separated sufficiently to accommodate the tube itself or a hollow Pyrex water thermostated condenser in which the Guoy tube could be freely suspended.

Measurements were first made on each species at room temperature after flushing the solutions with nitrogen. Density was determined by pycnometer. The field was maintained at 8000 G for these measurements, by using 4-in. pole caps at a separation of 1 in. and a current of 6.2 A.

For the second set of measurements, the water-jacketed cavity was used to maintain constant temperature. The Guoy tube, suspended in the cavity, was allowed to come to equilibrium with its surrounding for about 1 h or until readings with the field off were constant. The temperature of the cavity, assumed to be the same as the temperature of the sample, was determined by hanging a NBS mercury thermometer in the cavity, under the same conditions. The pole gap was increased to 2 in. to accommodate the water jacket, and the field was reduced to 6000 G at the same amperage (6.2 A). The temperature range covered was limited because of the decomposition of the dimers at high temperatures.

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Registry No. SBD, 77153-84-5; DBD, 23852-05-3; $[Cr(H_2O)_6]^{3+}$, 14873-01-9; $[(H_2O)_4Cr(OH)_2Cr(H_2O)_2(OH)_2Cr(H_2O)_4]^{5+}$, 60938-70-7.

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Normal-Coordinate Analyses for the Vibrations of Tetraphenyl- and Tetramethyldithioimidodiphosphinate and the Adamantane-like Cage Structure $Cu^I_4S_6$

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Normal-coordinate analyses have been performed for 1:1 metal-ligand models of bis(tetraphenyldithioimidodiphosphinato)manganese(II) and bis(tetramethyldithioimidodiphosphinato)cobalt(II) and for the $Cu^I_4S_6$ core of the tris(tetraphenyldithioimidodiphosphinato)tetracopper(I) cation in C_2 and T_d point symmetries, respectively. Results of the calculations support the assignment of ν_{as}(PNP) and ν_s(PNP) to bands near 1210 and 820 cm^{-1}, ν(PC) to bands between 680 and 750 cm^{-1}, ν_{as}(PS) and ν_s(PS) to bands between 500 and 600 cm^{-1}, and ν_{as}(MS) and ν_s(MS) to bands between 240 and 320 cm^{-1}. Bonding stretching force constants show that Co-S bonds in the tetramethyl compound are stronger than Mn-S bonds in the tetraphenyl compound, and this is compensated by a lower K(P-S) value in the Co(II) complex. The lack of infrared and Raman intensity in ν_s(PNP) is explained in terms of opposing σ and π contributions to the dipole moment and polarizability changes during the symmetric PNP stretching vibration. Only in resonance Raman spectra where other contributions to the band intensity are operative was ν_s(PNP) observed. Analysis of the $Cu^I_4S_6$ cluster vibrations showed that only weak Cu···Cu bonding interactions were present. ν(Cu(I)-S) modes were located between 280 and 170 cm^{-1} in the infrared and Raman spectra. The K(Cu-S) value was about the same magnitude as K(Mn-S) for the bis chelate.

Introduction

Dithioimidodiphosphinates, $SPR_2NR_2PS^-$, where R = phenyl (L) or methyl (L'), coordinate to divalent first-row transition-metal ions to form bis complexes[1] that contain a tetrahedral $M^{II}S_4$ core geometry. The preference for tetrahedral[2,1b] over square-planar geometry, even for the nickel complex, was thought at first to reflect a low ligand field strength with this bidentate sulfur ligand. Yet analyses of ligand field spectra[1a,b] of Mn(II), Fe(II), Co(II), and Ni(II) complexes showed that L^- presented a field of intermediate strength. To clarify the metal-sulfur and chelate ring bonding picture in these chelates, we undertook an infrared-Raman spectral study[1d] and herein present the results of normal-coordinate calculations on several metal dithioimidodiphosphinates.

Measurement of Raman intensities has been useful in studies of molecular structure and bonding, particularly in the estimation of bond orders. In the theory of Raman intensities the mean molecular polarizability, $\bar{\alpha}$, is directly related[3] to the observed intensity of a totally symmetric Raman band. Approximate methods have been devised[4] to express terms in the molecular polarizability derivative as a superposition of principal polarizability components of individual bonds. Bond polarizabilities, $\bar{\alpha}_u$, are related to molecular polarizabilities by the equation

$$\frac{\partial \bar{\alpha}}{\partial Q_i} = \sum_u l_{ui} \frac{\partial \bar{\alpha}_u}{\partial R_u}$$

where l_{ui} is the L matrix (eigenvectors for the normal vibrations Q_i) element between internal coordinates R_u and Q_i. The sum is taken over bonds, u. We suggest that further division of bond polarizabilities into two components, σ and π, may be justified in cases where the two contributions occur in opposing directions, i.e., are of opposite sign. One of the apparent anomalies in the vibrational spectra of imidodiphosphinates[1d,5] was the absence of any intensity in the symmetric P···N···P stretching band in either infrared or Raman spectra. Only in resonance Raman spectra was it observed. The reasons for a very small change in polarizability as well as in dipole moment with respect to this normal coordinate are explored in terms of σ and π bonding in the imidodiphosphinate group.

Short Cu···Cu distances within several copper cluster compounds have been cited as evidence for some metal-metal bonding.[6] Raman intensities of metal cluster[7] related vibrational bands are expected to depend on the extent of metal-metal interaction. Since Cu···Cu distances in the

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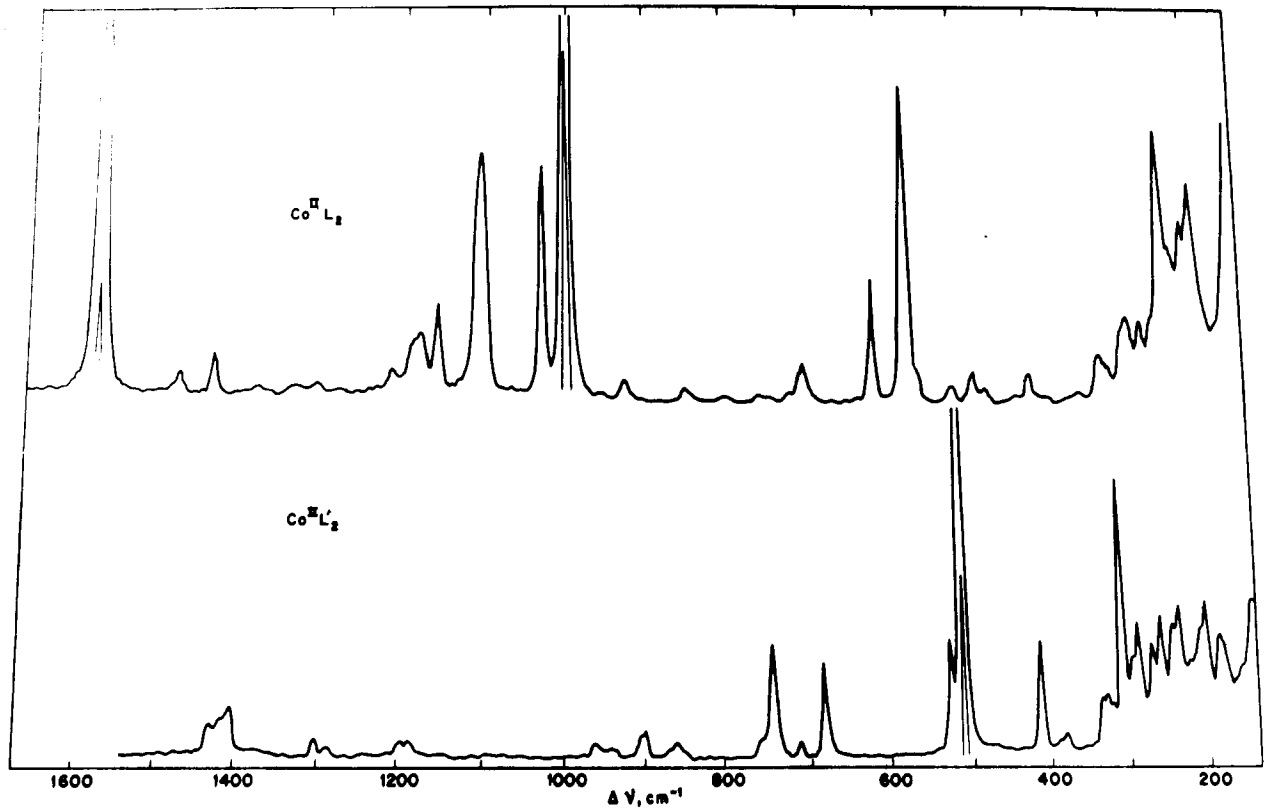

