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A Normal-Coordinate Analysis of Bis(*O,O'*-dialkyldithiophosphato)nickel(II) Complexes

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The infrared spectra of $Ni[S_2P(OCH_3)_2]_2$, $Ni[S_2P(OCD_3)_2]_2$, and $Ni[S_2P(OC_2H_5)_2]_2$ have been recorded in the range 4000–50 cm^{-1} and interpreted on the basis of a 1:1 metal ligand, molecular model of $Ni[S_2P(OCH_3)_2]_2$. A normal-coordinate analysis using a Urey–Bradley force field was carried out to assign infrared vibrational frequencies over a broad spectral range. The infrared band assignments for the metal complexes have been compared with those of analogous molecules. A good correlation was found between the results of the normal-coordinate analysis and previous assignments based on empirical evidence.

Introduction

Structural and spectral studies have shown that the four-membered chelate rings formed by the interaction of metal ions with dithiophosphates have significant differences that can be attributed to either electronic or steric effects that arise from the substituents on the phosphorus atom.[1-4] Variation of the alkyl or alkoxy substituent on the phosphorus atom affects the character of the phosphorus hybrid orbitals and causes marked changes in the phosphorus–sulfur bond distance and the sulfur–phosphorus–sulfur angle in the chelate ring. The phosphorus–sulfur bond order as well as the extent of charge localization on the metal atom and the sulfur donor atoms have been inferred from these investigations.[5] It has been presumed that the participation of phosphorus d orbitals in the bonding in the chelate ring is the primary reason for the differences in the geometry and the charge distribution in the chelate ring, but there are no experimental results that can substantiate this statement. A normal-coordinate analysis of the model compound, bis(*O,O'*-dimethyldithiophosphato)nickel(II), of known structure, was undertaken to establish a firm basis for understanding the factors that influence the stability and configuration of the metal complexes of the dithiophosphates.

Experimental Section

Synthesis of Bis(*O,O'*-dimethyldithiophosphato)nickel(II), Ni(DMP)$_2$.[6] Methanol (100 mL) was added slowly over a period of 1.5 h to 110 g of finely powdered P_2S_5 (Eastman Chemical Co.). The reaction mixture was heated under reflux for 3 h and the H_2S gas that was evolved was passed through scrubbers containing H_2O_2 and NaOH. The reaction product which consisted of a black oily liquid was filtered and the filtrate was extracted with three 50-mL portions of water. Finely powdered $NiSO_4 \cdot 6H_2O$ was added to the aqueous extract containing the *O,O'*-dimethyldithiophosphonic acid. Violet crystals of the nickel complex which formed on standing were filtered, dried, and dissolved in hot ethanol. The unreacted nickel sulfate precipitated as green crystals and was separated by filtration. When the filtrate was cooled to −15 °C, violet crystals of the pure nickel complex were obtained.

Bis(*O,O'*-diethyldithiophosphato)nickel(II), Ni(DEP)$_2$, was synthesized in the same manner as above by using ethanol instead of methanol.

Synthesis of Bis(*O,O'*-dimethyldithiophosphato-d_6)nickel(II), Ni(DMP-d_6)$_2$. The method used for the synthesis of the deuterio analogue of Ni(DMP)$_2$ was essentially that described by Nyquist.[7] CD_3OD (5 mL) (Aldrich Chemical Co.) was dissolved in 10 mL of toluene and added dropwise over a period of 1.5 h to a stirred mixture of 6.5 g of P_2S_5 in 20 mL of toluene. The toluene was dried over sodium metal and freshly distilled before use. The reaction mixture was maintained at 85 °C for 4.5 h in an atmosphere of nitrogen, cooled to room temperature, filtered to remove the sulfur precipitate, and distilled under reduced pressure to remove the toluene. The viscous liquid that remained was extracted with three 2-mL portions of D_2O (Stohler Isotope Chemicals). Finely powdered $NiSO_4 \cdot 6H_2O$ was added to the D_2O extract and allowed to stand. The violet crystals that formed were separated, dried under reduced pressure, and dissolved in hot ethanol. The unreacted $NiSO_4$ was separated by filtration and the filtrate was cooled to −15 °C for about 2 h. The violet crystals that formed were filtered, dried under vacuum, and stored in a desiccator over molecular sieves (3 Å).

