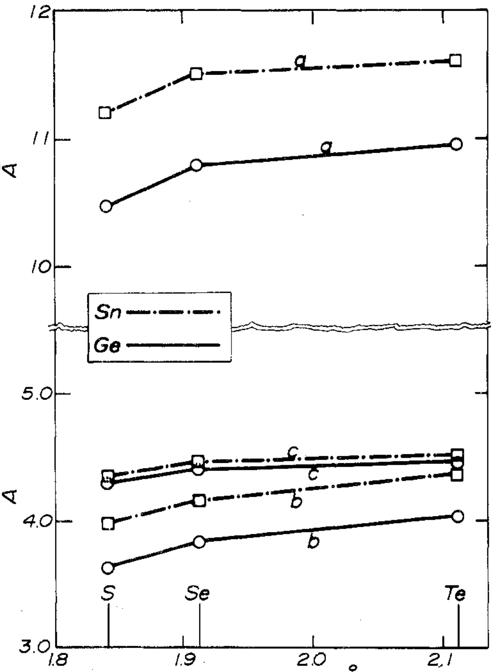

Figure 2. Lattice parameters of the S-Se-Te series of Sn and Ge; the phases are all of the SnS (or GeTe-II) structure. The unit axes are all referred to those of GeTe-II.

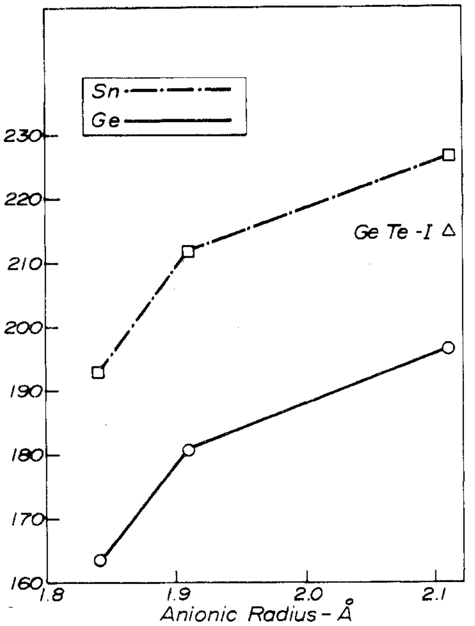

Figure 3. Unit cell volumes of the S-Se-Te series of Sn and Ge. The value for the rhombic phase, GeTe-I, not belonging to the isostructural orthorhombic series, is plotted for comparison.

olating these results to 100% GeTe we find the lattice parameters (under pressure) would be a = 10.82, b = 4.04, and c = 4.10 Å with V = 179.5 Å^3. The values are in good agreement with those of GeTe-II as quenched to 1 atm.

Attention is called both to an important difference and an important similarity between GeTe-II and the corresponding SnTe.[6] In the series GeS, GeSe, and GeTe-II, the sulfide and selenide are stable at atmospheric pressure, and GeTe-II must be formed at high pressures but can be quenched to room conditions. In the Sn series, however, although the sulfide and selenide are also stable at atmospheric pressure, SnTe (as indicated above[5,6]) may be observed only under high pressures using x-ray diffraction techniques and thus appears not to be quenchable. The ionic radius ratios of SnTe and GeTe are 0.44 and 0.34, respectively. These values indicate that the bonding character of SnTe is more metallic than that of GeTe. This focuses attention on a possible relationship between quenchability and degree of metallicity of similar, closely related phases.

In other work[7] on the SnTe–GeTe system, the high-pressure phase formed by compositions containing up to 35 mol % GeTe could not be retained or quenched even on cooling to 100 K before removing pressure. However, on diluting the same mixtures with boron, the pressure and cooling procedures are successful in retaining about 50% of the high-pressure phase at atmospheric pressure and 100 K for compositions containing up to 20 mol % GeTe. Thus with the system of SnTe–GeTe, differences in quenching behavior are beginning to fall within a framework of ionic parameters, temperature, pressure, and friction effects that may lend themselves to more than qualitative treatment.

