tach]$^{2+}$ and that of the trigonal-prismatic Co[(py)$_3$tach]$^{2+}$ is particularly vivid. The latter consists of an extremely broad band at 8430 cm^{-1} and two overlapping bands at 19,100 and 20,200 cm^{-1}.[2] The spectra of the corresponding Ni(II) compounds do not differ markedly in band position but the spectrum of the hydrogenated complex ion is somewhat less intense than that of Ni[(py)$_3$tach]$^{2+}$. However, if the spectrum of the latter is interpreted in terms of an octahedral ligand field, *B* has a remarkably high value of 980 cm^{-1}.[2] This result is undoubtedly due to the unusual coordination geometry found in that complex ion.

Oxidation of Co[(pic)$_3$tach]$^{2+}$ with $S_2O_8^{2-}$ afforded the corresponding Co(III) species whose spectra consisted of only one observable ligand field band (Table I). The band position compares favorably with the $^1A_1 \rightarrow {}^1T_1$ transition at 21,400 cm^{-1} in Co(en)$_3{}^{3+}$. The second spin-allowed transition in the (pic)$_3$tach complex is obscured by high-intensity transitions in the near-ultraviolet region of the spectrum. The vibrational spectrum is very similar to those of 2+ complexes.

The conclusion deduced from the experimental data is then in complete accord with that drawn from the inspection of molecular models. Consequently, it becomes clear that the trigonal-prismatic complexes of (py)$_3$tach owe their coordination geometry to the rotational barriers within the conjugated, acyclic C═N bonds.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY 08540

Metal–Metal Frequencies and Force Constants for a Platinum–Tin Cluster[1]

BY ARISTIDES TERZIS, THOMAS C. STREKAS,
AND THOMAS G. SPIRO*

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An unusual platinum–tin metal atom cluster was postulated recently by Lindsey, *et al.*,[2] as the basic unit of some trichlorotin complexes of platinum. The cluster was formulated as Pt$_3$Sn$_2$, a trigonal bipyramid with platinum atoms in the equatorial plane and tin atoms at the apices. Guggenberger has established this molecular configuration by X-ray crystallography[3] in the case of L$_3$Pt$_3$(SnCl$_3$)$_2$, where L is cycloocta-1,5-diene bound to the platinum atoms.[3] The structure is reproduced in Figure 1.

As part of a continuing study of the vibrational spectra of metal-cluster compounds,[4] we have examined the low-frequency Raman and ir spectra of L$_3$Pt$_3$(SnCl$_3$)$_2$. These provide the first opportunity to assign vibrational modes associated with the stretching of Pt–Pt bonds, and of bonds to bridging tin atoms. A simple normal-coordinate analysis provides an estimate of the force constants associated with these novel bonding features.

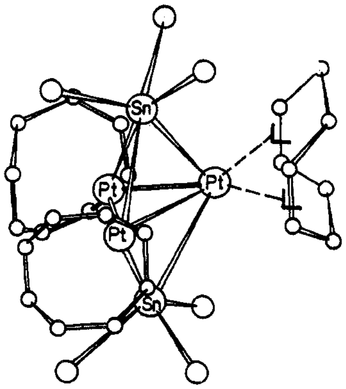

Figure 1.—The molecular configuration of (C$_8$H$_{12}$)$_3$Pt$_3$(SnCl$_3$)$_2$ (taken from ref 3). For the normal-coordinate analysis, the cyclooctadiene rings were each replaced by two point mass ligands, effective mass 26, located at the midpoints of the double bonds coordinated to the platinum atoms. Molecular parameters: distances (Å): Pt–Pt, 2.58; Pt–Sn, 2.80; Sn–Cl, 2.39; Pt–L, 2.15; angles (deg): Cl–Sn–Cl, 109.6; L–Pt–L, 90 (see J. A. Ibers and R. G. Snyder, *J. Amer. Chem. Soc.*, **84**, 495 (1962)).

Spectral Assignments

Metal–metal stretching frequencies are expected below 250 cm^{-1}. For an isolated Pt$_3$Sn$_2$ cluster with D_{3h} symmetry there are six fundamental vibrational modes. The representations spanned by Pt–Pt and Pt–Sn internal coordinates are

$$\Gamma_{\text{Pt-Pt}} = A'_1 + E'$$
$$\Gamma_{\text{Pt-Sn}} = A'_1 + A''_2 + E' + E''$$

The A$'_1$ and E$''$ modes are Raman active only while the A$''_2$ mode is infrared active only and the E$'$ modes are active in both spectra. While the crystal symmetry[3] for L$_3$Pt$_3$(SnCl$_3$)$_2$ is lower than D_{3h}, previous experience with metal-cluster spectra[4] suggests that site symmetry effects are unlikely to be important for the cluster modes.