Synthesis of Bis(*O,O'*-diethyldithiophosphato)platinum(II), Pt(DEP)$_2$.[8] $PtCl_2$ (133 mg) was digested in 10 mL of aqua regia, and KCl (320 mg) was added to the solution followed by 10 mL of concentrated HCl. The mixture was heated for 1.5 h and 10 mL of water was added. The resultant solution was red brown and contained $PtCl_4^{2-}$. The addition of an excess of the ammonium salt of *O,O'*-diethyldithiophosphonic acid to the solution containing $PtCl_4^{2-}$ produced a lemon yellow precipitate which was separated, recrystallized from hot acetone, and stored in a desiccator.

Spectral Measurements. The infrared spectra from 4000 to 200 cm^{-1} were obtained with a Beckman IR-12 double-beam spectrophotometer. The KBr disk method was used between 4000 and 600 cm^{-1}; the Nujol mull technique and polyethylene pellets were used to record the spectra from 600 to 200 cm^{-1}.

The far-infrared spectra from 300 to 50 cm^{-1} were obtained in polyethylene pellets and carbon disulfide solutions with a Beckman IR-11 spectrophotometer equipped with a bolometer detector cooled by liquid helium. Wavelength calibrations were made with polystyrene film and water vapor.

Calculations

The calculations were simplified by treating the planar Ni(DMP)$_2$ complex as a 1:1 metal–ligand system conforming to the molecular model shown in Figure 1. The two methoxy groups bonded to the phosphorus atom were treated as single atoms X_1 and X_2 having an effective mass of 15.994 amu. This six-atom model contains 15 internal coordinates having the following molecular parameters obtained from a single crystal x-ray structure determination:[9] $r_1 = r_2 = 2.22$ Å, $r_3 = r_4 = 1.98$ Å, $r_5 = r_6 = 1.565$ Å, $\alpha = 88°$, $\beta_1 = \beta_2 = 84.5°$, $\nu = 103°$, $\delta_1 = \delta_2 = \theta_1 = \theta_2 = 115°$, $\epsilon = 96°$. Since the model has C_{2v} symmetry, its 12 normal vibrations may be classified into four

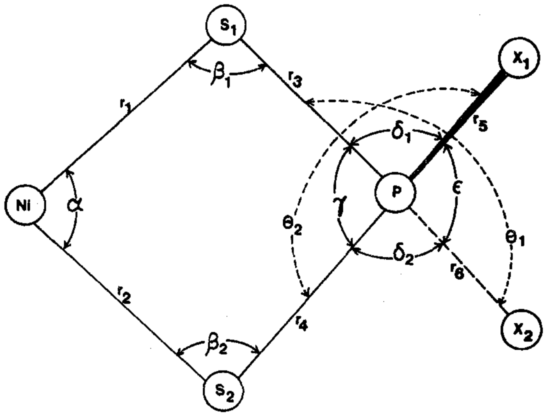

Figure 1. Molecular model and internal coordinates of $Ni(DMP)_2$.

Table I. Symmetry Coordinates

Species		
A_1	$S_1 = (1/2^{1/2})(\Delta r_1 + \Delta r_2)$	ν_{sym}(NiS)
	$S_3 = (1/2^{1/2})(\Delta r_3 + \Delta r_4)$	ν_{sym}(PS)
	$S_5 = (1/2^{1/2})(\Delta r_5 + \Delta r_6)$	ν_{sym}(PO)
	$S_7 = (1/2^{1/2})(\Delta \beta_1 + \Delta \beta_2)$	δ(SPS)
	$S_{11} = (-1/(20)^{1/2})(\Delta \delta_1 + \Delta \delta_2 + \Delta \theta_1 + \Delta \theta_2 - 4\Delta \epsilon)$	δ(OPO)
A_2	$S_8 = (1/2)(\Delta \delta_1 + \Delta \delta_2 - \Delta \theta_1 - \Delta \theta_2)$	ρ_t(OPO)
B_1	$S_6 = (1/2^{1/2})(\Delta r_5 - \Delta r_6)$	$\nu_{antisym}$(PO)
	$S_9 = (1/2)(\Delta \delta_1 - \Delta \delta_2 + \Delta \theta_1 - \Delta \theta_2)$	ρ_r(OPO)
B_2	$S_2 = (1/2^{1/2})(\Delta r_1 - \Delta r_2)$	$\nu_{antisym}$(NiS)
	$S_4 = (1/2^{1/2})(\Delta r_3 - \Delta r_4)$	$\nu_{antisym}$(PS)
	$S_{10} = (1/2)(\Delta \delta_1 - \Delta \delta_2 - \Delta \theta_1 + \Delta \theta_2)$	ρ_w(OPO)

