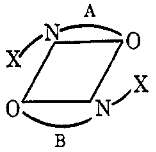
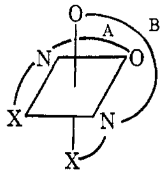
in parentheses. It is best to consider the values of ΔH° and ΔS° to be of qualitative significance only.

One interesting observation is that ΔH° for the transformation planar → octahedral is uniformly positive. This transformation can be represented as **6** → **7**. In the simplest model the conversion **6** → **7** can be visualized as a two-step process: (1) the relative orientation of rings A and B changes; (2) two long Ni–X bonds are formed. The change in geometry is also attended with a change in multiplicity of nickel(II). The first step may be expected to be endothermic.[32] The second step is most likely to be exothermic. The observed sign of ΔH° shows that energetically the first step plays the dominant role. This is not surprising since the Ni–X bonds are likely to be very weak (on the basis of the known structure of $(CH_3Cl)_2Co$). The sign of ΔS° can be rationalized along similar lines using the same model. We have not carefully examined the effect of varying the solvent on the position of equilibrium 1. However, spectral results suggest that it shifts to the right in going from benzene to chloroform.



6



7

Concluding Remarks

One general result of this research is that halo groups suitably attached to the aromatic ring of triazene 1-oxides can occupy a pseudooctahedral coordination position around cobalt(II) and nickel(II). The metal–halogen bond, though weak, observably affects properties of these systems. The complexes deviate considerably from O_h symmetry and this is neatly reflected in electronic spectral data. In the case of nickel(II) complexes, the population of the octahedral configuration in the solution phase follows the order F < Cl < Br ≪ OCH_3 ∼ SCH_3. The iodo complex is too insoluble for reliable magnetic measurements. However, if the intensity of the ∼9300-cm^{-1} band is taken as an index of the population of the pseudooctahedral species, the above series may be completed for the halo groups: F < Cl < Br > I. In cobalt(II) complexes also the iodo group behaves differently. Probably the large size of the iodo group is a determining factor.

One further observation to make is that for a given ligand the extent of halo coordination follows the order cobalt(II) ≫ nickel(II). Thus while $(CH_3Cl)_2Ni$ shows an equilibrium in solution, the corresponding cobalt(II) complex exists essentially ∼100% in the pseudooctahedral form. At least for this class of ligands the octahedral quartet state of cobalt(II) is populated with greater facility than the octahedral triplet state of nickel(II).[33]

The behavior of nickel(II) complexes clearly demonstrates that ether and thioether groups are better coordinating agents than the halo groups. This is not unexpected. In fact the X = OCH_3, OC_2H_5, and SCH_3 complexes were synthesized in order to establish the behavior in the 100% pseudooctahedral limit.

Acknowledgment.—Our sincere thanks are due to Dr. R. C. Srivastava for supplying advance information on the structure of $(CH_3Cl)_2Co$. The grant of a Senior Research Fellowship to P. S. Z. by the Department of Atomic Energy, New Delhi, India, is gratefully acknowledged. Microanalyses were done by Mr. A. H. Siddiqui of this department.

[32] The step (1) involves a distortion from a planar *toward* a tetrahedral NiN_2O_2 coordination. Planar → tetrahedral conversions are usually endothermic. See for example: R. H. Holm, A. Chakravorty, and G. O. Dudek, *J. Amer. Chem. Soc.*, **86**, 379 (1964); R. H. Holm, A. Chakravorty, and L. J. Theriot, *Inorg. Chem.*, **5**, 625 (1966); D. H. Gerlach and R. H. Holm, *J. Amer. Chem. Soc.*, **91**, 3457 (1969).

[33] An interesting parallel to this is provided by the higher population of the tetrahedral configuration in the case of cobalt(II) compared to nickel(II) complexes of some Schiff bases: G. W. Everett, Jr., and R. H. Holm, *Inorg. Chem.*, **7**, 776 (1968).

