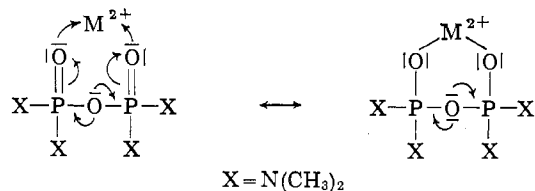


establish the chelate structure the P—O—P stretch must be examined. The frequency shift of the P—O—P stretch in all cases except two is in the direction of higher frequency, which indicates a stronger bond or higher bond order. This may be explained by considering the structures



After forming the proposed chelate structure, the polarization effects of the metal ion will tend to decrease the double bond character of P=O and at the same time draw the electron pairs from the P—O—P oxygen into $p_\pi-d_\pi$ overlap with phosphorus. The overall effect is to decrease the P=O stretching frequency and increase the P—O—P stretching frequency. The decrease in P=O stretching frequency is observed in all complexes prepared in this study, and all but two show an increase in the P—O—P stretching frequency.

Further evidence for coordination through the phosphoryl oxygen is found by looking at the P—N stretching frequency, which shifts to higher frequencies in all cases. The decrease in the P=O bond order that occurs when the metal ion coordinates to the phosphoryl oxygen can cause the lone pair on nitrogen to delocalize into the available d_π orbitals on the phosphorus. This would increase the P—N bond order.

The presence of coordinated water in $Mg(NO_3)_2 \cdot 2OMPA \cdot 2H_2O$, $MgCl_2 \cdot 2OMPA \cdot 2H_2O$, $LiCl \cdot OMPA \cdot 2H_2O$, $LiNO_3 \cdot OMPA \cdot 3H_2O$, and $CaCl_2 \cdot OMPA \cdot 4H_2O$ was established by an absorption peak in the infrared spectrum of each of these compounds in the 3300–3400 cm^{-1} region.²² This peak is absent in all of the other complexes.

The positions and relative intensities of d_{hkl} for the

(22) F. A. Miller and C. H. Wilkins, *Anal. Chem.*, **24**, 1253 (1952).

3:1 complexes are given in Table III. The d_{hkl} values for $Ni(ClO_4)_2 \cdot 3OMPA$ are included for comparison. The X-ray data indicate that the 3:1 complexes are isomorphous. Earlier work with spectra of $Ni(ClO_4)_2 \cdot 3OMPA$ dissolved in nitromethane supported the assignment of an octahedral configuration to this complex in solution.⁴ The similarity of the X-ray data for the 3:1 complexes in this study supports the assignment of an octahedral configuration to the metal ions in these complexes.

TABLE III
X-RAY POWDER PATTERN DATA^a

$Mg(ClO_4)_2 \cdot 3OMPA$		$Ca(ClO_4)_2 \cdot 3OMPA$		$Pb(ClO_4)_2 \cdot 3OMPA$	
d_{hkl}	I/I_{100}	d_{hkl}	I/I_{100}	d_{hkl}	I/I_{100}
11.78	57	11.62	32	11.78	100
9.82	29	9.30	24	9.82	57
7.37	64	7.19	75	7.62	51
6.23	81	6.23	100	5.98	78
5.75	88	5.94	71	5.64	86
4.87	64	4.92	61	4.67	38
4.23	100	4.23	83	4.29	43
3.93	52	3.93	66	3.81	48
3.85	52	3.60	17	3.55	20
3.53	18	3.58	17	3.31	21
3.13	33	3.16	27	2.89	17
2.95	15	2.88	17		
2.79	15				
$Al(ClO_4)_3 \cdot 3OMPA$		$Cd(ClO_4)_2 \cdot 3OMPA$		$Ni(ClO_4)_2 \cdot 3OMPA$	
d_{hkl}	I/I_{100}	d_{hkl}	I/I_{100}	d_{hkl}	I/I_{100}
10.27	78	11.62	65	10.77	77
9.50	62	9.30	32	9.02	25
6.32	100	8.93	33	7.13	99
5.43	79	7.19	100	6.02	63
4.44	57	6.41	70	5.37	100
4.19	47	4.92	47	4.77	46
3.98	60	4.23	64	4.09	77
3.49	19	3.90	82	3.81	60
2.98	10	3.62	14	3.08	31
2.79	11	3.15	29	2.88	19

