be separated by fractional crystallization. A small sample was isolated by g.l.c.; however, this procedure introduced a few per cent of new impurities from decomposition in the detector cell. It melted quite sharply at 135°; g.l.c. retention time, 13 min. The reflections from the X-ray pattern were at 9.06 (m), 8.35 (m), 7.99 (s), 7.16 (w), 4.74 (w), 4.60 (w), 4.47 (w), 4.36 (w), 4.14 (w), 4.05 (w), 3.89 (w), and 3.78 (w) Å. The infrared spectrum (in CS_2) showed a strong siloxane absorption at 1125 cm.$^{-1}$, a shoulder near 1085 cm.$^{-1}$ characteristic of the $SiOC_2H_5$ group, and a weak absorption at 788 cm.$^{-1}$ on the side of the 774 cm.$^{-1}$ band.

Anal. Calcd. for $C_{11}H_{32}O_{14}Si_9$: mol. wt., 641.2. Found: mol. wt. (mass spectrum), 640 ± 5.

Relative Thermodynamic Stabilities.—A solution containing 0.50 g. of methyl-T_{10} and 0.050 ml. of 0.1610 N ethanolic KOH (equilibration catalyst) in 25 ml. of toluene was refluxed for 84 hr. The composition of the solution was determined by g.l.c. at 24-hr. intervals; equilibrium was attained within 24 hr. G.l.c. detected only five volatile components, almost equally spaced as to retention times. The first, second, third, and fifth of these corresponded in retention times to T_8, $T_9(OC_2H_5)$, T_{10}, and T_{12}, respectively. It was assumed that the fourth peak was due to a $T_{11}(OC_2H_5)$ species. In addition, a non-volatile oil, presumably of higher polymers, was present. The over-all composition (% by weight; reliable to ±15%) of the equilibrated

species was found to be 8% methyl-T_8, 7% methyl-$T_9(OC_2H_5)$, 19% methyl-T_{10}, 6% "methyl-$T_{11}(OC_2H_5)$," 10% methyl-T_{12}, and 50% non-volatile oil. There were no peaks with retention times expected for such species as methyl-T_6, methyl-$T_7(O-C_2H_5)$, methyl-$T_{13}(OC_2H_5)$, or methyl-T_{14}; if any of those species were present their concentrations were below 0.15%. Thus, at equilibrium in 2% solution in toluene at 110° the relative molar concentrations of the completely condensed species, methyl-T_6, -T_8, -T_{10}, -T_{12}, and -T_{14}, were in the ratios <0.01: 1.2:2.3:1.0: <0.01, respectively.

Phosphine Sulfides and Selenides: The Phosphorus–Sulfur and Phosphorus–Selenium Stretching Frequencies

By RALPH A. ZINGARO

The fundamental P=X stretching frequency, where X is a sulfur or selenium atom, has been assigned in 15 phosphine sulfides and 13 phosphine selenides. The effect of coördination with halogen molecules on this vibration also has been observed. A statistically significant correlation has been shown to exist between the position of the P=S band and the nature of the substituents attached to the phosphorus atom.

Introduction

Prior to the investigations of Hooge and Christen,[1] who reported the spectra of trimethyl- and triethylphosphine sulfides, no additional spectra of $R_1R_2R_3P=S$ molecules, in which the three R- substituents are all linked directly to the phosphorus atom *via* carbon atoms, have been reported. Gore[2] and Daasch and Smith[3] have investigated a number of thiophosphates and McIvor, Grant, and Hubley[4] have investigated the monothionopyrophosphates.

The highest observed frequency for the P–S fundamental vibration is that at 860 cm.$^{-1}$ for $PS(NH_2)_3$,[5] while the lowest observed value is that at 535 cm.$^{-1}$ reported for triethylphosphine sulfide.[1] A proposed

range for the P=S vibration of 840–600 cm.$^{-1}$ has been suggested.[6]

In some recent studies[7] on the effect of halogen complexing on the spectra of phosphine oxides and sulfides, tentative assignments were made for the P=S frequencies in a few phosphine sulfides. It is now established that when three phosphorus–carbon links are present these frequencies lie beyond the range of rock salt and a revision of these earlier assignments is necessary.