Figure 1. Raman spectra of solid samples. Experimental conditions [excitation (nm), power (mW), slit width (cm^{-1}), sensitivity (counts/s), time constant (s), scan rate (cm^{-1}/s)]: for $Co^{II}L_2$, 488.0 (Ar^+), 20, 9.8, 2000, 1, 1; for $Co^{II}L'_2$ 488.0 (Ar^+), 200, 4.8, 4000, 2, 0.5.

Table I. Chelate Ring and P-C Stretching-Mode Frequencies (cm^{-1})

	$Mn^{II}L_2$		$Co^{II}L_2$		$Co^{II}L'_2$		$Cu^{I}_4L_3^+$	
	IR	R	IR	R	IR	R	IR	R
ν_{as}(PN)	1218 vs	···	1215 vs	1215 w	1198 vs	1198 vw	1216 vs	···
					1187 vs	1187 vw		
ν(PC)	715 m	718 vw	715 m	718 vw	749 m	749 m	718 m	···
	700 vs	705 mw	700 vs	704 mw	713 m	718 vw	···	700 vw
	692 sh	···	692 sh	···	674 vs	684 m	692 vs	···
ν_{as}(PS)	568 vs	567 w, sh	565 vs	560 sh	505 m	···	551 vs	···
ν_s(PS)	585 mw	580 s		572 s	···	511 vs	570 vs, sh	570 s
								575 s
ν_s(MS)	···	245 s	···	240 s	···	306 ms	275 m	272 vs
ν_{as}(MS)	275 w	275 w		270 mw	318 m	···	242 m	245 w
	285 w	285 w		288 mw				

tetraphenyldithioimidodiphosphinate–Cu(I) cluster,[8] $Cu^{I}_4L_3^+$, were smaller than the sum of van der Waals radii but larger than the sum of covalent radii, the influence of metal–metal bonding on intensities of ν(Cu–S) Raman bands was of interest. Vibrations of the copper–sulfur clusters were further analyzed.

Experimental Section

The preparation of all compounds was discussed in a previous paper.[1d] Raman spectra were recorded with a Jarrell-Ash 25-500 double Ebert monochromator using a water-cooled Hammamatsu R500 photomultiplier tube for detection. A Spectra-Physics Model 165 argon- or krypton-ion laser was used for excitation. Samples were rotated in a cylindrical stainless-steel cell, which had a circular groove packed with powdered material. Incident laser light reached the sample at an angle of ~45°. Scattered light was collected at 90° to the incident beam.

Results and Discussion

A. Infrared and Raman Spectra. 1. P–C and Chelate Ring Stretching Vibrations. IR and Raman (R) spectra of $Mn^{II}L_2$, $[Cu^{I}_4L_3^+][Cu^{I}Cl_2^-]CCl_4$, and $[Cu^{I}_4L_3^+][ClO_4^-]$ and the IR spectrum of $Co^{II}L'_2$ were previously[1d] recorded. The IR spectrum of $Co^{II}L_2$ is very similar to that of $Mn^{II}L_2$. R spectra of $Co^{II}L_2$ and $Co^{II}L'_2$ between 1600 and 100 cm^{-1} are shown in Figure 1. Electronic absorption spectra of the Co(II) complexes indicated[1a] that they too contain a tetrahedral $Co^{II}S_4$ core that was verified by single-crystal X-ray analyses[1b,2] for $Mn^{II}L_2$ and for $Fe^{II}L'_2$ and $Ni^{II}L'_2$. Vibrational assignments for phosphorus–neighboring atom, phenyl ring, and some metal–sulfur IR and R bands were made before.[1d] With a few revisions the chelate ring and ν(P–C) band assignments are summarized in Table I. In all compounds chelated L and L' showed a broad intense ν_{as}(PNP) infrared band near 1200 cm^{-1} and a very weak Raman counterpart. One very intense ν(P–C) infrared band occurs at or below 700 cm^{-1}. Weak ν(P–C) Raman bands were observed when R = phenyl whereas medium R bands occur at 749 and 684 cm^{-1} when R = methyl. The tetraphenyl derivatives show a lower frequency strong ν_{as}(P···S) IR band and a higher frequency strong R band, ν_s(P···S). With the acquisition of the R spectrum of $Co^{II}L'_2$ our revised assignments of L' chelates show a similar trend but a smaller frequency difference between ν_{as}(P···S) at 506

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cm^{-1}, an intense IR band, and ν_s(P···S) at 511 cm^{-1}, an intense R band. The strongest low-frequency Raman band is observed near 240 cm^{-1} in $Mn^{II}L_2$ and $Co^{II}L_2$ but at 306 cm^{-1} in $Co^{II}L'_2$. In L chelates, it was previously assigned[1d] to ν_s(M–S) on the basis of vibrational fine structure in the low-temperature single-crystal electronic absorption spectrum[1b] of $Mn^{II}L_2$. In the comparison of methyl against phenyl derivative chelate stretching frequencies, the methyl shows a higher ν_s(Co—S), Δ = 66 cm^{-1}, but a lower ν(P···S), Δ = 45 or 60 cm^{-1}, and ν_{as}(P···N···P), Δ = 23 cm^{-1}. Very nearly the same lowering of ν(P=S) and ν_{as}(P—N—P) frequencies was observed in comparing the respective ligand, HL and HL', band frequencies: ν(P=S), Δ = 52 or 64 cm^{-1}; ν_{as}(P—N—P), Δ = 18 cm^{-1}. In addition, ν(PS) band positions of HL (HL') compared to chelated L (L') were ~60 cm^{-1} lower in $Co^{II}L_2$ ($Co^{II}L'_2$). Therefore, the higher ν_s(Co—S) frequency in $Co^{II}L'_2$ might not directly be linked to the further lowering of ligand ν(PS) and ν(PNP) band frequencies. A change in coupling of other lower frequency modes to ν(M–S) may be involved. Force constants derived from normal-coordinate calculations offer a more reliable basis for comparing metal–sulfur bond strengths.

