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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713618290>

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To cite this Article Brownridge, Scott , Calhoun, Larry , Laitinen, Risto S. , Passmore, Jack , Pietikäinen, Jarkko and Saunders, Jeremy(2001) 'Reversible Dissociation of $(\text{SeI}_6)_2(\text{AsF}_6)_2$ in $\text{SO}_2(\text{l})$ ', Phosphorus, Sulfur, and Silicon and the Related Elements, 168: 1, 105 – 110

To link to this Article: DOI: 10.1080/10426500108546538

URL: <http://dx.doi.org/10.1080/10426500108546538>

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Reversible Dissociation of (Se₆I₂)(AsF₆)₂ in SO₂(l)

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The dissociation of (Se₆I₂)(AsF₆)₂ in SO₂(l) has been investigated by ⁷⁷Se NMR spectroscopy at -80 °C involving both a natural-abundance sample as well as that containing selenium enriched in the ⁷⁷Se-isotope (enrichment 92 %). In addition to the previously characterized cations Se₆I₂²⁺, SeI₃⁺, 1,1,4,4-Se₄I₄²⁺, Se₁₀²⁺, Se₈²⁺, and Se₄²⁺, the NMR spectra of the equilibrium solution exhibited additional resonances the assignment of which has been carried out by ⁷⁷Se-⁷⁷Se COSY, selective irradiation experiments, and spectral simulation. Combining this information with the trends in the chemical shifts as well as with iodine, selenium, and charge balances that were calculated from quantitative integrated intensities, the presence of cyclic cations Se₇I⁺ and 1,4-Se₇I₂²⁺, as well as acyclic Se₂I⁺, and 1,1,6,6-Se₆I₄²⁺ (two rotamers) could be inferred. Upon evaporation of the solvent only Se₆I₂²⁺ was found to be present in the solid state.

Keywords: Selenium-iodine cations; ⁷⁷Se NMR spectroscopy

INTRODUCTION

The structural chemistry of selenium-iodine cations has seen rapid progress in recent years.^[1,2] The solid state structures have been established for (Se₆I₂)(AsF₆)₂·2SO₂ and (Se₆I)_n(MF₆)_n (M = As, Sb)^[3]

containing cyclic cations, and for acyclic $(\text{SeI}_3)(\text{AsF}_6)$,^[4,5] $(\text{Se}_2\text{I}_4)(\text{AsF}_6)_2\cdot\text{SO}_2$, and $(\text{Se}_2\text{I}_4)(\text{Sb}_2\text{F}_{11})_2$.^[6] The present work was initiated in order to explore the nature of the complex equilibrium that is set when $(\text{Se}_6\text{I}_2)(\text{AsF}_6)_2\cdot 2\text{SO}_2$ is dissolved in $\text{SO}_2(\text{l})$ and to identify the cationic dissociation products.

EXPERIMENTAL

$(\text{Se}_6\text{I}_2)(\text{AsF}_6)_2\cdot 2\text{SO}_2$ was prepared from elemental selenium, iodine, and arsenic pentafluoride as described previously.^[3] Two samples were prepared one involving natural-abundance selenium and the other selenium enriched in the ^{77}Se -isotope (enrichment 92 %). The ^{77}Se NMR spectra were recorded in $\text{SO}_2(\text{l})$ at -80°C employing Bruker DXP400 and Varian Unity 400 spectrometers. Spectral simulation was carried out by using the program Perch.^[7]

RESULTS AND DISCUSSION

The ^{77}Se NMR spectrum of the equilibrium mixture of the ^{77}Se -enriched sample of $(\text{Se}_6\text{I}_2)(\text{AsF}_6)_2$ dissolved in $\text{SO}_2(\text{l})$ is shown in Figure 1. The chemical shifts have previously been reported for $1,4\text{-Se}_6\text{I}_2^{2+}$, $1,1,4,4\text{-Se}_4\text{I}_4^{2+}$, SeI_3^+ ,^[8,9] Se_4^{2+} ,^[10,11] Se_8^{2+} , and Se_{10}^{2+} .^[12] These species could be identified in the spectrum. Spectral simulation reproduced well the coupling patterns of $1,4\text{-Se}_6\text{I}_2^{2+}$ and $1,1,4,4\text{-Se}_4\text{I}_4^{2+}$, yielded reasonable coupling constants, and thus verified their identities. The coupling patterns of the resonances assigned for Se_8^{2+} were also in agreement with those reported earlier.^[12] The resonances due to SeI_3^+ and Se_4^{2+} appeared expectedly as singlets and those of Se_{10}^{2+} showed the expected fluxional behaviour.^[12] The ^{77}Se - ^{77}Se COSY connectivities provided further confirmation of this assignment.