Thomas and Chittenden[8] have reported the range from 473–577 cm.$^{-1}$ as the region of the P=Se fundamental vibration in five phosphorus–selenium bonded compounds and 568–835 cm.$^{-1}$ as that of the P=S vibration, but we have no details as to the structures of

(1) F. N. Hooge and P. J. Christen, *Rec. trav. chim.*, **77**, 911 (1958).
(2) R. C. Gore, *Discussions Faraday Soc.*, **9**, 138 (1950).
(3) L. W. Daasch and D. C. Smith, *Anal. Chem.*, **23**, 853 (1951).
(4) R. A. McIvor, G. A. Grant, and C. E. Hubley, *Can. J. Chem.*, **34**, 1611 (1956).
(5) E. Steger, *Z. Elektrochem.*, **61**, 1004 (1957).

(6) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., Second Ed., 1958, pp. 321, 322.
(7) R. A. Zingaro and R. M. Hedges, *J. Phys. Chem.*, **65**, 1132 (1961).
(8) L. C. Thomas and R. A. Chittenden, *Chem. Ind.* (London), 1913 (1961).

the compounds investigated.[9] The present studies corroborate these assignments.

Experimental

The spectra were recorded on a Perkin-Elmer Model 21 double-beam spectrophotometer, using NaCl and CsBr optics. Calibration in the rock salt region was carried out by comparison with a polystyrene standard. In the cesium bromide region the 14.986 μ band of carbon dioxide and water bands at 21.84, 23.86, and 25.14 μ were used as calibration standards.

The preparation of all of the phosphines, phosphine sulfides and selenides,[10] and their halogen addition compounds[11] is described elsewhere.

The phosphines were handled in a closed, dry nitrogen atmosphere. Hygroscopic materials such as triethylphosphine sulfide were handled similarly up to pressing of the plate, after which no special precautions were taken to exclude moisture. All samples were measured immediately after removal from sealed glass vials, in which they had been stored under nitrogen.

Results and Discussion

Except in the case of the trimethyl compound, or when the selenide was not prepared, the assignment of the P=S or P=Se vibration was based upon a comparison of the series of molecules R_3P, R_3PS, and R_3PSe. When the R groups are identical, these molecules possess C_{3v} symmetry and the P–C stretching vibrations should be displaced only very slightly in such a series of compounds. A band present in the sulfide, but absent in the spectra of both the phosphine and the phosphine selenide, can plausibly be assigned to the P=S band. The validity of this approach is described in more detail elsewhere.[1] Fortunately, among all of the compounds studied, the P=S and P=Se vibrations were strong and easily characterized. Also, the phosphines are quite transparent in the 400–600 cm.$^{-1}$ range. The symmetric P–C vibrations are located at the long wave length limit of the rock salt region ($\geq$600 cm.$^{-1}$),[1,3] and what are presumably skeletal ring vibrations appear at *ca.* 500 cm.$^{-1}$. Thus, provided that no halogen atoms are present, the identification of the P=S or P=Se stretching frequency can be made with confidence.

Examination of Fig. 1 readily demonstrates the facts just discussed. The strong vibrations due to the carbon skeleton can be observed in the 500 cm.$^{-1}$ region and they obviously are characteristic of all three molecules. Comparison of the spectra between 667 and 525 cm.$^{-1}$ readily demonstrates the ease with which the vibrations of interest may be located. Such assignments were even simpler to make in the case of the trialkyl derivatives because of their transparency in the 500 cm.$^{-1}$ region.

Because previous studies[6] suggest that the P=S vibration is frequently found in the rock salt region, each series of molecules also was investigated with a sodium chloride prism. Only in the case of diphenyl-

(9) An abstract of a paper by the same authors, *viz.*, L. C. Thomas and R. A. Chittenden, Parton Technical Paper No. 784, July 28, 1961, reveals essentially the same information as in ref. 8. The original paper has not yet become available to us for examination.