2. Chelate Ring Bending Modes. Analysis of the distribution of vibrations in the C_2 symmetry 10-atom model of $MS_2P_2R_4N$ shows that the 12 A + 12 B normal vibrations can be divided into 5 bond stretching modes, 3 ring angle bending modes, and 4 P–R bending modes for each representation. The five stretching modes, ν(PN), ν(PS), ν(MS), and two ν(PR), were previously[1d] identified. One ring bending mode from the A and the B species predominantly involves δ(PNP) and δ(SPN), respectively. These are expected to be the highest frequency ring bending vibrations. δ(PNP) belongs to A species normal modes and is both IR and R active in C_2 symmetry. The Raman band is expected to be more intense than its IR counterpart. Phosphonitrilic trimers exhibit[9] the following P_3N_3 ring bending vibrations: in-plane ring deformations at 669 cm^{-1} (a'_1) and 529 cm^{-1} (e'); out-of-plane ring deformations at 619 cm^{-1} (a''_2) and 202 cm^{-1} (e''). Since some of the ring stretching modes, ν_s(PNP) and ν_s(PS), appeared very intense in the resonance Raman (RR) spectrum of $Cu^{II}L_2$, we expect that bands due to symmetric bending modes that are associated with SPNPS in the chelate ring might be enhanced to a similar degree. This is especially appropriate since extensive mixing of the totally symmetric ν(PNP) and δ(PNP) modes was proposed in one Raman study[9b] of phosphonitrilic trimers. An intense RR band at 420 cm^{-1} in $Cu^{II}L_2$ is therefore assigned to δ_s(PNP) with some mixing with ν_s(PNP). Medium-intensity normal-Raman bands at 420 cm^{-1} in $Mn^{II}L_2$ and other L chelates and at 410 cm^{-1} in $Co^{II}L'_2$ are also assigned to δ_s(PNP). The slightly lower δ_s(PNP) frequency in $Co^{II}L'_2$ parallels a lower ν_{as}(PNP) frequency in the IR spectrum of $Co^{II}L'_2$ relative to $Co^{II}L_2$. IR and R spectra[10] of the centrosymmetric compound bis(dimethylphosphine) disulfide show that it has no other IR or R bands between 550 and 300 cm^{-1} apart from an intense R band at 437 cm^{-1} for ν(P–P). Another RR band in $Cu^{II}L_2$ appears weakly at 530 cm^{-1}. Since the remaining RR bands at 213 and 287 cm^{-1} in $Cu^{II}L_2$ can be assigned to symmetric and asymmetric ν(Cu–S) modes, we tentatively assign the 530 cm^{-1} band to the highest frequency asymmetric B species ring deformation. Spectra of $M^{II}L_2$ complexes show a medium IR and a weak R band in this region. A medium-weak IR and R band at 524 cm^{-1} in $Co^{II}L'_2$ is also observed. Other ring-deformation modes are expected at lower frequencies since they are metal dependent or have a torsional mode contribution.

Table II[a]

	$\delta_s(CH_3)$	$\delta_{as}(CH_3)$	$\rho_r(CH_3)$	CH_3 wag
IR	1299 s	1422 w	965 w	863 s
	1288, 1285 s	1411 ms	943 s	853 w
		1397 w	932 s	
			896 ms	
R	1300 w	1426 w	962 w	860 w
	1288 vw	1418 vw	942 vw	
		1403 w	935 vw	
			900 w	

[a] Units: cm^{-1}.

Raman spectra of both HL and HL' ligands show medium bands near 408 and 388 cm^{-1}, respectively, which occur very weakly in the IR spectra and are ~20 cm^{-1} downshifted from Raman bands that were assigned to δ(PNP) in the metal chelates. Although bond stretching modes, ν(P···N···P) in metal complexes and ν(P—N—P) in protonated ligands, differ widely in frequency due to the change in bonding, we do not expect very much difference in the bending mode, δ(P···N···P) and δ(P—N—P), frequencies. Therefore, δ(PNP) in the ligands is assigned to bands at 408 and 388 cm^{-1}.

3. PR_2 and CH_3 Group Bending Vibrations. δ(P–CH_3) bands in bis(tetramethylphosphine) disulfide are observed[10] between 300 and 150 cm^{-1}. Four bands, as in tetramethyldithioimidodiphosphinates, are predicted and are observed in the R spectrum of the solid at 290 (s), 230 (mw), 208 (mw), and 177 (s) cm^{-1}. Four similar bands occur in the R spectrum of $Co^{II}L'_2$ as doublets with the more intense peaks of the pairs at 286, 234, 198, and 181 cm^{-1}. An extra R band is found at 257 cm^{-1}. Geometric nonequivalence of the two ligands in $Co^{II}L'_2$ might explain the presence of doublet R bands associated with δ(P–CH_3). Similar splitting of methyl group vibrational bands (vide infra) is observed in the IR and R spectra of $Co^{II}L'_2$. The P–CH_3 bending modes are distributed into four basic types of motion that occur, in general, for XY_2 groups: PMe_2 deformation (scissor), twist, rock, and wag. Analysis of characteristic methyl group vibrations shows that two symmetrical deformations, four asymmetrical deformations, four rocking modes, and two wagging modes are assignable to both A and B species as shown in Table II. δ(P–Ph) modes should be located at lower frequency from corresponding δ(P–CH_3) ones. Three medium-to-strong R bands that fit this description are found between 150 and 300 cm^{-1} in both HL and HL' ligands: 258, 223, and 164 cm^{-1} in HL; 285, 225, and 182 cm^{-1} in HL'. Some of the bands in $Co^{II}L_2$ at 290, 270, 240, 212, and 200 cm^{-1} may, thus, be assigned to δ(P–Ph) vibrations.

B. Normal-Coordinate Analyses. 1. MnL_2 and CoL_2. Since the chelate rings of $Mn^{II}L_2$ were found by X-ray analysis[1b] to have very nearly an S_4 axis of symmetry down the N–Mn–N line, a 1:1 metal–ligand model possessing C_2 symmetry, shown in Figure 2, was adopted for normal-mode calculations. The phenyl group carbon and hydrogen atoms were treated as a single mass to simplify the calculations. Previous calculations[11] have shown this approximation to be justified, but it does lead to an overestimation of some force constants associated with the R group. Geometric parameters that were used are shown in Table III.

The 24 normal vibrations possible after excluding translations and rotations (12 A + 12 B) were analyzed. The 10-atom model gave 32 internal (10 bond stretching, 16 angle bending, and 6 torsional angle bending) coordinates, which could be

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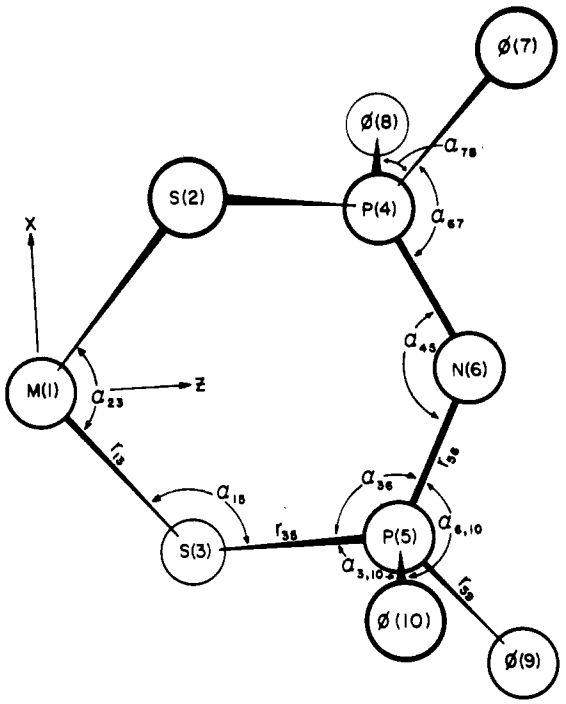

Figure 2. The 1:1 metal–ligand model for ML_2.