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The Stereochemistry of Four-Coordinate Bis(methinodiphosphinate)metal(II) Chelate Complexes

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A series of bivalent metal complexes of the type $[YP(C_6H_5)_2CHP(C_6H_5)_2Y]_2M^{II}$ (M = Fe, Co, Ni; Y = S, Se) have been synthesized. The sulfur and selenium complexes of iron(II) and cobalt(II) are tetrahedral while the nickel(II) complexes are planar. The selenium complexes of iron(II) and cobalt(II) are the first examples of tetrahedral coordination of four seleniums to these metals.

Introduction

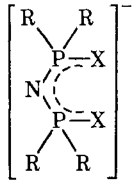
A large amount of comparative chemistry on four-coordinate metal(II) bis-chelate compounds[1] has produced some generalizations on their stereochemical behavior. (A) All nickel(II) complexes with donor atoms which are not sterically hindered (*e.g.*, O, S, Se, NH donors) have been found to be planar. (B) For a given ligand backbone, the order of stabilization of planar *vs.* tetrahedral[2] forms in cobalt(II) complexes

[1] R. H. Holm and M. J. O'Connor, *Progr. Inorg. Chem.*, in press.

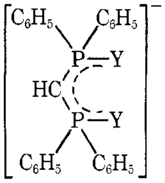
[2] The chelate rings reduce the symmetry of the molecule from T_d to D_{2d} or lower; however, the local symmetry around the metal is tetrahedral.

as a function of the donor atom set is[3] $S_4 \leftrightarrows (NH)_4 > (NH)_2O_2 > O_2S_2 > O_4$. (C) The stereochemical pattern for iron(II) complexes has not been as extensively explored as the cobalt(II) and nickel(II) cases, although those systems studied seem to indicate that tetrahedral geometry is preferred.

We have recently investigated[4] a series of bis-chelate metal(II) complexes with "imidodiphosphinate" ligands (I) where R = CH_3 or C_6H_5 and X = S, O, or NH. The single most interesting stereochemical feature which emerged from this work was the establishment of a tetrahedral geometry[5] imposed by four sulfurs coordinated to the nickel. There are no obvious restrictions in the backbone of the chelate ring to preclude the adoption of a planar structure. This complex and the related $[((C_6H_5)_2PS)_2N]_2Ni^{II}$ are the only known exceptions to generalization A. The iron compound, $[((CH_3)_2PS)_2N]_2Fe^{II}$, which was not isomorphous with the nickel complex, was the first example of a simple iron compound to have tetrahedral coordination of four sulfurs to iron.[6] This is of particular importance as the only other documented examples of tetrahedral FeS_4 units occur in the oxidized[7] and reduced[8] forms of the non-heme iron protein rubredoxin.


I

We have prepared a series of complexes of the ligands of type II (where Y = S or Se) which are isoelectronic with the "imidodiphosphinates." By analogy[4] with the previous system these will be named from the generic root "methinodiphosphinate." This system allows the first comparisons of sulfur *vs.* selenium as the donor sets in a series of bis chelates, with six-membered rings, of iron(II), cobalt(II), and nickel(II). The only known example of a complex of this type is the brief report of bis(diselenoacetylacetonato)nickel(II)[9a] which is similar to its sulfur analog.[9b] Previous comparisons of bis chelates, having five-membered rings, containing sulfur or selenium as the donor sets[10] have indicated a fairly close similarity between the respective complexes except that the selenium complexes are more prone to decomposition.