(10) R. A. Zingaro and R. E. McGlothlin, "Phosphines, Phosphine Sulfides and Phosphine Selenides," *J. Chem. Eng. Data*, in press.

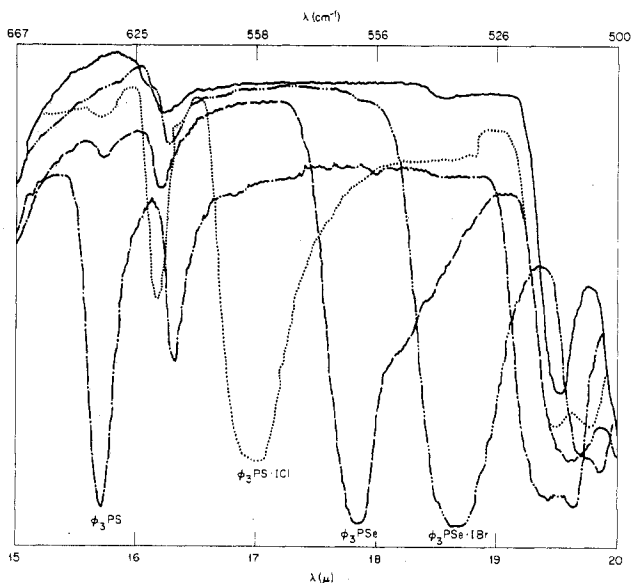(11) R. A. Zingaro and E. A. Meyers, *Inorg. Chem.*, **1**, 771 (1962).

Fig. 1.—Infrared absorption of some phosphine sulfides and selenides and their halogen addition compounds in the 15–20 μ region. The spectrum of triphenylphosphine is shown by the solid trace.

chlorophosphine sulfide was searching in the rock salt region fruitful.

The liquid prepared by fusion of sulfur with phenyldichlorophosphine and subsequent vacuum distillation was examined carefully throughout the 1000–500 cm.$^{-1}$ region, but revealed no evidence of a P=S band. Even careful searching with a grating instrument (Beckman IR-VII) under high resolution failed to disclose the presence of any bands other than those observed in the parent phosphine. A strong absorption at $\sim$685 cm.$^{-1}$, characteristic of both compounds, was easily resolved into a pair of absorptions at 691 and at 683 cm.$^{-1}$ in the case of the phenyldichlorosphine, which exhibits C_s symmetry. Under the same conditions, or at even higher resolution, the sulfide derivative did not show such splitting. Inasmuch as this is the region of P–C stretching absorptions, this is not unexpected. We suggest that this may be due to isomerization to $C_6H_5ClPSCl$ with an accompanying change from C_s to the lower C_i symmetry.

Gore,[2] using Gordy's rule,[12] calculated the region from 500–750 cm.$^{-1}$ as that in which the P=S stretching frequency should occur. Analogous calculations were carried out for the P=Se vibration. Using a value of 2.07 Å. for the internuclear distance and a bond order of two, we obtain a value of 559 cm.$^{-1}$ for an isolated P=Se vibration having "pure, double-bond" character. A lower limit of 388 cm.$^{-1}$ is calculated for an isolated P–Se vibration using 2.27 Å. as the internuclear distance and a bond order of one. The force constants for P=Se, in dynes/cm., calculated according to Gordy's rule, are 2 × 10^5 and 4 × 10^5, corresponding to bond orders of one and two, respectively.

Examination of Table I reveals (neglecting the trimethyl and triethyl compounds for the moment) that

(12) W. Gordy, *J. Chem. Phys.*, **14**, 305 (1946).