^a d_{hkl} is reported in Å; I_{100} is the most intense line.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF
TEXAS A&M UNIVERSITY, COLLEGE STATION, TEXAS

The Synthesis of Tetraphosphorus Triselenide: Preliminary Infrared, Nuclear Magnetic Resonance, and Raman Studies

BY KURT IRGOLIC, RALPH A. ZINGARO, AND MOHAN KUDCHADKER

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A highly simplified method for the preparation of the soluble modification of P_4Se_3 is described. Very simple apparatus is used and the material is obtained in good yield and a high degree of purity. Some preliminary studies of the infrared, Raman, ³¹P n.m.r., visible, and ultraviolet spectra of this molecule are reported.

Tetraphosphorus triselenide has been prepared in two ways. Meyer¹ fused a stoichiometric mixture of

(1) J. Meyer, *Z. anorg. Chem.*, **30**, 249 (1902).

red or yellow phosphorus with selenium and isolated P_4Se_3 as a red solid by distillation at 360–400°. He reported it to be only slightly soluble in carbon disul-

fide. Behrens² purified this compound by high vacuum sublimation. Mai³ prepared P_4Se_3 by heating a mixture of yellow phosphorus and selenium in tetralin. The product thus obtained was easily soluble in warm carbon disulfide, benzene, and tetrachloroethane. These differences in behavior led Mai³ to suggest that this compound exists in two different crystalline modifications.

We have had need of the soluble material in relatively large amounts for use in synthetic work, and because of the extremely disappointing results obtained both with respect to purity and yield, we have reinvestigated the preparation of this compound. This paper describes a highly simplified method for the preparation of P_4Se_3 with the use of very simple apparatus, which gives the material in good yield and in a high degree of purity.

Although the crystal structure of the soluble form of P_4Se_3 has been studied in detail,⁴ we have been unable to locate any information on its vibrational spectrum and the results of a preliminary investigation of the infrared, Raman, and ³¹P n.m.r. spectra of this molecule are also reported.

Experimental

Preparation of Tetraphosphorus Triselenide.—A three-necked 500-ml. flask was equipped with a stirrer and distilling head while the third neck was sealed with a stopper. The flask was charged with 170 ml. of *n*-heptane, 5 g. (0.16 g.-atom) of yellow phosphorus (purified grade), 10 g. (0.127 g.-atom) of finely powdered gray selenium,⁵ and 15 g. of powdered charcoal. The mixture was refluxed⁶ for 1 hr., after which time 75 ml. of reagent grade tetralin was added through the third neck. After the addition of the tetralin, the heptane was removed by distillation through the distilling head. The temperature was slowly raised over a period of 45 min. until it reached 207°. The hot solution was allowed to settle and the clear hot liquid was passed through a coarse filter. The residue in the flask, which consisted of charcoal, selenium, and the phosphorus selenide, was extracted with three 30-ml. portions of hot tetralin, and the washings were added to the first filtrate. The combined tetralin solutions were cooled in ice and the tetraphosphorus triselenide separated as a fine yellow-orange crystalline powder. The product was easily recrystallized from benzene. The yield of recrystallized product, m.p. 245–246°, was 55–60%.

Anal. Calcd. for P_4Se_3 : P, 34.34; Se, 65.66. Found: P, 34.15; Se, 65.29.

Spectra.—Infrared spectra were measured in saturated carbon disulfide and benzene solutions, as KBr pellets and as Nujol mulls. Absorption in the rock-salt region was measured on a Beckman Model IR-9. The region from 600 to 250 cm^{-1} was measured on a Perkin-Elmer Model 21 equipped with cesium bromide optics.

