Three-Centre, Four-Electron Bonding and Structural Characteristics of Two-Coordinate Iodine(I) Complexes with Halogen and Chalcogen Ligands. Synthesis, Spectroscopic Characterization and X-Ray Structural Studies of (Triiodo)[tris(dimethylamino)phosphaneselenide]iodine(I) and Bis{(triiodo)[tri(*N*-morpholyl)phosphaneselenide]-iodine(I)}/Diiodine Molecular Complex

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The two title compounds have been synthesized and their structures have been studied by X-ray crystallographic methods. The crystals of (triiodo)[tris(dimethylamino)phosphaneselenide]iodine(I) (I) are orthorhombic; at 103 K, $a = 14.003(4)$, $b = 10.958(2)$, $c = 11.801(2)$ Å, $Z = 4$, space group $Pna2_1$, final conventional $R = 0.023$. The crystals of bis{(triiodo)[tri(*N*-morpholyl)phosphaneselenide]iodine(I)}/diiodine (II) are monoclinic; at 103 K $a = 8.999(4)$, $b = 16.874(8)$, $c = 16.996(6)$ Å, $\beta = 103.98(3)°$, $Z = 4$, space group $P2_1/c$, final conventional $R = 0.033$. The two compounds represent hypervalent complexes of I^I with nearly linear $Se–I^I–I$ sequences with $Se–I$ bond lengths of 2.596(1) and 2.590(1) Å for I and II, respectively. Corresponding $I^I–I$ bonds are weakened and their bond lengths are 3.215(1) and 3.186(1) Å. The bonding of I and II is studied within the framework of three-centre, four-electron bonding (3c,4e) centered on the I^I atom. Based on a literature survey, we have found many similar compounds mostly with the sequence $Y–I^I–X$, where $Y = S$ or Se and $X = $ halogen. The majority of these compounds fit well into this 3c,4e scheme. The relative *trans*-influences of the chalcogen ligands are found to be dependent upon the ligand's ability to accept positive charge from the central I^I atom. A systematic study of the inter-relationship between bond lengths $Y–I$ and $I–X$ shows that this depends on secondary interactions of Y and X in a predictable manner.

Recently, we reviewed some complexes of divalent three-coordinated tellurium with a general formula L=Y–Te(Ar)–X, where X is a halogen ligand and Y is a double-bonded chalcogen atom from a large neutral organic or phosphorus containing ligand (the remainder of the ligand is marked as L).[1] We considered them in a framework of a three-centre, four-electron (3c,4e) bonding scheme. In summary, this scheme (also known as 'hypervalent bonding' or 'secondary bonding') considers a linear three-centre group of atoms A–B–C comprising,

for instance, a σ-bonded covalent A–B molecule and an additional, 'secondary' ligand C donating its lone electron pair onto the A–B σ-antibonding orbital and inducing the weakening of the A–B bond (or vice versa).[2]

In the particular case of the Te complexes studied, it was possible to represent this in such resonance forms (Scheme 1).

We have to note that in this paper we are using the symbol '→' not in its conventional meaning of a coordination bond (i.e. a lone electron pair of a ligand donated onto a vacant atomic orbital of the central atom) but to designate a lone electron pair of a ligand

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Ar
|
L=Y—→Te—X   ←——→   L⁺—Y—Te←——X⁻.
(a)   (b)
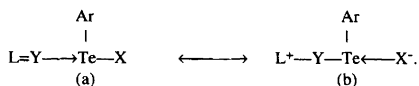
Scheme 1.

only initially oriented toward the molecular σ*-orbital of the central atom bond with another ligand. This oriented lone pair becomes a convenient σ-bonding pair expelling the σ-bonding electrons of the opposite, initially σ-bonded ligand, which in turn becomes an oriented two-electron donor. In practice, the central atom always has a completed eight-electron sp-shell, and both the opposite hypervalent bonds have bond orders less than 1 and their comparative 'strength' (a 'primary' character) or 'weakness' (a 'secondary' character) is dependent on the *trans*-influence[3] of the corresponding ligands. The *trans*-influence can be physically estimated as a function of the polarizability of the ligands (considered in the concept of 'soft' and 'hard' ions) in combination with a smaller contribution from the electronegativity. Now, among the halogens, iodine has a larger *trans*-influence than bromine, which again has a larger *trans*-influence than chlorine. In the same manner, the *trans*-influence decreases in the order $Se > S > O$ for chalcogens.

In our previous work[1] we suggested that the ability of the rest of the ligand L to accept (to delocalize) additional positive charge [Scheme 1(b)] can modify the *trans*-influence of the chalcogen atom in these complexes. We have also confirmed this conclusion from a literature survey of a large variety of organic ligands containing in most cases chalcogenureas, $(H/R)_2N-C(=Y)-N(H/R')_2$, and also taken into consideration some chalcogen phosphortriamide ligands $(R_2N)_3P=Y$.[1] Now we can add that, in the same way, any factors facilitating the delocalization of the negative charge from X should modify its *trans*-influence as well.

It was found that the delocalization of the positive charge takes place with the chalcogen phosphortriamide ligands also, even though this is less effective than with the urea derivatives. A thorough investigation has shown an unexpected mechanism of charge delocalization in the chalcogen phosphoramide ligands upon their coordination. These ligands possess a unique nitrogen atom whose hybridization changes from sp^3 towards sp^2 upon complexation. Usually, this 'special' nitrogen is *trans*-situated (less often *cis*) relative to the coordination centre and its lone electron pair has a very stable *anti*-orientation relative to the P=Y bond. Moreover, we found a very unexpected distribution of the valence electron density in $(Me_2N)_3P=S$ which does not correspond to the classical representation of the phosphorus atom in such compounds as being sp^3-hybridized (a model of Ω bonding proposed for phosphine oxides[4] gives a better approximation for the electron distribution observed).

Surprisingly, the sulfide and selenide derivatives of the phosphortriamides (as well as the phosphortriamides themselves) have not been widely investigated in com-

plexes or as individual ligands. Only the simplest representative, hexamethylphosphortriamide is known as a ligand (but the structure of the individual, liquid compound was only recently investigated)[5] in a large variety of structures of molecular complexes and coordination compounds (but only a few complexes involving non-transition elements are known). Because of this, we have made an attempt to diversify the list of coordination compounds of non-transition elements with the triaminophosphanesulfide and triaminophosphaneselenide ligands for a better understanding of their coordinating behaviour.

In this paper, the syntheses and results of X-ray structural investigations of the two complexes of I[1]: $[(Me_2N)_3PSe]I[I_3{}^-]$ (I) and $[morph_3PSe]I[I_3{}^-] \cdot \frac{1}{2}I_2$ (II), are reported. Here, we are considering these as isoelectronic analogues of the aforementioned complexes of Te[II] in the framework of the 3c,4e bonding scheme (Scheme 2).

Lp   Lp
| |
L=Y—→I—X   ←——→   L⁺—Y—I←——X⁻.
(a)   (b)

Scheme 2.

However, looking for the literature analogues of these compounds, we have found that no groups have systematically used this useful approach for the complexes of two-coordinated iodine(I) before. The theoretical views in this field often represent a mixture of particular opinions put forward by different authors and used only for separate groups of the complexes. Usually, most of these theories can not be applied to the whole variety of complexes studied. This has prompted us to look more widely at this class of chemical compounds to give a general consideration of these.

Experimental

Materials. Tris(dimethylamino)phosphane selenide[6] and tri(morpholino)phosphane selenide[7] were prepared according to published procedures. Iodine (Aldrich) was sublimed before use. Dichloromethane was of ACS grade. Melting points are uncorrected. NMR spectra were recorded on a Bruker DMX600 spectrometer in $CDCl_3$; [1]H 600 MHz, [13]C 150.9 MHz and [31]P 242.93 MHz. Infrared spectra were recorded on a Nicolet Impact 400 FT-IR spectrometer, with samples as Nujol mulls placed between KBr plates.

Syntheses. (I). To a stirred solution of tris(dimethylamino)phosphane selenide (0.10 g, 0.41 mmol) dissolved in dichloromethane (25 ml), was added iodine (0.210 g, 0.83 mmol) in the same solvent (20 ml) to give an immediate deep red, clear solution. This was stirred at room temperature for 30 min. Evaporation of the solution to approximately 8 ml followed by slow cooling to −10 °C over several hours yielded a crop of deep red

crystals with a black metallic appearance. Yield 0.26 g, 84%. M.p. 63–65 °C. IR v_{max}/cm^{-1} (Nujol): 1290, 1158, 1060, 980, 744, 650, 497 (P=Se). ^{1}H NMR (δ ppm): 2.88s, 2.87s (J 11.5 Hz) (N(CH$_3$)$_2$); ^{13}C{^{1}H} NMR: 38.88, 38.85 (N(CH$_3$)$_2$) (J 3.7 Hz); ^{31}P{^{1}H} NMR: 61.53s [^1J (^{31}P–^{77}Se) 595 Hz]; UV–VIS: λ 319 nm, ε 46970 mol^{-1} dm^3 cm^{-1}.

(II). Iodine (0.138 g, 0.54 mmol) in dichloromethane (15 ml) was added to a stirred solution of tri(morpholino)phosphane selenide (0.10 g, 0.27 mmol) in the same solvent (15 ml) to give an immediate dark red–brown clear solution. This was allowed to stir at room temperature for an hour and then filtered. Concentration of the solution to 10 ml followed by cooling at -20 °C overnight gave small deep red–brown block crystals with a grey metallic appearance. Yield 0.14 g, 59%, m.p. 156–158 °C. IR v_{max}/cm^{-1} (Nujol): 1258, 1136, 1114, 1072, 1014, 958, 724, 669, 585, 510 (P=Se). ^{1}H NMR (δ ppm): 3.76–3.74 m (12H), 3.27–3.24 m (12H); ^{13}C{^{1}H} NMR: 47.04s, 67.00s, 66.95s (J 6.5 Hz); ^{31}P{^{1}H} NMR: 65.03s [^1J(^{31}P–^{77}Se) 709 Hz]; UV–VIS: λ 321 nm, ε 30595 mol^{-1} dm^3 cm^{-1}.

The NMR spectra of both complexes **I** and **II** do not give any useful information concerning the structures of the products. The ^{1}H and ^{13}C NMR spectra show resonances close to those of the free ligands, but the ^{31}P spectra are significantly altered. In **I** a singlet at 61.53 ppm appears with ^1J(^{31}P–^{77}Se) 595 Hz whereas the uncomplexed ligand displays a resonance at approx. 83 ppm with ^1J(^{31}P–^{77}Se) 805 Hz. This change in both the chemical shift and coupling constant is much greater than seen in the corresponding tellurium(II) complex [BrTe(Ph)SeP(NMe$_2$)$_3$].[1] A similar but smaller shift is seen in **II** from ca. 77 ppm to 65.03 ppm, but in this case the decrease in the ^{31}P–^{77}Se coupling constant is only from 814 to 709 Hz. This decrease is typical of coordination of the Se=P moiety to an electron acceptor fragment (PhTeX (X=hal) or the isoelectronic I$_2$). The infrared spectra also show vibrations typical of the coordination of the ligands; bands at 497 cm^{-1} (**I**) and 510 cm^{-1} (**II**) are indicative of a P=Se stretch and are found 31 and 16 cm^{-1}, respectively, to lower energy than in the free ligands. Both the infrared and NMR spectra confirmed the conclusions of the X-ray structural study in that the P=Se bond in **I** and **II** is lengthened upon coordination to iodine.

Structure determinations. Crystal data are given in Table 1, together with some data collection and refinement details. Data for both crystals were collected with MoKα radiation at low temperature using an Enraf-Nonius CAD4 diffractometer. The unit cell parameters and orientation matrices were obtained by a least-squares fit of 25 randomly orientated intense reflections in both cases. The diffracted intensities were collected using a variable scan speed. Three standard reflections were measured at regular intervals. All corrections needed

Table 1. Crystal data and structure refinement parameters for compounds **I** and **II**.

Compound	I	II
Empirical formula	C$_6$H$_{18}$I$_4$N$_3$PSe	C$_{12}$H$_{24}$I$_5$N$_3$O$_3$PSe
M	749.76	1002.77
Crystal system	Orthorhombic	Monoclinic
Space group	Pna2$_1$	P2$_1$/c
a/Å	14.003(4)	8.999(4)
b/Å	10.958(2)	16.874(8)
c/Å	11.801(2)	16.996(6)
α/°	90	90
β/°	90	103.98(3)
γ/°	90	90
T/K	103(2)	103(2)
V/Å^3	1810.8(7)	2504(2)
Z	4	4
D_c/mg m^{-3}	2.750	2.660
μ/mm^{-1}	8.964	7.745
F(000)/e	1344	1820
Crystal size (mm)	0.15 × 0.2 × 0.3	0.1 × 0.2 × 0.2
θ range/°	2.0–30.0	2.5–30.0
hkl ranges	0/19, 0/15, 0/16	0/12, 0/23, −23/23
Total no. of reflections	2760	8202
Crystal decay correction	0.946–1.000	0.941–1.000
Transmission coeff.	0.066–0.340	0.145–0.260
Independent reflections $I > 2\sigma(I)$ (R_{int})	2555 (0)	4871 (0.055)
Data (all)/parameters	2745/148	7256/226
Goodness of fit on F^2 (obs/all data)	0.575/0.617	1.057/0.953
Final R-indices:		
R_1 (obs/all data)	0.0233/0.0289	0.0327/0.0805
wR_2 (obs/all data)	0.0729/0.0870	0.0748/0.0866
Largest difference peak and hole/e Å^{-3}	1.058, −0.938	1.920, −2.059

(including empirical psi-scan absorption correction) were made using Blessing's program package.[8] The structures were solved using direct methods with the SHELXS86 program.[9] All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were put in idealized calculated positions and processed with a least-squares refinement as a 'riding' model (for Me groups the torsion angle was optimized). In structure **I**, each set of hydrogens belonging to the same Me group had a common isotropic thermal parameter refined separately; in structure **II**, hydrogens' isotropic thermal parameters were set as 1.5$U_{iso/eq}$ of the adjacent carbon atom. Refinement was with SHELXL93[10] on a MicroVax2000 computer.