II

Experimental Section

General Data.—All operations on complexes in solution were carried out under an atmosphere of prepurified nitrogen using solvents that were purified and degassed before use. Electronic spectra were recorded on a Cary (Model 14) spectrometer in methylene chloride. Proton nmr spectra were recorded on a Varian A-60 spectrometer, equipped with a variable-temperature probe, or a T-60 spectrometer. The magnetic susceptibilities of the solid samples were determined by the Faraday method using $HgCo(SCN)_4$ and $Ni(en)_3S_2O_4$ as calibrants. Pascal's constants were used for the diamagnetic susceptibilities.[11] The magnetic susceptibilities of the samples in solution were determined by the Evans method.[12] Melting points were determined, using a Kofler hot-stage microscope, in sealed capillaries and are uncorrected. Osmometric molecular weights were determined under nitrogen by Midwest Microlab, Inc., Indianapolis, Ind.

Bis(diphenylphosphinothioyl)methane.—A mixture of $((C_6H_5)_2P)_2CH_2$[13] (50 g, 0.13 mol) and sulfur (10 g, 0.31 g-atom) was stirred in 1000 ml of benzene overnight. The solution was then refluxed for 2 hr and the solvent was allowed to boil away until *ca.* 150 ml remained. This was cooled (0°) and brief pumping brought out white crystals. These were filtered, washed with CS_2 (40 ml) to remove excess sulfur, and dried briefly in air. Recrystallization from propanol (2000 ml) gave 50 g (86%) of large white needles, mp 175–176°.

Anal. Calcd for $C_{25}H_{22}P_2S_2$: C, 66.96; H, 4.91; P, 13.84; S, 14.29. Found: C, 66.90; H, 5.05; P, 13.81; S, 14.31. Nmr spectrum (δ in $CDCl_3$): 4.00, triplet (1); 7.46 (6); 7.92, broad (4).

Bis(diphenylphosphinoselenoyl)methane.—A warm solution of KSeCN (22.5 g, 0.16 mol) in acetonitrile (250 ml) was added rapidly to $((C_6H_5)_2P)_2CH_2$ (30 g, 0.078 mol) in hot acetonitrile (330 ml). The solution was stirred and refluxed for 2 days. The acetonitrile was evaporated and the white solid residue was washed carefully with water (five 100-ml portions) and cold methanol (50 ml). The resultant solid was dried *in vacuo* over P_2O_5 and recrystallized from propanol (1000 ml) to yield 27 g (64%) of white flakes, mp 190–191°.

Anal. Calcd for $C_{25}H_{22}P_2Se_2$: C, 55.36; H, 4.06; P, 11.44; Se, 29.15. Found: C, 55.20; H, 4.25; P, 11.35; Se, 29.17. Nmr spectrum (δ in $CDCl_3$): 4.33, triplet (1); 7.38 (6); 7.85, broad (4).

Bis(methinotetraphenyldithiodiphospino)iron(II).—A stirred solution of $((C_6H_5)_2PS)_2CH_2$ (2.24 g, 5 mmol) in THF (25 ml) was cooled to −70° and *n*-butyllithium (3.12 ml, 1.6 *N*, 5 mmol) was added dropwise. This caused a white solid to form which redissolved at room temperature. To this solution was added $[(C_2H_5)_4N]_2[FeBr_2Cl_2]$ (1.37 g, 2.5 mmol). The solvent was evaporated after 5 hr to yield a yellow-green solid. This was extracted with hot toluene (60 ml) and filtered, and hot heptane (30 ml) added. Slow evaporation of the solvent yielded yellow crystals. These were filtered, washed with hexane (two 20-ml portions), and dried *in vacuo* (1.5 g, 63%), mp 203–205°.

Anal. Calcd for $C_{50}H_{42}FeP_4S_4$: C, 63.17; H, 4.42; mol wt 949.8. Found: C, 63.09; H, 4.27; mol wt 900 (in toluene). λ_{max} (cm^{-1}) broad band centered *ca.* 3700–4299, ϵ (l. mol^{-1} cm^{-1}) 96. Nmr spectrum (δ in CD_2Cl_2): 6.67 (2), 9.07 (3). The complex is paramagnetic both in the solid form (5.24 BM) and in solution (5.22 BM, CH_2Cl_2). Solutions are extremely sensitive to air but the solid decomposes only slowly in air.