species: $5\ A_1 + 1\ A_2 + 3\ B_1 + 3\ B_2$ ($3\ A_1 + 1\ B_1 + 2\ B_2$ stretching and $2\ A_1 + 1\ A_2 + 2\ B_1 + 1\ B_2$ bending).

The **F** matrix was constructed using a Urey–Bradley force field.[10] The **G** matrix elements were determined using the method of Wilson, Decius, and Cross[11] and evaluated using the molecular parameters above.

Coordinate transformations applied to the **F** and **G** matrices[12] resulted in the removal of two redundant coordinates and their reduction to 13th order. One of the redundancies involved the sum of the changes in the angles around the phosphorus atom ($\Delta\nu + \Delta\delta_1 + \Delta\delta_2 + \Delta\theta_1 + \Delta\theta_2 + \Delta\epsilon = 0$) and the second redundancy involved the sum of the changes in the ring angles ($\Delta\alpha + \Delta\beta_1 + \Delta\beta_2 + \Delta\nu = 0$). A second coordinate transformation was used to factor the resulting 13th order matrices into the four symmetry species. A further simplification involves the deletion of the A_2 vibration which, being neither infrared nor Raman active, was not observed. The B_1 vibration, which concerns out-of-plane ring bending, is not described among the internal coordinates of the molecular model; it is expected to occur in the low-frequency region and is omitted from the calculation.

The remaining $6\ A_1 + 2\ B_1 + 4\ B_2$ species were solved as three independent secular equations of the form $|FG - E\lambda| = 0$ with the aid of a CDC-6400 computer. Twelve frequencies were calculated from 12 force constants. Zero frequencies were obtained for one of the A_1 and one of the B_2 species, representing coordinate redundancies which had not been removed explicitly, thus providing a check on the calculation procedure.

Since the initial set of frequencies varied considerably from the experimentally determined values, the force constants were systematically varied by using a Jacobian matrix until the computed frequencies agreed with the observed values. Although other sets of force constants will indeed give the same frequencies, they are unreasonable values because they do not agree with the force constants that have been determined by other workers for similar molecules.

Table II. Force Constants (mdyn/Å) for Bis(*O,O'*-dimethyldithiophosphato)nickel(II)

Stretching	
K(Ni–S) = 1.20	K(P–O) = 3.46
K(P$\overset{\cdots}{-}$S) = 2.80	
Bending	
H(S–Ni–S) = 0.30	H(S–P–O) = 0.05
H(Ni–S–P) = 0.12	H(O–P–O) = 0.39
H(S–P–S) = 0.15	
Repulsive	
F(S---S) = 0.05	F(S---O) = 0.23
F(Ni---P) = 0.35	F(O---O) = 0.40

Table III. A Comparison of Observed and Calculated Frequencies and Band Assignments of Bis(*O,O'*-dimethyldithiophosphato)nickel(II)

	Obsd	Calcd	Band assignment[a]
			A_1 Species
ν_1	823	831	ν_{sym}(PO) + ν_{sym}(PS)
ν_2	519	523	ν_{sym}(PS) + ν_{sym}(PO)
ν_3	395	391	δ(OPO) + δ(SPS) + ν_{sym}(PS)
ν_4	355	350	ν_{sym}(NiS)
ν_5	252	243	δ(SPS) + δ(OPO)
			B_1 Species
ν_6	796	792	$\nu_{antisym}$(PO)
ν_7	189	194	ρ_r(OPO)
			B_2 Species
ν_8	657	658	$\nu_{antisym}$(PS)
ν_9	328	327	$\nu_{antisym}$(Ni–S)
ν_{10}	214	214	ρ_w(OPO)

[a] Includes assignment contributions of 10% or more.

