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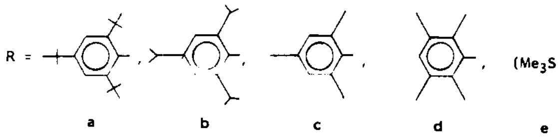
Reversible Dismutation and Coordination of Bis(2,4,6-triisopropylphenyl) Diselenide with Iodine: A Model Study That Relates to Iodine Intercalation between Selenium Chains[1]

It has long been known that iodine influences significantly the rate of crystallization of elemental selenium. It has been proposed that at very low concentration iodine atoms inhibit the crystallization by forming intercrystalline surfaces, whereas at higher iodine concentration "recombination of iodine atoms" takes place.[2-5] We report here a model study describing the role of iodine for reversible cleavage and formation of selenium–selenium bonds. Multinuclear NMR spectra reveal dismutation equilibria of a model diselenide with iodine in solution, whereas a very loose charge-transfer adduct of the same diselenide with iodine in the solid state allows one to predict how iodine molecules may intercalate between the chains of elemental selenium.

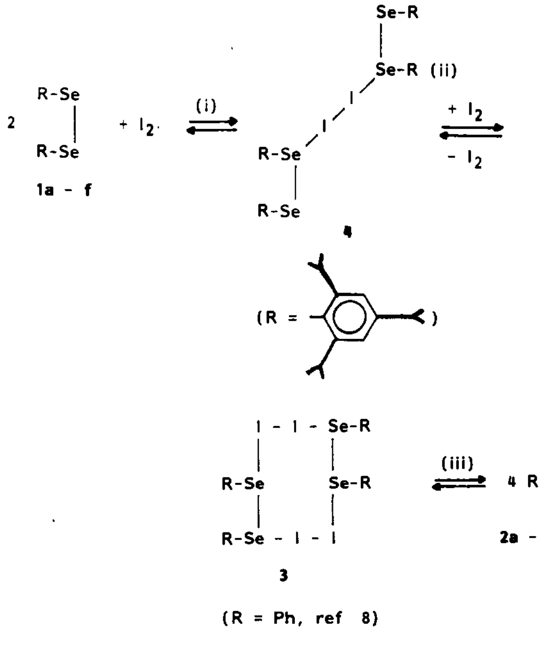
Uncharged binary compounds between selenium and iodine are still unknown,[3] but bulky aryl and alkyl groups may activate adjacent selenium–selenium bonds of organic diselenides for the reaction with molecular iodine to give stable molecules with covalent Se–I bonds[6,7] (eq 1), of which **2a** has been characterized

$$\underset{\mathbf{1a-e}}{R_2Se_2 + I_2} \xrightleftharpoons{\text{inert solvent}} \underset{\mathbf{2a-e}}{2\ RSeI} \qquad (1)$$



$$\underset{\mathbf{1f}}{2\ Ph_2Se_2 + 2\ I_2} \rightleftharpoons \underset{\mathbf{3}}{[Ph_2Se_2I_2]_2} \qquad (2)$$

by crystallographic data as the first iodoselane RSeI.[6] Quite differently, diphenyl diselenide gives a crystalline dimeric 1:1 adduct with iodine (**3**), in which (8-Se-3) selenium atoms act as donor atoms toward iodine [d(Se–I) = 2.992 Å] and (10-Se-3) selenium atoms behave as weak acceptors [d(Se–I) = 3.588 Å][8,9] (eq 2).



In solution, the diphenyl diselenide diiodine charge-transfer complex exists in equilibrium with the parent diselenide **1f** and iodine (the equilibration according to eq 3 is fast on the ^{1}H, ^{13}C, and ^{77}Se NMR time scales), but a species with a *covalent* Se–I bond (PhSeI) could not be detected by NMR spectroscopy.[8] Possible equilibration of a species PhSeI with Ph$_2$Se$_2$ (**1f**) and I$_2$ as a rapid process (on the ^{1}H, ^{13}C, and ^{77}Se NMR time scales) was ruled out by a crossing experiment of **3** with di-*p*-tolyl diselenide (observation of separate NMR signals for PhSeSe–*p*-Tol/I$_2$ beneath Ph$_2$Se$_2$/I$_2$, **1f**, and *p*-Tol$_2$Se$_2$/I$_2$ in the presence of iodine).