Bis(methinotetraphenyldiselenodiphosphino)iron(II).—This was prepared in a similar fashion to the above sulfur complex. More heptane was needed to bring the light yellow crystals of the product out of solution (yield 22%), mp 182–184°.

Anal. Calcd for $C_{50}H_{42}FeP_4Se_4$: C, 52.74; H, 3.67; mol wt 1137.69. Found: C, 52.94; H, 3.65; mol wt 1200 (toluene). λ_{max} (cm^{-1}) broad band centered *ca.* 3800–4200, ϵ (l. mol^{-1} cm^{-1}) 107. Nmr spectrum (δ in $CDCl_3$): 5.87 (2), 8.67 (3). The complex is paramagnetic both in the solid form (5.33 BM) and in solution (4.98 BM, CH_2Cl_2). The solid decomposes fairly rapidly in air and solutions are extremely air sensitive.

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Bis(methinotetraphenyldithiodiphosphino)cobalt(II).—The ligand (5 mmol) was prepared by deprotonation as described above and $[(C_2H_5)_4N]_2[CoCl_2Br_2]$ (2 g, 4 mmol) was added. The solvent was evaporated after 14 hr and the dark green solid extracted with hot toluene (50 ml). This was filtered and hot heptane (25 ml) was added dropwise to the stirred hot filtrate. Cooling overnight at $-20°$ yielded large green crystals. These were filtered, washed with heptane (two 15-ml portions), and dried *in vacuo* (1.8 g, 76%), mp 203–204°.

Anal. Calcd for $C_{50}H_{42}CoP_4S_4$: C, 62.97; H, 4.40; mol wt 952.9. Found: C, 63.21; H, 4.60; mol wt 910 (toluene). λ_{max} (cm^{-1}) 5713, 7380, 13,263, 14,327, 16,260; ϵ ($l.\ mol^{-1}\ cm^{-1}$) 144, 88, 366, 365, 375. Nmr spectrum (δ in CD_2Cl_2): 6.68 (2), 8.87 (3). The complex is paramagnetic both in the solid form (4.56 BM) and in solution (4.37 BM, CH_2Cl_2). It shows Curie behavior from -71 to $+36°$. The solid decomposes slowly in air but the solutions decompose fairly rapidly.

Bis(methinotetraphenyldiselenodiphosphino)cobalt(II).—This compound was prepared in a similar manner to that described for the sulfur complex. Considerably more heptane was needed to precipitate the product as green crystals (yield 62%), mp 184–186°.

Anal. Calcd for $C_{50}H_{42}CoP_4Se_4$: C, 52.59; H, 3.65. Found: C, 52.70; H, 3.62. λ_{max} (cm^{-1}) 5263, 7027, 12,492, 13,492, 15,518; ϵ ($l.\ mol^{-1}\ cm^{-1}$) 133, 118, 383, 426, 416. Nmr spectrum (δ in $CDCl_3$): 6.55 (2), 8.62 (3). The complex is paramagnetic both in the solid form (4.68 BM) and in solution (4.51 BM, CH_2Cl_2). The solid decomposes rapidly in air and solutions are extremely air sensitive.

Bis(methinotetraphenyldithiodiphosphino)nickel(II).—The ligand (10 mmol) was prepared by deprotonation as described above in 45 ml of THF and $[(C_2H_5)_4N]_2[NiBr_4]$ (*ca.* 11 mmol) was added. This was refluxed for 20 hr with stirring. The solvent was evaporated and the light red solid was extracted with boiling CH_2Cl_2 (100 ml). Hot heptane (30 ml) was added to the filtered extract. Cooling at $-20°$ for 35 hr caused small red crystals to separate. These were filtered, washed with hexane (two 20-ml portions), and dried at 0.05 mm and 100° for 24 hr (2.1 g, 44%), mp 208–210°.