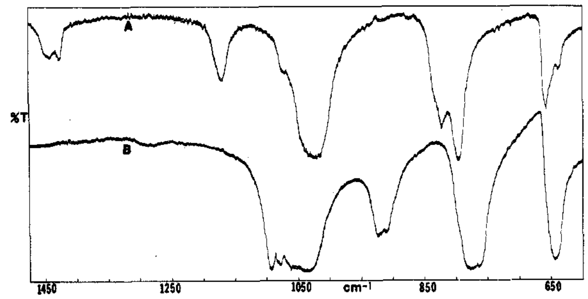

Figure 2. Infrared spectra of bis(*O,O'*-dimethyldithiophosphato)nickel(II) (A) and bis(*O,O'*-dimethyldithiophosphato-d_6)nickel(II) (B).

The symmetry coordinates with their assignments are presented in Table I. Table II lists the set of force constants which give the best agreement with the observed frequencies of $Ni(DMP)_2$. A comparison of calculated and observed frequencies is presented in Table III. The agreement is quite satisfactory, the average error is 1.2%, and the maximum error found is 3.6%.

The last column in Table III contains an approximate description of each normal mode as a linear combination of the symmetry coordinates of Table I. This was obtained from the calculation of the potential energy distribution.[13] The relative contributions are shown in Table IV.

Results and Discussion

Band Assignments. The infrared spectra of bis(*O,O'*-dimethyldithiophosphato)nickel(II) and its deuterio analogue from 1500 to 120 cm⁻¹ are shown in Figures 2 and 3. The high wavenumber regions of the spectra are not shown although they exhibit the characteristic C–H and C–D stretches

Table IV. Potential Energy Distribution

A_1 Species

Symmetry coordinate	Obsd freq, cm^{-1}				
	823	519	395	355	252
S_1	0.0077	0.0735	0.0155	1.0000	0.0190
S_3	0.5019	1.0000	0.0863	0.0200	0.0139
S_5	1.0000	0.4107	0.0136	0.0109	0.0006
S_7	0.0046	0.0340	0.1390	0.0263	1.0000
S_{11}	0.0020	0.1574	1.0000	0.0025	0.1847

B_1 Species

Symmetry coordinate	Obsd freq, cm^{-1}	
	796	188
S_6	1.0000	0.0014
S_9	0.0014	1.0000

B_2 Species

Symmetry coordinate	Obsd freq, cm^{-1}		
	657	328	214
S_2	0.0079	1.0000	0.0062
S_4	1.0000	0.0376	0.0307
S_{10}	0.0171	0.0170	1.0000

associated with the methyl moiety and its deuterio analogue. The observed frequencies that are collected in Table V show the expected shift upon deuterium substitution. Ni(DMP)$_2$ has two closely spaced bands at 1448 and 1431 cm^{-1} that arise from the antisymmetric and symmetric methyl bending modes.[14] Deuterium substitution shifts these bands to 1095 and 1085 cm^{-1}.

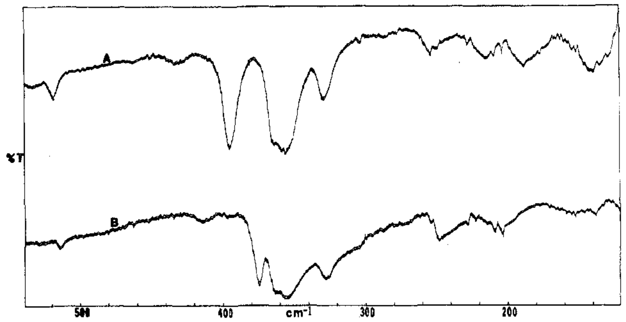

Figure 3. Infrared spectra in the low-frequency region of bis(*O,O'*-dimethyldithiophosphato)nickel(II) (A) and bis(*O,O'*-dimethyldithiophosphato-d_6)nickel(II) (B).