Raman spectra were measured in saturated carbon disulfide solutions on a Cary Model 81 spectrometer.⁷

The ³¹P n.m.r. spectrum was run as a saturated solution in carbon disulfide on a Varian HR 60 spectrometer operating at 24.3 Mc.

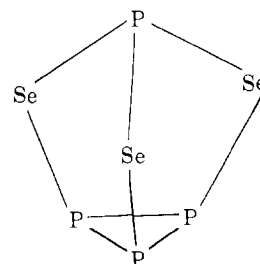


Figure 1.

Results and Discussion

The yellow-orange substance prepared by this method is the soluble modification of P_4Se_3 and it melted at 245–246° (Mai² reports 242°). We have varied all of the procedural parameters, and conditions described are close to optimum.

The heptane readily dissolves the phosphorus and the charcoal apparently functions as a catalyst. Indeed, in the absence of charcoal the reaction proceeds very inefficiently. The reaction takes place at temperatures above 160°. It is to be noted that no difficulties were encountered in spite of the fact that an inert atmosphere was not employed.

The molecule of the soluble form of P_4Se_3 ⁴ belongs to the same space group as the low-temperature modification of P_4S_3 . The structure is shown in Figure 1.

The vibrational spectrum of P_4S_3 has been examined by Gerding, Maarsen, and Nobel.⁸ This molecule has the same structure as P_4Se_3 (Figure 1) and possesses a C_{3v} symmetry. These authors describe a total of nine frequencies for this molecule; four symmetrical A_1 frequencies and five degenerate class E frequencies. However, a tenth fundamental class A_2 frequency is not mentioned.

Since P_4Se_3 is completely isomorphous with its sulfide analog, ten fundamentals, as defined above, should be expected. We have been able to observe a total of only six vibrations, and two of these are uncertain. The primary experimental difficulty involved observation of the Raman spectra. The sources of trouble have been twofold, *viz.*, the strong color of the compound and the rapid development of turbidity in the carbon disulfide solutions upon illumination. The turbidity can be attributed to the formation of colloidal selenium.

Saturated solutions of P_4Se_3 in carbon disulfide and Nujol mulls were transparent in the rock-salt region. The bands observed in the 600–250 cm^{-1} region of the infrared were as follows: 525 cm^{-1} , in the KBr pellet only, very weak; 420 cm^{-1} , weak; and 360 and 317 cm^{-1} , both intense.

The following Raman frequencies were observed, but their intensities are not estimated because of considerable background noise resulting from the high gain which was necessary in order to record the spectrum: 601, 363, 317, and 214 cm^{-1} . The last band

(2) H. Behrens, *Ber.*, **94**, 1196 (1961).

(3) J. Mai, *ibid.*, **59**, 1888 (1926); **61**, 1807 (1928).

(4) E. Keulen and A. Vos, *Acta Cryst.*, **12**, 323 (1959).

(5) Reagent grade selenium powder can be purchased from the Canadian Copper Refiners, Ltd.

(6) Best results were obtained by the use of an oil bath for heating. The use of a heating mantle or other warming devices gave decidedly poorer results.

(7) The exciting line was the Hg 5460 Å.

(8) H. Gerding, J. W. Maarsen, and P. C. Nobel, *Rec. trav. chim.*, **76**, 758 (1957).

was extremely weak and should be considered questionable.

The only definite assignments that can be made with some degree of certainty are those which give rise to the strong infrared absorptions at 360 and 317 cm^{-1} , which are also Raman active. They should parallel those in P_4S_3 , which means that the 360 cm^{-1} (363 cm^{-1} in the Raman) vibration corresponds to the symmetric stretch of the apex phosphorus atom with respect to the three attached selenium atoms, while the 317 cm^{-1} vibration involves the fundamental symmetrical stretching of the P-Se bonds of the triangular phosphorus base atoms with respect to each of the selenium atoms.⁹