Anal. Calcd for $C_{50}H_{42}NiP_4S_4$: C, 62.98; H, 4.41. Found: C, 62.81; H, 4.59. λ_{max} (cm^{-1}) 19,275; ϵ ($l.\ mol^{-1}\ cm^{-1}$) 476. Nmr spectrum (δ in CD_2Cl_2): 4.08, triplet (1); 7.42 (12); 7.95 (8). The complex is diamagnetic in the solid form and in solution. It decomposes slowly in air as a solid but rapidly in solution.

Bis(methinotetraphenyldiselenodiphosphino)nickel(II).—This compound was prepared in a manner similar to the other two selenium complexes but was extremely difficult to isolate pure. The THF reaction mixture was filtered and the solvent was removed. The resulting red oil was dissolved in CH_2Cl_2 and filtered. Addition of an equal amount of hexane and reduction of the solvent yielded a deep red solid, mp 152–154°. This red solid frequently was contaminated with a paramagnetic impurity which successive recrystallization could not remove.

Anal. Calcd for $C_{50}H_{42}NiPSe_4$: C, 52.59; H, 3.68; P, 10.87; Se, 27.69. Found: C, 52.70; H, 3.61; P, 10.58; Se, 27.61. λ_{max} (cm^{-1}) 20,000 (sh); ϵ ($l.\ mol^{-1}\ cm^{-1}$) 560. Nmr spectrum (δ in $CDCl_3$): 4.28, triplet (1); 7.35 (12); 7.80, broad (8). As a solid the complex is air stable but in solution it decomposes slowly to its red paramagnetic impurity noted above and free ligand.

Results and Discussion

Sulfur Complexes.—The complex $[((C_6H_5)_2PS)_2CH]_2Fe^{II}$ is a light yellow crystalline solid which decomposes slowly in air. It has been shown to be monomeric in toluene solution; exposure of these solutions to air causes rapid decomposition. The magnetic moments (5.24 BM, solid; 5.22 BM, CH_2Cl_2 solution) are essentially the same as those found for the known[6] tetrahedral $[((CH_3)_2PS)_2N]_2Fe^{II}$ (5.25 BM, solid; 4.99 BM, CH_2Cl_2 solution[4]). These lie in the same range expected for high-spin tetrahedral iron(II) complexes. However, this alone is not structurally conclusive because the planar FeO_4 unit in the mineral gillespite[14] gives a high-spin moment of 5.12 BM.

More conclusive evidence for a tetrahedral chromophore is obtained from the electronic spectrum which shows a very broad band centered at *ca.* 3800 cm^{-1} (ϵ 96). The position and appearance of this band are very similar to those found for $[((CH_3)_2PS)_2N]_2Fe^{II}$ [4] and for iron(II) ions doped into ZnS[15] and CdS[16] lattices. This band is most reasonably assigned to the $^5E \rightarrow {}^5T_2$ transition of a high-spin tetrahedral d^6 complex. The magnitude of the ligand field transition is similar to those found in tetrahaloiron(II) complexes.[17] Eaton and Lovenberg[8] have recently assigned the broad band centered at about 6250 cm^{-1} (ϵ 20) in the reduced form of rubredoxin from *Clostridium pasteurianum* as the spin-allowed $^5E \rightarrow {}^5T_2$ transition. This band appears very similar in shape to the bands in $[((CH_3)_2PS)_2N]_2Fe^{II}$ and $[((C_6H_5)_2PS)_2CH]_2Fe^{II}$, but, as these authors noted, the magnitude of the ligand field is considerably larger than that found in tetrahedral chromophores of Fe(II). However, no direct comparisons to simple complexes containing tetrahedral FeS_4 units could be made. Thus $[((C_6H_5)_2PS)_2CH]_2Fe^{II}$ and $[(R_2PS)_2N]_2Fe^{II}$, where R = C_6H_5 or CH_3, are extremely important compounds for spectral comparisons. The magnitude of the ligand field in reduced rubredoxin is considerably larger than that found in our studies. This supports the contention that constraints imposed on the sulfur atoms by the protein configuration produces a ligand field greater than that expected for mercaptide sulfides. Further, the magnetic moment of reduced rubredoxin[18] (5.05 BM) is similar to those found for the simple tetrahedral iron chelates described here.