Positional and displacement parameters of non-hydrogen atoms of the structures **I** and **II** are given in Tables 2 and 3. Bond distances and angles, and selected torsion angles are listed in Tables 4 and 5. Molecular structures of the complexes are shown in Figs. 1 and 2. Additional material, available from the Cambridge Crystallographic Data Centre, comprises anisotropic thermal parameters of non-hydrogen atoms, H-atom coordinates, remaining geometrical parameters, and tables of structure factors.

Table 2. Non-hydrogen atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\times 10^3$) for compound I.

Atom	x	y	z	$U_{iso/eq}{}^a$
I(1)	−6418.8(3)	1009.9(4)	184.1(4)	19.5(1)
I(2)	−7287.2(3)	344.1(4)	−2261.0(4)	21.1(1)
I(3)	−9183.8(3)	215.1(4)	−792.2(4)	18.7(1)
I(4)	−10 708.3(3)	82.9(4)	708.6(5)	22.2(1)
Se(1)	−5793.2(6)	1739.7(8)	2141.0(7)	27.3(2)
P(1)	−6712(1)	669(1)	3311(1)	15.2(3)
N(1)	−6243(4)	−651(5)	3572(5)	19(1)
N(2)	−6710(4)	1412(5)	4522(5)	17(1)
N(3)	−7781(4)	562(5)	2803(6)	20(1)
C(11)	−6501(5)	−1344(6)	4598(6)	22(1)
C(12)	−5731(5)	−1381(7)	2713(8)	27(1)
C(21)	−5778(5)	1633(7)	5063(7)	25(1)
C(22)	−7442(6)	2278(5)	4850(6)	22(1)
C(31)	−8233(5)	−618(7)	2562(6)	24(1)
C(32)	−8311(6)	1600(6)	2375(6)	24(1)

$^a U_{iso/eq} = (1/3) \Sigma_i \Sigma_j U_{ij} a_i{}^* a_j{}^* a_i a_j$.

Table 3. Non-hydrogen atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\times 10^3$) for compound II.

Atom	x	y	z	$U_{iso/eq}{}^a$
I(1)	3278.6(4)	6814.0(2)	1109.5(2)	14.1(1)
I(2)	−201.2(4)	6261.4(3)	794.2(2)	23.1(1)
I(3)	338.2(4)	5848.3(2)	2618.6(2)	21.3(1)
I(4)	808.1(6)	5493.3(3)	4261.4(3)	39.4(1)
I(5)	−3555.1(4)	5325.9(2)	208.7(2)	17.7(1)
Se(1)	6203.8(6)	7065.5(3)	1442.0(3)	13.4(1)
P(1)	6359(1)	7910(1)	2456(1)	10.9(2)
O(1)	5621(5)	6641(2)	4648(2)	22(1)
O(2)	4619(5)	10 249(2)	1913(3)	28(1)
O(3)	11 297(4)	8634(3)	3023(3)	24(1)
N(1)	6113(5)	7508(3)	3296(3)	12(1)
N(2)	5056(5)	8603(3)	2206(3)	15(1)
N(3)	8177(5)	8171(3)	2665(2)	13(1)
C(11)	4548(6)	7291(3)	3359(3)	16(1)
C(12)	4554(6)	7219(3)	4254(3)	20(1)
C(13)	7126(6)	6844(3)	4595(3)	20(1)
C(14)	7227(6)	6907(3)	3714(3)	15(1)
C(21)	4493(7)	8902(4)	1376(3)	24(1)
C(22)	5049(8)	9744(4)	1325(4)	29(1)
C(23)	5238(7)	9965(4)	2703(4)	27(1)
C(24)	4716(6)	9142(3)	2827(3)	17(1)
C(31)	8913(6)	8402(4)	2012(3)	20(1)
C(32)	10 632(6)	8231(4)	2295(4)	26(1)
C(33)	10 592(6)	8425(4)	3661(3)	24(1)
C(34)	8876(6)	8610(3)	3428(3)	17(1)

^{a}See Table 2.

Results and discussion

The main principles and features of chemical bonding in hypervalent complexes of two-coordinated iodine(I). Most of the compounds of two-coordinated iodine(I) studied are derived from elemental iodine (diiodine, I_2) and are considered by many authors as a diiodine molecule perturbed by a secondary interaction with a neighbouring ligand. The unperturbed σ-bonded diiodine molecule is characterized by an interatomic distance I–I of

2.667(2) Å [in the vapor phase;[11] in the crystalline state at 110 K the longer distance of 2.715(6) Å is influenced by intermolecular interactions;[12] no more recent data are available]. The molecule contains filled molecular σ-, π- and π*-orbitals and an unfilled σ*-orbital. An iodide anion can easily attack the σ*-orbital of the diiodine molecule giving the simplest (and widely known) compound of two-coordinated iodine(I), the symmetrical linear triiodide anion $I_3{}^-$ with the completely delocalized 3c,4e bonding molecular orbital (Scheme 3). We can consider the bond order of both I–I interactions in this anion to be equal to 0.5. The Cambridge Structural Database (CSD)[13] contains precise ($R \leqslant 0.05$) low-temperature ($T \leqslant 200$ K) data on 11 well ordered structures containing the $I_3{}^-$ ion with bond distances in the range 2.823–3.054 Å [av. 2.921(9) Å] which correspond to this bond order. Finally, the van der Waals radius of the iodine atom is 1.98 Å.[14] So, the distances I–I lying in the interval 2.67–2.92 Å can be considered as 'primary' bonds and the distances belonging to the interval 2.92–3.96 Å, as 'secondary' bonds.

Other symmetrical halogen complexes of two-coordinate iodine(I) are known. These are the linear Br–I–Br and Cl–I–Cl anions. The most precise low-temperature data give the half bond distances I–Br 2.683 Å[15] [single bond I–Br 2.470(5) Å in vapor[16] and 2.521(4) Å in solid[17]] and I–Cl 2.557 Å.[18,19]

Symmetrical dichalcogen complexes of two-coordinate iodine(I) are also known. However, unlike the halogen complexes, these compounds are still considered by many authors as 'iodonium' complexes,[20] even though in an early paper on one of these, the thiourea (tu) complex $[Itu_2]^+I^-$, Lin and Hope paid special attention to the fallibility of such a point of view and proposed to differentiate between two types of these two-coordinated iodine(I) compounds.[21] We will return to this discussion here.

Genuine iodonium compounds are well known in organoelement chemistry. Although we are not going to give a complete review of all compounds of two-coordinated iodine(I), it would be useful to dwell briefly upon some of its organic complexes. The 16-electron ion I^+ assumes a high-spin $(5p_x)^2(5p_y)^1(5p_z)^1$ electronic state and gives two mutually orthogonal, single σ-bonds with two organic (usually aryl) radicals [CSD's statistics on more than 50 iodonium structures gives the average $C-I^+$ bond length as 2.090(5) Å, which coincides well with the standard value[22] of 2.095(15) Å for a C(aryl)–I single bond; the average $C-I^+-C$ bond angle is 93.3(6)°].

Organic compounds with the linear moiety C–I–C are much less numerous. However, they are derived from the corresponding organic iodides (with C–I σ-bonds) as a result of the addition, not of a cation-radical, but a carbene (neutral or ionic) group, which acts as a donor of a lone electron pair (Scheme 4). This gives neutral or charged complexes with a halved bond order for both the C–I interactions. We wish to emphasize the following: the iodine atom in these compounds is not formally

Table 4. Bond lengths (d/Å) and angles (ω/°), and selected torsion angles (τ/°) in molecule I.

Bond	d	Bond	d
I(1)–I(2)	3.215(1)	P(1)–N(3)	1.615(6)
I(1)–Se(1)	2.596(1)	N(1)–C(11)	1.474(9)
I(2)–I(3)	3.175(1)	N(1)–C(12)	1.477(10)
I(3)–I(4)	2.778(1)	N(2)–C(21)	1.472(8)
Se(1)–P(1)	2.222(2)	N(2)–C(22)	1.450(9)
P(1)–N(1)	1.619(6)	N(3)–C(31)	1.468(8)
P(1)–N(2)	1.644(6)	N(3)–C(32)	1.450(8)

Angle	ω	Angle	ω
Se(1)–I(1)–I(2)	174.77(3)	P(1)–N(1)–C(11)	121.1(5)
I(1)–I(2)–I(3)	80.59(2)	P(1)–N(1)–C(12)	123.4(5)
I(2)–I(3)–I(4)	173.44(2)	C(11)–N(1)–C(12)	113.9(5)
I(1)–Se(1)–P(1)	101.21(5)	P(1)–N(2)–C(21)	117.5(5)
Se(1)–P(1)–N(1)	110.8(2)	P(1)–N(2)–C(22)	123.7(5)
Se(1)–P(1)–N(2)	106.1(2)	C(21)–N(2)–C(22)	113.7(6)
Se(1)–P(1)–N(3)	110.2(2)	P(1)–N(3)–C(31)	122.4(5)
N(1)–P(1)–N(2)	106.0(3)	P(1)–N(3)–C(32)	123.1(5)
N(1)–P(1)–N(3)	112.4(3)	C(31)–N(3)–C(32)	113.7(6)
N(2)–P(1)–N(3)	111.1(3)		

Angle	τ	Angle	τ
I(1)–Se(1)–P(1)–N(1)	87.6(2)	Se(1)–P(1)–N(2)–C(21)	−57.5(5)
I(1)–Se(1)–P(1)–N(2)	−157.8(2)	Se(1)–P(1)–N(2)–C(22)	95.5(5)
I(1)–Se(1)–P(1)–N(3)	−37.4(2)	Se(1)–P(1)–N(3)–C(31)	121.1(5)
Se(1)–P(1)–N(1)–C(11)	157.7(5)	Se(1)–P(1)–N(3)–C(32)	−48.3(6)
Se(1)–P(1)–N(1)–C(12)	−37.7(6)		

positively charged; it contains eight electrons (not ten, as many authors assume!) in its sp-valence shell, and acts rather as a conductor of electrons between two neighbouring coordinated groups.

These hypervalent compounds may be anionic in the case of the addition of a negatively charged carbene particle (the [NC–I–CN]⁻ anion[23,24] and the anionic [F₅C₆–I–C₆F₅]⁻ adduct[25] are known), they may be cationic (a product of the addition of a neutral carbene derived from N,N'-dimesitylimidazoline to the 2-iodo-1,3-dimesitylimidazolium cation has been studied)[26] or neutral as in the (NAdR–CH=CH–NAd)C–I–C₆F₅ complex.[27] In all these cases the bond length C–I varies in the range 2.159–2.754 Å (av. 2.357 Å). It is very remarkable that these bonds are on average ca. 0.26 Å longer than in genuine organic iodonium compounds, and this lengthening is quite comparable with the 0.25 Å difference between bond lengths I–I in diiodine and triiodide (see above). Therefore, we can actually consider these bonds as having bond orders equal to 0.5.

Coming back to the symmetrical dichalcogen *hypervalent two-coordinated complexes of iodine(I)* we can ascertain that the half bond length I–S is ca. 2.63 Å [2.619(2) Å in the {[en₂Co(SCH₂CH₂NH₂)]₂I}⁵⁺ cation,[28] 2.63 Å in the aforementioned bis(tu) cationic complex[21], 2.600 and 2.634(2) Å in the analogous bis(mbtt) [mbtt = N-methylbenzothiazole-2(3H)-thione] cationic complex[20] and 2.674(7) Å in the [I(IS₇)₂]³⁺ cation],[29] i.e. on average 0.26 Å longer than the sum of the corresponding covalent radii 2.37 Å[30a] (compare with

the lengthening of the halved I–I and I–C bonds, see above; there are no accurate data on the length of true single halogen–chalcogen bonds due to the tendency of both elements to take part in secondary interactions). In the only known symmetrical Se-complex [bis(mbts)I]⁺I₃⁻ [mbts = N-methylbenzothiazole-2(3H)-selone], the Se–I bond lengths are 2.719 and 2.800(1) Å.[20] (The sum of the corresponding covalent radii is 2.50 Å.[30a])

A very interesting feature of the bis(tu), bis(mbtt) and bis(mbts) complexes is the mutually coplanar orientation of the ligands [as well as in the previously mentioned organic (NAd–CH=CH–NAd)C–I–C₆F₅ complex[25]]. In the framework of the bonding scheme used in this paper, one of the resonance forms comprises a σ-bonded positively charged chalcogen ligand [Scheme 2(b)]. We have proposed[1] that the better the delocalization of this charge over the ligand, the larger the contribution of this resonance form to the structure observed. However, an additional opportunity exists to delocalize this positive charge: not only via conjugation of the p_z-orbital of the chalcogen atom with the π-electron system of the rest of the ligand but via π-conjugation of the p_z-orbital of the chalcogen atom with the p_z-orbital of the central iodine atom (i.e. donation of lone p_z-electron pair of the iodine atom onto π*-orbital of the L=Y double bond). In this case the π-orbital of the second, electron-rich ligand Y'=L' can become conjugated with the newly obtained Y=I π*-orbital, giving in addition to the three-centre, four-electron σ-bond a five-centre, six-electron π-bond

Table 5. Bond lengths (*d*/ Å) and angles (ω/°), and selected torsion angles (τ/°) in molecule II.