The assignment of the 22 unknown resonances has been carried out by ^{77}Se - ^{77}Se COSY, selective irradiation experiments, as well as by spectral simulation that together yielded information on the number of species and their spin systems. It was established that these resonances could be assigned to five cationic species the chemical identity of which was inferred to be as follows: Se_7I^+ (7 resonances), $1,4\text{-Se}_7\text{I}_2^{2+}$ (4 resonances), $1,1,6,6\text{-Se}_6\text{I}_2^{2+}$ (asymmetric rotamer, 6 resonances; symmetric rotamer, 3 resonances), and Se_2I^+ (2 resonances). The inferred molecular structures are shown in Figure 2. The spectral

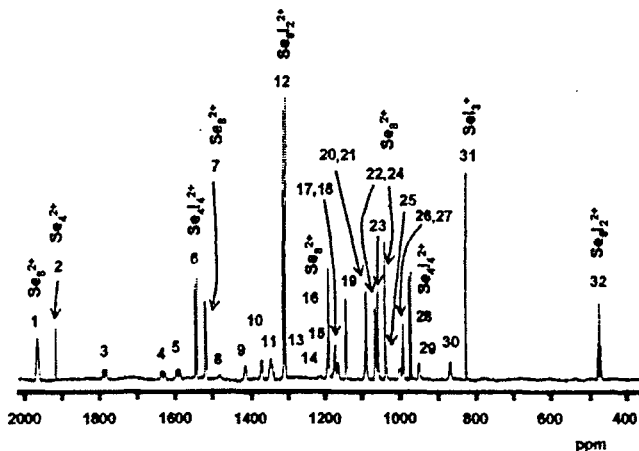


FIGURE 1. The ^{77}Se NMR spectrum of ^{77}Se -enriched $(\text{Se}_6\text{I}_2)(\text{AsF}_6)_2$ in $\text{SO}_2(\text{l})$ recorded at -80°C .

simulation showed a close agreement between the calculated and observed coupling patterns with reasonable coupling constants as exemplified for Se_7I^+ in Figure 3.

While ^{77}Se - ^{77}Se COSY and spectral simulation can be used to determine the ^{77}Se spin systems of the species, additional information is needed to establish their chemical identities. This can be done by considering the iodine, selenium, and charge balances in the reaction mixture. Let there be initially 100 mol of $\text{Se}_6\text{I}_2^{2+}$ implying 600 mol of selenium and 200 mol of iodine. The quantitatively integrated intensities

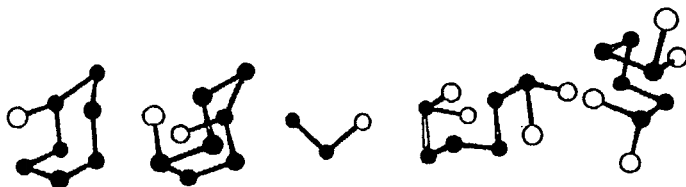


FIGURE 2. Selenium-iodine cations that are generated upon dissociation of $(\text{Se}_6\text{I}_2)(\text{AsF}_6)_2$.

of the resonances in the equilibrium mixture enables the determination of the relative abundances of the cationic species and therefore also the final amounts of selenium and iodine. This has been shown in Table 1. It can be seen that the equilibrium amount of iodine is almost exactly identical to the initial amount. Not all selenium, however, is accounted for. This is due to the fact that because of the fluxionality and exchange of Se_{10}^{2+} [12] the intensities of its resonances cannot be converted to the abundance of the species. Therefore the amount of selenium should be higher, but it does not affect the iodine balance. For the same reason not all of the charge has been accounted for (total positive charge in the equilibrium mixture is 174.1 mol as compared to 200 mol initially present).

The trends in the chemical shifts are consistent with the present assignment (see Table 1). All resonances of the selenium atoms that are bound to iodine expectedly lie at higher field than those of other

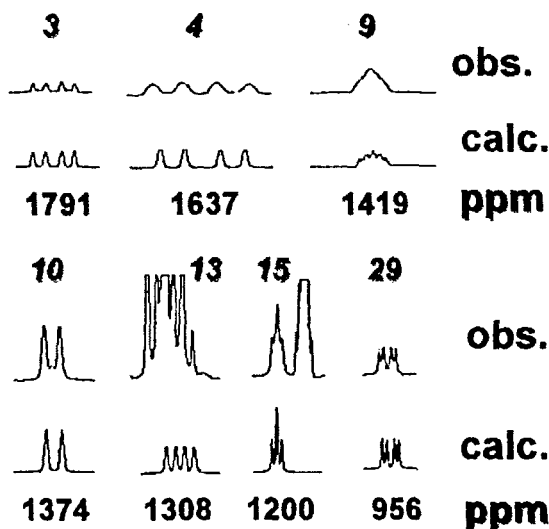


FIGURE 3. The observed and calculated resonances Se_7I^+ ($^1J_{\text{SeSe}} = 1, 66, 69, 104, 199, 214, 484 \text{ Hz}$; $^2J_{\text{SeSe}} = 3, 20, 23, 173 \text{ Hz}$; $^3J_{\text{SeSe}} = 1, 27, 33 \text{ Hz}$).