Table III. Geometric Parameters for Metal-Ligand Models

	av values			idealized values for C_2 symmetry		av values for
	$Mn^{II}L_2$	$Fe^{II}L'$	$Ni^{II}L'$	$Mn^{II}L_2$	$Co^{II}L'$	$Cu^{I}_4L_3^+$
r_{M-S}, Å	2.443	2.360	2.282	2.443	2.321	2.266[a]
r_{P-S}, Å	2.013	2.020	2.023	2.013	2.022	2.053
r_{P-N}, Å	1.588	1.591	1.580	1.588	1.586	1.579
r_{P-Ph}, Å	1.815	1.806	1.825	1.815	1.816	1.799
α_{SMS}, deg	111.9	109.3	109.5	111.6	111.0	123.6
α_{MSP}, deg	99.9	99.5	104.6	99.9	102.1	102.5
α_{SPN}, deg	118.7	116.7	116.6	118.2	116.6	118.2
α_{PNP}, deg	133.5	132.3	128.4	133.5	130.4	138.0
α_{SPPh}, deg	107.9	107.9	107.6	107.9	108.3	106.7
α_{NPPh}, deg	107.8	109.0	108.6	107.9	108.3	108.8
α_{PhPPh}, deg	106.1	105.7	107.2	106.3	106.5	107.2

	av values	idealized values for T_d $Cu^{I}_4S_6$ symmetry
α_{CuSCu}, deg	76.0	70.6
α_{SCuS}, deg	118.5	120.0
$r_{S\cdots S}$, Å	3.920	3.920

[a] Idealized value for T_d $Cu^{I}_4S_6$ symmetry 2.263 Å.

divided into the 17 A and 15 B symmetry coordinates listed in Table IV. Torsional ring angle bending coordinates were introduced after it was discovered that a complete set of 12 A + 12 B nonzero frequencies was not obtained with the listed stretching and bending coordinates alone. The redundancies, 5 A + 3 B, yielded zero frequencies in the eigenvalue problem. Diagonalization of the G matrices for A and B also gave 5 A + 3 B zero eigenvalues, demonstrating the presence of this number of dependent coordinates in the symmetry coordinate sets. The GF matrix problem was solved by procedures similar to the ones described previously.[12] Modified Urey–Bradely

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Table IV. Symmetry Coordinates for 1:1 Metal–Ligand Model of Bis(tetraphenyldithioimidodiphosphinato)manganese(II) in C_2 Symmetry

coordinate	mode
A Species	
$S_1 = (1/2^{1/2})(\Delta r_{46} + \Delta r_{56})$	ν(P=N)
$S_2 = (1/2^{1/2})(\Delta r_{47} + \Delta r_{59})$	ν(P–Ph)
$S_3 = (1/2^{1/2})(\Delta r_{48} + \Delta r_{5,10})$	ν(P–Ph)
$S_4 = (1/2^{1/2})(\Delta r_{24} + \Delta r_{35})$	ν(P=S)
$S_5 = (1/2^{1/2})(\Delta r_{12} + \Delta r_{13})$	ν(Mn–S)
$S_6 = (1/2)(\Delta\alpha_{67} + \Delta\alpha_{68} + \Delta\alpha_{69} + \Delta\alpha_{6,10})$	δ(NPPh)
$S_7 = (1/2)(\Delta\alpha_{67} - \Delta\alpha_{68} + \Delta\alpha_{69} - \Delta\alpha_{6,10})$	δ(NPPh)
$S_8 = (1/2)(\Delta\alpha_{27} + \Delta\alpha_{28} + \Delta\alpha_{39} + \Delta\alpha_{3,10})$	δ(SPPh)
$S_9 = (1/2)(\Delta\alpha_{27} - \Delta\alpha_{28} + \Delta\alpha_{39} - \Delta\alpha_{3,10})$	δ(SPPh)
$S_{10} = (1/2^{1/2})(\Delta\alpha_{78} + \Delta\alpha_{9,10})$	δ(PhPPh)
$S_{11} = \Delta\alpha_{45}$	δ(PNP)
$S_{12} = (1/2^{1/2})(\Delta\alpha_{26} + \Delta\alpha_{36})$	δ(SPN)
$S_{13} = (1/2^{1/2})(\Delta\alpha_{14} + \Delta\alpha_{15})$	δ(MnSP)
$S_{14} = \Delta\alpha_{23}$	δ(SMnS)
$S_{15} = (1/2^{1/2})(\Delta\tau_{1246} + \Delta\tau_{1356})$	τ(MnSPN)
$S_{16} = (1/2^{1/2})(\Delta\tau_{2465} + \Delta\tau_{3564})$	τ(SPNP)
$S_{17} = (1/2^{1/2})(\Delta\tau_{3124} + \Delta\tau_{2135})$	τ(SMnSP)
B Species	
$S_{18} = (1/2^{1/2})(\Delta r_{46} - \Delta r_{56})$	ν(P=N)
$S_{19} = (1/2^{1/2})(\Delta r_{47} - \Delta r_{59})$	ν(P–Ph)
$S_{20} = (1/2^{1/2})(\Delta r_{48} - \Delta r_{5,10})$	ν(P–Ph)
$S_{21} = (1/2^{1/2})(\Delta r_{24} - \Delta r_{35})$	ν(P=S)
$S_{22} = (1/2^{1/2})(\Delta r_{12} - \Delta r_{13})$	ν(Mn–S)
$S_{23} = (1/2)(\Delta\alpha_{67} + \Delta\alpha_{68} - \Delta\alpha_{69} - \Delta\alpha_{6,10})$	δ(NPPh)
$S_{24} = (1/2)(\Delta\alpha_{67} - \Delta\alpha_{68} - \Delta_{69} + \Delta\alpha_{6,10})$	δ(NPPh)
$S_{25} = (1/2)(\Delta\alpha_{27} + \Delta\alpha_{28} - \Delta_{39} - \Delta\alpha_{3,10})$	δ(SPPh)
$S_{26} = (1/2)(\Delta\alpha_{27} - \Delta\alpha_{28} - \Delta\alpha_{39} + \Delta\alpha_{3,10})$	δ(SPPh)
$S_{27} = (1/2^{1/2})(\Delta\alpha_{78} - \Delta\alpha_{9,10})$	δ(PhPPh)
$S_{28} = (1/2^{1/2})(\Delta\alpha_{26} - \Delta\alpha_{36})$	δ(SPN)
$S_{29} = (1/2^{1/2})(\Delta\alpha_{14} - \Delta\alpha_{15})$	δ(MnSP)
$S_{30} = (1/2^{1/2})(\Delta\tau_{1246} - \Delta\tau_{1356})$	τ(MnSPN)
$S_{31} = (1/2^{1/2})(\Delta\tau_{2465} - \Delta\tau_{3564})$	τ(SPNP)
$S_{32} = (1/2^{1/2})(\Delta\tau_{3124} - \Delta\tau_{2135})$	τ(SMnSP)

Table V. Bending Stretching (K), Angle Bending (H), and Repulsive (F) Force Constants (mdyn/Å)

	$Co^{II}L'_2$, R = methyl	$Mn^{II}L_2$, R = phenyl		$Co^{II}L'_2$, R = methyl	$Mn^{II}L_2$, R = phenyl
K(M–S)	0.80	0.45	K(P–N)	5.30	5.00
K(P–S)	2.20	3.70	K(P–R)	2.60	4.80
H(SPN)	0.15	0.20	H(RPR)	0.13	0.08
H(PNP)	0.40	0.40	H(SMS)	0.05	0.05
H(SPR)	0.14	0.10	H(MSP)	0.05	0.05
H(NPR)	0.16	0.12			
F(S···N)	0.30	0.30	F(R···R)	0.30	0.50
F(P···P)	0.35	0.35	F(S···S)	0.05	0.05
F(S···R)	0.18	0.45	F(M···P)	0.08	0.05
F(N···R)	0.13	0.45			

force field force constants (K, bond stretching; H, angle bending; F, nonadjacent repulsive) for the present stage of refinement are shown in Table V. Also, calculated and observed frequencies and predominant mode assignments from a potential energy distribution calculation are shown in Table VI.

The same procedure was carried out for a 1:1 metal–ligand model of $Co^{II}L'_2$, taking average geometric parameters (Table I) determined by X-ray analysis[2] for $Fe^{II}L'_2$ and $Ni^{II}L'_2$. Electronic absorption spectra[1a] of both $Co^{II}L_2$ and $Co^{II}L'_2$ indicated a tetrahedral CoS_4 core structure. The methyl groups of L″ were assumed to exist as a single mass to simplify calculations. The results of this calculation are displayed in Tables V and VI.