Metal–metal stretching vibrations are expected to show up strongly in Raman scattering. The low-frequency Raman spectrum of a single crystal of L$_3$Pt$_3$(SnCl$_3$)$_2$ (Figure 2) shows four prominent bands, at 170, 143, 112, and 81 cm^{-1}, which may be assigned with some confidence to cluster modes. In addition there are several weaker bands. Mononuclear platinum cycloocta-1,5-diene complexes show four Raman bands in this region, assignable as Pt–L deformation modes: LPtCl$_2$: 186, 160, 120, and 101 cm^{-1}; LPtBr$_2$: 187, 160, 125, and 98 cm^{-1}. The only other features found in the low-frequency spectra of these reference compounds are the X–Pt–X bending frequencies, at 170 cm^{-1} for X = Cl and 116 cm^{-1} for X = Br. Accordingly we assign to Pt–L deformation modes the weak features in Figure 2 at 185, 160, 125 (sh), and 95 (sh) cm^{-1}. Other weak bands at 130, 89, and 54 cm^{-1} are shown by the normal-coordinate analysis below to be assignable to mixed Sn–Cl deformation and Pt–Sn stretching modes. The low-frequency infrared spec-

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[1] This investigation was supported by Public Health Service Grant GM-13498, from the National Institute of General Medical Sciences, and by National Science Foundation Grant GP-10122.

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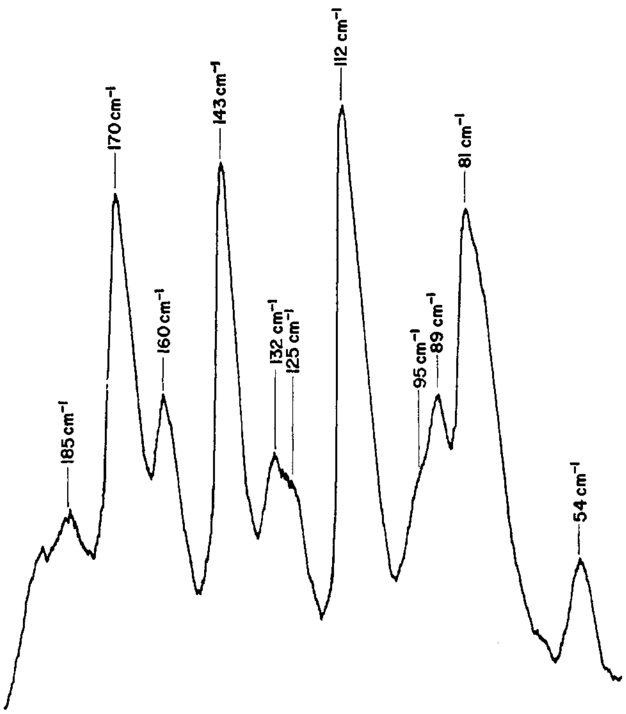

Figure 2.—Low-frequency Raman spectrum of a single crystal (∼3 mm per edge) of $L_3Pt_3(SnCl_3)_2$ (arbitrary orientation). He–Ne (6328 Å) laser excitation. Instrument conditions: slit width, 1.0 cm^{-1}; scan rate, 20 cm^{-1}/min; time constant, 3 sec.

trum (Table I) shows bands at 180, 158, 144, 130, 125 (sh), and 53 cm^{-1}. These are all coincident with Raman bands, indicating E′ symmetry. However the calculations below suggest an A''_2 assignment for the 130-cm^{-1} mode, and its appearance in the Raman spectrum may arise from selection rule breakdown due to lowered site symmetry in the crystal.