Bond	*d*	Bond	*d*
I(1)–I(2)	3.186(1)	O(3)–C(32)	1.412(7)
I(1)–Se(1)	2.590(1)	O(3)–C(33)	1.426(7)
I(2)–I(3)	3.100(1)	N(1)–C(11)	1.484(6)
I(2)–I(5)	3.338(1)	N(1)–C(14)	1.482(6)
I(3)–I(4)	2.786(1)	N(2)–C(21)	1.470(7)
I(5)–I(5′)	2.754(1)	N(2)–C(24)	1.479(6)
Se(1)–P(1)	2.214(1)	N(3)–C(31)	1.476(6)
P(1)–N(1)	1.643(4)	N(3)–C(34)	1.494(6)
P(1)–N(2)	1.638(5)	C(11)–C(12)	1.525(7)
P(1)–N(3)	1.649(4)	C(13)–C(14)	1.525(7)
O(1)–C(12)	1.418(7)	C(21)–C(22)	1.514(9)
O(1)–C(13)	1.421(7)	C(23)–C(24)	1.497(8)
O(2)–C(22)	1.436(8)	C(31)–C(32)	1.532(8)
O(2)–C(23)	1.408(8)	C(33)–C(34)	1.531(8)

Angle	ω	Angle	ω
I(2)–I(1)–Se(1)	172.01(2)	P(1)–N(2)–C(21)	123.6(4)
I(1)–I(2)–I(3)	89.29(3)	P(1)–N(2)–C(24)	120.9(4)
I(1)–I(2)–I(5)	165.87(2)	C(21)–N(2)–C(24)	113.0(4)
I(3)–I(2)–I(5)	95.95(3)	P(1)–N(3)–C(31)	120.7(4)
I(2)–I(3)–I(4)	179.35(2)	P(1)–N(3)–C(34)	120.5(3)
I(2)–I(5)–I(5′)	174.43(2)	C(31)–N(3)–C(34)	110.5(4)
I(1)–Se(1)–P(1)	98.32(4)	N(1)–C(11)–C(12)	108.5(4)
Se(1)–P(1)–N(1)	114.5(2)	O(1)–C(12)–C(11)	111.3(4)
Se(1)–P(1)–N(2)	110.6(2)	O(1)–C(13)–C(14)	111.2(5)
Se(1)–P(1)–N(3)	102.3(2)	N(1)–C(14)–C(13)	108.9(4)
N(1)–P(1)–N(2)	106.3(2)	N(2)–C(21)–C(22)	109.6(5)
N(1)–P(1)–N(3)	104.9(2)	O(2)–C(22)–C(21)	111.7(5)
N(2)–P(1)–N(3)	118.5(2)	O(2)–C(23)–C(24)	112.6(5)
C(12)–O(1)–C(13)	110.6(4)	N(2)–C(24)–C(23)	110.1(4)
C(22)–O(2)–C(23)	110.5(5)	N(3)–C(31)–C(32)	108.4(5)
C(32)–O(3)–C(33)	112.0(4)	O(3)–C(32)–C(31)	111.5(5)
P(1)–N(1)–C(11)	119.6(3)	O(3)–C(33)–C(34)	111.1(5)
P(1)–N(1)–C(14)	118.8(3)	N(3)–C(34)–C(33)	108.1(4)
C(11)–N(1)–C(14)	109.9(4)		

Angle	τ	Angle	τ
I(1)–Se(1)–P(1)–N(1)	71.8(2)	O(1)–C(13)–C(14)–N(1)	58.0(6)
I(1)–Se(1)–P(1)–N(2)	−48.3(2)	C(24)–N(2)–C(21)–C(22)	51.6(6)
I(1)–Se(1)–P(1)–N(3)	−175.3(2)	C(21)–N(2)–C(24)–C(23)	−51.2(6)
Se(1)–P(1)–N(1)–C(11)	−76.1(4)	C(23)–O(2)–C(22)–C(21)	59.4(7)
Se(1)–P(1)–N(1)–C(14)	63.2(4)	C(22)–O(2)–C(23)–C(24)	−59.3(6)
Se(1)–P(1)–N(2)–C(21)	−31.8(5)	N(2)–C(21)–C(22)–O(2)	−55.2(7)
Se(1)–P(1)–N(2)–C(24)	167.6(3)	O(2)–C(23)–C(24)–N(2)	54.7(6)
Se(1)–P(1)–N(3)–C(31)	47.4(4)	C(34)–N(3)–C(31)–C(32)	57.9(6)
Se(1)–P(1)–N(3)–C(34)	−167.2(4)	C(31)–N(3)–C(34)–C(33)	−58.2(6)
C(14)–N(1)–C(11)–C(12)	57.5(5)	C(33)–O(3)–C(32)–C(31)	58.4(7)
C(11)–N(1)–C(14)–C(13)	−57.3(5)	C(32)–O(3)–C(33)–C(34)	−58.7(6)
C(13)–O(1)–C(12)–C(11)	60.0(6)	N(3)–C(31)–C(32)–O(3)	−57.4(6)
C(12)–O(1)–C(13)–C(14)	−59.4(6)	O(3)–C(33)–C(34)–N(3)	57.5(6)
N(1)–C(11)–C(12)–O(1)	−58.8(6)		

(of course, only in the case of a coplanar orientation of the ligands)! If this is so, the hypervalent system considered should have additional π-bonding (Scheme 5).

An application of the three-centre, four-electron bonding scheme to the mixed halogen/chalcogen hypervalent complexes of two-coordinated iodine(I). Most of the structurally studied hypervalent complexes of iodine(I) of the type LY–I–X represent compounds where X = I and Y =

S^{II} or Se^{II}. There are only a few examples with X = Cl or Br, and structures with X = F or with Y = O or Te^{II} are not known (evidently, because of the negligible *trans*-effects of fluorine and oxygen, and the presumably large *trans*-effect of tellurium which exceeds that of iodine).

The sulfur and selenium complexes may be divided into two separate classes when looking at the valence state of the chalcogen in a ligand: these are the thiane and selane ligands containing a two-coordinate doubly
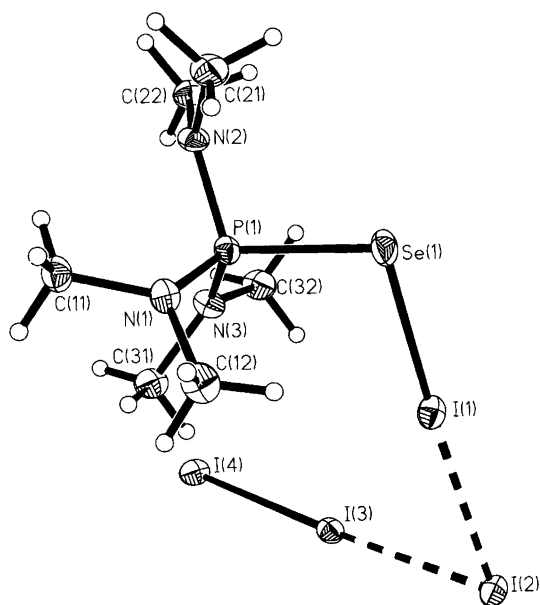
Fig. 1. Perspective projection of the molecule I with numbering of the atoms. Weakened (secondary) bonds I–I are shown by dashed solid lines. The thermal displacement ellipsoids are given at 50% probability level.
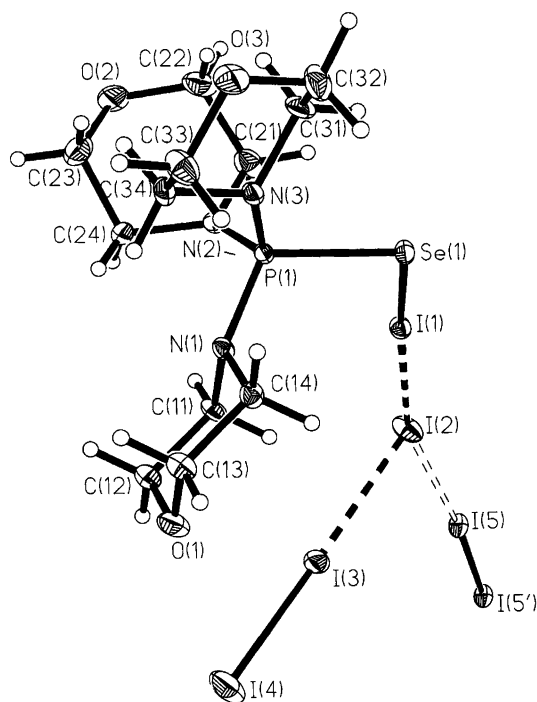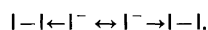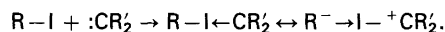

Fig. 2. Perspective projection of the molecule II and a complexed diiodine molecule (situated in a centre of symmetry) with numbering of the atoms. Weakened (secondary) bonds I–I are shown by dashed solid lines and a short bonding intermolecular interaction I···I by a dashed open line. The thermal displacement ellipsoids are given at 50% probability level.
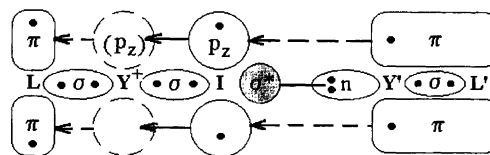
$$I-I\leftarrow I^- \leftrightarrow I^- \rightarrow I-I.$$

Scheme 3.

$$R-I + :CR_2' \rightarrow R-I\leftarrow CR_2' \leftrightarrow R^-\rightarrow I-{}^+CR_2'.$$

Scheme 4.

Scheme 5.

σ-bonded chalcogen, R–Y–R' (or L > Y), and then the thione and selone ligands containing a one-coordinate π-double-bonded chalcogen, L=Y. The principal difference between these classes of ligands is that the former can only donate a lone electron pair onto the central iodine atom without the possibility to delocalize the accepted positive charge upon the rest of the ligand (this is true in most cases, but we shall see that for some selenium ligands there are some specific effects), while the second can delocalize this positive charge owing to the resonance $L=Y\rightarrow M^+ \leftrightarrow L^+-Y-M$.

Tables 6 and 7 contain the most complete up to date summary of all these complexes based on CSD data and the data on our two complexes, I and II.

The interrelationship between the Y–I and I–X bond lengths is graphically presented in Fig. 3. Such a graph was first given by Herbstein and Schwotzer,[46] and this 'hyperbola' (in general it is not in a hyperbola, see below, but the overall reciprocal shape of this curve is in very good agreement with the hypervalent character of these iodine complexes, though only very few authors have pointed this out!) became a favourite reference of many subsequent papers. However, neither the authors of that graph nor subsequent workers have undertaken any attempt to explain the nature of this curve and what the factors are that determine the ratio $d(Y\!-\!I)/d(I\!-\!X)$ for each specific complex, i.e. why the corresponding point on the graph not only 'fits this curve well' but why it is positioned at that special point on the graph. A similar type of curve have been presented for 3c,4e systems based on Te^{II}.[46]

We can expect that for the 3c,4e hypervalent system Y–I–X, the total bond order of the bonds Y–I and I–X should be equal to unity:

$$N_Y + N_X = 1, \tag{1}$$

where N_Y is the bond order of the Y–I interaction and N_X is the bond order of the I–X interaction.

In accordance with Pauling's classical point of view,[30b] the length of a chemical bond is dependent upon the logarithm of its bond order. For an absolute change of the C–C bond length, the equation is:

$$d_N - d_1 = -0.6 \lg N \tag{2}$$

(where d_N is the bond length for bond order N and $d_1 = 1.54$ Å is the length of the corresponding single bond) and works well. This equation may be rewritten for a

Table 6. The main geometrical parameters of the hypervalent interactions L=Y–I–X (in an approximate order of increasing Y–I interaction) and intermolecular interactions with the strongest perturbing effect on the hypervalent moiety in thiane and selane complexes of iodine(I). Full names of the compounds are given in footnote below.

