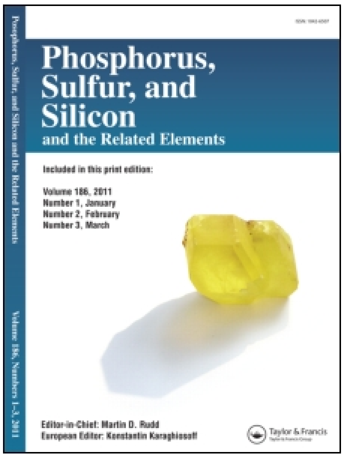

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From $P_4Se_3I_2$ via P_3Se_4I to P_2Se_5

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FROM $P_4Se_3I_2$ VIA P_3Se_4I TO P_2Se_5

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Abstract The reaction of phosphorus with selenium in the molten state yields a glass from which the new molecule P_2Se_5 can be extracted with CS_2. By using ^{31}P- and ^{77}Se-nmr techniques it was shown, that the molecule is not a P_4O_{10} homologue. It has a norbornane-like structure, which is also realized in the related compounds P_3Se_4I and $P_4Se_3I_2$. By using the same technique the new compounds $P_3Se_{4-n}S_nI$ (n=1 and 2) could be synthesized. ^{31}P- and ^{77}Se-nmr spectra show, that Se could only be replaced by S in the monochalcogenide bridge positions.

INTRODUCTION

The synthesis of the compounds α- and β-$P_4X_3I_2$ (X = Se, S) are well known and their structure had been determined[1–4]. The substitution of one PI- group by Se in $P_4Se_3I_2$ gave the compound P_3Se_4I (Figure 1B), whose structure was analysed by Blachnik et al[5] in 1986. The analogous P_3S_4I is still unknown. We are now able to show that in a thermal reaction selenium can be partially replaced by sulphur.

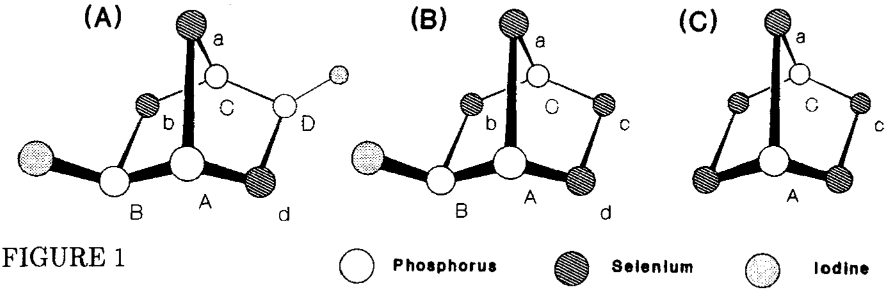

FIGURE 1

THE $P_3Se_{4-n}S_nI$ COMPOUNDS

Experimental

The Elements P, Se, S and I (molar ratio 3:2:2:1) were sealed in an evacuated glass ampoule, heated for one week at 250°C and cooled down to room temperature. After recrystallization of the pulverized product in CS_2, dark red crystals were obtained.

Analysis and results

It has been reported that, in solution at room temperature, P_A and P_B of P_3Se_4I (Figure 1B) undergo mutual exchange.[5] This fluctuation, which produces broadened peaks in the nmr, can be suppressed only at low temperatures. Under these conditions the solubility of the new compounds is so sparing, that a complete analysis of the ^{77}Se-isotopomers was not possible. It is known, that the exchange rates increase in the order $P_3Se_4Cl < P_3Se_4Br < P_3Se_4I$.[6]

Conversion of the reaction product into the chlorides and bromides was effected by reaction with HgX_2 ($X = Cl, Br$) in CS_2 solution.[7] Identification of the ^{77}Se-isotopomers in the chloride mixture was difficult, due to overlap of the signals. Therefore an nmr-analysis was performed only on the bromide mixture. In this case a measuring temperature of 270 K for ^{31}P, 298 K for ^{77}Se and long accumulation times (^{31}P, 16 h; ^{77}Se, 64 h) had to be used, in order to obtain the signals for the ^{77}Se isotopomers. These ^{31}P and ^{77}Se-nmr spectra showed, that, by using the preparation method described in the experimental part, the molecules P_3Se_4I, P_3Se_3SI and $P_3Se_2S_2I$ were present.