In the infrared spectra of compounds that have a P–O–C linkage there are three regions in which characteristic absorption bands are found:[15] 1065–905 cm^{-1}, very intense bands that arise from (P)–O–C stretching modes; 875–730 cm^{-1}, strong absorption bands that arise from P–O(C) stretching modes; 1240–1085 cm^{-1}, bands of variable intensity that arise from deformations involving the carbon atom. The assignments of the absorption bands in the infrared spectra of Ni(DMP)$_2$ and Ni(DEP)$_2$ are consistent with the above generalizations for compounds with a P–O–C linkage.

Table V. Observed Frequencies of Bis(*O,O'*-dialkyldithiophosphato)nickel(II) Complexes[14]

Ni(DMP)$_2$	Assignment	Ni(DMP-d_6)	Assignment	Ni(DEP)$_2$	Assignment
355	ν_{sym}(NiS)	355	ν_{sym}(NiS)	357	ν_{sym}(NiS)
328	ν_{antisym}(NiS)	328	ν_{antisym}(NiS)	329	ν_{antisym}(NiS)
324	140 + 189 = 329	325	189 + 151 = 340	323	
303		304 (vw)		303 (vw)	
283	2(140) = 280	286 (vw)		274 (vw)	
252	δ(SPS) + δ(OPO)	245	δ(SPS) + δ(OPO)		
240 (sh)		238 (sh)			
214	ρ_ω(OPO)	205	ρ_ω(OPO)	224	ρ_ω(OPO)
189	ρ_r(OPO)	189 (sh)	ρ_r(OPO)	184	ρ_r(OPO)
140		151		123	
				109	
				80	
1172	δCH_3 (out of plane)	918	δCH_3 (out of plane)	1159	δCH_3 (out of plane)
				1103	δCH_3 (in plane)
1072 (sh)	$\nu_{\text{sym}}P(-O-C)_2$	1061 (sh)	$\nu_{\text{sym}}P(-O-C)_2$	1049	$\nu_{\text{sym}}P(-O-C)_2$
1025	$\nu_{\text{antisym}}P(-O-C)_2$	1035	$\nu_{\text{antisym}}P(-O-C)_2$	1004	$\nu_{\text{antisym}}P(-O-C)_2$
				970	ν(C–C)
823	ν_{sym}(PO) + ν_{sym}(PS)	772 (sh)		823	ν_{sym}(PO) + ν_{sym}(PS)
796	ν_{antisym}(PO)	762		807	ν_{antisym}(PO)
657	ν_{antisym}(PS)	650 (sh)	ν_{antisym}(PS)	643	ν_{antisym}(PS)
635 (sh)	2(328) = 656	635	2(328) = 656		
534	2(252) = 504				
519	ν_{sym}(PS) + ν_{sym}(PO)	514	ν_{sym}(PS) + ν_{sym}(PO)	544	ν_{sym}(PS) + ν_{sym}(PO)
433	2(214) = 428	414	2(205) = 410		
395	δ(OPO) + δ(SPS) + ν_{sym}(PS)	374	δ(OPO) + δ(SPS) + ν_{sym}(PS)	396	δ(OPO) + δ(SPS) + ν_{sym}(PO)
362 (sh)	2(188) = 376	361 (sh)	2(189) = 378		
2998	$\nu_{\text{antisym}}CH_3$	2270	$\nu_{\text{antisym}}CH_3$	2984	$\nu_{\text{antisym}}CH_3$
				2979 (sh)	
				2961	$\nu_{\text{antisym}}CH_2$
2948	$\nu_{\text{sym}}CH_3$	2254	$\nu_{\text{sym}}CH_3$	2935	$\nu_{\text{sym}}CH_3$
				2923	$\nu_{\text{sym}}CH_2$
2892	2(1448) = 2896	2196	2(1095) = 2190	2898	2(1453) = 2906
2843	2(1431) = 2862	2140	2(1085) = 2170	2862	2(1441) = 2882
2620	1172 + 1448 = 2620	2074	918 + 1095 = 2013		
	1172 + 1431 = 2603		918 + 1085 = 2003		
2254					
1835	796 + 1025 = 1821			1828	807 + 1004 = 1811
1630	2(823) = 1646				
1448	$\delta_{\text{antisym}}CH_3$	1095	$\delta_{\text{antisym}}CH_3$	1453	$\delta_{\text{antisym}}CH_3$
1431	$\delta_{\text{sym}}CH_3$	1085	$\delta_{\text{sym}}CH_3$	1441	$\delta_{\text{sym}}CH_3$
				1391	ωCH_2