Compound[a]	d(Y–I)	d(I–X)	Intermolecular contacts[b]
Y=–S–; X=I			
'weak Y–I/strong I–X'			
yewnuj[1/5]	3.239	2.755	$-\beta$-D [SR$_2$; I···S 3.089 Å]
pelxuz[1/5,lt]	3.197	2.754	$-\beta$-D [SR$_2$; I···S 3.055 Å]
			α-H-b⊥ [H–(C–S); I···H 2.97 Å, ∠IHC 145°]
yewnuj[2/5]	3.089	2.755	$-\beta$-D [SR$_2$; I···S 3.239 Å]
pelxuz[2/5,lt]	3.055	2.754	$-\beta$-D [SR$_2$; I···S 3.197 Å]
			β-H-b⊥ [H–(C–S); I···H 2.97 Å, ∠IHC 145°]
'weakened Y–I/strengthened I–X'			
yewpar[1/3]	2.934	2.751	$-\alpha$-A⊥ [II(S); I···I 3.786 Å]
			$+\beta$-A⊥ [II(S); I···I 3.952 Å]
fajraj[1/2]	2.901	2.768	β-H-b⊥ [H–(C–S); I···H 2.95 Å, ∠IHC 153°]
yewpar[2/3]	2.880	2.773	$-\beta$-D⊥ [I(S)I; I···I 3.786 Å]
yewnuj[3/5]	2.886	2.782	$-\beta$-D⊥ [II(S); I···I 4.017 Å]
			$-\alpha$-A⊥ [II(S); I···I 4.064 Å]
pelxuz[3/5,lt]	2.870	2.785	$-\beta$-D⊥ [II(S); I···I 3.983 Å]
			$-\alpha$-A⊥ [II(S); I···I 4.023 Å]
dthini[ph]	2.870	2.789	$-\beta$-D⊥ [II(S); I···I 4.067 Å]
			$+\beta$-A⊥ [II(S); I···I 4.067 Å]
yewnuj[4/5]	2.878	2.792	$-\beta$-D⊥ [II(S); I···I 3.843 Å]
pelxuz[4/5,lt]	2.862	2.799	$-\beta$-D⊥ [II(S); I···I 3.777 Å]
yewpar[3/3]	2.865	2.768	$-\beta$-D⊥ [II(S); I···I 3.952 Å]
vutpef[1/4]	2.847	2.774	±β-DA∠ [II(S); I···I 3.784 Å, ∠III 140.6, 129.4°]
fajpub[1/2]	2.825	2.796	±β-DA∠ [II(S); I···I 3.721 Å, ∠III 154.2, 154.2°]
'undisturbed Y–I–X'			
fajpub[2/2]	2.805	2.796	
fajraj[2/2]	2.802	2.796	
benzsi[ph]	2.779	2.819	
'strengthened Y–I/weakened I–X'			
yewnuj[5/5]	2.791	2.818	$+\beta$-A⊥ [II(S); I···I 3.843 Å]
			$+\beta$-A⊥ [II(S); I···I 4.017 Å]
			$-\beta$-D⊥ [I(S)I; I···I 4.064 Å]
vutpef[2/4]	2.773	2.821	$+\beta$-A⊥ [II(I); I···I 3.551 Å]
			±β-DA∠ [II(S); I···I 3.720 Å, ∠III 153.5, 156.3°]
vutpef[3/4]	2.763	2.809	±β-DA∠ [II(S); I···I 3.784 Å, ∠III 129.4, 140.6°]
pelxuz[5/5,lt]	2.760	2.816	$+\beta$-A⊥ [II(S); I···I 3.777 Å]
			$+\beta$-A⊥ [II(S); I···I 3.983 Å]
			$-\beta$-D⊥ [I(S)I; I···I 4.023 Å]
'strong Y–I/weak I–X'			
isbcls[lt]	2.716	2.818	$+\beta$-A// [ClSb(S); I···Cl 3.517, Cl–Sb 2.450,
			Sb···S 3.106 Å, ∠IICl 175.7, IClSb 173.6°]
hemdim[SM]	2.720	2.853	$+\beta$-A// [II(S); I···I 3.629 Å, ∠III 170.0°]
vutpef[4/4]	2.653	2.902	$+\beta$-A⊥ [II(I); I···I 3.403 Å]
Y=–S–; X=Br			
'undisturbed Y–I–X'			
dthibr	2.687	2.646	
Y=–Se–; X=I			
'weakened Y–I/strengthened I–X'			
dseiod[ph]	2.830	2.870	±β*-DA∠ [(Se)II; I···Se 3.994 Å, ∠ISeI 148.8, IISe 148.4°]
			$+\beta$*-D// [(Se)II; I···Se 3.889 Å]
			$+\beta$*-D// [I(Se)I; I···Se 4.008 Å]
			$-\alpha$-A⊥ [SeC; I···Se 4.008 Å]
			±β-DA∠ [SeI(I); I···Se 3.994 Å, ∠IISe 148.4, ISeI 148.8°]
			$+\beta$-A⊥ [SeC; I···Se 3.889 Å]
thseli[ph]	2.765	2.913	$-\beta$*-A// [(Se)II; I···Se 3.636 Å, ∠ISeI 167.2, IISe 166.6°]
			$+\beta$*-D// [(Se)II; I···Se 4.200 Å]
			$+\beta$*-D// [(Se)II; I···Se 4.249 Å]
			$+\beta$-A// [SeI(I); I···Se 3.636 Å, ∠IISe 166.6, ISeI 167.2°]
			$+\beta$-A⊥ [SeC; I···Se 4.200 Å]
			$+\beta$-A⊥ [SeC; I···Se 4.249 Å]

Table 6. (Continued.)

Compound[a]	d(Y–I)	d(I–X)	Intermolecular contacts[b]
'strengthened Y–I/weakened I–X'			
oxseli[ph]	2.755	2.955	$+\beta^*$–D// [(Se)II; I···Se 3.708 Å]
			$+\beta^*$–D// [(Se)II; I···Se 4.001 Å]
			$+\beta$-A⊥ [SeC; I···Se 3.708 Å]
			$+\beta$-A⊥ [SeC; I···Se 4.001 Å]
Y =–Se–; X = Cl			
'weakened Y–I/strengthened I–X'			
oxseic[ph]	2.630	2.731	$-\beta^*$–A// [(Se)ICl; Cl···Se 3.605 Å, ∠ClSeI 176.9, IClSe 177.°]
			$+\beta^*$–D⊥ [(Se)ICl; Cl···Se 3.541 Å]
			$+\beta^*$–D⊥ [(Se)ICl; Cl···Se 3.588 Å]
			$+\beta$-A// [SeI(I); Cl···Se 3.605 Å, ∠IClSe 177.7, ClSeI 176.9°]
			$+\beta$-A⊥ [SeC; Cl···Se 3.541 Å]
			$+\beta$-A⊥ [SeC; Cl···Se 3.588 Å]
Y =–Se–(Se–); X = I			
'weak Y–I/strong I–X'			
kigfel	3.483	2.722	$-\beta$-D [Se(SeR)C; I···Se 3.483 Å]
'weakened (?) Y–I/strengthened (?) I–X'			
gihzig	2.992	2.774	$+\beta^*$–D⊥ [η²–(Se)II; I···Se 4.153, 4.252 Å
			(3.967 Å from the middle point I–I)]
			±β-DA∠ [II(Se); I···I 4.127 Å, ∠III 120.4, 120.4°]
			$+\beta$-A⊥ [SeSe(I); I···Se 3.588 Å]
			$-\alpha$-A⊥ [SeSe(I); I···Se 4.252 Å]
			$+\beta$-A⊥ [SeSe(I); I···Se 4.153 Å]

[a]To designate the compounds, the CSD refcodes have been used (here in alphabetical order): **benzsi**,[31] benzyl sulfide-iodine; **dseiod**,[32] 1,4-diselenane bis(iodine); **dthibr**,[33] 1,4-dithiane bis(iodine monobromide); **dthini**,[34] 1,4-dithiane bis(iodine); **fajpub**,[35] dithia(3.3.1)propellane bis(iodine); **fajraj**,[35] dithia(3.3.2)propellane bis(iodine); **gihzig**,[36] diphenyldiselenide iodine; **hemdim**,[37] bis((μ²-diiodosulfido-*S,S*)-(η⁵-cyclopentadienyl)-*tert*-butyliminomolybdenum); **isbcls**,[38] 1,4-dithiane trichloro-antimony iodine (at 113 K); **kigfel**,[39] bis(2,4,6-triisopropylphenyl) diselenide diiodide; **oxseic**,[40] 1-oxa-4-selenacyclohexane iodine monochloride complex; **oxsseli**,[41] 1,4-oxaselenane iodine; **pelxuz**,[42] catena(tetrakis(μ²-diiodo)-bis-(1,4,7-trithiacyclononane)) (≡**yewnuj**, see below) (at 150 K); **thseli**,[43] tetrahydroselenophene iodine; **vutpef**,[44] bis-(1,10-bis(diiodo)-4,7,13,16-tetraoxa-1,10-dithiacyclooctadecane) diiodine (at 153 K); **yewnuj**,[45] 1,4,7-trithiacyclononane bis-(diiodine) (≡ **pelxuz**, see above); **yewpar**,[45]-1,4,7-trithiacyclononane tris(diiodine). [b]Designations for intermolecular contacts (see text and Schemes 6–8 for more details): – or +, resulting character of the contact on the Y–I interaction (weakening or strengthening, respectively); β*, α or β, an atom influenced (Y, central I or X, respectively); A, D or H-b, a character of the influence of the neighbouring group on the Y–I–X moiety attacked (acceptor, donor, H-bonding); ⊥, ∠ or //, an orientation of the linear neighbouring molecule attacking (often iodine) relative to the axis of the Y–I–X group (orthogonal, inclined or colinear, respectively); the type of the neighbouring group is shown in brackets (if the neighbouring group, often I₂, is under strong apical influence too, the influencing atom is given in parentheses after the influenced atom), as well as the main geometrical parameters of the contact (in sequences Y–I–X···A–B the angle IXA is given first, then – XAB; in sequences A–B···Y–I–X the angle BYI is given first, then – ABY). [m]/[n] [n] = The total number of independent Y–I–X moieties in the structure (if any), and [m] is the number assigned each such moiety. [t]Low temperature data (see also the designations of the compounds above). [ph] Photomethod. [SM] Y=μ-(Mo₂)S.

relative change of the C–C bond length:

$$d_N/1.54 - 1 = -(0.6/1.54)\lg N \quad (3)$$

and then may be generalized for bonds of any type:

$$k(d_1 - d_N)/d_1 = \lg N \quad (4)$$

where the dimensionless coefficient '*k*' has a physical meaning of relative 'softness' of the bonding interaction (for the C–C bonding it is $1.54/0.6 = 2.57$; unfortunately, some authors still think this is a universal constant, see, for example, Ref. 59, but we shall demonstrate that this is not so).

The bond order may be expressed as

$$N = 10^{**}[k(d_1 - d_N)/d_1] \quad (5)$$

and eqn. (1) may be rewritten as:

$$10^{**}[k_Y(d_{Y1} - d_Y)/d_{Y1}] + 10^{**}[k_X(d_{X1} - d_X)/d_{X1}] = 1 \quad (6)$$

where d_{Y1} and d_{X1} are standard lengths of the single bonds Y–I and I–X, respectively, and d_Y and d_X are the running values of these bond lengths. Now, it is easy to see that the reciprocal dependence of d_Y on d_X is not a simple hyperbola $(y = a/x - b)$ but has a more complicated character.

The main question under discussion is how to determine particular values of the 'softness coefficients' k_Y and k_X. In general, it might be more correct to use separate values for each interaction, Y–I and I–X. On other hand, the nature of the 3c,4e bonding requires a common softness parameter. We have found that a common k_{YX} coefficient (which is individually adjusted

Table 7. The main geometrical parameters of the hypervalent interactions L=Y–I–X (in an approximate order of increasing Y–I interaction) and intermolecular interactions with the strongest disturbing effect on the hypervalent moiety in thione and selone complexes of iodine(I). Full names of compounds are given in footnote below.

Compound[a]	Ligand[b]	d(Y–I)	d(I–X)	Intermolecular contacts[c]
Y = (C)=S; X = I				
'weak Y–I/strong I–X'				
msnrod	⊥NR,S(5/7)	3.099	2.751	–β-D [S = ; I···S 3.099 Å]
'weakened Y–I/strengthened I–X'				
giglox$^{1/4}$	//C,NR(a)	2.920	2.751	–β-D⊥ [II(S); I···I 3.931 Å]
				+β-A⊥ [II(S); I···I 3.758 Å]
giglox$^{2/4}$	//C,NR(a)	2.892	2.738	–β-D⊥ [II(S); I···I 3.705 Å]
kuwdip$^{1/2}$	//C,NH(5/s)	2.843	2.767	β-H-b⊥ [H(N); H···I 2.97 Å, ∠NHI 144°]
giglox$^{3/4}$	//C,NR(a)	2.801	2.787	–β-D⊥ [II(S); I···I 3.758 Å]
				+β-A⊥ [II(S); I···I 3.931 Å]
giglox$^{4/4}$	//C,NR(a)	2.789	2.805	–β-D⊥ [II(S); I···I 3.746 Å]
				+β-A⊥ [II(S); I···I 3.705 Å]
'undisturbed or weakly influenced Y–I–X'				
pyitcc	=N–Co	2.796	2.804	
kuwdov	//NH,NH(5/s)	2.774	2.801	
vebcek	⊥NR,NR(5/7)	2.774	2.822	±β-DA∠ [II(S); I···I 3.608 Å, ∠III 148.9, 148.9°]
kuwdel	//NH,NH(5/s)	2.748	2.818	
kuwdip$^{2/2}$	//NH,NH(5/s)	2.738	2.849	
pejkiy	//S,S(5/s)	2.715	2.823	
varcia	//C,S(5/7)	2.711	2.832	±β-DA∠ [II(S); I···I 3.767 Å, ∠III 157.9, 157.9°]
				+β-A⊥ [S–S; I···S 3.537 Å, ∠ISS 145.5°]
tcapli	//C,NR(7/s)	2.687	2.879	
bzhtic	⊥NN,NN(a)	2.663	2.917	
gegnub/α	⊥NR,NR(5/7)	2.616	2.967	
gegnub/β	⊥NR,NR(5/7)	2.607	2.985	
'strengthened Y–I/weakened I–X'				
cewmog	//NH,NH(5/s)	2.580	2.984	+β-A⊥ [II(I); I···I 3.475 Å]
cewnat	//NH,NH(5/s)	2.588	2.986	+β*-D// [C=S; S···S 3.448 Å, ∠SSI 164.9, CSS 173.5°
				+β-A⊥ [II(I); I···I 4.091]
'strong Y–I/weak I–X'				
bzhtid	⊥NN,NN(a)	2.502	3.213	+β-A⊥ [II(I); I···I 3.282 Å]
				+β-A⊥ [II; I···I 3.152 Å]
				+β-A⊥ [II(I); I···I 3.712 Å]
cewmia	//NH,NH(5/s)	2.487	3.148	+β-A⊥ [II; I···I 3.003 Å]
yeshaf	//Ar$^+$,=S(a)	2.583	2.964	
Y = (P)=S; X = I				
'strengthened Y–I/weakened I–X'				
tphpsi	Ph,Ph,Ph(a)	2.730	2.837	+β-A⊥ [II(I); I···I 3.570 Å]
Y = (C)=Se; X = I				
'undisturbed or interinfluenced Y–I–X'				
yeyfen	//NR,S(5/s)	2.725	2.983	
yeyfox$^{1/3}$	//NR,S(5/7)	2.720	2.959	+β-A⊥ [II(I); I···I 3.381 Å]
				–α-A// [Se(II); I···Se 3.718 Å]
				+β*-D// [I(Se)I; Se···I 3.718 Å]
kuwdub	//NH,NH(5/s)	2.698	2.963	+β-A [Se(II); I···Se 3.750 Å]
				β-H-b⊥ [H(N); I···H 2.81 Å, ∠IHN 156°]
				+β*-D// [I(Se)II; I···Se 3.750 Å]
'strengthened Y–I/weakened I–X'				
yeyfox$^{2/3}$	//NR,S(5/7)	2.661	3.058	+β-A⊥ [II(I); I···I 3.341 Å]
				+β-A⊥ [II(I); I···I 3.526 Å]
				–α-A// [Se(II); I···Se 3.895 Å]
				–α-A⊥ [II(I); I···I 3.970 Å]
				+β*-D// [I(Se)I; I···Se 3.620 Å]
yeyfox$^{3/3}$	//NR,S(5/7)	2.639	3.071	+β-A⊥ [II(I); I···I 3.156 Å]
				+β-A⊥ [II(I); I···I 3.670 Å]
				–α-A// [Se(II); I···Se 3.620 Å]
				+β*-D// [I(Se)I; I···Se 3.895 Å]