We found that S is only inserted in the monochalcogenide bridge position (position a and / or b in figure 1B) but not into the dichalcogenide selenium bridge (position c and / or d in figure 1B). More information was available from the intensities of the signals in the P_3Se_3SI nmr spectra. As shown in Figure 2 the two diastereomers interconvert as a result of the dynamic process described above. The ratio of the integrals indicate, that the $P_3Se_3S_aI$ molecule, with sulphur in position a (Figure 1B and 2) is more stable than $P_3Se_3S_bI$ which has sulphur in position b. This can be rationalized in steric terms, with the smaller sulphur being prefered over selenium for occupation of the bridging position (a in figure 2). This is also in accordance with our results found for the α- and β-$P_4Se_{3-n}S_nI_2$ (n=1, 2) molecules.

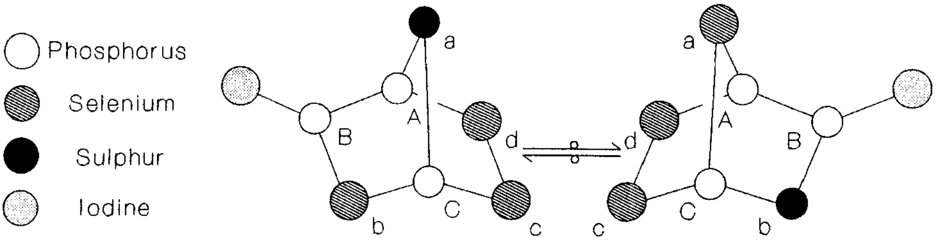

FIGURE 2

DIPHOSPHORUS PENTASELENIDE

Substitution of both PI-groups in $P_4Se_3I_2$ by selenium gives the compound P_2Se_5, first presumed by Berzelius[8] about 200 years ago, but not previously isolated. Our experiments show that P_2Se_5 could be prepared by direct thermal reaction of the elements followed by an extraction with CS_2. Its geometry, shown in Figure 1C, is a result of the ^{31}P- and ^{77}Se-nmr analysis.[9]

Attempts to substitute selenium by sulphur in a thermal reaction have been successful. A ^{31}P- and ^{77}Se-nmr analysis indicates, that sulphur could only be inserted in the monochalcogenide bridge position (Se_a in Figure 1C), which is in excellent agreement with our results found for the $P_3Se_{4-n}S_nI$ series described above and theoretical calculations performed by R. O. Jones and G. Seifert.[10] They have been able to show, that the symmetric isomer with sulphur in position a is about 13.5 $kJmol^{-1}$ (0.14 eV) more stable than the asymmetric one with sulphur in position c (Figure 1C).

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REFERENCES

1. G. W. Hunt and A. W. Cordes, Inorg. Chem., 10, 1935 (1971)
2. G. J. Penney and G. M. Sheldrick, J. Chem. Soc.(A), 1100 (1971)
3. G. J. Penney and G. M. Sheldrick, Acta Cryst., B26, 2092, (1970)

4. R. Blachnik, G. Kurz and U. Wickel, Z. Naturforsch., 39b, 778 (1984)
5. R. Blachnik, W. Buchmeier, C. Schneider and U. Wickel., Z. Naturforsch., 42b, 47 (1987)
6. H. P. Baldus, R. Blachnik, P. Lönnecke and B. W. Tattershall, J. Chem. Soc. Dalton Trans., in publication
7. H. P. Baldus, R. Blachnik, K. Hackmann, Z. Naturforsch., 46b, in publication

8.a J. Berzelius, Briefwechsel J. Berzelius und F. Wöhler, II, 426

8.b J. Meyer, Z. Anorg. Chem., 30, 258 (1902)

9. R. Blachnik, P. Lönnecke, H. P. Baldus and B. W. Tattershall, Angew. Chem. Int. Ed. Engl., 30, No.5, 605 (1991)

10 R. O. Jones and G. Seifert, Institut für Festkörperforschung, D-5170 Jülich, private communication