TABLE I

INFRARED AND RAMAN FREQUENCIES OF $(C_8H_{12})_3Pt_3(SnCl_3)_2$[a]

Infrared (35–300 cm^{-1}, Nujol mull)	Raman (30–3000 cm^{-1}, single crystal and powder)			
226 m	2975 vw	1430 m	845 w	297 s
180 m, br	2923 w	1337 w	833 vw	292 sh
158 s	2915 w	1316 m	792 vw	242 w, sh
144 m	2906 m	1306 w	775 w	229 m
130 m	2904 m, sh	1254 vs	558 w	192 w, sh
125 sh	2898 w	1247 m	553 w	185 w
53 m	2887 w	1235 w	504 w	170 s
	2842 w	1230 m	499 w	160 m
	1520 vvs	1199 w, sh	452 m, br	143 vs
	1495 vw	1196 m	426 w	132 m
	1482 w, sh	1185 m	413 s	112 vs
	1479 m	1094 w	352 w	95 sh
	1451 w	1017 w	328 vs	89 m
	1441 m	1003 w	320 s	81 s
	1436 m	979 m	309 s	77 sh
		866 w		54 w

[a] Key: w, weak; m, medium; s, strong; v, very; br, broad; sh, shoulder.

Of the numerous features at higher frequencies (Table I) a strong Raman band at 328 cm^{-1} may confidently be assigned to the A'_1 Sn–Cl stretch, while another strong band at 413 cm^{-1} is probably the Pt–C breathing mode of the coordinated cyclooctadiene ligands (compare 405 cm^{-1} for the Pt–ethylene symmetric stretch in Zeise's salt[5]).

The assignment of symmetry species to the vibrational modes would be aided by Raman polarization measurements in solution. Unfortunately $L_3Pt_3(SnCl_3)_2$ is insufficiently soluble in a variety of solvents tried to provide a solution spectrum. However the single-crystal Raman spectrum shows distinct polarization properties. While these are difficult to interpret rigorously because of the low crystal symmetry, they do exhibit regularities which aid in the assignment of symmetry species. Specifically, when the crystal was rotated 90° from the orientation which gave the spectrum shown in Figure 2, it was found that the two bands at 170 and 112 cm^{-1} became considerably weaker, as did the 328-cm^{-1} A'_1 Sn–Cl stretch. At the same time the bands at 143 and 54 cm^{-1} became stronger, while the 81-cm^{-1} band stayed about the same. In conjunction with the ir coincidences these observations confirm E′ assignments for the 143- and 54-cm^{-1} bands and suggest that the modes at 170 and 112 cm^{-1} are of A'_1 symmetry while the 81-cm^{-1} mode belongs to E″.

For the Pt–Sn coordinates, the diagonal symmetry G matrix elements are in the ratios 2:1:0.6 for the A'_1, E″, and E′ modes, respectively. The frequencies are expected to be roughly proportional to the square roots of the G matrix elements, and since the E″ band occurs at 81 cm^{-1}, it seems reasonable to assign the 112 (A'_1) and 54 (E′) cm^{-1} bands primarily to Pt–Sn stretching. The 170 (A'_1) and 143 (E′) cm^{-1} modes are then left primarily to Pt–Pt stretching, in reasonable accord with the ratios of the corresponding G matrix elements, 2:1.

Normal-Coordinate Analysis

Normal-coordinate calculations were carried out using the *FG* matrix method of Wilson, *et al.*,[6] with the aid of Schachtschneider's programs GMAT and FPERT.[7] For this analysis we used a model containing the $Pt_3(SnCl_3)_2$ structure described by Guggenberger.[3] Inclusion of the cyclooctadiene ligands would have made the analysis impossibly complicated. Previous experience with heavy-metal carbonyl clusters[4] suggests that mixing of metal–metal and metal–ligand modes should be unimportant, because of the great disparity in mass between the carbon atoms of the cylooctadiene ligands and the platinum atoms to which they are attached. An estimate of the magnitude of the coupling was obtained by including in the calculation six point mass ligands located at the centers of the double bonds to which the platinum atoms are coordinated[3] (see Figure 1). The effective mass for each ligand was taken as that of C_2H_2, 26. In the calculation an effective Pt–L force constant was obtained from the assigned metal–ligand breathing mode at 413 cm^{-1}. This model cannot, of course, test realistically for coupling with C–Pt–C or other ligand deformation modes. Again experience with carbonyl-cluster calculations[4] suggests that such coupling is slight.