2. Cu_4S_6 Cluster. A second normal-mode calculation was performed for the $Cu^{I}_4S_6$ core structure that was found by X-ray analysis[8] in $Cu^{I}_4L_3^+$ clusters. A model possessing ex-

Table VI. Calculated and Observed Frequencies (cm^{-1}) and Predominant Mode Assignments

$Co^{II}L'_2$				$Mn^{II}L_2$			
	obsd				obsd		
calcd	IR	R	predominant mode(s)	calcd	IR	R	predominant mode(s)
			A Species				
876	···	···	$S_1(64) + S_{11}(17)$[a]	873	···	···	$S_1(49) + S_{11}(18) + S_4(14)$
731	749 m	749 m	$S_2(82)$	723	715 m	718 vw	$S_2(62) + S_1(17)$
703	713 m	718 w	$S_3(85)$	706	692 sh	690 w, sh	$S_3(54) + S_4(30)$
506	···	511 vs	$S_4(82)$	579	585 mw	580 s	$S_4(42) + S_3(24) + S_{11}(16)$
441	410 m	410 m	$S_{11}(25) + S_{12}(20)$	335	400 m	418 m	$S_8(15) + S_{12}(14)$
305	···	306 ms	$S_5(39) + S_9(27)$	246	···	245 s	$S_5(40) + S_9(39)$
271		286 mw	$S_{10}(33) + S_8(28) + S_9(22)$	193	···	200 s	$S_8(38) + S_{10}(25)$
232		234 mw	$S_5(33) + S_7(18)$	182		187 w	$S_7(21) + S_{12}(19)$
207		198 mw	$S_6(41) + S_{10}(15) + S_7(15)$	131		128 mw	$S_{14}(32) + S_{13}(19)$
183		181 mw	$S_7(33) + S_5(22) + S_9(21)$	105			$S_6(42) + S_{10}(40)$
138			$S_{14}(34) + S_{13}(34)$	96			$S_7(61)$
74			$S_{15}(23) + S_9(18) + S_{13}(17)$	45			$S_9(26) + S_{15}(20) + S_{13}(16)$
			B Species				
1196	1198 vs	1198 vw	$S_{18}(97)$	1212	1218 vs	···	$S_{18}(96)$
	1187 vs	1187 vw					
747	765 vw	765 vw	$S_{20}(51) + S_{19}(26)$	771	741 m	···	$S_{20}(40) + S_{31}(18)$
689	674 vs	684 m	$S_{19}(63) + S_{20}(23)$	712	700 vs	705 mw	$S_{21}(55) + S_{19}(34)$
545	518 mw	524 mw	$S_{21}(31) + S_{20}(18) + S_{31}(22)$	546	568 s	567 w, sh	$S_{21}(45) + S_{19}(26)$
507	505 ms	···	$S_{21}(54)$	511	518 s	522 w	$S_{20}(49) + S_{31}(24)$
318	318 m	~331 w	$S_{22}(43)$	277	275 m	275 w	$S_{25}(43) + S_{23}(26) + S_{22}(14)$
					285 w, sh	285 w	
303			$S_{27}(55)$	256			$S_{22}(37) + S_{26}(29)$
287			$S_{25}(37) + S_{27}(19)$	190			$S_{28}(28) + S_{29}(25)$
217			$S_{26}(37) + S_{22}(22) + S_{24}(16)$	167			$S_{27}(38)$
186			$S_{28}(36)$	131			$S_{22}(39) + S_{21}(23)$
132			$S_{32}(53)$	87			$S_{32}(27)$
85			$S_{24}(36) + S_{31}(24)$	52			$S_{24}(49) + S_{31}(30)$

[a] Percent contribution in parentheses.

actly T_d point symmetry, shown in Figure 3, was adopted. The adamantane-like cage structure in $Cu^I_4L_3^+$ very closely approaches the idealized structure, with sulfur atoms at the corners of an octahedron and Cu atoms at the centers of alternate octahedral faces. Bond distances and angles in the model were r(Cu–S) = 2.263 Å, α(CuSCu) = 70.6°, α(SCuS) = 120°. An average S···S edge distance of 3.920 Å was transferred from the $Cu^I_4L_3^+$ structure. The 24 genuine normal vibrations (2 A_1 + 2 E + 2 T_1 + 4 T_2) were analyzed. The 10-atom model gave 30 internal (12 Cu–S bond stretching, 12 SCuS angle bending, and 6 CuSCu angle bending) coordinates which were divided into the 3 A_1, 3 E, 2 T_1, and 5 T_2 symmetry coordinates listed in Table VII. Symmetry coordinates were constructed in the usual way[13] such that the E species transformed as the components of the two-dimensional matrix for $(2z^2 - x^2 - y^2, x^2 - y^2)$, T_1 species transformed as the components of the three-dimensional matrices for the rotations (R_x, R_y, R_z), and T_2 species transformed as the components of the three-dimensional matrices for the translations (x, y, z) under all symmetry operations of the T_d point group. In the T species care was taken to group degenerate species, unstarred, starred, and double-starred, according to whether they transformed like the twofold rotations $C_2(x)$, $C_2(y)$, or $C_2(z)$, respectively. This[13,14] prevents the occurrence of cross terms when the G and F matrices are blocked by the symmetry coordinate transformation. Redundancies, 1 A_1 + 1 E + 1 T_2, gave zero eigenvalues in the G and GF matrices. Force constants and calculated–observed frequencies are shown in Table VIII.

C. PNP Bonding. The noticeable absence of an infrared or Raman band assignable to ν_s(P···N···P) in dithioimidodiphosphinates was somewhat surprising. In any case the most intense resonance Raman band in $Cu^{II}L_2$ was identified as ν_s(P···N···P) at 813 cm^{-1}. Normal-mode calculations further support this assignment. When the calculated ν_{as}(PNP) frequency is fitted to an observed band at 1220 cm^{-1}, ν_s(PNP) is calculated to appear in the 750–850-cm^{-1} region. Also, RR band intensities[15] depend on the nature of the electronic excited state that is involved, and, therefore, large bond polarizability derivatives are not the only source of intensity. Rather, Franck–Condon overlaps[16] that depend on ΔK (force constant)

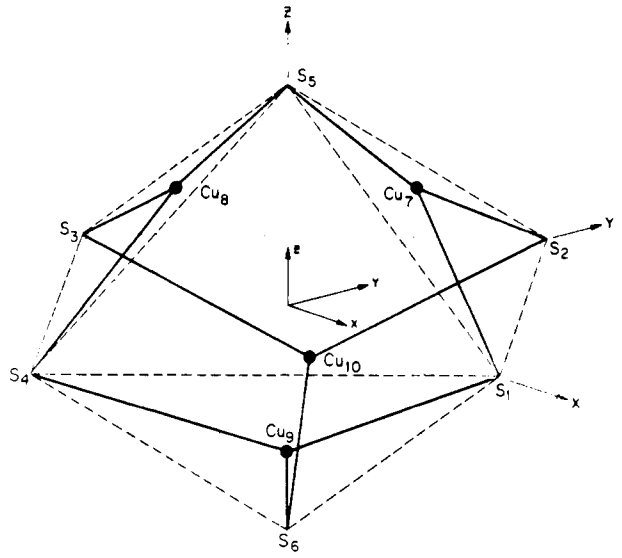


Figure 3. Structural model for the $Cu^I_4S_6$ core of copper cluster compounds.

(13) Wilson, E. B., Jr.; Decius, J. C.; Cross, P. C. "Molecular Vibrations"; McGraw-Hill: New York, 1955.
(14) Siiman, O.; Fresco, J. *Spectrochim. Acta, Part A* **1971**, *27A*, 673.
(15) (a) Siebrand, W.; Zgierski, M. Z. *Excited States* **1979**, *4*, 1. (b) Clark, R. J. H.; Stewart, B. *Struct. Bonding (Berlin)* **1979**, *36*, 1.