The lower limit of an isolated single-bonded P-Se vibration has been calculated from Gordy's rule¹⁰ as 388 cm^{-1} . It is obvious that both of the observed P-Se stretching frequencies in P_4Se_3 are lower than the lower limit calculated for $\bar{\nu}_{\text{P-Se}}$. Gerding, Maarsen, and Nobel⁸ made a similar observation in their studies of P_4S_3 , *viz.*, that the frequencies calculated from force constants obtained from the F matrix elements of P_4S_3 were higher than the observed P-S stretching frequencies. We were unable to improve the agreement between the observed frequencies and those calculated by the use of the rules of Badger¹¹ or Jensovsky.¹² The use of Herzberg's equation,¹³ which takes into account the P-Se-P bond angle, also failed to furnish any improvement.

Inasmuch as the effect of coupling of the two P-Se vibrations is to *increase* one frequency, while lowering the other, coupling between these frequencies does not offer an explanation for the low values observed ex-

perimentally. The most plausible explanation is that the P-Se force constant in P_4Se_3 must be lower than that which is expected for a single P-Se bond, since the bond distances, as shown from the X-ray data, are very close to the values expected for a single bond.

The n.m.r. spectrum was very similar in appearance to that of P_4S_3 as determined by Callis, Van Wazer, Shoolery, and Anderson.¹⁴ It consisted of a doublet at +106 p.p.m. and a quartet at -38 p.p.m., both relative to 85% H_3PO_4 . The coupling constant, $J_{\text{P-Se-P}}$, as measured from the splitting of the doublet was 85 c.p.s. The spectrum is obviously in accord with the structure shown in Figure 1. The quartet is due to the apex phosphorus atom being split by the three basal phosphorus atoms. The doublet is due to the basal phosphorus atoms being split by the apex phosphorus.

The visible and ultraviolet absorption spectra of dilute solutions ($\sim 10^{-4} M$) of P_4Se_3 in heptane were also measured. Absorption of radiation in this region was characterized by a weak band at 3840 Å. ($\epsilon \sim 2.7 \times 10^2$) and an intense absorption at 2360 Å. ($\epsilon \sim 1.0 \times 10^4$). The latter absorption obeys the Beer-Lambert law in the concentration range studied. The lower frequency absorption was too weak to test the Beer-Lambert law.

Because of the experimental difficulties we have encountered, we do not plan any further spectral studies of the vibrational spectrum of this molecule, but it does provide an interesting challenge to the spectroscopist.

Acknowledgments.—We are indebted to Dr. Alan H. Cowley of the University of Texas for running the n.m.r. spectrum and furnishing helpful comments and to the Perkin-Elmer Corporation, Houston, Texas, for making their infrared equipment available to us. Financial support was furnished by the United States Atomic Energy Commission under Contract AT-(40-1)-2733, by the Selenium and Tellurium Development Association, Inc., and by the Robert A. Welch Foundation, Houston, Texas.

(9) The observation of a Raman-active, but infrared-inactive frequency at 363 cm^{-1} in P_4 vapor has been reported [S. Bhagavantam and T. Venkataramduy, *Proc. Indian Acad. Sci.*, **A8**, 119 (1938)]. This raises the question of whether the 363 cm^{-1} absorption observed in P_4Se_3 may arise from a symmetric stretching of the base phosphorus atoms since, in this molecule, this vibration is also infrared active. However, such a vibration would be accompanied by only a very small change in dipole moment and must be very weak. Also, because of the large difference in their masses, the coupling between P-Se and P-P vibrations should be, at best, very weak. Hence, because the 360 and 317 cm^{-1} absorptions are strong, and of approximately equal intensity, the assignments, as given, are very probably correct.

(10) R. A. Zingaro, *Inorg. Chem.*, **2**, 192 (1963).

(11) R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934); **3**, 710 (1935).

(12) L. Jensovsky, *Z. Chem.*, **2**, 334 (1962).

(13) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand and Co., Inc., New York, N. Y., 1945.

(14) C. F. Callis, J. R. Van Wazer, J. N. Shoolery, and W. A. Anderson, *J. Am. Chem. Soc.*, **79**, 2719 (1957).