Table 7. (Continued.)

Compound[a]	Ligand[b]	d(Y–I)	d(I–X)	Intermolecular contacts[c]
Y = (P)=Se; X = I				
'strong Y–I/weak I–X'				
I[t]	NR₂,NR₂,NR₂	2.596	3.215	+ β-A⊥ [II(I); I···I 3.175 Å] + β*-D// [(I)II; I···Se 3.872 Å] ± β-DA∠ [II(I); I···I 3.720 Å, ∠III 153.1, 175.°]
II[t]	NR₂,NR₂,NR₂	2.590	3.186	+ β-A⊥ [II(I); I···I 3.100 Å] + β-A// [II(I); I···I 3.338 Å, ∠III 165.9, 174.4°] + β*-D// [(I)II; I···Se 3.644 Å]
Y = (C)=Se; X = Br[d]				
'undisturbed Y–I–X'				
yeyfir	//NR,S(5/s)	2.689	2.907	
'strong Y–I/weak I–X'				
yeyfud	//NR,S(5/7)	2.565	3.129	+ β-A⊥ [IBr(Br); Br···I 2.803 Å] + β-A [Se(IBr); Br···Se 3.600 Å] + β*-D// [(Se)IBr; Br···Se 3.600 Å]

[a] To designate the compounds, the CSD refcodes have been used (here in alphabetical order): **bzhtic**,[46] 1,5-diphenylthiocarbazone diiodine; **bzhtid**,[46] bis(1,5-diphenyl-iodothiocarbazone) bis(pentaiodide) diiodine; **cewmia**,[46] ethylenethiourea bis(diiodine); **cewmog**,[46] bis(ethylenethiourea) tris(diiodine); **cewnat**,[46] 1-(1-imidazolin-2-yl)-2-thioxo-imidazolidinium triiodide ethylenethiourea diiodine; **gegnub/α**,[47] 1,3-dimethyl-2-thioimidazolium diiodine (alpha modification); **gegnub/β**,[47] 1,3-dimethyl-2-thio-imidazolium diiodine (beta modification); **giglox**,[48] bis(morpholinothiocarbonyl) bis(diiodine); **kuwdel**,[49] 5,5-dimethylimidazolidine-2,4-dithione diiodine; **kuwdip**,[49] 5,5-dimethylimidazolidine-2,4-dithione bis(diiodine); **kuwdov**,[49] 5,5-dimethyl-2-thioxoimidazolidin-4-one diiodine; **kuwdub**,[49] 5,5-dimethyl-2-selenoimidazolidine-4-one diiodine; **msnrod**,[50] 5-(2-methylmercapto-4-methyl-4,5-dihydro-1',3',4'-thiadiazol-5-ylidene)-3-ethylrhodanine iodine; **pejkiy**,[51] 1,3-dithiolan-2-thione-diiodine; **pyitcc**,[52] tetra(pyridine)-di(diiodothiocyanato) cobalt(III); **tcapli**,[53] N-methylthiocaprolactam iodine complex; **tphpsi**,[54] bis(S-iodine triphenylphosphinesulfide) iodine; **varcia**,[55] dithiolodithiole diiodine; **vebcek**,[56] 4,5,6,7-tetrathiocino(1,2-b:3,4-b')diimidazolyl-1,3,8,10-tetraethyl-2,9-dithihone bis(diiodine); **yeshaf**,[57] diiodide 1,3-diisopropyl-4,5-dimethylimidazolium-2-dithiocarboxylate (at 150 K); **yeyfen**,[58] (N-methyl-1,3-thiazolidine-2(3H)-selenone) diiodine; **yeyfir**,[58] (N-methyl-1,3-thiazolidine-2(3H)-selenone)-(0.75 iodine monobromide/0.25 diiodine); **yeyfox**,[58] (N-methylbenzothiazole-2(3H)-selenone) bis(diiodine); **yeyfud**,[58] N-methylbenzothiazole-2(3H)-selenone iodine dibromoiodide.
[b] Designations for ligands: // or ⊥, relative orientation of (A)(B)C=Y group of the ligand and the Y–I–X moiety (coplanar or orthogonal, respectively); then types of the (A) and (B) groups are given. Symbols in parentheses: (a) acyclic ligand; ([k]/[l]) k-membered cyclic ligand with l π-electrons ('s' instead of [l] means that the cyclic system is partially saturated).
[c] Designations for intermolecular contacts (see text and Schemes 6–8 for more details): − or +, resulting character of the contact on the Y–I interaction (weakening or strengthening, respectively); β*, α or β, the atom influenced (Y, central I or X, respectively); A, D or H-b, the type of influence of the neighbouring group on the Y–I–X moiety attacked (acceptor, donor, H-bonding); ⊥, ∠ or //, the orientation of the linear neighbouring molecule attacking (often iodine) relative to the axis of the Y–I–X group (orthogonal, inclined or colinear, respectively), the type of the neighbouring group is shown in brackets (if the neighbouring group, often I₂, is under strong apical influence too, the influencing atom is given in parentheses after the influenced atom), as well as the main geometrical parameters of the contact (in sequences Y–I–X···A–B the angle IXA is given first, then XAB; in sequences A–B···Y–I–X the angle BYI is given first, then ABY). [m]/[n] [n] = The total number of independent Y–I–X moieties in the structure (if any), and [m] is the number assigned each such moiety. [t] Low temperature data. [d] X = 0.75Br/0.25I in **yeyfir**.

for each YX combination) will fit each experimental bond length distribution well. Thus, $k_{SI} = 2.82$ gives an average total bond order of 0.99(4) for all the experimental examples of the S–I–I interaction (within the overall range 0.93–1.10), and $k_{SeI} = 3.04$ gives an average total bond order of 1.01(3) for all the experimental examples of the Se–I–I interaction (within the overall range 0.96–1.06). An attempt to apply Pauling's coefficient $k = 2.57$ (which has been calculated for C–C bonding only!) has failed: see dashed curves in Fig. 3. Intuitively, it is quite understandable that the 'softness' of the bonding interaction between the heavier atoms should be larger than that between carbon atoms: $k_{SeI} > k_{SI} > k_{CC}$.

To calculate these curves (Fig. 3), we have used the standard value 2.67 Å for the I–I single bond,[11] the sum

of Pauling's covalent radii 2.50 Å for the Se–I single bond[30a] and the modified sum of Pauling's covalent radii 2.35 Å for the S–I single bond (we have taken the covalent radius of sulfur equal to 1.02 Å, derived from the average value of the S–S single bond in dithianes,[22] instead of Pauling's value 1.04 Å[30a] and found that it fits better). As expected, the largest deviations of experimental points from the theoretical curves are in the areas with N values close to zero. The Pauling equation works well for bonds with significant covalent character but considerably overestimates bond order of interactions with mainly van der Waals character.

Mixed halogen/chalcogen hypervalent complexes of two-coordinated iodine(I) with thiane and selane ligands. To consider specific factors controlling the particular ratio
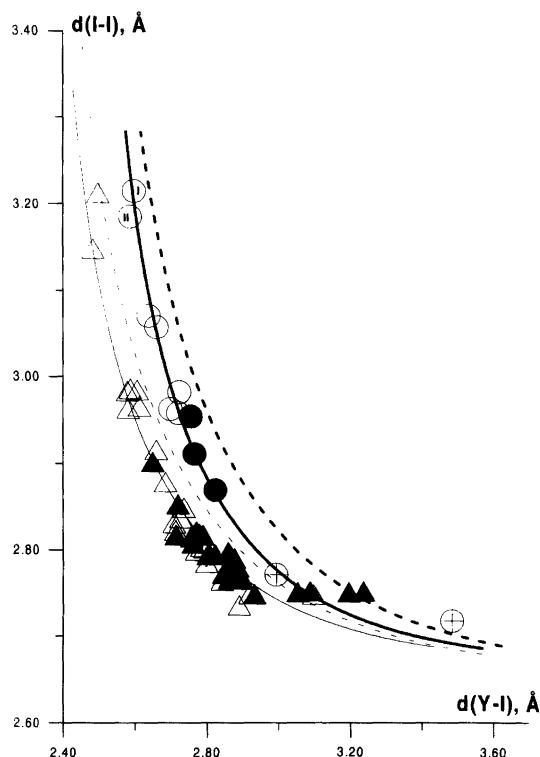
Fig. 3. Graph of Y–I vs. I–I bond distances in the hypervalent complexes of type Y–I–I (Tables 6 and 7). Points corresponding to Y = S are marked by triangles (open for thione and shaded for thiane complexes), and to Y = Se by circles (open for selone complexes, including **I** and **II**: see the labels, shaded for selane and crossed for diselane complexes). Theoretical curves are given by a thin line for the *S*-derivatives and by a bold line for the Se-derivatives [corresponding normalized Pauling's curves (see text) are shown by dashed lines].

of the Y–I and I–X interactions in the Y–I–X 3c,4e hypervalent moiety, we are first considering complexes of thiane and then selane ligands because of their simpler coordination behaviour, before we continue with the more complicated thione and selone derived systems.

Most of the thiane complexes are addition compounds of elemental diiodine with the corresponding aliphatic thianes, R_2S–I–I, with a few exceptions (Table 6). Looking at these ligands, we do not expect to see any large differences between the electron donating properties of sulfur in them. Nevertheless, the bond distances S–I and I–I exhibit very large ranges: 3.239–2.653 and 2.751–2.902 Å (theoretically corresponding to bond order variations from 0.08 to 0.43 and from 0.82 to 0.57), respectively. The wide variations are found not only from structure to structure but also for some independent interactions in the same structure (Table 6, Fig. 3).*

A very common way to explain this variation is that 'this is dependent on intermolecular interactions'. However, if the 'intermolecular interactions' can change

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*Moreover, there is a significant temperature dependence on this interaction: compare structures **pelxuz** and **yewnuj**.

the bond orders in the system investigated by ½ (!) we feel that we should analyse them systematically, especially since nobody has done this before.

Theoretically, the sulfur atom in the thianes may have both sp³-hybrid and non-hybrid electronic states. But in practice there is not a single structure where the thiane group acts as a donor of two lone pairs, and we have to assume its electron configuration as being of the non-hybridized variant. Therefore, the sulfur atom of the S–I–I/X group does not take part in any additional intermolecular interactions (its lone p-electron pair is just drawn into the hypervalent bond). On the contrary, the dihalogen moiety has some additional possibilities to be drawn into various intermolecular donor–acceptor interactions. To begin with, the central α-iodine in the Y–I–I/X group, has two lone p-electron pairs and can act as a donor. The peripheral β-iodine/X has two lone p-electron pairs as well, but it can act not only as a donor but as an acceptor through the σ*-orbital of the I–I bond at its apical site, especially if, upon complex formation, the 'diiodine molecule' is not particularly perturbed (i.e. that orbital is available) by a stronger hypervalent interaction with the sulfur atom at its opposite end. We can see that the participation of the α- and β-iodine atoms in additional donor–acceptor interactions leads to different consequences for the stability of the original 3c,4e-system.

Thus, any outer acceptors attacking the β-iodine/X lone electron pairs (in the plane orthogonal to the Y–I–I/X axis) should promote delocalization of a negative charge from the terminal iodine/X and thereby stabilize the resonance form R_2S^+–I←I⁻ with a resulting strengthening of the S–I interaction. In the same way, the acceptors attacking this atom in its apical site (*trans* to the I–I bond) should stabilize that resonance form as well. On the other hand, any outer donors at the same site of this atom compete with the opposite thia group for the 'diiodine' σ*-orbital and should cause a weakening of the S–I interaction. Moreover, any acceptors of lone electron pairs of the central iodine atom will destroy the original 3c,4e system, redirecting valence orbitals of this atom into the orthogonal plane.