Table VII. Symmetry Coordinates for $Cu^{I}_4S_6$ Core Model in T_d Symmetry

coordinate	mode
A_1 Species	
$S_1 = (1/2(3^{1/2}))(\Delta r_{71} + \Delta r_{91} + \Delta r_{10,3} + \Delta r_{83} + \Delta r_{72} + \Delta r_{84} + \Delta r_{10,2} + \Delta r_{75} + \Delta r_{10,6} + \Delta r_{85} + \Delta r_{96})$	ν(Cu-S)
$S_2 = (1/2(3^{1/2}))(\Delta\alpha_{1,7,2} + \Delta\alpha_{4,9,1} + \Delta\alpha_{2,10,3} + \Delta\alpha_{3,8,4} + \Delta\alpha_{2,7,5} + \Delta\alpha_{4,8,5} + \Delta\alpha_{4,9,6} + \Delta\alpha_{2,10,6} + \Delta\alpha_{1,7,5} + \Delta\alpha_{3,10,6} + \Delta\alpha_{3,8,5} + \Delta\alpha_{1,9,6})$	δ(SCuS)
$S_3 = (1/6^{1/2})(\Delta\alpha_{7,5,8} + \Delta\alpha_{10,6,9} + \Delta\alpha_{9,1,7} + \Delta\alpha_{10,3,8} + \Delta\alpha_{7,2,10} + \Delta\alpha_{8,4,9})$	δ(CuSCu)
E Species	
$S_4 = (1/2(6^{1/2}))(2\Delta r_{75} + 2\Delta r_{10,6} + 2\Delta r_{85} + 2\Delta r_{96} - \Delta r_{71} - \Delta r_{91} - \Delta r_{10,3} - \Delta r_{83} - \Delta r_{72} - \Delta r_{84} - \Delta r_{94} - \Delta r_{10,2})$	ν(Cu-S)
$S_5 = (1/2(6^{1/2}))(2\Delta\alpha_{1,7,2} + 2\Delta\alpha_{4,9,1} + 2\Delta\alpha_{2,10,3} + 2\Delta\alpha_{3,8,4} - \Delta\alpha_{2,7,5} - \Delta\alpha_{4,8,5} - \Delta\alpha_{4,9,6} - \Delta\alpha_{2,10,6} - \Delta\alpha_{1,7,5} - \Delta\alpha_{3,10,6} - \Delta\alpha_{3,8,5} - \Delta\alpha_{1,9,6}$	δ(SCuS)
$S_6 = (1/2(3^{1/2}))(2\Delta\alpha_{7,5,8} + 2\Delta\alpha_{10,6,9} - \Delta\alpha_{9,1,7} - \Delta\alpha_{10,3,8} - \Delta_{7,2,10} - \Delta\alpha_{8,4,9})$	δ(CuSCu)
$S_4^* = (1/2(2^{1/2}))(\Delta r_{71} + \Delta r_{91} + \Delta r_{10,3} + \Delta r_{83} - \Delta r_{72} - \Delta r_{84} - \Delta r_{94} - \Delta r_{10,2})$	ν(Cu-S)
$S_5^* = (1/2(2^{1/2}))(\Delta\alpha_{2,7,5} + \Delta\alpha_{4,8,5} + \Delta\alpha_{4,9,6} + \Delta_{2,10,6} - \Delta\alpha_{1,7,5} - \Delta\alpha_{3,10,6} - \Delta\alpha_{3,8,5} - \Delta\alpha_{1,9,6})$	δ(SCuS)
$S_6^* = (1/2)(\Delta\alpha_{9,1,7} + \Delta\alpha_{10,3,8} - \Delta\alpha_{7,2,10} - \Delta\alpha_{8,4,9})$	δ(CuSCu)
T_1 Species	
$S_7 = (1/2(2^{1/2}))(\Delta r_{72} - \Delta r_{84} + \Delta r_{94} - \Delta r_{10,2} - \Delta r_{75} + \Delta r_{10,6} + \Delta r_{85} - \Delta r_{96})$	ν(Cu-S)
$S_8 = (1/2(2^{1/2}))(\Delta\alpha_{1,7,3} + \Delta\alpha_{4,9,1} - \Delta\alpha_{2,10,3} - \Delta_{3,8,4} - \Delta\alpha_{1,7,5} + \Delta\alpha_{3,10,6} + \Delta\alpha_{3,8,5} - \Delta\alpha_{1,9,6})$	δ(SCuS)
$S_7^* = (1/2(2^{1/2}))(\Delta r_{71} - \Delta r_{91} + \Delta r_{10,3} - \Delta r_{83} - \Delta r_{75} - \Delta r_{10,6} + \Delta r_{85} + \Delta r_{96})$	ν(Cu-S)
$S_8^* = (1/2(2^{1/2}))(\Delta\alpha_{1,7,2} - \Delta\alpha_{4,9,1} + \Delta\alpha_{2,10,3} - \Delta\alpha_{3,8,4} - \Delta\alpha_{2,7,5} + \Delta\alpha_{4,8,5} + \Delta\alpha_{4,9,6} - \Delta\alpha_{2,10,6})$	δ(SCuS)
$S_7^{**} = (1/2(2^{1/2}))(\Delta r_{71} - \Delta r_{91} - \Delta r_{10,3} + \Delta r_{83} - \Delta r_{72} - \Delta r_{84} + \Delta r_{94} + \Delta r_{10,2})$	ν(Cu-S)
$S_8^{**} = (1/2(2^{1/2}))(\Delta\alpha_{2,7,5} + \Delta\alpha_{4,8,5} - \Delta\alpha_{4,9,6} - \Delta\alpha_{2,10,6} - \Delta\alpha_{1,7,5} + \Delta\alpha_{3,10,6} - \Delta\alpha_{3,8,5} + \Delta\alpha_{1,9,6})$	δ(SCuS)
T_2 Species	
$S_9 = (1/2)(\Delta r_{71} + \Delta r_{91} - \Delta r_{10,3} - \Delta r_{83})$	ν(Cu-S)
$S_{10} = (1/2(2^{1/2}))(\Delta r_{72} - \Delta r_{84} + \Delta r_{94} - \Delta r_{10,2} + \Delta r_{75} - \Delta r_{10,6} - \Delta r_{85} + \Delta r_{96})$	ν(Cu-S)
$S_{11} = (1/2(2^{1/2}))(\Delta\alpha_{2,7,5} - \Delta\alpha_{4,8,5} + \Delta\alpha_{4,9,6} - \Delta\alpha_{2,10,6})$	δ(SCuS)
$S_{12} = (1/2(2^{1/2}))(\Delta\alpha_{1,7,2} + \Delta\alpha_{4,9,1} - \Delta\alpha_{2,10,3} - \Delta\alpha_{3,8,4} + \Delta\alpha_{1,7,5} - \Delta\alpha_{3,10,6} - \Delta\alpha_{3,8,5} + \Delta\alpha_{1,9,6})$	δ(SCuS)
$S_{13} = (1/2^{1/2})(\Delta\alpha_{9,1,7} - \Delta\alpha_{10,3,8})$	δ(CuSCu)
$S_9^* = (1/2)(\Delta r_{72} - \Delta r_{84} - \Delta r_{94} + \Delta r_{10,2})$	ν(Cu-S)
$S_{10}^* = (1/2(2^{1/2}))(\Delta r_{71} - \Delta r_{91} + \Delta r_{10,3} - \Delta r_{83} + \Delta r_{75} + \Delta r_{10,6} - \Delta r_{85} - \Delta r_{96})$	ν(Cu-S)
$S_{11}^* = (1/2)(\Delta\alpha_{1,7,5} + \Delta\alpha_{3,10,6} - \Delta\alpha_{3,8,5} - \Delta\alpha_{1,9,6})$	δ(SCuS)
$S_{12}^* = (1/2(2^{1/2}))(\Delta\alpha_{1,7,2} - \Delta\alpha_{4,9,1} + \Delta\alpha_{2,10,3} - \Delta\alpha_{3,8,4} + \Delta\alpha_{2,7,5} - \Delta\alpha_{4,8,5} - \Delta\alpha_{4,9,6} + \Delta\alpha_{2,10,6})$	δ(SCuS)
$S_{13}^* = (1/2^{1/2})(\Delta\alpha_{7,2,10} - \Delta\alpha_{8,4,9})$	δ(CuSCu)
$S_9^{**} = (1/2)(\Delta r_{75} - \Delta r_{10,6} + \Delta r_{85} - \Delta r_{96})$	ν(Cu-S)
$S_{10}^{**} = (1/2(2^{1/2}))(\Delta r_{71} - \Delta r_{91} - \Delta r_{10,3} + \Delta r_{83} + \Delta r_{72} + \Delta r_{84} - \Delta r_{94} - \Delta r_{10,2})$	ν(Cu-S)
$S_{11}^{**} = (1/2)(\Delta\alpha_{1,7,2} - \Delta\alpha_{4,9,1} - \Delta\alpha_{2,10,3} + \Delta\alpha_{3,8,4})$	δ(SCuS)
$S_{12}^{**} = (1/2(2^{1/2}))(\Delta\alpha_{2,7,5} + \Delta\alpha_{4,8,5} - \Delta\alpha_{4,9,6} - \Delta\alpha_{2,10,6} + \Delta\alpha_{1,7,5} - \Delta\alpha_{3,10,6} + \Delta\alpha_{3,8,5} - \Delta\alpha_{1,9,6})$	δ(SCuS)
$S_{13}^{**} = (1/2^{1/2})(\Delta\alpha_{7,5,8} - \Delta\alpha_{10,6,9})$	δ(CuSCu)