Figure 1 summarizes results obtained with a 1:1 amorphous GeTe composition. It is evident that high pressures alone are not sufficient to produce noticeable crystallinity, at least to the experimental limit of 120 kbars. Complete conversion to GeTe-II occurred only at 80–100 kbars at 300°C, with mixtures of I and II forming at lower pressures.

A few runs made with a limited supply of amorphous films of 70:30 Ge:Te composition showed the formation of mixtures of I and II near 400 °C and 10 kbars. Much more work with other compositions and forms of starting materials will be necessary to detail phase relations in the system Ge–Te.

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Registry No. GeTe, 12025-39-7.

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Metal Atom Evaporation Synthesis and Intramolecular Exchange: (1,3-COD)FeL$_3$ Complexes from 1,5-COD

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In recent years, metal atom evaporation has emerged as a valuable technique for the synthesis of gram quantities of organometallic complexes, some of which cannot be readily obtained by conventional methods.[1-6] Following the report of Timms[7] on the preparation of Fe(1,5-COD)$_2$ (COD = cyclooctadiene), we thought its reaction with phosphites would provide an easy route to FeL$_5$ complexes. [1,5-COD is rapidly

Table I. ^{31}P NMR Data[a] and Thermodynamic Parameters

	(1,3-COD)FeL_3							FeL_5[b]
L	δ_A	δ_B	T, °C	J, Hz	$\Delta H^{\ddagger}_{298}$, kcal/mol	$\Delta S^{\ddagger}_{298}$, cal/(mol K)	$\Delta G^{\ddagger}_{298}$ kcal/mol	$\Delta G^{\ddagger}_{200}$, kcal/mol
$P(OMe)_3$	−187.2	−177.9	−91	39	9.9	−2.8	10.7	8.8
$P(OEt)_3$	−181.9	−175.5	−70	39	11.7	2.7	10.9	11.2
$P(O\text{-}i\text{-}Pr)_3$	−181.6	−174.7	−70	36	11.3	−3.3	12.3	

[a] In pentane. Negative shifts are downfield from external H_3PO_4. [b] Data from ref 21.

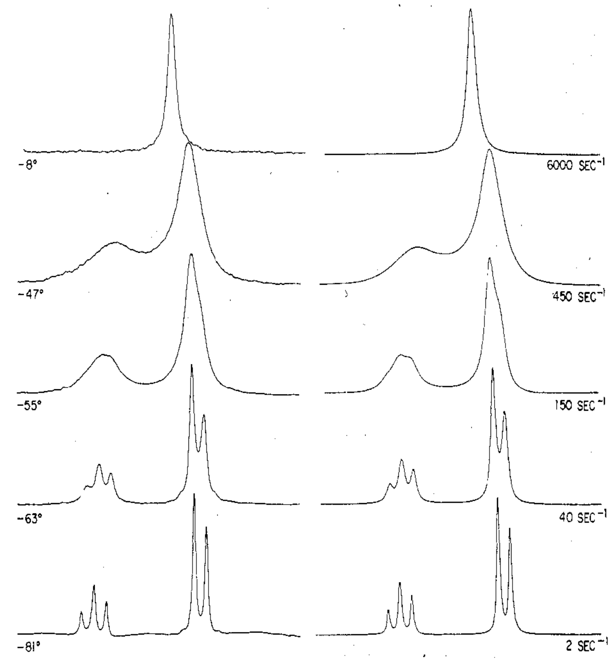


Figure 1. $^{31}P\{^1H\}$ spectra at 36.43 MHz of (1,3-COD)Fe[$P(OMe)_3$]$_3$ in pentane at various temperatures on the left. Simulated spectra at various rates of intramolecular exchange on the right.

displaced from Ni(1,5-COD)$_2$ by small phosphites, such as $P(OMe)_3$, to form NiL_4 complexes.][8] We had previously prepared Fe[$P(OMe)_3$]$_5$,[9] in a mixture with other iron-containing products, by the direct cocondensation of Fe atoms with $P(OMe)_3$.