The most common 'outer' donor/acceptor group in the considered structures is an iodine molecule (just coordinated or individual), and the most common mutual arrangements of these groups are shown in Scheme 6 (designation of the configurations is given in correspondence with Tables 6 and 7). However, there are some intermediate cases when an inclined 'outer' diiodine molecule can attack the β-iodine in its apical position as
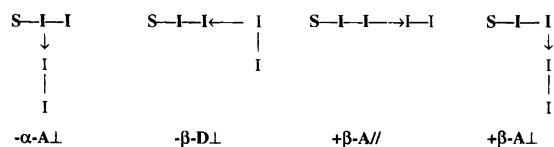
Scheme 6.

a donor and, simultaneously, in its orthogonal position
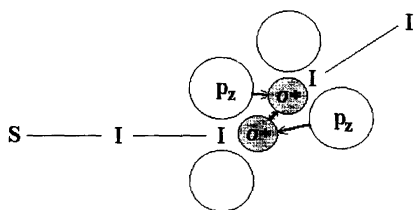
Scheme 7.

as an acceptor (Scheme 7). Depending on a specific mutual orientation of these linear moieties (S–I–I and I–I), any one of two these contributing interactions (designated as $-\beta$-D$\angle$ and $+\beta$-A$\angle$ in Tables 6 and 7) may predominate.

Now, we can classify the structures of the known thiane complexes by looking at the donor/acceptor nature of the additional intermolecular contacts and their effect on the 3c,4e system. Indeed, the 'antibonding' contacts dominate at the top of the Table 6 (structures labelled as 'weak Y–I' and 'weakened Y–I') and, in the opposite way, the 'bonding' contacts are characteristic of structures at the bottom of this list (labelled as 'strengthened Y–I' or 'strong Y–I') in good agreement with our assumptions.

In fact, the top four lines in this table (labelled as 'weak' interactions) belong to the same type: there is a bridging diiodine molecule symmetrically disposed between two thiane donor groups. Their strong dative influences are mutually exclusive and leave the diiodine molecule only slightly perturbed.

We can see for the 'weakened' structures, that the short $-\alpha$-A$\perp$ contacts are indeed the most unfavourable. The $-\beta$-D$\perp$ contacts with an 'outer' diiodine are not so destructive for the main 3c,4e system as the abovementioned $-\beta$-D interactions with a thiane sulfur, but they weaken this system as well. The 'inclined' contacts $-\beta$-D$\angle$ and $+\beta$-A$\angle$ give only a very small effect on the geometry of the 3c,4e hypervalent system because of their 'mixed' action.
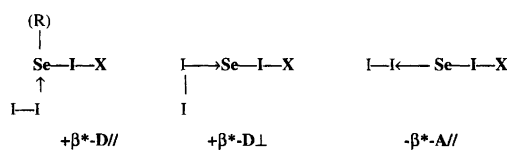
There are some structures which may be considered 'undisturbed'. With an exception of the rather imprecise **benzsi** structure, two other structures, **fajpub** and **fajraj** demonstrate an excellent coincidence of their structural parameters [S–I 2.805(2) and 2.802(2) Å; I–I 2.796(1) Å in both cases] in the absence of specific intermolecular interactions, and are examples of a pure $R_2S{\rightarrow}I_2$ interaction. The **dthibr** structure is an example of an 'undisturbed' $R_2S{\rightarrow}IBr$ interaction, and we can see that the *trans*-influence of the bromide anion at iodine(I) is quite comparable with that of thiane [the bond length S–I 2.687(2) Å is only a little longer than 2.674(7) Å in the symmetrical S–I–S complex of heptasulfur[25]] and both of them have a weaker *trans*-influence than the iodide ion.

However, additional $+\beta$-A$\perp$ contacts can reduce the iodide *trans*-influence to the bromide level, especially if the ability of the 'outer' acceptor (I_2 molecule) is not
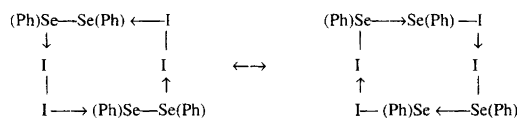
weakened by a participation in other 3c,4e systems: the shortest distance S–I found in this group of complexes [2.653(3) Å, **vutpef**[4/4], Table 6] as well as the longest I–I distance [2.902(1) Å] are a result of such interaction with an essentially isolated diiodine molecule.

It seems that weak H bonds with β-halogen atoms do not give a similar acceptor effect (evidently due to the mainly electrostatic character of this interaction) and act rather as sterical hindrances (see **fajraj**[1/2], Table 6). On the other hand, the $+\beta$-A// contacts give, in general, nearly the same influence on the S–I interaction as the $+\beta$-A$\perp$ contacts (an especially interesting example is the **isbcls** structure where the acceptor is another 3c,4e system, Cl–Sb–S), even though they should be statistically more rare because of the more strict geometrical conditions imposed.

The coordination behaviour of selanes and especially 1,2-diselanes is more complicated than that of thianes. The Se^{II} atom displays a much more pronounced ability to take part in additional hypervalent interactions than S^{II} and has a tendency to attain an octahedral coordination environment. In addition to three-coordination through p-orbitals, it forms two Se–C σ^*-orbitals which can be attacked at the Se contiguous end by some 'outer' donors with a large enough *trans*-influence. Besides, its coordination site opposite to the main Se–I–X 3c,4e system (the newly formed Se–I σ^*-orbital) may be the object of an 'outer' donor or acceptor influence as well. Of course, the effect of the Se-coordinated 'outer' donors and acceptors on the Se–I interaction is inverted as compared with those at the X atom [the resonance form $L{=}Y^+{-}I{\leftarrow}X^-$ should be stabilized by donors at Se (Y) and by acceptors at X]. The main possible types of such interactions with I_2 molecules (the most common donors/acceptors in these systems) may be as shown in Scheme 8. Indeed, the $+\beta^*$-D// interactions are common for the compounds known, even though their effect on the main 3c,4e system does not seem to be as large as that of the $-\beta^*$-A// interactions, which are very common and predominate (the only example with an incomplete octahedral environment of the Se atom in such complexes is the structure of **oxseli**; Table 6). There is no example of the $+\beta^*$-D$\perp$ interactions for selane complexes (the bond order of the main Se–I interaction is small in these complexes, so the acceptor ability of this group at the apical site of Se is not great enough) but there is one example (**dseiod**) of a contact of the same geometry as in the abovementioned mixed $-\beta$-D$\angle/+\beta$-A$\angle$ interactions. It may be labelled as a $+\beta^*$-D$\angle/-\beta^*$-A$\angle$

Scheme 8.

(Ph)Se—Se(Ph) ←—I   (Ph)Se—→Se(Ph) —I
    ↓ | | ↓
    I   I   ←—→   I   I
    | ↑   ↑ |
    I—→ (Ph)Se—Se(Ph)   I— (Ph)Se ←—Se(Ph)

Scheme 9.

interaction, and its total effect seems to be antibonding in this particular case.

The ability of the Se atom to be a separate centre of a 3c,4e system is more fully expressed in 1,2-diselanes (diselenides). In this case, the interplay between the Se–Se–I and Se–I–I 3c,4e systems should give very interesting results. Unfortunately, only two representatives of these compounds are known, **kigfel** and **gihzig**. The former is only a trivial case of a practically undisturbed diiodine bridging two equally strong donor centres (Table 6; cf. **pelxuz/yewnuj**$^{1/5,2/5}$) but the second is of special interest. This is a cyclic aggregate comprising different Se–Se–I and Se–I–I 3c,4e systems interacting in a way very favourable for the resonance* (Scheme 9). This aggregate may be considered as a model of a preliminary state of a dismutation reaction, $2R_2Se_2 + 2I_2 \rightarrow 4RSeI$.[36] Nevertheless, the bond length distribution in this compound does not correspond to our (and the authors of that paper)[36] expectations. The hypervalent interaction Se→I is unexpectedly weak in this crystal structure (Table 6), and we can only propose that this might be a consequence of some alternative (though weak) antibonding intermolecular interactions (Table 6). In any case, more structural examples of these interesting complexes would be desirable to make a more definite conclusion.

Mixed halogen/chalcogen hypervalent complexes of two-coordinated iodine(I) with thione and selone ligands. The thione and selone complexes of iodine(I) comprise an additional factor which affects the L=Y–I–X interaction. The double-bonded Y atom of the ligands has an extra opportunity to delocalize the positive charge accepted, thus the Y–I interaction can become stronger [see the resonance formula above, Scheme 2(b)]. To demonstrate this, we can compare the bond lengths S–I in 'undisturbed' (with an absent or weak effect of intermolecular interactions on the S–I–X group) thiane (2.78–2.81 Å; Table 6) and thione complexes (2.61–2.80 Å; Table 7). Moreover, we can see that the points corresponding to the thione and selone complexes preferentially populate the top part of the curves in Fig. 3, as compared with the thiane and selane complexes.

However, as distinct from the clearly pronounced $d(Y–I)/d(I–X)$ inter-relationship (Fig. 3), the mutual correspondence between the L=Y and Y–I bonding interactions is not so unambiguous. In Fig. 4 it is shown in terms of the corresponding bond orders, $N(C=Y)$ and

* The designation (Ph) means that bonds Se–Ph are orthogonal to the plane of the main Se–I interactions, and their σ^*-orbitals do not take part in this bonding.
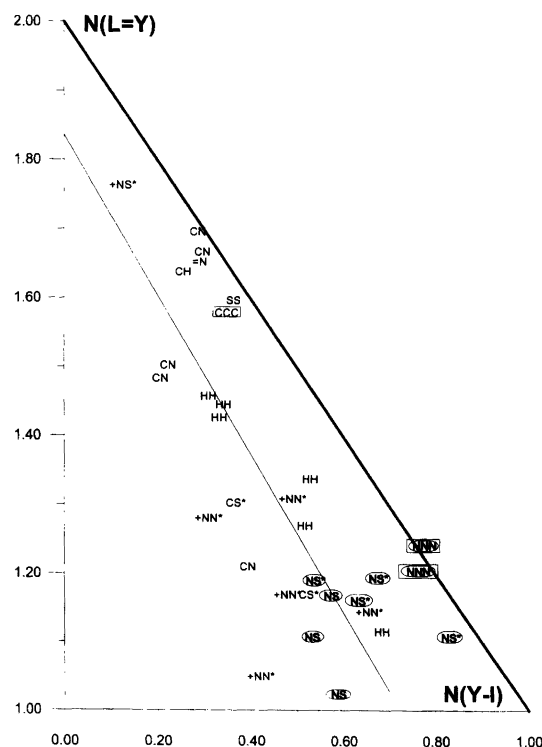
Fig. 4. Graph of bond order of C=Y bonds (or in a few cases P=Y bonds) [N(L=Y)] vs. bond order of Y–I bonds [N(Y–I)] in the thione and selone hypervalent complexes of type L=Y–I–X (Table 8). Shortened designations for ligands are used: (+) orthogonal relative orientation of (A)(B)C=Y group of the ligand and the Y–I–X moiety. Then types of the (A) and (B) groups are given ('N' and 'H' mean NR and NH groups, respectively); (*) ligands with increased ability to delocalize the positive charge accepted (pre-aromatic cyclic structures or extended π-conjugated chains). Points corresponding to Y = Se are marked by ovals, and two phosphane derivatives by rectangles. The best-fit-line (a linear approximation) for the (A)(B)C=S–I–I complexes [eqn. (10)] is given by a thin line. Theoretical dependence [eqn. (8)] is shown by a bold line.

$N(Y–I)$. These values have been calculated from the corresponding bond lengths (Table 8) according to eqn. (5) using the standard bond lengths $d_1 = 1.76$ Å [C(sp^2)–S] and 1.91 Å [C(sp^2)–Se] [derived from the covalent radius[60] 0.74 Å for C(sp^2) and the aforementioned values for S and Se]. The corresponding 'softness' coefficients for the bonds C(sp^2)–S ($k = 3.31$) and C(sp^2)–Se ($k = 2.61$) have been calculated according to the equation:

$$k = (d_1 \lg 2)/(d_1 - d_2) \tag{7}$$

using the standard bond lengths $d_2 = 1.60$ Å for the localized double C=S bond[22] and 1.69 Å for the C=Se bond (based on the structure of carbon diselenide[61]).

Presumably, if the chalcogen atom in these complexes acts as an 'ideal' conductor of the positive charge accepted, i.e. the structure of the complexes represents a superposition of the resonance forms (a) and (b) (Scheme 2), all the points in Fig. 4 should lie on the bold

Table 8. The bond lengths L=Y [d(L=Y), Å] as compared with bond distances Y–I [d(Y–I), Å], and the corresponding bond orders [N(L=Y) and N(Y–I)] in hypervalent moieties L=Y–I–X of the thione and selone complexes of iodine (I) given in order of increasing the resulting negative charge localized on the Y atom [Q(Y) = N(L=Y) + N(Y–I) − 2; e]. The names of the compounds and designations for the ligands are given as in Table 7.