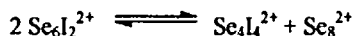
TABLE 1. The ⁷⁷Se NMR spectroscopic information and the relative abundance of the cationic species of the equilibrium SO₂ solution of Se₆I₂²⁺.

Species	δ (ppm)	Int. ^a	Abund.	mol Se	mol I
Se ₆ I ₂ ²⁺	1313, 476 (2:1)	80	15.5	93.0	31.0
Se ₄ I ₄ ²⁺	1548, 978 (1:1)	42	8.1	32.4	32.4
SeI ₃ ⁺	830	61	11.8	11.8	35.4
Se ₄ ²⁺	1922	10	1.9	7.6	0.0
Se ₈ ²⁺	1970, 1521, 1196, 1071, 1046 (2:2:1:2:1)	105	20.3	162.4	0.0
Se ₇ I ⁺	1791, 1637, 1419, 1374, 1308, 1200, 956 (1:1:1:1:1:1:1)	43	8.3	58.1	8.3
Se ₇ I ₂ ²⁺	1149, 1064, 1044, 998 (2:2:1:2)	50	9.7	67.9	19.4
Se ₆ I ₄ ²⁺ a ^b	1597, 1351, 1350, 1170, 1007, 873 (1:1:1:1:1:1)	45	8.7	52.2	34.8
Se ₆ I ₄ ²⁺ s ^b	1181, 1096, 1094 (1:1:1)	51	9.9	59.4	39.6
Se ₂ I ⁺	1486, 1219 (1:1)	30	5.8	11.6	5.8
Total			100.0	556.4	206.7

^a The integrated intensity has been calculated as an average of all resonances of the cationic species as scaled for one selenium atom. ^b a denotes asymmetric rotamer and s symmetric rotamer.

selenium atoms The chemical shift gets larger as the spatial separation from the iodine atoms grows. The trends in one-bond coupling constants are also consistent with the expected variations of the Se-Se bond lengths as a function of the distance from the Se-I bond {see for instance the molecular structure of (Se₆I₂)(AsF₆)₂·2SO₂ [13]}.

The dissociation of Se₆I₂²⁺ and the setting up of the equilibrium can be considered in terms of the well-known equilibria:^[1]





It is quite conceivable that other species observed in the SO_2 solution also take part in the formation of equilibrium. This finds confirmation from the observation that upon removal of the solvent only $(\text{Se}_6\text{I}_2)(\text{AsF}_6)_2 \cdot 2\text{SO}_2$ is found in the solid state.

Acknowledgments

The financial support from Academy of Finland, Emil Aaltonen Foundation, and NSERC is gratefully acknowledged.

References

- [1] T. Klapötke and J. Passmore, *Acc. Chem. Res.*, **22**, 234 (1989).
- [2] S. Brownridge, T.S. Cameron, J. Passmore, G. Schatte, and T.C. Way, *J. Chem. Soc., Dalton Trans.*, 2553 (1996).
- [3] W.A.S. Nandana, J. Passmore, P.S. White, and C.-M. Wong, *Inorg. Chem.*, **28**, 3320 (1989).
- [4] J. Passmore and P. Taylor, *J. Chem. Soc., Dalton Trans.*, 804 (1976).
- [5] J.P. Johnson, M.P. Murchie, J. Passmore, M. Tajik, P.S. White, and C.-M. Wong, *Can. J. Chem.*, **65**, 2744 (1987).
- [6] W.A.S. Nandana, J. Passmore, P.S. White, and C.-M. Wong, *Inorg. Chem.*, **29**, 3529 (1990).
- [7] PERCH, Version 1/96, University of Kuopio (1996).
- [8] J. Passmore, in *Studies in Inorganic Chemistry*, ed. R. Steudel, Elsevier, New York 1992, vol. 14, ch. 19, p. 373, and references therein.
- [9] M.M. Carnell, F. Grein, M.P. Murchie, J. Passmore, and C.-M. Wong, *J. Chem. Soc., Chem. Commun.*, 225 (1986).
- [10] G.J. Schrobilgen, R.C. Burns, and P. Granger, *J. Chem. Soc., Chem. Commun.*, 957 (1978).
- [11] M.J. Collins, R.J. Gillespie, J.F. Sawyer, and G.J. Schrobilgen, *Inorg. Chem.*, **25**, 2053 (1988).
- [12] R.C. Burns, M.J. Collins, R.J. Gillespie, and G.J. Schrobilgen, *Inorg. Chem.*, **25**, 4465 (1986).