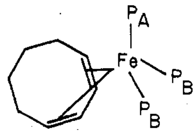
1,5-COD and Fe atoms were cocondensed at liquid nitrogen temperature in a conventional apparatus[10] and the resulting (1,5-COD)$_2$Fe washed down with cold THF (−50 °C)[11] into excess $P(OMe)_3$. The solution was warmed to room temperature with stirring, and the THF and excess $P(OMe)_3$ were stripped off. The resulting tarry product was taken up in pentane, chromatographed through alumina, and crystallized from cold pentane. Pale yellow crystals[12] of (1,3-COD)Fe[$P(OMe)_3$]$_3$ (mp 143–143.5 °C) were obtained in 5% yield based on the amount of Fe evaporated.

The composition is established by the high-resolution mass spectrum (*m/e* 536.1142, calculated for $C_{17}H_{39}P_3O_9Fe$ 536.1154), which also showed peaks corresponding to loss of 1,3-COD and $P(OMe)_3$. The 220-MHz proton NMR spectrum[13] at 25 °C shows broad resonances at δ (relative intensity) 5.00 (2), 3.00 (2), 2.27 (4), and 1.66 (4) and a quartet [J_{wings} = 10.0 Hz] at δ 3.55 (27). The pattern of chemical shifts for the COD is very similar to that reported for (1,3-COD)Fe(CO)$_3$ [δ 4.76 (2), 3.0 (2), 1.8 (4), 1.1 (4)] and not like that for (1,5-COD)Fe(CO)$_3$ [δ 3.4 (4), 2.0 (8)].[14]

The 22.63-MHz $^{13}C\{^1H\}$ spectrum[13] at 25 °C shows resonances at δ 86.3 (=CH–), 51.2 (–OCH_3), and 27.8 and 27.0 (–CH_2–). The large upfield coordination shift of olefinic carbons (~40 ppm) is consistent with bonding to a very electronic-rich center.[16] The distinction between –CH_2– carbons remains on heating to +60 °C.

The 36.43-MHz $^{31}P\{^1H\}$ spectrum[13] (Figure 1) shows a single resonance at −181 ppm above −10 °C. Addition of $P(OMe)_3$ gives a separate sharp resonance at −140 ppm, indicating an absence of intermolecular exchange on the NMR time scale. We have not observed intermolecular exchange even at 110 °C (in toluene).

When the pentane solution is cooled to −81 °C, a nearly first-order AB_2 pattern is observed. The NMR data are completely consistent with structure **1**,[17] which undergoes rapid



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intramolecular exchange of phosphites at room temperature.

Variable-temperature $^{31}P\{^1H\}$ spectra were analyzed using a full-density matric line shape analysis. The temperature dependence of δ_{AB} was extrapolated from spectra obtained near the slow-exchange limit. The exchange mechanism was assumed to involve exchange of the axial phosphite with either basal phosphite. A least-squares fit[18] of the Eyring equation gives the thermodynamic parameters in Table I.

We have similarly prepared (1,3-COD)Fe[$P(OEt)_3$]$_3$ and (1,3-COD)Fe[$P(O\text{-}i\text{-}Pr)_3$]$_3$. The increasing barriers to intramolecular phosphite exchange (Table I) parallel the increasing steric bulk of these ligands (cone angles 107, 109, and 130°).[19,20] The barriers are, however, relatively insensitive to changes in L when compared with the FeL_5 complexes[21] (Table I), where steric crowding in the transition state[22] must be much greater. Consistent with these idea is the fact that (1,3-COD)Fe[$P(O\text{-}i\text{-}Pr)_3$]$_3$ is isolable whereas Fe[$P(O\text{-}i\text{-}Pr)_3$]$_5$ has not been prepared.