Table VIII. Calculated and Observed Frequencies (cm^{-1}) and Predominant Mode Assignments for Cu_4S_6 Core[a]

$Cu^{I}_4L_3^+$			
	obsd		
calcd	IR	R	predominant mode
		A_1 Species	
272	275	272	ν(Cu-S)
171		175	δ(CuSCu)
		E Species	
267	···	255	ν(Cu-S)
127			δ(SCuS)
		T_1 Species	
219	···	···	ν(Cu-S)
145	···	···	δ(SCuS)
		T_2 Species	
271	275	277	ν(Cu-S)
244	242	245	δ(SCuS)
186		175	ν(Cu-S)
110			δ(SCuS)

[a] K(Cu-S) = 0.50 mdyn/Å; H(SCuS) = 0.10, F(S···S) = 0.15 mdyn/Å; H(CuSCu) = 0.05, F(Cu···Cu) = 0.20 mdyn/Å.

and Δr (bond distance) between ground and excited states are important in determining band intensities. In the quantum-mechanical view of Raman scattering the classical polarizability derivative is replaced by $(\alpha_{\rho\sigma})_{m,n}$, where m and n are the initial and final states, and is represented by the Kramers–Heisenberg dispersion equation[15]

$$(\alpha_{\rho\sigma})_{m,n} = \sum_e \left[\frac{\langle m|M_\sigma|e\rangle\langle e|M_\rho|n\rangle}{E_e - E_m - E_0} + \frac{\langle m|M_\rho|e\rangle\langle e|M_\sigma|n\rangle}{E_e - E_n + E_0} \right]$$

The sum is taken over excited electronic states, e, of the molecule. When $\nu_0 \rightarrow (\nu_e - \nu_m)$, a few terms dominate because of small denominators. If the Born–Oppenheimer approximation is applied

$$|e\rangle = \psi_e(q,Q)\phi_v(Q)$$

and ψ_e is expanded in a Taylor series

$$\psi_e(q,Q) = \psi_e(q,Q=0) + \left(\frac{\partial\psi_e}{\partial Q}\right)_{Q=0} Q + \ldots$$

then, for totally symmetric vibrations,[17] the first term in the series for $(\alpha_{\sigma\sigma})_{m,n}$ is nonzero. For a single excited state

$$(\alpha_{\sigma\sigma})_{0,1} = |\langle g|M_\sigma|e\rangle_0|^2 \sum_v \frac{\langle 0|v\rangle\langle v|1\rangle}{E_e - E_g - E_0}$$

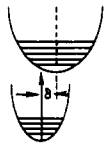
In the Condon approximation that is implied the value of M_σ is that at $Q = 0$ and M_σ is not a function of the vibrational transition that accompanies the electronic transition.

(16) (a) Ruamps, J. *C. R. Hebd. Seances Acad. Sci.* **1956**, *243*, 2034. (b) Sushchinskii, M. M. "Raman Spectra of Molecules and Crystals"; Keter: New York, 1972.

(17) Tang, J.; Albrecht, A. C. In "Raman Spectroscopy, Theory and Practice"; Szymanski, H. A., Ed.; Plenum Press: New York, 1967; Vol. 1, p 168.

Therefore, for $A_{1(g)}$ vibrations, resonance Raman intensity is large (1) when I absorption is large (given by value of transition moment $\langle g|M_\sigma|e\rangle$), (2) when some products of Franck–Condon overlaps, $\langle 0|v\rangle\langle v|1\rangle$, are large, and (3) when $\nu_0 \rightarrow \nu$ (electronic absorption band).

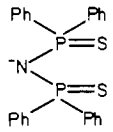
Franck–Condon overlaps[16] (shown pictorially by **1**) are large



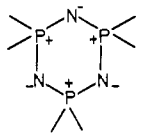
1

when δ and/or ΔK ($K = (\partial^2 V/\partial Q^2)_{Q=0}$) are large. In $Cu^{II}L_2$, relatively large intensification of ν_s(PNP) at 813 cm^{-1} and δ_s(PNP) at 425 cm^{-1}, compared to ν(P⋯S) at 580 cm^{-1} and ν(Cu—S) at 290 and 210 cm^{-1} suggests that Franck–Condon factors favor activation of PNP vibrations over others. Although a σ(S) → d_σ(Cu) transition assignment for the 585-nm absorption band is favored, the relatively low RR enhancement of ν(Cu–S) suggests that those orbitals, σ(S) and d_σ(Cu) directed along the Cu–S bond, cannot be the major contributors to MO levels in the resonant electronic transition. In a π(L) → d_σ(Cu) transition the symmetry of the two MO levels does not match; thus, we expect little overlap and a low transition moment. A reasonable assignment which takes into account the intensity of the absorption band as well as the RR data is d_π(Cu) → π^*(L). Franck–Condon factors favor activation of PNP vibrations if the π^*(L) contains a major contribution from N- and P-localized π orbitals.