Coupling with Sn–Cl stretching modes is expected to be somewhat more substantial. An effective Sn–Cl

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force constant is readily determined by assignment of the prominent A'_1 Raman band at 328 cm^{-1} to Sn–Cl stretching. The most serious coupling is with the Cl–Sn–Cl and Cl–Sn–Pt deformation modes, and there are no obvious assignments with which to fix the corresponding force constants. Starting values of $f_{Cl-Sn-Cl} = 0.08$ mdyn/Å and $f_{Cl-Sn-Pt} = 0.03$ mdyn/Å were taken from the calculations of Watters, Brittain, and Risen[8] on $(CO)_4CoSnCl_3$. The Pt–Pt and Pt–Sn force constants were then adjusted to calculate the four prominent Raman cluster bands, at 170, 143, 112, and 81 cm^{-1}. An adequate fit required the introduction of an interaction constant between Pt–Pt bonds. Moreover the preliminary calculations strongly pointed to assignment of the 89-cm^{-1} band to nearly coincident E′ and E″ modes involving Cl–Sn–Cl bending primarily. The values of the force constants were then refined to an acceptable fit to the assigned frequencies.

The results of the calculations are shown in Table II.

TABLE II

NORMAL-COORDINATE ANALYSIS RESULTS FOR $L_3Pt_3(SnCl_3)_2$

Freq, cm^{-1}		Potential energy distribution, %					
Calcd[a]	Obsd	V_{PtL}[b]	V_{SnCl}	V_{PtPt}	V_{PtSn}	V_{ClSnCl}	V_{ClSnPt}
413 (A'_1)	413	98.8	0.0	1.1	0.1	0.0	0.0
329 (A'_1)	329	0.0	96.5	0.0	2.6	0.8	0.1
170 (A'_1)	170	1.1	0.8	81.6	14.0	1.0	1.3
142 (E′)	143	0.7	0.1	91.3	6.5	0.2	0.1
131 (A''_2)	132[c]	...	3.6	0.0	67.5	23.8	3.6
116 (A'_1)	112	0.0	2.5	13.3	33.4	42.2	7.6
92 (E″)	89	...	0.9	0.0	32.7	66.5	5.1
89 (E′)	89	0.0	0.6	1.7	4.5	86.5	6.8
79 (A''_2)		...	0.0	0.0	26.7	49.8	22.9
77 (E″)	81	...	0.2	0.0	63.5	24.9	11.5
67 (E′)	54[c]	0.0	0.6	1.8	31.2	4.1	62.2
64 (A'_1)		0.0	0.2	3.0	46.8	30.6	18.3
51 (E″)	54[c]	...	0.2	0.0	7.9	0.2	91.8
28 (E′)		0.0	0.0	3.0	56.1	1.1	39.8

[a] Overall frequency match 2.4%. [b] V_i is the normalized contribution to the potential energy from *F* matrix elements of the type F_{ii}. [c] Not included in the force constant adjustment (see text).

Several low-frequency bands are calculated which were not included in the fitting procedure. The A''_2, primarily Pt–Sn stretching mode is calculated at 131 cm^{-1}, corresponding to the frequency observed at 132 cm^{-1}. The A''_2 band calculated at 79 cm^{-1}, however, was not observed in the infrared spectrum. The A'_1 band predicted at 64 cm^{-1} does not stand out in the Raman spectrum although it could be hidden in the tail of the 81-cm^{-1} band. The E′ mode observed at 54 cm^{-1} corresponds to the calculated frequency at 67 cm^{-1}. Attempts to reduce this discrepancy in the calculations were unsuccessful. Presumably further interaction constants are required for this purpose. The observed band at 54 cm^{-1} could also contain the calculated E″ mode at 51 cm^{-1}. The only remaining calculated low-frequency band is at 28 cm^{-1}, which is below the exciting line wing on our Raman spectrum.

Overall then, the analysis gives a reasonable account of the low-frequency vibrational spectrum. Seven force constants, the adjusted values for which are given in Table III, were used to calculate eight frequencies with an average error of 2.4%. The potential energy distribution, given in Table II, shows that the Pt–L and Sn–Cl modes are quite pure and that these coordinates contribute negligibly to the lower frequency modes. Moreover, the Pt–Pt modes at 170 and 143 cm^{-1} show only slight mixing with other coordinates. On the other hand, Pt–Sn stretching is heavily mixed with chlorine deformation coordinates. It is evident that the Pt–Pt force constant is well-determined, but the Pt–Sn force constant is not, being highly correlated with the equally ill-determined Cl–Sn–Cl and Cl–Sn–Pt force constants.

TABLE III

ADJUSTED VALENCE FORCE CONSTANTS FOR $L_3Pt_3(SnCl_3)_2$ MODEL (MDYN/Å)

$f_{Sn-Cl} = 1.80$ $f_{Pt-Pt} = 1.36$ $f_{Cl-Sn-Cl} = 0.06$
$f_{Pt-L} = 2.37$ $f_{Pt-Sn} = 0.38$ $f_{Pt-Sn-Cl} = 0.02$
$k_{Pt-Pt}{}^{a} = -0.16$

[a] Interaction constant between Pt–Pt coordinates.