Large green crystals of $[((C_6H_5)_2PS)_2CH]_2Co^{II}$ are readily prepared, from the ligand salt and tetrahalocobaltate(II) salts. It is monomeric in toluene solution, but like the iron complex its solutions decompose in air. The data in Table I clearly show that the complex is tetrahedral and that the ligand field is comparable to that found in the related "imidodiphosphinates." Apart from the four-membered chelated dithiophosphates[19] and dithiophosphinates,[20] the sulfur complexes in Table I are the only examples of tetrahedral CoS_4 coordination.

TABLE I

SUMMARY OF SPECTRAL AND MAGNETIC DATA FOR COBALT COMPLEXES, CoL_2

	ν_2,[a]	ν_3,[a]	Δ_t,	B',	μ_{eff}, BM	
L	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	Solid	Soln[b]
$((C_6H_5)_2PS)_2CH$	6539	14,974	3804	674	4.56	4.37[c]
$((C_6H_5)_2PSe)_2CH$	6195	14,205	3560	648	4.68	4.51
$((C_6H_5)_2PS)_2N$	6613	14,258	4027	586	4.54	...
$((CH_3)_2PS)_2N$	6576	14,399	3831	632	4.68	5.50

[a] Weighed averages of the several maxima. [b] CH_2Cl_2. [c] Curie behavior observed from $+36$ to $-71°$.

The complex $[((C_6H_5)_2PS)_2CH]_2Ni^{II}$ forms red crystals which slowly decompose in air. It is diamagnetic in the solid form indicating planar coordination. The sharp, nonshifted nmr spectrum indicates it remains diamagnetic in solution. Further evidence of planar

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geometry comes from the optical spectra. It shows one band centered at 19,275 cm^{-1} (ϵ 476). This is most likely due to the transition $(d_{x^2-y^2})^2 \rightarrow (d_{x^2-y^2})^1(d_{xy})^1$ in planar d^8 complexes.

The methinotetraphenyldithiodiphosphinate ligand shows a very close resemblance to the isoelectronic imidothiodiphosphinate particularly with respect to the similarity of the spectral and magnetic parameters of the iron(II) and cobalt(II) complexes. It gives the expected behavior of a sterically unencumbered bidentate ligand toward nickel(II), whereas the imidodiphosphinate gives the anomalous tetrahedral geometry. These results show conclusively that the factors which dictate the stereochemistry of coordination number 4 with bidentate ligands about nickel(II) are more complex than those previously anticipated.

Selenium Complexes.—The complex $[((C_6H_5)_2PSe)_2CH]_2Fe^{II}$ is obtained as small yellow crystals which decompose rapidly in air. It has been shown to be monomeric in toluene solutions which are extremely air sensitive. The magnetic moment and electronic spectrum indicate that it has a tetrahedral $FeSe_4$ unit. The spectral and magnetic data (Table I) for the green complex $[((C_6H_5)_2PSe)_2CH]_2Co^{II}$ show that it is also tetrahedral and like the iron complex is air sensitive in both solid and solution phases. These are the first examples of this geometry found for four-coordinate iron(II) and cobalt(II) complexes with selenium donor functions. The only other four-coordinate complexes of these metals are the 1,2-diselenolenes[10] $MSe_4C_4(CF_3)_4^-$ (M = Fe or Co) which are involved in monomer–dimer equilibria in solution and undoubtedly have planar monomeric units.