Bent triatomics (C_{2v} point symmetry) of the type XY_2, in particular,[18] Cl_2O, show all three fundamentals in both infrared and Raman spectra. The symmetric ν_1(Y–X–Y) stretching band appears as the most intense Raman band. Phosphazenes[9] that are cyclic trimers or tetramers of R_2PN also show an intense symmetric P_3N_3 ring stretching Raman band in the 750–800-cm^{-1} region. Bonding[19] within cyclophosphazene rings has been analyzed in detail. Both in-plane and out-of-plane p_π(N)–d_π(P) bondings have been proposed in addition to the σ-bonded P_3N_3 skeleton. Bonding about nitrogen in imidodiphosphinates, however, differs somewhat from that at nitrogen in cyclophosphazenes. In the L^- ligand the nitrogen atom is formally negatively charged as

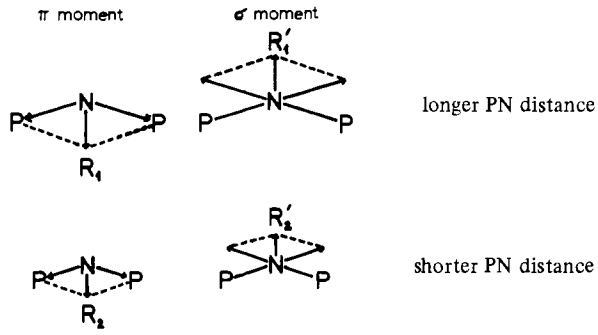


and this negative electron density is delocalized when binding through S atoms takes place to an electropositive metal ion. In $[R_2NP]_3$ the fifth valence electron of P is assumed to occupy a d orbital while the N atom has a one-electron p_π (out-of-plane) orbital and a doubly occupied in-plane lone pair. Only in the improbable ionic limit



does nitrogen carry an negative charge. We, therefore, anticipate that the degree of N→P, p_π→d_π back-bonding in imidodiphosphinates is much greater than in cyclophosphazenes. Substituent (methyl for phenyl, oxygen for sulfur, interchange of metal ion) and geometry (nonplanar vs. planar chelate ring, change in P–N–P angle) changes have no noticeable effect on the lack of intensity in ν_s(PNP). In compounds that contain the isoelectronic unit P–O–P a symmetric ν_s(POP) band has been identified[20] as a polarized Raman band near 611 cm^{-1}. No substantial p_π(O)–d_π(P) back-bonding can, however, be associated with the much lower ν_{as}(POP) and ν_s(POP) frequencies. These are similar to ν_{as}(P–N–P) and ν_s(P–N–P) frequencies of the N-protonated ligands. An explanation for the absence of IR and R intensity in ν_s(PNP) is offered in terms of the special bonding effects in the P–N^-–P moiety.

Chart I



σ (P→N, $\chi_N > \chi_P$) and π (N→P back-bonding) effects with regard to bond moments and polarizabilities are directly opposed to each other in the PNP group. Therefore, at extremes of the symmetric PNP bond stretching mode displacement we envision the situation shown in Chart I. If σ(P→N) and π(N→P) bonding effects have the same magnitude, then exact cancellation of resultant bond moments R_1 and R_1' or R_2 and R_2' can occur at the same bond stretching displacement values such that no change in the total moment takes place during the vibration. Similar arguments apply to bond polarizability changes. The result is very low $\partial\mu/\partial R$ and $\partial\alpha/\partial R$ values and thus very little or no infrared or Raman intensity in this fundamental.

During the PNP bending vibration no change in PN σ overlap or out-of-plane π overlap is expected if the PN bond distance does not change. However, the in-plane π overlap between the nitrogen lone pair and the in-plane d_π of the phosphorus atoms does change as the PNP angle changes during the bending mode. This contribution offsets the total balance of π- and σ-bond moment and polarizability changes and produces a net change in dipole moment and polarizability. Thus, δ(PNP) was observed in both infrared and Raman spectra near 420 cm^{-1}.

Though the same back-bonding arguments can be invoked for the P⋯S stretching mode, the extent of multiple bonding in the PS bond is much less. In addition, sulfur and phosphorus electronegativities are much closer in value and thus lead to a much less polar bond.

D. Metal–Ligand Bonding. Bond stretching force constants, K(Mn–S) = 0.45, K(Co–S) = 0.80, and K(Cu–S) = 0.50 mdyn/Å, show that metal–sulfur bonding in the tetraphenyl ligand is substantially weaker than in the tetramethyl ligand. The same trend is reinforced by the values of the force constants, K(PS) = 3.70 mdyn/Å in $Mn^{II}L_2$, and K(PS) = 2.20 mdyn/Å in $Co^{II}L'_2$. The 1.50 mdyn/Å lower value reflects stronger M–S bonding to the methyl-substituted ligand and a parallel decrease in the PS bond order. Values of PN

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constants, though, show little difference.

Relative to K(M-S) values that were obtained in normal-coordinate analyses of other metal-sulfur complexes[21] such as dithioacetylacetonates,[12a] monothioacetylacetonates,[12c] and dithienes,[11] results that were obtained herein for dithioimidodiphosphinates represent the lowest K(M-S) values. Both the tetrahedral geometry (as opposed to square planar) and the nature of the ligand (not a thiolate sulfur donor) probably contribute to the low metal-ligand bond strengths. Some intensification of Cu(I)-S Raman bands in the 200-300-cm^{-1} region for $Cu^{I}_3L_3$ and $Cu^{I}_4L_3^+$ clusters in comparison to Raman band intensities in the same region for bis chelates such as $Mn^{II}L_2$ might be surmised to arise from weak Cu···Cu bonding interactions.

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Bonding in $Ni(PH_3)_2(C_2H_4)$ and $Ni(PH_3)_2(C_2H_2)$. An ab Initio SCF-MO Study

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Ab initio MO calculations were carried out on $Ni(PH_3)_2(C_2H_4)$ and $Ni(PH_3)_2(C_2H_2)$. C-C bond lengths and bending angles of complexed ethylene and acetylene were determined. The binding energy was found to be larger in the acetylene complex than in the ethylene complex. The relative magnitude of σ donation and π back-donation was revealed through an analysis of binding energy and electron distribution. The influence of other ligands on the Ni-C_2H_4 bonding was discussed by comparing PH_3 with NH_3 as ligands.

Introduction

The Dewar-Chatt-Duncanson bonding model[2] has been the basis for qualitative understanding of chemical and physical properties of metal-olefin complexes. A number of semiempirical and ab initio MO calculations have been performed for a more quantitative description of the bonding.[3] However, most of these prior studies have discussed the relative importance of σ donation and π back-donation soley on the basis of the electron population on the metal atom and olefin. In the present work, we will attempt to reveal how σ donation and π back-donation contribute to the metal-olefin bond, through an analysis of the binding energy, as well as the electron distribution. We apply the scheme of energy decomposition analysis (EDA),[4] developed for studying intermolecular interactions. EDA enables us to understand the origin of bonding in terms of various meaningful interactions: electrostatic (Coulombic), exchange-repulsion, polarization, charge-transfer, and others. Though EDA and similar methods[5] have been widely applied to various types of intermolecular complexes,[4a] only a few applications have been made for transition-metal complexes.[6] Sakaki et al. have recently studied the bonding nature and stereochemistry of metal-carbon dioxide complexes by EDA with the ab initio SCF-MO method.[7] Ziegler and Rauk have carried out a similar analysis with a Hartree-Fock-Slater method for transition-metal ethylene and carbonyl complexes.[8]

In this paper, after giving the definition of energy components relevant to the σ donation and π back-donation, we will study the nature of bonding between $Ni(PH_3)_2$ and C_2H_4 in detail. The influence of other ligands on the Ni-C_2H_4 bonding will also be discussed. A comparison will be made between Ni-C_2H_4 and -C_2H_2 bonding.

Computational Procedures

We have assumed that the complexes $Ni(PH_3)_2(C_2H_4)$, $Ni(PH_3)_2(C_2H_2)$, and $Ni(NH_3)_2(C_2H_4)$ are singlets in their ground states, as was also assumed in previous studies.[21] As will be discussed later, with the stabilizing PH_3 ligands the electron configuration of these complexes is close to d^{10}, which would favor a singlet state. All calculations were performed with use of the closed-shell restricted Hartree-Fock (RHF) method.

Basis Set and Geometry. Ab initio SCF-MO calculations were carried out with use of the IMSPACK program system.[9] The basis sets used were the 4-31G set[10a] for ligand atoms and the [4s3p2d] contracted set for nickel atoms. The [4s3p2d] set was contracted from the (11s7p5d) primitive Gaussian set, which was modified from (12s6p4d)[10b] by deleting the two most diffuse s-type functions and adding an s-type, a p-type, and a d-type function with the exponents 0.2, 0.25, and 0.2, respectively. The 3s-type functions arising from the totally symmetric linear combination of d-type functions were removed from the basis set. The basis set used here was found to give reasonable binding energies and geometries.[11]

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