Compound	Y=*Ipso*-atom	Ligand	d(L=Y)	d(Y–I)	N(L=Y)	N(Y–I)	Q(Y)	Shortened designation[a]
II	Se=P	NR2,NR2,NR2	2.214	2.590	1.24	0.78	+0.02	NNN
giglox[3/4]	S=C	//C,NR(a)	1.638	2.801	1.70	0.29	−0.02	CN
I	Se=P	NR2,NR2,NR2	2.222	2.596	1.20	0.76	−0.03	NNN
giglox[4/4]	S=C	//C,NR(a)	1.642	2.789	1.67	0.30	−0.04	CN
pejkiy	S=C	//S,S(5/s)	1.652	2.715	1.60	0.36	−0.04	SS
pyitcc	S=C	=N–Co(a)	1.644	2.796	1.65	0.29	−0.06	=N
yeyfud	Se=C	//NR,S(5/7)	1.878	2.565	1.11	0.83	−0.06	NS*
tphpsi	S=P	Ph,Ph,Ph	2.008	2.730	1.58	0.35	−0.07	CCC
kuwdip[1/2]	S=C	//C,NH(5/s)	1.646	2.843	1.64	0.26	−0.11	CH
msnrod	S=C	⊥NR,S(5/7)	1.629	3.099	1.76	0.13	−0.11	+NS*
yeyfox[3/3]	Se=C	//NR,S(5/7)	1.854	2.639	1.19	0.68	−0.13	NS*
cewmog	S=C	//NH,NH(5/s)	1.693	2.580	1.34	0.53	−0.13	HH
bzhtid	S=C	⊥NN,NN(a)	1.729	2.502	1.14	0.66	−0.20	+NN*
gegnub/β	S=C	⊥NR,NR(5/7)	1.698	2.607	1.31	0.49	−0.20	+NN*
cewmia	S=C	//NH,NH(5/s)	1.735	2.487	1.11	0.68	−0.20	HH
yeyfox[2/3]	Se=C	//NR,S(5/7)	1.863	2.661	1.16	0.64	−0.20	NS*
kuwdip[2/2]	S=C	//NH,NH(5/s)	1.675	2.738	1.44	0.34	−0.21	HH
cewnat	S=C	//NH,NH(5/s)	1.705	2.588	1.27	0.52	−0.21	HH
kuwdov	S=C	//NH,NH(5/s)	1.673	2.774	1.46	0.31	−0.23	HH
kuwdel	S=C	//NH,NH(5/s)	1.678	2.748	1.43	0.33	−0.24	HH
kuwdub	Se=C	//NH,NH(5/s)	1.861	2.698	1.17	0.57	−0.26	NS
yeyfox[1/3]	Se=C	//NR,S(5/7)	1.855	2.72	1.19	0.54	−0.27	NS*
giglox[2/4]	S=C	//C,NR(a)	1.666	2.892	1.50	0.22	−0.27	CN
yeshaf	S=C	//Ar+,=S(a)	1.724	2.583	1.17	0.53	−0.31	CS*
giglox[1/4]	S=C	//C,NR(a)	1.669	2.92	1.48	0.21	−0.31	CN
varcia	S=C	//C,S(5/7)	1.699	2.711	1.30	0.37	−0.33	CS*
gegnub/α	S=C	⊥NR,NR(5/7)	1.724	2.616	1.17	0.48	−0.35	+NN*
yeyfen	Se=C	//NR,S(5/s)	1.878	2.725	1.11	0.53	−0.36	NS
yeyfir	Se=C	//NR,S(5/s)	1.903	2.689	1.02	0.59	−0.39	NS
tcapli	S=C	//C,NR(7/s)	1.716	2.687	1.21	0.39	−0.40	CN
vebcek	S=C	⊥NR,NR(5/7)	1.703	2.774	1.28	0.31	−0.41	+NN*
bzhtic	S=C	⊥NN,NN(a)	1.749	2.663	1.05	0.42	−0.53	+NN*

[a] Shortened designations of ligands as used in Fig. 4.

line in Fig. 4, defined as:

$$N(C=Y) + N(Y–I) = 2 \qquad (8)$$

similar to eqn. (1). However, all the experimental points are situated to the left and below this line. It means, that the total bond order at the chalcogen atom is always less than 2:

$$N(C–Y) + N(Y \cdots I) < 2 \qquad (9)$$

and this atom always keeps a noticeable negative charge (Table 8). Generally, all the points are closer to another line, which can be given as the best-fit line by the equation:

$$N(C–Y) + 1.16N(Y \cdots I) = 1.84 \qquad (10)$$

for the thione complexes.

It is possible to explain this fact, keeping in mind that the majority of these ligands have a structure with partially separated charges due to the resonance shown in Scheme 10 if they contain one or two π-electron donor groups A and B which can be conjugated with the double bond C=Y. Indeed, according to eqn. (7), the bond C=S
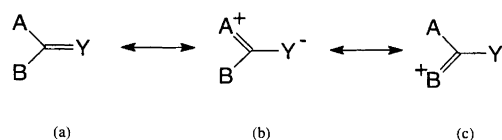
Scheme 10.

in, e.g., non-coordinated thioureas (av. 1.68 Å)[22] has a bond order of only 1.41 [A, B=(R/H)₂N-], i.e. the sulfur atom has a negative charge of 0.59 e. We can expect that ligands with large π-donor effects of the A and B groups should form more stable complexes and give a larger bond order of the Y–I interaction. In general, it means that the points on the bottom of the graph represent complexes with good π-donor ability of L which results both in a large charge on Y (ΣN < 2, distinct shift left and down from the theoretical line) and in good complexing ability of the ligand (bottom right corner of the graph). This is in a good agreement with the observed mutual orientation of the lines [eqns. (8) and (10)] in Fig. 4. The corresponding points on the top of the graph (Fig. 4) should be less distant from the theoretical line.

These points represent complexes with low π-donor ability of L, which results both in a small charge on Y ($\Sigma N \approx 2$, small shift left and down from the theoretical line) and in poor complexing ability (top left corner of the graph).

However, this is only a general trend, because the particular positions of the points in Fig. 4 are also dependent on other factors: (a) Moderate quality of most of the experimental data available; there are no low temperature experiments (with an exception of our data). Thus, the precision of the C=S bond lengths in these structures (containing many heavy atoms) is usually 0.01–0.02 Å. This corresponds to an uncertainty in the calculated bond orders of 0.07–0.13 (in addition to the very approximate character of the calculations used). (b) The aforementioned intermolecular interactions with participation of the X counterpart of the complexes can enable the L=Y ligands with poor complexing ability to give stronger Y–I bonds and vice versa. (c) In turn, the π-donor ability of L can be modified by outside factors, such as π-donor–acceptor intermolecular interactions and intermolecular H bonds.

The effect of the modest quality of several experimental data used may be illustrated well by the **giglox** structure.[48] The four independent C=S bond lengths determined in that work with $\sigma = 0.02$ Å show an abnormal interrelationship as compared with corresponding S–I bond lengths [shorter C=S bonds correspond to shorter S–I bonds; see Table 8 and Fig. 4 (the four 'CN' points on the top of the graph)].

The most preferable situation for the delocalization of the positive charge upon the ligand should be, for instance, when L represents a cyclic π-conjugated system which can become aromatic in the case of the loss of one electron [ligands marked as (5/7) in Tables 7 and 8]. We can see that the complexes **gegnub** reach a bond order for the S–I interaction equal to ca. 0.5 due solely to this effect, without any additional 'outer' factors (Tables 7 and 8).[47] Moreover, it is quite obvious that the points corresponding to such ligands (marked by an asterisk in Fig. 4) are concentrated on the bottom of the graph (Fig. 4) with a medium or large $Q(Y)$ value (Table 8). The only exception is the **msnrod** structure[50] (see the upper '+NS*' point in Fig. 4) where the S–I interaction is suppressed by a very unfavourable $-\beta$-**D** intermolecular interaction (the symmetrically bridging I_2 molecule between two ligands; cf. the aforementioned analogous **kigfel, yewnuj** and **pelxuz** structures, Table 6).

On the other hand, there are several thione and selone complexes where the strengthening effect of the crystalline environment gives some further shortening of the Y–I bond in combination with the strong π-donor properties of ligands (these examples are labelled as 'strengthened Y–I' or 'strong Y–I' in Table 7). In the extreme cases (such as **bzhtid, cewmia, yeyfox**) we can observe a practically complete transfer of the positive charge to the L group (comparable with that in ionic **yeshaf**) and delocalization of the negative charge over

extended $[I_3]^-$ or even $[I_{12}]^{2-}$ (**bzhtid**) outgoing ionic groups. The *trans*-influence of these bulky poly-iodide groups becomes comparable (or even smaller) to that of the bromide ion (cf. **yeyfir** or **yeyfud**; Table 7).

In many cases the increased single-bonded character of a strongly coordinated L=Y group is indicated by its orthogonal orientation (even when this is forced by sterical reasons) of the π-conjugated part of the ligand relative to the Y–I–X moiety (complexes marked by '$\perp$' in Tables 7 and 8 and by '+' in Table 8 and in Fig. 4). Indeed, in the case of a non-conjugated ligand [Scheme 10(a)] only one p-electron pair of the Y atom (in the plane of the L=Y group) is available for coordination.* However, in the ylide resonance form [Scheme 10(b,c)] another p-electron orbital of Y (the one formerly involved in the L=Y π-bond, orthogonal to the L=Y plane) becomes a lone pair accessible for coordination.

In general, the data in Table 7 show a wide variety of bond length distribution in the Y–I–X group. This is dependent on the possibilities for delocalization of both the positive charge (over an L group) and the negative charge (through donor–acceptor intermolecular interactions). Finally, we want to emphasize that the hypervalent 3c,4e scheme, used in this paper for their description, not only works well on the crystallographic data. In addition, we find it a very productive theoretical approach to explain, classify and, maybe, to predict mechanisms of reactions in the system $[L=Y]/[X_2]$. We hope that the following chemical diagram can give a more clear and systematic view of this approach as distinguished from some old[46,47] and still existing[62,63] approaches (Scheme 11).

The positively charged L^+ part of many of these intermediates and derivatives can act, in turn, as a regular organic cation/carbocation in some subsequent reactions (depending on the specific conditions and its particular chemical structure). It can, for instance, eliminate H^+ (or another cationic group), becoming an electroneutral molecule, or be the object of a nucleophilic attack by Lewis acids, giving addition products, or undergo a combination of these transformations as illustrated by the Johnson–Edens reaction.[46,64]

Mixed halogen/chalcogen hypervalent complexes of two-coordinated iodine(I) with phosphanesulfide and -selenide ligands. Chalcogen compounds of phosphorus(V) are known as ligands in iodine(I) complexes by a single (structurally investigated) example: **tphpsi**,[54] bis(*S*-iodine-triphenylphosphinesulfide)iodine. In general, this class of ligands should be quite a good reservoir for the positive charge, especially phosphortriamide derivatives owing to the resonance shown in Scheme 12,

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* We are assuming that the S and Se atoms in the thione and selone complexes have a non-hybrid electronic state (proceeding from origins similar to those used for thiane and selane complexes; see above).
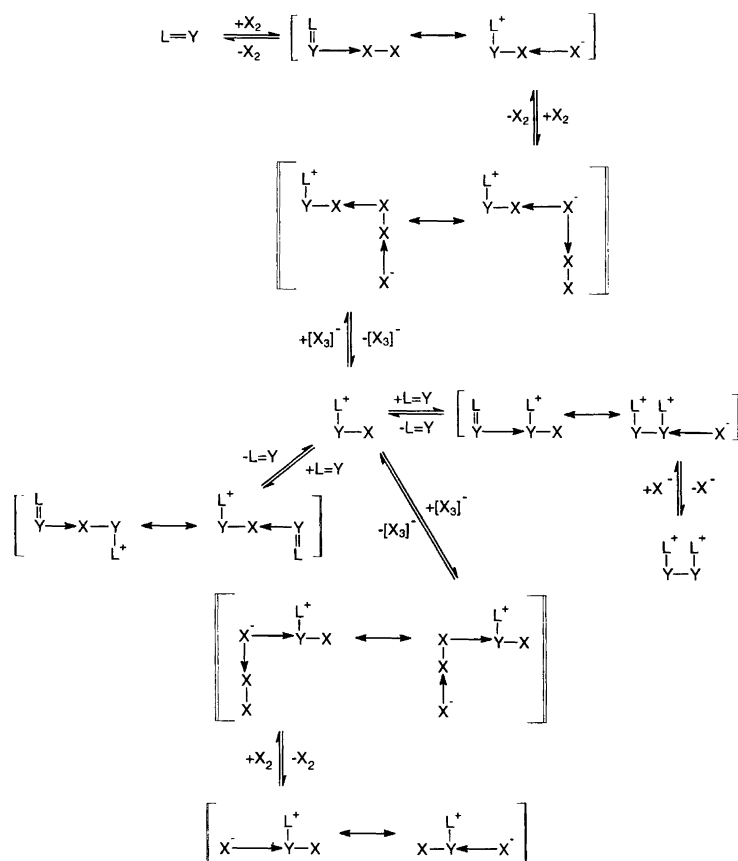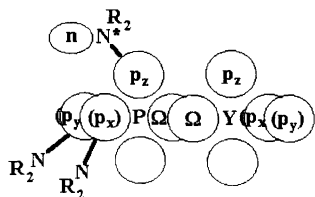
Scheme 11.
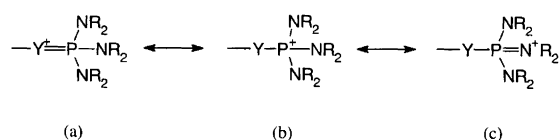
Scheme 12.

and therefore their complexing ability should be comparable with, for instance, that of thio- and selenourea.