In the spectrum of Ni(DMP)$_2$ the band at 1172 cm^{-1} arises from an out-of-plane bending of the methyl group;[14-16] deuterium substitution shifts this band to 918 cm^{-1}. The shoulder at 1072 cm^{-1} and the band at 1025 cm^{-1} are assigned to the symmetric and antisymmetric C–O stretching modes which are most probably coupled with the motions of other atoms in their vicinity. This assignment is supported by the presence of corresponding bands at 1050 and 1037 cm^{-1} in dimethyldithiophosphoric acid, and at 1040 and 1017 cm^{-1} in diethyldithiophosphoric acid, and their assignment to ν_{sym}(C–O)$_2$ and ν_{antisym}(C–O)$_2$ stretching modes.[14] The P–O symmetric stretching frequency occurs at 823 cm^{-1} and is assigned to ν_1, A$_1$ species coupled extensively with the P–S stretch (ν_2, A$_2$ species). The band at 796 cm^{-1} is essentially a pure P–O antisymmetric stretching frequency (ν_6, B$_2$ species). Deuterium substitution shifts the two bands to 772 and 762 cm^{-1}, respectively. The increased mass of the CD$_3$ group affects the C–O stretch which interacts with the P–O stretching frequencies and causes the observed shift upon deuterium substitution.

The P$\overset{\cdots}{-}$S antisymmetric and symmetric stretching frequencies occur at 657 and 519 cm^{-1}, respectively. The band at 657 cm^{-1} is assigned to the ν_8, B$_2$ species and that at 519 cm^{-1} to the ν_2, A$_1$ species with a contribution of approximately 33% from the ν_1, A$_1$ species. As expected, there is essentially no shift in these frequencies upon deuterium substitution since the methyl group frequencies are well separated from the metal chelate ring system frequencies. The P–S stretching frequencies are well documented.[17] It has been reported that there are two frequency ranges which correspond to the P–S stretch, 702–640 cm^{-1} in which a high intensity band is usually observed, and 575–532 cm^{-1} in which a weak to medium intensity absorption band is found.[18] The antisymmetric and symmetric P–S stretches are found at 657 and 519 cm^{-1} in Ni(DMP)$_2$. The position of the high-frequency band is well within the reported range, but the low-frequency band is outside the range that is reported for the symmetric P–S stretching frequencies. It is noteworthy, however, that ν_{sym}(P–S) in Ni(DMP)$_2$ is observed at 519 cm^{-1} when a Nujol mull or polyethylene pellet technique is used whereas the band appears at 532 cm^{-1} when the spectrum is recorded in a KBr disk. In another study of five phosphorotetrathioate salts,[19] in which the P–S bond order is 1.25, the P–S stretches occurred in the region 570–520 cm^{-1}. In Ni(DMP)$_2$ the P–S bond order is 1.5 and the P–S antisymmetric stretch should appear at a frequency that is higher than 570 cm^{-1}. It is not surprising therefore that the P–S antisymmetric stretching frequency in Ni(DMP)$_2$ occurs at 657 cm^{-1}.

The band at 395 cm^{-1} is assigned to the O–P–O bend (ν_3, A$_1$ species) coupled to a small extent with the symmetric P–S stretch and the symmetric ring breathing vibration (ν_5, A$_1$ species). In the deuteriated compound this band is shifted to 374 cm^{-1}. Analogous bands were found in the infrared spectra of CH$_3$OP(=S)Cl$_2$ and CD$_3$OP(=S)Cl$_2$.[20] The two bands at 373 and 393 cm^{-1} that occur in the former compound are shifted to 361 and 379 cm^{-1} in the deuteriated compound. These two bands had been assigned to the C–O–P bending modes.