We were surprised to find that the reaction of $P(OMe)_3$ with Fe(COD)$_2$ gives (1,3-COD)Fe[$P(OMe)_3$]$_3$, especially since we started with 1,5-COD. Since Mackenzie and Timms[7] have established that the COD in Fe(COD)$_2$ is the 1,5 species, we must conclude that isomerization to the 1,3 species must occur while warming in the presence of the phosphite. A catalytic isomerization of 1,5- to 1,3-cyclooctadiene by Fe(CO)$_5$ was reported by Arnet and Pettit.[23]

Treatment of Fe(COD)$_2$ with CO gave Fe(CO)$_5$, identified by comparing its infrared spectrum in the carbonyl region (2013 (m), 1990 cm^{-1} (s), toluene) with that of an authentic sample. A stronger band at 1970 cm^{-1} has almost the same frequency as that reported[24] for (CO)Fe(1,3-cyclohexadiene)$_2$ (1964.5 cm^{-1}), suggesting formation of (CO)Fe(1,3-COD)$_2$.

Note Added in Proof. Professors P. L. Timms and M. Greene at Bristol have independently prepared (1,3-COD)Fe[$P(OMe)_3$]$_3$ by a method similar to ours. By way of contrast PF_3 gave the (1,5-COD)Fe(PF_3)$_3$ complex (private communication).

Acknowledgment. We gratefully thank Dr. C. L. Hoover for his help in designing and constructing the metal atom evaporation apparatus and Dr. P. Meakin for the use of his computer programs. We also wish to thank Mssrs. D. W. Reutter and G. Watunya for skilled technical assistance.

Registry No. (1,3-COD)Fe(P(OMe)$_3$)$_3$, 59034-03-6; (1,3-COD)Fe(P(OEt)$_3$)$_3$, 59034-02-5; (1,3-COD)Fe(P(O-*i*-Pr)$_3$)$_3$, 59034-04-7; 1,5-COD, 111-78-4; Fe, 7439-89-6; P(OMe)$_3$, 121-45-9; Fe(COD)$_2$, 55823-33-1.

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(12) A satisfactory elemental analysis was obtained. The compound melted sharply in a sealed, evacuated tube and recrystallized on cooling.
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Pentamolybdobis[*cis*-phosphatobis(ethylenediamine)aquocobalt(III)]. A "Neutral" Heteropoly Complex

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We have recently reported some of the first examples of organic derivatives of heteropoly anions.[1,2] Among the new complexes were pentamolybdobisphosphonates, (RP)$_2$Mo$_5$O$_{21}$$^{4-}$, that are structurally analogous[3] to the corresponding molybdophosphate,[4] (OP)$_2$Mo$_5$O$_{21}$$^{6-}$. In these heteropoly complexes the heteroatom, phosphorus, utilizes only three oxygens to bind to the oxometalate structure. The pentamolybdophosph(on)ate anions form rapidly and are hydrolytically stable at pH 4–5. Under these conditions, complexes where R contains an amino group are protonated, and the resulting heteropoly anions are zwitterionic, e.g., [(H$_3$N$^+$C$_2$H$_4$P)$_2$Mo$_5$O$_{21}$$^{4-}$]$^{2-}$. In this paper we describe the synthesis of an electrically neutral zwitterion of the same type in which the hetero group is a monodentate phosphate ligand of an inert coordination complex.