In our previous paper[1] we made a review of the structurally studied chalcogen phosphortriamides and their hypervalent complexes with tellurium(II) – isoelectronic analogues of the complexes of iodine(I) (see above). We have shown that the complexing ability (trans-influence) of these compounds in the hypervalent system is slightly lower than that of the corresponding urea derivatives. Indeed, the trans-influence of triphenylphosphinesulfide in the complex tphpsi is relatively weak (Table 7). Moreover, the data in Table 8 and Fig. 4 indicate a comparatively small ability of this ligand to accept/delocalize positive charge from the sulfur atom. To calculate the bond order of the P=S bond in the coordinated ligand (as well as bond order of P=Se bonds in compounds I and II), we have used eqns. (7) and (5), Pauling's covalent radius of P (1.10 Å),[30a] the aforementioned radii for S (1.02 Å) and Se (1.17 Å) and standard[22]

bond lengths for the double bonds P=S (1.95 Å) and P=Se (2.09 Å).

An interesting feature of the chalcogen phosphortriamides[1,5,65-68] is their asymmetry, quite unexpected from the classical point of view. Every one of these compounds contains two different sorts of nitrogen atoms: one 'special' nitrogen (N*) which has a pronounced sp^3-hybridized pyramidal configuration with the lone n-electron pair directed in an antiparallel fashion to the P=Y bond (its coordination plane is nearly perpendicular to the P=Y bond). The other two nitrogens are essentially sp^2-hybridized, with their coordination planes only slightly inclined (usually less than 30°) to the P=Y bond. As a result, the P–N bond lengths and N–P–N and N–P=Y bond angles differ very noticeably [the P–N* bond is noticeably lengthened [1.65–1.68, av. 1.669(14) Å] and the bond angle N*–P=Y is significantly enlarged [114–117, av. 115.5(11)°] as compared with the two others [1.62–1.67, av. 1.650(13) Å; 110–113, av. 111.6(11)°]. In our previous paper[1] we showed that valence electron density distribution in these compounds is very unusual, and does not correspond to the classical notion of an sp^3-hybridized electronic state of the phosphorus atom. Instead, it is most likely that the phosphorus atom and the chalcogen atom have unhybridized electronic states, and are bonded in a manner similar to

that proposed by the Ω-bonding model for phosphine oxides[4] (Scheme 13). Stereoelectronic conditions for the three amino groups are therefore unequal.

Scheme 13.

A very interesting transformation of these geometrical parameters occurs upon complexation of the ligands:[1,69] the N* atom becomes practically sp^2-hybridized, in line with the other two nitrogen atoms, though still keeps its special orientation. Also, the P–N* bond becomes much shorter (1.62–1.65, av. 1.634 Å), even shorter than the two other P–N bonds (these are practically unchanged: 1.62–1.67, av. 1.645 Å). Finally, the coordinated (central) atom lies very close to the plane defined by the N*–P=Y group, *trans* or *cis* to N*.

We can conclude using the available facts, that π-conjugation of the amine groups with the phosphorus–chalcogen moiety has a different character (we can not state definitely yet what type) for the special nitrogen atom on one side and the two other nitrogen atoms on the other. It seems the acceptance of positive charge by the phosphorus atom upon ligand coordination in a hypervalent system leads to a change of its electronic state from non-hybridized to sp^3-hybridized, and that all three substituents (amino groups in our case) become more or less equivalent. Such a reorganization of the electronic system in the phosphortriamides upon coordination differs, in principle, from that found in chalcogenurea analogues and seems to be less effective for acceptance of positive charge. This is seen by comparing the *trans*-influences of the chalcogenphosphorus ligands and organic chalcogenides[1] (Table 7) and looking at estimates of charge transfer in the phosphorus-derived ligands (Table 8, Fig. 4).

Nevertheless, the complexes investigated by us, I and II, have the strongest Se–I interaction among the selone-iodine complexes. The Se–I bond lengths are 2.596(1) Å in I and 2.590(1) Å in II. These are much shorter than in oxseic (2.630 Å, Table 6) with chloride as the outgoing ion and comparable with that found in yeyfud (2.565 Å, Table 7) with bromide (actually [BrIBr]$^-$) as the outgoing group.

Correspondingly, the Se–P distance, 2.222(2) Å in I and 2.214(1) Å in II, is lengthened not only as compared with that in non-coordinated ligands [2.120(1) Å in tris(dimethylamino)phosphaneselenide, **tdmse**, and 2.106(1) Å in tris(N-morpholino)phosphaneselenide, **trmse**],[57] but also compared to the similar isoelectronic tellurium(II) hypervalent complexes [2.183(2) Å in BrTePhtdmse,[1] and 2.182(2) Å in BrTePhtrmse and 2.176(2) Å in ClTePhtrmse[62]]. It is practically equal

to the single Se–P bond length in the [$(Me_2N)_3P$–Se–Se–$P(NMe_2)_3$]$^{2+}$ dication, 2.227(8) Å[70] (see the estimated bond orders in Table 8). This means that both of the complexes investigated correspond very closely to the resonance form [Scheme 12(b)] comprising an R_3P^+SeI cation which is only slightly disturbed by a halide counterion, and that the *trans*-influence of the phosphaneselenide ligands predominates in these hypervalent compounds.

However, both of the coordinated ligands, **tdmse** and **trmse**, still retain the special nitrogen atom, N*. The N* atom is represented by N(2) in I and N(1) in II (Figs. 1 and 2, Tables 4 and 5). In I, the values of ψN* and τN* are 153.0 and −161.0°, respectively,† (ψN are 164.6 and 169.4°, τN are 60.0 and 36.4°). For comparison, in **tdmse**, ψN* and τN* are 132.3 and 170.7°, in BrTePh**tdmse** 163.9 and 156.7°, respectively; values of ψN and τN remain more or less constant in all the compounds.[1] This means that the special N(2) atom in I still has a pyramidal configuration (though much less pronounced than that in the non-coordinated molecule), and its lone electron pair is *anti*-oriented relative to P–Se bond. The P–N* bond is shortened as compared with the 'free' ligand [1.644(6) and 1.679(3) Å, respectively], but to a lesser degree than in the corresponding Te complex [1.620(5) Å], being closer to the two other P–N bonds [1.619 and 1.615(6) Å]. The Se–P–N bond angles [110.8 and 110.2(2)°] remain the same as in the ligand and the Te complex (108–113°) but the Se–P–N* bond angle becomes smaller: 106.1(2)° instead of 114.4(1)° in **tdmse** and 114.7(2)° in BrTePh**tdmse**. Perhaps the reason for this lies in a different relative orientation of N* and the central atom (I or Te) in I [relatively rare, *trans*, torsion angle N*–P–Se–I −157.8(2)°] and in BrTePh**tdmse** [*cis*, torsion angle N*–P–Se–Te 27.8(2)°] though in both of them the N*–P–Y–M moiety keeps the abovementioned planar arrangement.

The situation with the special nitrogen atom is more intricate in complex II. The special N(1) atom is the most pyramidal (ψN = 139.3°) and its lone electron pair is directed *anti* relative to the P–Se bond (τN = −173.5°). Nevertheless, the torsion angle I–Se–P–N(1) is 71.8(2)°. On other hand, though both of the usual nitrogens keep the typical orientation relative to the P–Se bond [τN is 67.9° for N(2) and −59.9° for N(3)], one of them, N(3), changes its configuration to pyramidal, up to ψN = 145.4° [ψN(2) = 160.6°], being disposed *trans* relative to the iodine atom [torsion angle I–Se–P–N(3) is −175.3(2)°]. All P–N bond lengths become practically equal [1.638–1.649(4) Å], but the bond angle N(3)–P–Se becomes the smallest [102.3(2)°] and N(1)–P–Se the largest [114.5(2)°].

We have mentioned above for organic thione and selone ligands in complexes with orthogonal orientation

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† ψ is the difference between two coupled torsion angles Y–P–N–C (must be 120 and 180° for ideally sp^2- and sp^3-hybridized nitrogen, respectively); τ is the torsion angle Y–P–N–(lone pair).

of L and Y–I–X moieties, that the bond Y=L assumes more single bond character during the increase of σ-character in the Y–I interaction, so the sterical limitations on orientation of the lone pair of the ligand become invalid. It seems that this situation is found in complex **II**, and it is quite interesting that a coordinated atom can influence the electronic state of a *trans* disposed amino group in such a ligand.

The strong Se–I bonding in the complexes **I** and **II** is rather unexpected. In the known tellurium(II) complexes and in an iodine(I) complex (**tphpsi**), the phosphanechalcogenide ligands display rather weak *trans*-influences. Most likely, the strong *trans*-influence of the **tdmse** and **trmse** ligands in **I** and **II** is a result of a comparative weakening of the *trans*-influence of the X$^-$ counterion (iodide). Indeed, the iodide *trans*-influence in **I** and **II** is comparable with the *trans*-influence of a separate bromide anion. However, we have seen above that intermolecular interactions can modify *trans*-effects of both X and Y significantly.

The crystal structure of **I** may be represented (as an extreme case) as built up of $[(Me_2N)_3PSeI]^+$ cations, I$^-$ anions and solvate diiodine molecules (1:1:1). However, the 'solvate' diiodine makes close contacts with the 'iodide anion'. This $I(3) \cdots I(2)$ contact [3.175(1) Å] is even shorter than the hypervalent distance $I(1) \cdots I(2)$ [3.215(1) Å] and the diiodine and the iodide are arranged linearly [bond angle $I(2)–I(3)–I(4)$ 173.44(3)°]. The bond distance in the diiodine unit [2.778(1) Å] is 0.111 Å longer than in a unique diiodine molecule but 0.143 Å shorter than in triiodide anion (see above). In fact, we can consider the $I(2)I(3)I(4)$ moiety as a strongly distorted (asymmetric) triiodide anion, and the $I(2)$ ion/atom takes a part in two mutually orthogonal [bond angle $I(1)–I(2)–I(3)$ 80.59(2)°] 3c,4e systems $(-Se–I \leftarrow I^-$ and $I–I \leftarrow I^-$; Fig. 1) with resulting weakening of its *trans*-influence in both systems.

There are some additional short intermolecular (interionic) contacts in the structure of **I**. The triiodide anions form zigzag chains in the crystal along *z* (2_1-axis) owing to additional $I(2) \cdots I(4')(-2–x, –y, –½+z)$ interactions $[I \cdots I$ 3.720(1) Å; angles $I(1)–I(2) \cdots I(4')$ 153.1°, $I(3)–I(2) \cdots I(4')$ 73.4°, $I(2) \cdots I(4')–I(3')$ 175.7°]. Moreover, these chains [including the attached (phosphaneselenide)iodine cations] are crosslinked to each other along *x* (*yz* plane) by short $Se(1) \cdots I(4'')(½+x, ½–y, z)$ contacts $[Se \cdots I$ 3.872(1) Å; angles $P(1)–Se(1) \cdots I(4'')$ 139.8°, $I(1)–Se(1) \cdots I(4'')$ 84.2°, $Se(1) \cdots I(4'')–I(3'')$ 104.8°]. In general, all these additional interactions should have a strengthening effect on the Se–I hypervalent interaction (see considerations above and Table 7).

In the same way, the crystal structure of **II** may be represented as an ionic structure too, built up of $[(morph)_3PSeI]^+$ cations, I$^-$ anions and solvate diiodine molecules (1:1:1.5). One 'solvate' diiodine molecule (lying in a general position) forms with the 'iodide anion' a linear triiodide 3c,4e unit as in the previous case: the

$I(2) \cdots I(3)$ distance 3.100(1) Å is even shorter than the corresponding interaction in the structure of **I**, the $I(4)–I(3) \leftarrow I(2)$ moiety is virtually linear with a bond angle I–I–I 179.35(2)° and is quite orthogonal to the other coupled 3c,4e system, $Se(1)–I(1) \leftarrow I(2)$ $[I(1) \cdots I(2)$ distance 3.186(1) Å; $I(1) \cdots I(2) \cdots I(3)$ angle 89.29(3)°]. The diiodine unit is more perturbed than in **I** $[I(3)–I(4)$ bond length 2.786(1) Å].

However, as compared with **I**, **II** contains an additional 'hemisolvate' diiodine molecule occupying the special position on an inversion center and bridging the above-mentioned aggregates pairwise by short contacts $I(2) \cdots I(5)$ of 3.338(1) Å [angles $I(1) \cdots I(2) \cdots I(5)$ 165.87(2)°, $I(3) \cdots I(2) \cdots I(5)$ 95.95(3)°, $I(2) \cdots I(5)–I(5')(-1–x, –y, 1–z)$ 174.43(2)°]. As expected, the bridging diiodine molecule is less perturbed $[I(5)–I(5')$ distance 2.754(1) Å].

It is possible to consider the aggregates of the diiodine molecules and the iodide ions in structure **II** as octa-iodide dianions or as indefinite polyanion chains $[\cdots I–I \cdots I^- \cdots I–I \cdots I^- \cdots I–I \cdots]_n$ if the additional contacts are taken into account, $I(4) \cdots I(4'')-(-x, 1–y, 1–z)$ of 3.599 Å [angle $I(3)–I(4) \cdots I(4'')$ 144.0°]. There is one more short contact, $Se(1) \cdots I(5''')-(1+x, y, z)$ of 3.644 Å [angles $P(1)–Se(1) \cdots I(5''')$ 98.3°, $I(1)–Se(1) \cdots I(5''')$ 86.6°, $Se(1) \cdots I(5''') \cdots I(2''')$ 67.8°, $Se(1) \cdots I(5''')–I(5'''')$ 106.6°]. In general, the total effect of all these additional interactions should strengthen the Se–I hypervalent interaction (see considerations above and Table 7).

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