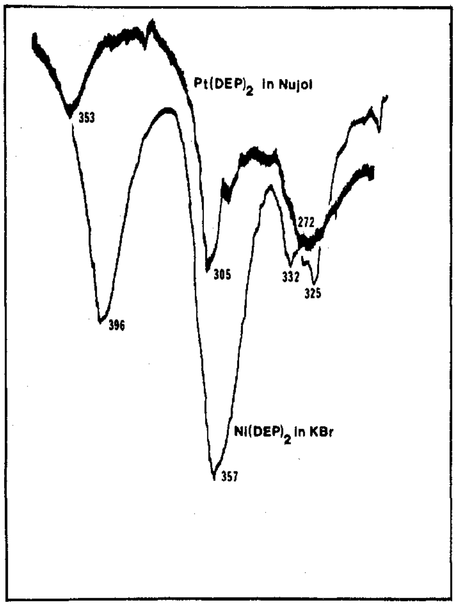

Figure 4. Stretching frequencies associated with Pt–S and Ni–S.

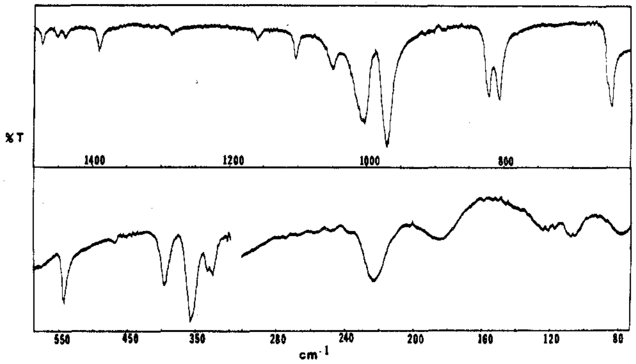

Figure 5. Infrared spectra of bis(*O,O'*-diethyldithiophosphato)-nickel(II).

The symmetric and antisymmetric Ni–S stretching frequencies in Ni(DMP)$_2$ are found at 355 and 328 cm^{-1}, respectively, the symmetric stretch being assigned to the ν_4, A$_1$ species and the antisymmetric stretch to the ν_9, B$_2$ species. In a study of the metal chelates of monothio-β-diketones and related ligands,[21] the Ni–S stretching frequency was found to occur at 358 cm^{-1}. Confirmation of the assignment of the Ni–S stretch was obtained by substitution of Pt for Ni in Ni(DEP)$_2$. In the spectra shown in Figure 4, the band shapes of Ni(DEP)$_2$ and Pt(DEP)$_2$ are similar, and the predicted values (based on a change in the reduced mass) of the Pt–S stretching frequencies (308 and 284 cm^{-1}) are very close to the observed values (305 and 272 cm^{-1}). It is asumed that substitution of the heavy Pt atom for Ni in Ni(DEP)$_2$ does not change its molecular geometry. This assumption is valid because the infrared bands present in the Ni(DEP)$_2$ spectrum are also present in the Pt(DEP)$_2$ spectrum.

The bands at 252, 214, and 188 cm^{-1} correspond to the ν_5, A$_1$ species coupled to a small extent with the O–P–O bend, the ν_{10}, B$_2$ species and the ν_7, B$_1$ species, respectively. The band at 252 cm^{-1} corresponds to the ring breathing vibration, the 214 cm^{-1} band to the in-plane bending or rocking motion, and the 188 cm^{-1} band to the out-of-plane bending or wagging motion. The absorption band at 140 cm^{-1} is tentatively assigned to the out-of-plane (B$_1$ species) bending vibration of the ring.

The infrared spectrum of bis(*O,O'*-diethyldithiophosphato)nickel(II), from 1500 to 80 cm^{-1}, is shown in Figure 5. Although the high wavenumber region of the spectrum is not shown, the observed frequencies are given in Table V. The characteristic C–H stretches of the methyl and methylene groups in the (OCH$_2$CH$_3$) moiety are readily distinguished in the list of observed frequencies. The band assignments in Table V correlate well with the assignments by other workers.[14,17] A comparison of the spectra of Ni(DMP)$_2$ and Ni(DEP)$_2$ (Figures 2, 3, and 5; Table V) clearly shows the normal vibrations which can be attributed to new interactions that are found in the ethoxy group.

Force Constants. The initial Urey–Bradley force constants were transferred from the following compounds: $H_2PO_4^-$,[22] PS_4^{3-},[23] $Ni(S_2CSC_2H_5)_2$,[24] and $Ni(S_2COC_2H_5)_2$.[25] The force constants that were used to give the best fit with the observed frequencies are collected in Table II.