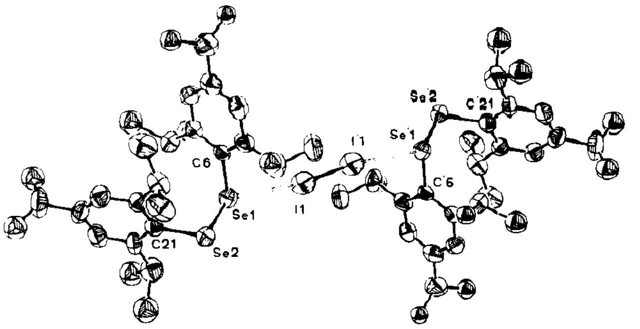


Figure 1. ORTEP drawing of **4**, showing only one position of the disordered isopropyl groups. Hydrogen atoms are omitted for clarity.

Table I. Selected Bond Lengths (Å) and Bond Angles (deg) for the Central Se$_2$·I$_2$·Se$_2$ Unit of (C$_{30}$H$_{46}$Se$_2$)$_2$I$_2$ (**4**) with Estimated Standard Deviations in Parentheses

I′(1)[a]–I(1)	2.772 (2)	I(1)–Se(1)	3.483 (1)
Se(1)–Se(2)	2.353 (2)	Se(1)–C(6)	1.945 (9)
Se(2)–C(21)	1.934 (10)		
I′(1)[a]–I(1)–Se(1)	169.2 (1)	I(1)–Se(1)–Se(2)	140.9 (1)
I(1)–Se(1)–C(6)	101.1 (3)	Se(2)–Se(1)–C(6)	101.0 (3)
Se(1)–Se(2)–C(21)	100.3 (3)		

[a] With reference to transformation operation $-x$, $1 - y$, $1 - z$.

A novel unique type of behavior of Se–Se bonds toward iodine is shown by the rather bulky bis(2,4,6-triisopropylphenyl) diselenide (**1b**). In inert solvents, equilibrium mixtures according

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(10) With chlorine and bromide, diselenide **1b** provides quantitative yields of monomeric selenenyl halides i-Pr$_3$C$_6$H$_2$SeCl [δ(^{77}Se) 926.1 ppm] and i-Pr$_3$C$_6$H$_2$SeBr [δ(^{77}Se) 757.7 ppm; Me$_2$Se standard and C$_6$D$_6$ solvent in all cases; spectra recorded at 54.24 MHz on a Bruker AM 300 instrument). Both compounds were isolated in a pure state: Martens, A. Diplomarbeit, University of Oldenburg, 1988.

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(12) X-ray diffraction data for (C$_{30}$H$_{46}$Se$_2$)$_2$I$_2$ (**4**): M_r = 1383.0356, orthorhombic, space group *Pbca* (No. 61); a = 16.256 (1) Å, b = 17.336 (2) Å, c = 22.408 (1) Å; V = 6314.9 Å^3, D = 1.455 g cm^{-3} (the linear absorption coefficient was 26.94 cm^{-1}, absorption correction by empirical ψ scan); diffractometer Siemens Stoe AED 2; Mo Kα, λ = 0.71069 Å; the intensities of 4207 symmetry-independent reflections determined by an ω–2θ scan. In the range 3.0° $\leq 2\theta \leq$ 48°, 2661 reflections with I$_o$ $\geq 2\sigma(I_o)$ were observed (number of variables = 289). R_1 = 0.0615; R_2 = 0.0527.[18] Anal. Calcd for C$_{60}$H$_{92}$I$_2$Se$_4$: C, 51.88; H, 6.68; I, 18.7. Found: C, 52.17; H, 6.72; I, 18.46. Purple-black crystals, mp 77–79 °C, were formed.

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to eq 1 contain iodoselane **2b** [$\delta(^{77}$Se) 370.8 ppm] as the predominant species[10] but minor amounts of the educt diselenide **1b** [$\delta(^{77}$Se) 359.1 ppm][11] are still present. With iodine in excess, diselenide **1b** is completely consumed.

Removal of the solvent from mixtures containing **1b**, I_2, and **2b** proceeds with loss of iodine, and subsequent crystallization from 40/60 petroleum ether leads to purple-black crystals of the composition $(R_2Se_2)_2I_2$ (**4**) (R = 2,4,6-triisopropylphenyl). Crystals of **4** were orthorhombic, space group *Pbca*, and allowed a single-crystal X-ray structure determination.[12] Surprisingly, solid **4** is not an iodoselane but a very weak adduct of molecular iodine with two molecules of diselenide **1b** (Figure 1 and Table I). The diselenide molecules are related by a center of inversion in the middle of the I–I bond. The I–I bond length of **4** (2.72 Å) is comparable to that of solid I_2 (2.715 Å);[13] it is less elongated than in any other known adduct of selenium ligands with iodine molecules. Accordingly, the geometry of diselenide **1b** within the complex **4** appears very much like an undistorted organic diselenide, quite different from the Ph_2Se_2 moiety in complex **3**, which shows distinctly different coordination geometries of the two three-coordinated [(8-Se-3) and (10-Se-3)] selenium atoms[8] as well as a much stronger Se$\rightarrow$I interaction (2.99 Å) and weaker I–I bonds (2.77 Å)[8] than those of **4**.