While the normal-coordinate analysis presented here is highly approximate, we feel that the approximations are reasonable, and we are confident that a more complete analysis would not significantly alter the metal–metal force constants, of primary interest here. Indeed a simple calculation using only the Pt_3Sn_2 cluster, without any ligands, and the assigned cluster frequencies gives a Pt–Pt force constant only 5% lower and a Pt–Sn force constant some 20% higher than the values reported here.

Discussion

The value of the Sn–Cl stretching force constant, 1.80 mdyn/Å, suggests that the electron density on the tin atoms is greater than that for $SnCl_4$[9] or $(CO)_4CoSnCl_3$[8] ($f_{Sn-Cl} = 2.56$ and 2.46 mdyn/Å, respectively) but less than that for $SnCl_3^-$ [9] ($f_{Sn-Cl} = 1.22$ mdyn/Å). The Pt–Sn force constant, 0.38 mdyn/Å, is very low, as might be expected if one considers $SnCl_3^-$ as a triply bridging ligand, donating an electron pair to the Pt_3^{2+} triangle. Indeed the force constant is roughly one-third that of f_{Co-Sn} in $(CO)_4CoSnCl_3$,[8] which has a Co–Sn single bond. The internuclear distances (Pt–Sn = 2.80 Å,[3] Co–Sn = 2.50 Å[8]) are consistent with this interpretation. Similarly in the complex $Pt(SnCl_3)_5^{3-}$ the Pt–Sn distance is 2.54 Å,[10] and a Pt–Sn frequency has been assigned[11] in the ir spectrum at 210 cm^{-1}, much higher than any of the Pt–Sn frequencies of the Pt_3Sn_2 cluster.

As to the strength of the Pt–Pt interaction, it is of interest that a formal electron count requires a bond order of $^5/_3$ if each Pt atom is to have an 18-electron environment: 4 electrons from each cyclooctadiene ligand, 2 from each $SnCl_3^-$, 28 from Pt_3^{2+} with 10 of them available for Pt–Pt bonding. This arrangement leaves each Pt atom with 6 nonbonding d electrons. Alternatively one could allocate 4 electrons to Pt–Pt bonding (bond order of $^2/_3$) leaving each Pt atom with a d^8 nonbonding configuration and a 16-electron environment. The latter alternative is perhaps more consistent with the Pt–Pt force constant, 1.36 mdyn/Å, which is somewhat lower than might be expected for a normal single bond at the Pt–Pt internuclear distance, 2.58 Å, considering the trend observed for metal–metal force constants and distances in polynuclear complexes of the third transition row elements: $Re_2(CO)_{10}$

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(f_{MM} = 0.82 mdyn/Å,[12] d = 3.02 Å[13]), $Os_3(CO)_{12}$ (f_{MM} = 0.91 mdyn/Å,[4] d = 2.89 Å[14]), $Ir_4(CO)_{12}$ (f_{MM} = 1.69 mdyn/Å,[4] d = 2.68 Å[15]), and $Hg_2(OH_2)_2^{2+}$ (f_{MM} = 1.93 mdyn/Å,[16] d = 2.54 Å[17]). These force constants are not strictly comparable, because of differences in geometry and in required interaction constants. Nevertheless the trend is clear and the position of $L_3Pt_3(SnCl_3)_2$ is anomalous.

Experimental Section

Orange-red crystals of $L_3Pt_3(SnCl_3)_2$ were kindly provided by Dr. L. J. Guggenberger, Central Research Department, Experimental Station, E. I. du Pont de Nemours and Co. Wilmington, Del. The compounds $LPtX_2$ (X = Cl, Br) were prepared by Chatt's method.[18] Infrared spectra were kindly recorded by Miss B. Prescott of Bell Telephone Laboratories, Murray Hill, N. J., with a Beckman IR 11 spectrometer using Nujol mulls. Raman spectra were obtained with microcrystalline samples of $LPtX_2$ and a single crystal as well as powder samples of $L_3Pt_3(SnCl_3)_2$, using a spectrometer[19] equipped with a He–Ne laser source.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF KENTUCKY, LEXINGTON, KENTUCKY 40506

Complexes with Sulfur and Selenium Donors. IV. Bis(*O*,*O'*-diisopropyldithiophosphato)nickel(II) and Its Pyridine and Picoline Adducts[1]

