(II) complex can be varied systematically by changing the coordinated polyethylenamine and since the actual rate of water exchange on each nickel(II) complex is known,[9,10] direct comparisons between the ligand-substitution rates and water-exchange rates can be made. The specific ligands used to investigate these substitution reactions are 1,10-phenanthroline, 2,2'-bipyridine, and 2,2',2''-terpyridine. These neutral heterocyclic molecules were used in an attempt to minimize rate differences due to electrostatic effects and to allow a direct examination of the effects of bidentate and tridentate chelation on the water-substitution reaction for a homologous series of nickel(II) complexes.

Experimental Section

Reagents.—Reagents of the highest quality available were used. The white crystals of phenanthroline (phen) and bipyridine (bipy) were used without further purification. Terpyridine (terpy) was purified prior to use by sublimation.[7] Reagent grade $NiCl_2 \cdot 6H_2O$ was used to prepare stock solutions of nickel(II) which were standardized[11] either by direct titration with EDTA or by gravimetric methods with dimethylglyoxime.

(1) (a) Abstracted in part from the Ph.D. thesis of W. S. Melvin, submitted to the University of Iowa, Aug 1971. (b) Visiting scientist.
(2) (a) R. G. Wilkins and M. Eigen, *Advan. Chem. Ser.*, **49**, 55 (1965); (b) D. J. Hewkin and R. H. Prince, *Coord. Chem. Rev.*, **5**, 45 (1970), and references therein.
(3) R. H. Holyer, C. D. Hubbard, S. F. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **4**, 929 (1965).
(4) D. W. Margerum and H. M. Rosen, *J. Amer. Chem. Soc.*, **89**, 1008 (1967).
(5) J. P. Jones, E. J. Billo, and D. W. Margerum, *ibid.*, **92**, 1875 (1970).
(6) G. G. Hammes and J. I. Steinfeld, *ibid.*, **84**, 4639 (1962).
(7) R. H. Holyer, C. D. Hubbard, S. F. Kettle, and R. G. Wilkins, *Inorg. Chem.*, **5**, 622 (1966).
(8) D. Rablen and G. Gordon, *ibid.*, **8**, 395 (1969).

(9) A. G. Desai, H. W. Dodgen, and J. P. Hunt, *J. Amer. Chem. Soc.*, **91**, 5001 (1969).
(10) D. Rablen and J. P. Hunt, private communication, 1970.
(11) A. I. Vogel, "Quantitative Inorganic Analysis," Wiley, New York, N. Y., 1961, pp 435, 479.