Dihalogen molecules tend to give 1:2 complexes only with very weak donors.[14] Quite typical for such adducts, the arrangement Se–I–I–Se of **4** is not far from linear ($\angle$Se–I–I = 169.1°).

Dissolving crystals of **4** in inert solvents allows one to detect immediately an equilibrium mixture of diselenide **1b**, iodoselane **2b**, and iodine (NMR, UV); these molecules are also observed in the gas phase (EI-MS at 70 eV).

Remarkably, complex **4**, containing an iodine molecule "intercalated" weakly between two diselenide molecules, is of very similar energy compared with both the educts (diselenide **1b**/iodine) and the iodoselane species **2b** containing a covalent Se–I bond. Packing effects will contribute to make CT complex **4** (not **2b**, which predominates in solution) a stable compound in the solid state. From less bulky bis(2,3,5,6-tetramethylphenyl) diselenide (**1d**) with iodine, iodo(2,3,5,6-tetramethylphenyl)selane (**2d**), the predominant species in solution, was isolated as a pure crystalline compound.[15]

The barriers of transformation of these species into each other (eq 3) are lowest for the charge-transfer complex association/dissociation equilibria (steps i and ii are fast at all NMR time scales) and still rather low for the diselenide–diiodine dismutation (immediate equilibration according to eq 3 upon dissolving **4**).

The (low) strength of the interaction of diselenide **1b** with iodine in solid **4** [*d*(Se–I) = 3.48 Å] is quite comparable with intermolecular interactions in solid iodine or with interchain contacts in hexagonal selenium [*d*(I···I) = 3.50 Å; *d*(Se···Se) = 3.43 Å].[16,17] The solid-state structure and the reversible dismutation in solution make the diselenide **1b**/I_2 system the most suitable molecular model currently available for the modes of interaction between elemental selenium and elemental iodine[2,4,5] wherein catalysis of selenium crystallization (i.e. Se–Se bond breaking and bond making) is favored by iodination/deiodination via covalent and charge-transfer Se–I bonded intermediates.

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Supplementary Material Available: Tables of crystallographic data and positional and thermal parameters and a figure with the numbering scheme of compound **4** (4 pages). Ordering information is given on any current masthead page.

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Wavelength Dependence of Unquenchable Photoaquation in the Tris(1,3-diaminopropane)chromium(III) Ion

We have discovered a wavelength dependence of product stereochemistry in $[Cr(tn)_3]^{3+}$ (tn = 1,3-diaminopropane) photoaquation that indicates the unquenchable photochemistry competes with vibrational relaxation. An earlier study[1] of wavelength dependence of unquenchable photoracemization yield in $[Cr(phen)_3]^{3+}$ was interpreted similarly, while wavelength-dependent quenching in *trans*-$[Cr(en)_2F(NCS)]^+$ was interpreted in terms of reaction via two quartet states.[2] All these results are important in the context of previous reports[3,4] of wavelength independence of product yields.

It is known that chromium(III) complexes may photosubstitute by two pathways,[5–8] one via the doublet state with product[9,10] forming with the doublet lifetime, the rate of the other pathway, often about 20–30% of the reaction, being faster than nanoseconds. The details of the fast pathway have not been established experimentally. It has been proposed to occur directly from a thermally equilibrated, solvent-shell-relaxed electronically excited (thexi) quartet state[11] or by surface crossing to a ground-state transition state.[12,13]

Intersystem crossing yields[14] and product yields have been observed to vary with excitation wavelength, and phosphorescence risetime lies in the picosecond or faster domain.[15,16] These features suggest the quartet route is very fast, but there is need for more information on its rate.

Previous studies[17,18] have shown that $[Cr(tn)_3]^{3+}$ photosubstitutes to *cis*- and *trans*-$[Cr(tn)_2(tnH)(H_2O)]^{4+}$ with quantum yield 0.15. Here, we have examined, at 20 °C, the overall quantum yields for photoaquation and the product isomer composition on irradiation into the quartet and doublet states as well as for quartet irradiation in the presence of a quencher that eliminates the

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