Nickel(II) forms four-membered chelate rings with dithiophosphates, dithiocarbamates, and xanthates. The anomalous properties of the four-membered chelate rings in the dithiophosphate complexes can be attributed to the presence of the large phosphorus atom with available d orbitals. The Ni–S bond in the four-membered ring containing a phosphorus atom is more prone to disruption than the Ni–S bond in the corresponding ring systems in which the phosphorus is replaced by a carbon atom.[24-26] The Ni–S distances that have been determined by x-ray crystallographic techniques do not reflect these bonding differences in the chelate rings. For instance, the Ni–S distance in bis(ethylxanthato)nickel(II) is 2.23 Å and in bis(*O,O'*-dimethyldithiophosphato)nickel(II) it is 2.222 Å. It might be deduced from these bond distances that the Ni–S bond in the dithiophosphate complex is somewhat stronger than the Ni–S bond in the xanthate complex and that the dithiophosphate complex of nickel(II) is more stable than the xanthate complex. The force constants, however, imply correctly that the xanthate is much more stable than the dithiophosphate. The bond distances in these metal chelates are quite insensitive to variations in metal–ligand bonding. The interpretation of subtle but significant variations in x-ray crystallographic bond parameters in terms of the electronic structures of these systems can be quite misleading.

Registry No. $Ni(DMP)_2$ (salt form), 25764-05-0; $Ni(DMP)_2$ (coordination form), 15844-04-9; $Ni(DMP\text{-}d_6)_2$ (salt form), 61812-69-9; $Ni(DMP\text{-}d_6)_2$ (coordination form), 61813-20-5; $Pt(DEP)_2$ (salt form), 31596-89-1; $Pt(DEP)_2$ (coordination form), 37583-01-0; $Ni(DEP)_2$ (salt form), 3911-05-5; $Ni(DEP)_2$ (coordination form), 16743-23-0.

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Electrode Potentials of Nickel(III,II)–Peptide Complexes

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Standard electrode potentials from 0.96 to 0.79 V are determined for a series of 30 $Ni^{III,II}$–peptide couples in aqueous solution. The values of $E°$ decrease with the number of deprotonated peptide groups and can increase with bulky C substituents depending upon their position in the amino acid residues. Histidine-containing peptide complexes have relatively high electrode potentials. Ligand effects on the values of $E°$ are much smaller for the nickel peptides than for the corresponding copper peptides, which is indicative of the relative advantages in ligand field stabilization of d^8 vs. d^9 and d^7 electronic configurations in the square-planar and tetragonal environments of the peptide complexes.

Introduction

A number of trivalent nickel complexes with nitrogen donors have been prepared in nonaqueous solution[1-5] or in the solid state.[6,7] The formation of Ni(III) complexes with several pyridine oxime ligands in nonaqueous solution prompted the proposal of some qualitative criteria for ligands which stabilize complexes of Ni(III) rather than Ni(IV).[8] In addition, an extensive series of tetraaza macrocyclic nickel complexes in acetonitrile has been used to quantitatively correlate potentials of the $Ni^{III,II}$ couples with the nature of the ligands.[2] Characterization of trivalent nickel complexes in aqueous solution until recently has been limited to transient species,[9] although there is a preliminary report of a relatively stable Ni^{III}–EDTA complex.[10]

We have recently prepared and characterized several relatively stable nickel(III)–peptide complexes in aqueous solution.[11] In the present work a more extensive series of nickel peptides is electrochemically oxidized and characterized in aqueous solution. The electrode potentials have been measured for 30 $Ni^{III,II}$–peptide complexes in order to determine what factors affect the relative thermodynamic stability of the divalent and trivalent oxidation states. The changes in the values of $E°$ for the nickel complexes with changes in the nature of ligands are compared with the results obtained from a similar study of copper–peptide complexes.[12] A correlation between the visible absorption maxima of the divalent complexes and the electrode potentials is used to explain the differences in the relative stability of the oxidation states for the two metal–peptide systems.

Experimental Section

The wavelengths of the visible absorption maxima of the fully deprotonated Ni(II) complexes of the peptides and peptide amides used are listed in Table I. The commercial sources for the chromatographically pure peptides also are given. The following ab-