Considerable difficulty was experienced in preparing pure samples of the dark red complex $[((C_6H_5)_2PSe)_2CH]_2Ni^{II}$. Pure samples are diamagnetic; however it is frequently contaminated by a paramagnetic impurity. The optical spectrum and its diamagnetism indicate that like the sulfur analog it is planar.

Conclusions.—The two ligands, described in this work, give compounds of similar properties. The selenium ones are more soluble and more prone to decomposition in a number of solvents. The electronic spectra show slight shifts to lower energy of the d–d transitions of the $CoSe_4$ chromophore compared to the sulfur complex. The $NiSe_4$ complex, on the other hand, shows a slight shift to higher energy *vs.* the sulfur complex for the band usually assigned to the $(d_{x^2-y^2})^2 \rightarrow (d_{x^2-y^2})^1(d_{xy})^1$ transition. Previous spectral comparisons[21] of a variety of transition metal chromophores with selenium and sulfur donors usually show small shifts to longer wavelengths of both d–d and charge-transfer bands for the selenium derivatives. However, the separation of the mainly metal $d_{x^2-y^2}$ and d_{xy} orbitals for planar d^8 complexes is expected to be a sensitive function of both in-plane π and σ interactions. Thus, the slight blue shift found in this case is not unreasonable. Lastly, the "methinodiphosphinate" complexes are less stable than the related "imidodiphosphinate" ones with respect to decomposition of their solutions in air.

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Spectroscopic Studies of Metal–Metal Bonding. II. The Variation of Metal–Metal Bond Strengths with Substituents from the Vibrational Analyses of $X_3MCo(CO)_4$ (M = Sn, Ge; X = I, Br, Cl)

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The complete absorption spectra (33–55,000 cm^{-1}) for the four metal–metal bonded molecules $Br_3SnCo(CO)_4$, $I_3SnCo(CO)_4$, $Br_3GeCo(CO)_4$, and $I_3GeCo(CO)_4$ and the results of laser Raman measurements, where obtainable, are reported. From 16 to 12 of the 20 predicted Raman- and infrared-active fundamentals for each molecule have been observed and the symmetry type of each vibration was assigned. Assignments of the ν(CO) overtone bands in the 4050–4250-cm^{-1} region are given. Vibrational normal-coordinate analyses for each of these molecules yield close agreement between the calculated and assigned spectra and are based upon a valence force field and reasonable spectroscopic assumptions including the transfer to this study of the portions of the force fields for the $Co(CO)_4$ moieties obtained in an earlier work. Series of solutions to the equations of motion have been obtained by continuously varying only four force field elements directly associated with the Co–M and M–X motions to give the correct calculated spectra while all other force field elements were left unchanged. Solutions obtained in this manner yield loci of the many acceptable values of $k_{\text{Co-M}}$ and $k_{\text{M-X}}$ for each molecule. The experimental evidence accumulated from other types of studies on these molecules is discussed along with the bonding implications of the values found for $k_{\text{Co-M}}$: $k_{\text{Co-Ge}}(\text{X = Cl}) = 1.10$, $k_{\text{Co-Ge}}(\text{X = Br}) = 0.96$, $k_{\text{Co-Ge}}(\text{X = I}) = 0.52$, $k_{\text{Co-Sn}}(\text{X = Cl}) = 1.23$, $k_{\text{Co-Sn}}(\text{X = Br}) = 1.05$, $k_{\text{Co-Sn}}(\text{X = I}) = 0.64$ mdyn/Å, each of which falls at the minimum of the accceptable range of values of $k_{\text{Co-M}}$ as discussed in the text.

Introduction

The series of molecules $X_3MCo(CO)_4$ (X = I, Br, Cl; M = Sn, Ge, Si) is well suited for the investigation of metal–metal bond strengths and the dependence of these strengths upon the nature of the ligand X and of the metal M because the vibrational problem can be made tractable and also because both M and X can be

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