Table I
P=S and P=Se Frequencies of Phosphine Sulfides and Selenides

Derivative	Physical state	$\bar\nu_{P-S}$ μ	cm.$^{-1}$	$(\Delta\bar\nu_{P-S})^{1/2}$,[e] cm.$^{-1}$	$\bar\nu_{P-Se}$ μ	cm.$^{-1}$
1. Trimethyl-	Solid, KBr plate	17.55	570		22.69	441
2. Triethyl-	Solid, KBr plate	18.59	538		23.70	422
	Satd. soln. in CS$_2$	18.13	552			
3. Tris-(*n*-propyl)-	Pure liquid	16.79	⌈596⌉[a]	36	20.18	496
		17.15	⌊583⌋		(21.54 ?	464)[b]
4. Tris-(*n*-butyl)-	Pure liquid	16.79	596	38	19.56	511
5. Tris-(*n*-amyl)-	Pure liquid	16.69	⌈599⌉[a]	30	19.74	507
		17.01	⌊588⌋			
6. Triphenyl-	Solid, KBr plate	15.94	627			
7. (C$_6$H$_5$)$_3$PS·1.5I$_2$	Solid, KBr plate	16.95	590			
8. (C$_6$H$_5$)$_3$PS·ICl	Solid, KBr plate	16.99	589			
9. Triphenyl-	Solid, KBr plate				17.86	560
10. (C$_6$H$_5$)$_3$PSe·IBr	Solid, KBr plate				18.70	535
11. Tricyclohexyl-	Solid, KBr plate	16.16	619		18.42	543
12. (Tricyclohexyl)-PSe·IBr	Solid, KBr plate				19.38	516
13. Diphenylmethyl-	Pure liquid	16.18	⌈618⌉[a]	26	18.90	529
		16.43	⌊609⌋			
14. Diphenylethyl-	Solid, KBr plate	16.65	⌈601⌉[c]		19.06	525
		16.69	⌊599⌋			
		16.73	598			
15. Diphenyl-(*n*-butyl)-	Solid, KBr plate	16.20	⌈617⌉[d]		18.98	527
		16.54	⌊605⌋			
16. Dimethylphenyl-	Solid, KBr plate	17.10	585			
17. Dimethylphenyl-	Pure liquid				20.58	486
18. Diethylphenyl-	Pure liquid	17.30	578	22	19.38	516
19. Bis-(*n*-butyl)-phenyl-	Solid, KBr plate	16.76	597		19.38	516
20. Diphenylchloro-	Pure liquid	15.15	660			
21. Dichlorophenyl-	Pure liquid	Undetermined				

[a] Poorly resolved doublet. [b] Weak band. [c] Shoulders. [d] Clearly resolved doublet. [e] The band width at half-intensity is given only in those cases where the shape and symmetry of the band was such that the calculation could be made with relative ease and reasonable accuracy.

in the case of trialkyl or triaryl phosphine sulfides, the P=S vibration is found in the rather limited range of 610 ± 20 cm.$^{-1}$. The low frequencies observed for the methyl and ethyl compounds are most reasonably associated with very strong intermolecular forces which tend to enhance the ionic character of the bond and reduce the bond order. The triethyl compound exhibits the lowest observed P=S vibration in the entire homologous series. This corroborates previous observations.[1] It is of further interest to note that the very same situation prevails among the phosphine selenides in which the triethyl compound again exhibits the lowest frequency of any of the observed P=Se vibrations. As would be expected, proceeding from the solid to solution leads to a weakening of the intermolecular forces and a higher observed frequency (Table I, 2).

The replacement of an alkyl group by the electron withdrawing phenyl group should lead to an increase in the P=S bond order and consequent increase in the vibrational frequency. This is observed in the R$_3$PS, R$_2$C$_6$H$_5$PS, R(C$_6$H$_5$)$_2$PS sequences, where R is an ethyl, methyl, or *n*-butyl group (Table I). The increase, however, is relatively small when only one phenyl group is present and the extremely slight difference observed in the P=S frequencies between the triphenyl and tricyclohexyl compounds suggests that mass effects and steric factors may play an important role. An attempt to place these observations on a more quantitative basis will be given subsequently.
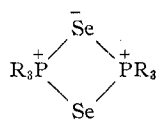
The observations made in the case of the phosphine sulfides hold equally well for the selenides. Excepting the triphenyl, trimethyl, and triethyl derivatives for the moment, all of the other ten derivatives exhibit the characteristic P=Se vibration in the rather narrow range from 496–543 cm.$^{-1}$. The effect of replacing an alkyl group by a phenyl group also parallels that observed for the phosphine sulfides.