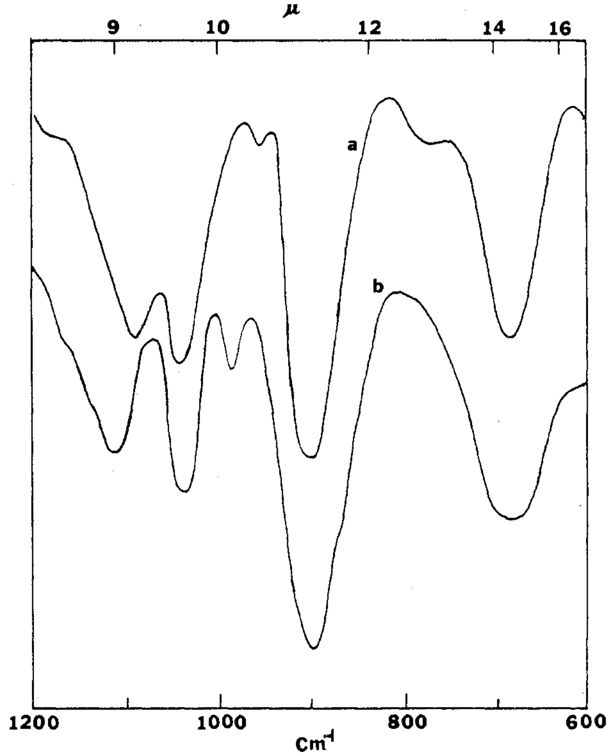

Figure 1. Infrared spectra, in KBr disks, of (a) {[Co(en)$_2$(H$_2$O)OPO$_3$]$_2$Mo$_5$O$_{15}$}·8H$_2$O and (b) Na$_6$[P$_2$Mo$_5$O$_{23}$]·13H$_2$O.

Experimental Section

The complexes *cis*-[Co(en)$_2$(H$_2$O)(HPO$_4$)]ClO$_4$·0.256H$_2$O, [Co(en)$_2$PO$_4$]·H$_2$O, and *cis*-[Co(en)$_2$(H$_2$O)$_2$](NO$_3$)$_3$ were prepared as previously described.[5,6] The last named complex was converted to the perchlorate salt by treatment with sodium perchlorate. Optical spectra of these complexes agreed with those reported.[5,7]

Preparation of [Co$_2$(en)$_4$(H$_2$O)$_2$P$_2$Mo$_5$O$_{23}$]·8H$_2$O. The complex *cis*-[Co(en)$_2$(H$_2$O)(HPO$_4$)]$^+$ was prepared by dissolving 0.56 g of [Co(en)$_2$PO$_4$]·H$_2$O (2 mmol) in 100 ml of water and adjusting the pH to 4.7 with dilute sulfuric acid.[5] A solution containing 1.45 g of Na$_2$MoO$_4$·2H$_2$O (6 mmol) in 20 ml of water was adjusted to pH 4.4 with dilute sulfuric acid. Both solutions were separately filtered to remove dust and the filtrates were chilled to 10–15 °C in an ice bath. The molybdate solution was added dropwise to the cobalt solution, keeping the pH of the mixture at 4.4–4.7 by the addition of sulfuric acid and keeping the temperature at 10–15 °C. A brick red precipitate began to form when ca. 2 ml of the molybdate solution had been added. After the final addition of the molybdate solution, the suspension was kept in a refrigerator for 2 h. The precipitate was collected by filtration, washed successively with large amounts of water acidified to pH 4.5 and acetone, and air-dried. The dried product was red-violet and weighed 1.1 g. Anal. Calcd for Co$_2$C$_8$N$_8$H$_{32}$P$_2$Mo$_5$O$_{23}$·8H$_2$O: C, 6.64; H, 3.62; N, 7.73; P, 4.28; Mo, 33.12; H$_2$O, 9.95. Found:[8] C, 6.69; H, 3.63; N, 7.82; P, 4.41; Mo, 33.14; H$_2$O (weight loss at 110–115 °C), 11.26.

Results and Discussion

The complex is insoluble in water at pH 3–5 and in common polar and nonpolar solvents (alcohols, dimethyl sulfoxide, dimethylformamide, propylene carbonate, acetonitrile, nitromethane, benzene, etc.). At pH 6 or above the complex dissolves to give a clear solution of [Co(en)$_2$PO$_4$] (maximum at 529 nm) and, presumably, MoO$_4$$^{2-}$ ions. If this solution is reacidified to pH ca 4., the heteropoly complex is re-formed.

The analytical data support the formulation as a neutral zwitterion (or alternatively as a binuclear cobalt complex), [(en)$_2$(H$_2$O)CoOPO$_3$(Mo$_5$O$_{15}$)O$_3$POCo(H$_2$O)(en)$_2$]·8H$_2$O [I].

The infrared spectrum of the complex in the metal–oxygen stretching region is shown in Figure 1, together with that of sodium pentamolybdodiphosphate, and is characteristic[2] of the