BY H. E. FRANCIS, G. L. TINCHER, W. F. WAGNER,
J. R. WASSON,* AND G. M. WOLTERMANN

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Planar, diamagnetic, four-coordinate compounds of nickel(II) are known readily to form paramagnetic five- and six-coordinate complexes upon addition of amines.[1-4] Purple bis (*O*,*O'*-diethyldithiophosphato)-nickel(II), $Ni(C_2H_5dtp)_2$, and its green amine adducts have been the subject of several investigations.[4-6] The crystal structures of $Ni(C_2H_5dtp)_2$[5] and its trans pyridine diadduct have been determined.[6] The Ni–S distance increases from 2.21 Å in $Ni(C_2H_5dtp)_2$ to 2.49 Å in the pyridine diadduct. For both compounds is can be argued,[4] on the basis of P–S bond distances, that the Ni–S bond has appreciable ionic character. Similar proposals can be made for vanadium(III),[7] zinc(II), and cadmium(II)[8] substituted-dithiophosphate complexes. However, studies of the electronic spectra[1-4] of dithiophosphate complexes, particularly of the oscillator strengths of the transitions and nephelauxetic parameters,[9] have led to the conclusion that there is considerable covalency in the metal–ligand bonding.

It is well-known that the observation of proton magnetic resonance shifts in paramagnetic transition metal complexes can be used to obtain information about electronic structure.[10] Pmr studies of paramagnetic pyridine and other heterocyclic-amine complexes have demonstrated that unpaired electron density is delocalized into these amine ligands by a mechanism principally involving the ligand σ molecular orbitals.[11] In order to obtain more definitive information regarding the electronic structure of dithiophosphate complexes, we have undertaken pmr studies of bis(*O*,*O'*-diisopropyldithiophosphato)nickel(II), $Ni(i\text{-}C_3H_7dtp)_2$, and its paramagnetic pyridine and picoline adducts. Additional characterization of the complexes was obtained by investigations of the thermal properties and electronic spectra of the compounds.

Experimental Section

Preparation of Complexes.—Phosphorus(V) sulfide was obtained from Matheson Coleman and Bell, Norwood, Ohio. All other chemicals were of the best available commercial, reagent, or spectroscopic grades. Carbon and hydrogen analyses were obtained by Mr. D. G. Sharp of the departmental analytical services. Nickel was determined by the dimethyl glyoximate method. Carbon, hydrogen, and nickel analyses for the complexes are given below. *Anal.* Calcd for $C_{12}H_{28}O_4P_2S_4Ni$: C, 29.70; H, 5.83; Ni, 12.1. Found: C, 29.73; H, 5.78; Ni, 12.1. Calcd for $C_{22}H_{42}N_2O_4P_2S_4Ni$: C, 42.93; H, 6.30; Ni, 8.74. Found: C, 42.74; H, 7.33; Ni, 8.87.

***O*,*O*-Diisopropyldithiophosphoric Acid.**—A stoichiometric amount of absolute isopropyl alcohol was added to phosphorus(V) sulfide and the mixture was stirred magnetically until it became clear (about 3 hr). The acid obtained from the alcoholysis[12] of phosphorus(V) sulfide was used immediately for the preparation of the nickel complex. Before the acid can be stored, it is necessary to bubble nitrogen gas through it for several minutes.

$Ni(i\text{-}C_3H_7dtp)_2$.—Stoichiometric amounts of nickel(II) chloride and *O*,*O'*-diisopropyldithiophosphoric acid were stirred together for 1 hr and the mixture was extracted with chloroform. The chloroform extract was filtered and the solvent was allowed to evaporate. The purple crystals of $Ni(i\text{-}C_3H_7dtp)_2$ were then recrystallized several times from chloroform.

Diadducts of $Ni(i\text{-}C_3H_7dtp)_2$.—Pyridine and 3- and 4-methylpyridine diadducts were obtained as green crystals by evaporating amine solutions of $Ni(i\text{-}C_3H_7dtp)_2$. Attempts to prepare adducts with 2-picoline by this method were without success since the brown products rapidly lost amine at room temperature.

Nmr Spectra.—The nmr spectra were recorded on Varian T-60 (operating at 35°) and HA-60-IL (operating at 33°) spectrometers. Tetramethylsilane was employed as a internal calibrant. Assignments of the peaks were made on the basis of relative intensities, spin–spin splittings, and decoupling experiments.

The diamagnetic ligand resonances are as follows: for 12.41 *M*

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