The effect of halogen complexing on both the P=S and the P=Se vibrations (Table I, 7, 8, 10, 12) is to lower the frequencies by 25–60 cm.$^{-1}$. This is in the same direction and of the same order of magnitude as was observed[7] in the case of the halogen–phosphine oxide interaction. Conclusions arrived at from previous observations[7] which have been presently shown to be based upon incorrect P=S assignments still appear to be plausible. The most reasonable explanation is that there is a net decrease in electron density around the S or Se atom following halogen complexing. There naturally follows a decrease in $p\pi_{S(or\ Se)} \rightarrow d\pi_P$ backbonding and a net decrease in the P–S bond order. This means there is a lowering of the P–S force constant and a lowering of the frequency. This explanation, along with a discussion of the mass coupling effect, already has been reported in greater detail.[7]

Gordy[12] has found that an increase in the formal charge on one of the atoms of a bond should increase the stretching force constant, providing the bond order remains unchanged. The fact that the triphenyl

derivative in both series of compounds possesses the highest vibrational frequency for the atom pair is in line with such a suggestion. The strongly electron-withdrawing power of the phenyl group would impose a positive formal charge on the phosphorus atom. From the equation for a simple harmonic oscillator, a value of 4.1×10^5 dynes/cm. is calculated for the force constant, k_{P-Se}, in triphenylphosphine selenide.

The low values observed for the frequencies of the P–S vibration in the trimethyl and triethyl derivatives suggest strong intermolecular association involving the P=S (or P=Se) links. Using the observed experimental value for $\tilde{\nu}_{P-Se}$ in triethylphosphine selenide, a value of 2.3×10^5 dynes/cm. is estimated for k_{P-Se}. This low value suggests a decreased bond order, which would arise from strong molecular association *via* $\overset{+}{P}\text{–}\overset{-}{Se}$, (or $\overset{+}{P}\text{–}\overset{-}{S}$) dipoles, *e.g.*

$$R_3\overset{+}{P} \diagdown_{\overset{\displaystyle \bar{Se}}{}}^{\diagup \overset{\displaystyle \bar{Se}}{}} \overset{+}{P}R_3$$

Intermolecular association has been proposed as an explanation for splitting of the P=S bond both here and elsewhere.[1]

Hooge and Christen[1] have shown that the location of the P=S vibration can be correlated with the number of heavy atoms attached to the phosphorus atom. Their straightforward treatment involving the dependency of the P=S vibration upon the mass of the phosphorus substituents, X, and the P–X force constant does an acceptable job of explaining the observed experimental facts.

We have made a reasonably thorough attempt to correlate the fundamental P=S vibration with the steric and polar nature of the phosphorus substituents. The molecules chosen were the 14 which were the subject of this investigation in addition to the trichloro, tribromo, dichloromethyl, and dichloroethyl compounds whose P=S vibrational frequencies are tabulated.[1] Two sets of steric factors, E_s, were used, both taken from the published literature.[13] Set A[14] assigns a value of 1.24 to the phenyl group, while set B[15] assigns a value of -0.31 to the phenyl group and also furnishes the values -0.17 for Cl and -0.20 for Br, all normalized to a zero value for the methyl group. Thus, the E_s values of set A differ from those in set B only if phenyl groups are present in the molecule. The values of σ^*, the polar substituent constants, were taken from the same source[16] and are largely a measure of electron withdrawing power.

The experimentally observed values of $\tilde{\nu}_{P-S}$ were fitted to an empirical equation of form 1 by the method of least squares.

$$\tilde{\nu}_{P-S} = \tilde{\nu}_0 + a\Sigma E_s + b\Sigma\sigma^* + c\Sigma(E_s)(\sigma^*) \qquad (1)$$

(13) M. S. Newman, Ed., "Steric Effects in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1956.

(14) Reference 13, Chapter 13, Table VI, p. 598.

(15) Reference 13, Chapter 13, Table VII, series 2-2.

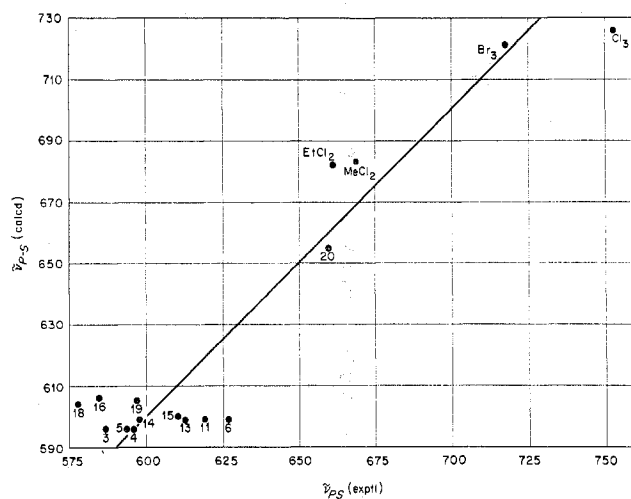(16) Reference 13, Chapter 13, Tables XIb and XII.

Fig. 2.—Correlation of the observed values of $\tilde{\nu}_{P-S}$ in trisubstituted phosphine sulfides with values calculated according to eq. 3. The numbered points correspond to the compounds listed in Table I.

A total of 21 equations was obtained, seven equations corresponding to each of three groups of molecules. These equations measured the regression of $\tilde{\nu}_{P-S}$ on E_s alone using values corresponding to either set A or set B as previously defined; on σ^* alone; on σ^* and E_s using each set of E_s values; and on σ^*, E_s, and $(E_s)(\sigma^*)$ using each of the two sets of E_s values.

The first group of molecules chosen included all of the 18 previously indicated. None of the empirical equations obtained by use of this set of molecules gave predicted values of statistical significance. The deviations in the predicted values were much too high for Cl_3PS and Br_3PS and much too low for $(CH_3)_3PS$ and $(C_2H_5)_3PS$.

The second group included all of the compounds, but excluded the two trihalo-substituted derivatives. The maximum value of the multiple correlation coefficient, R, using this second set of molecules, was 0.673 by eq. 2,

$$\tilde{\nu}_{P-S} = 591 - 2.81\Sigma E_s + 15.1\Sigma\sigma^* + 7.87\Sigma(E_s)(\sigma^*) \quad (2)$$

in which the values of E_s correspond to those of set B. If the regression of $\tilde{\nu}_{P-S}$ upon σ^* alone was considered, the multiple correlation coefficient was 0.636. The regression of $\tilde{\nu}_{P-S}$ upon E_s alone was completely insignificant, R being -0.021.

The most useful correlation was obtained when the trimethyl and triethyl derivatives were excluded, and the halogen derivatives were retained. This set gave eq. 3, using E_s values of B, and R is 0.890.

$$\tilde{\nu}_{P-S} = 599 - 2.81\Sigma E_s + 14.1\Sigma\sigma^* - 0.406\Sigma(E_s)(\sigma^*) \quad (3)$$

The regression of $\tilde{\nu}_{P-S}$ on σ^* is given by eq. 4, for which R is 0.887.

$$\tilde{\nu}_{P-S} = 599 + 14.3\Sigma\sigma^* \qquad (4)$$

These correlations must be considered highly significant,[17] as the correlation coefficients lie within the 1% point.

(17) G. W. Snedecor, "Statistical Methods," Iowa State College Press, Ames, Iowa, 1946, p. 351.

In Fig. 2 the values of $\bar{\nu}_{P-S}$ calculated by use of eq. 3 are plotted against the experimentally observed values. It will be noted that the largest deviations are observed for the cyclohexyl compound, 11; the phenyl-bearing compounds, 16, 18, 6; and the trichloro derivative.

These results clearly indicate that the electronegativity of the substituents on the phosphorus atom plays a most important role in determining the frequency of the fundamental P=S vibration. The steric factors appear to be of secondary importance. The very strong association among molecules containing ethyl and methyl substituents undoubtedly accounts for the unusually low frequencies observed for the P=S vibrations in these molecules.

The range of 770–750 cm.$^{-1}$ suggested by Thomas[18] for the frequency range of the P=S vibration in phosphine sulfides is obviously too narrow. The range for the P=Se vibration as reported by Thomas and Chittenden[8] is essentially correct but the limit at which

(18) Reference 6, p. 322.

this frequency may be observed needs to be lowered to at least 422 cm.$^{-1}$.

The use of a single force constant for the P=S link,[1] while it may provide a simplifying assumption made for the purpose of observing mass effects, must be considered a useful approximation. The wide range over which $\bar{\nu}_{P-S}$ is observed (535–860 cm.$^{-1}$) in addition to the obvious influence of the electronegativity of the phosphorus substituents means that k_{P-S} also must vary.

Contribution from the Department of Chemistry,
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Magnetic Oxides of Molybdenum(V) and Tungsten(V) with the Ordered Perovskite Structure[1]

By FRANK K. PATTERSON, CARL W. MOELLER, and ROLAND WARD

Compounds with the type formula $A_2B'B''O_6$ have been prepared in which A is an alkaline earth ion and B″ is pentavalent molybdenum or tungsten. When B′ is Fe(III), or Cr(III), ferrimagnetic compounds are obtained. The compounds are of the perovskite type and, in the case of the iron compounds, are shown by X-ray diffraction data to be ordered. Very weak superlattice lines were observed in the pattern of Sr_2CrWO_6 but none was found in that of Sr_2CrMoO_6. Partial ordering for these compounds is suggested on the basis of their magnetic properties. $Ba_3Cr_2MoO_9$ and $Ba_3Cr_2WO_9$ have the hexagonal barium titanate structure and are not ferrimagnetic.

Compounds of the type $A_2B'B''O_6$ tend to adopt the perovskite structure when A is a large cation capable of 12-fold coördination with oxygen while B′ and B″ are smaller cations suitable for octahedral coördination. If the difference in charge of the B′ and B″ cations is large, these ions assume an ordered arrangement in the perovskite lattice. This has been demonstrated with compounds such as Ba_2ZnWO_6,[2] Ba_2NaReO_6,[3] and Ba_2FeReO_6.[4]

In the ideal cubic perovskite structure the oxygen octahedra surrounding the B cations are regular, and each oxygen is shared by two B cations with a B–O–B angle of 180°. Such an arrangement is ideal for interaction of the B cations by the mechanism of super-

exchange.[5] With paramagnetic B cations of different moment in alternating B positions, the compound should exhibit ferrimagnetism. This was demonstrated in the case of rhenium(VI) compounds.[4,6] There was some doubt that this principle could be extended to the preparation of magnetic oxides of molybdenum(V) and tungsten(V) of the type $A_2{}^{II}B^{III}MoO_6$. A comparable compound, Ba_2FeTaO_6, showed no evidence of superstructure in its X-ray powder diffraction diagram.[7] On the other hand, differences in ionic radii of the two B cations has been shown to lead to an ordered arrangement in compounds such as $Ba_2B^{III}TaO_6$ when B^{III} is a rare earth ion.[8]

This paper describes the preparation and properties of the series of compounds $A_2B^{III}B^VO_6$, where B^{III} is Fe or Cr and B^V is Mo(V) or W(V).

(1) Abstracted from the Master's Thesis of Frank K. Patterson submitted to the Graduate School of the University of Connecticut, 1962.

(2) E. J. Fresia, L. Katz, and R. Ward, *J. Am. Chem. Soc.*, **81**, 4783 (1959).

(3) A. W. Sleight and R. Ward, *ibid.*, **83**, 1088 (1961).

(4) J. Longo and R. Ward, *ibid.*, **83**, 2816 (1961).

(5) E. O. Wollan, *Phys. Rev.*, **117**, 387 (1960).

(6) A. W. Sleight, J. Longo, and R. Ward, *Inorg. Chem.*, **1**, 245 (1962).

(7) F. Galasso, L. Katz, and R. Ward, *J. Am. Chem. Soc.*, **81**, 820 (1959).

(8) F. Galasso and W. Darby, *J. Phys. Chem.*, **66**, 131 (1962).