

Chalcogen-bonded complexes. Selenium-bound adducts of NH_3 , H_2O , PH_3 , and H_2S with OCSe , SCSe , and CSe_2

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Abstract Recent *ab initio* investigations of some complexes formed between carbon dioxide and its analogues carbonyl sulfide, carbonyl selenide, carbon disulfide, and thiocarbonyl selenide and the common bases ammonia, water, phosphine, and hydrogen sulfide have revealed significant differences between the properties of those complexes bound through the oxygen atom of the electron acceptor and their counterparts in which the interaction takes place through a sulfur atom. In each case the interaction is weak, but the structures, interaction energies, and vibrational spectra of the complexes show some regular variations in behavior as the base and the acid are systematically changed. The adducts bound through sulfur present examples of the type of non-covalent interaction known as the chalcogen bond. In this paper we extend the range of electron acceptors to include carbon diselenide, and we explore the effects of substituting selenium for sulfur as the acceptor atom in the complexes of OCSe , SCSe , and CSe_2 . These adducts are also classified as chalcogen-bonded complexes, and have many features in common with the sulfur-bonded species, but also exhibit some noticeable differences between the two series.

Keywords *Ab initio* calculations · Chalcogen-bonded complexes · Interaction energies · Molecular structures · Vibrational spectra

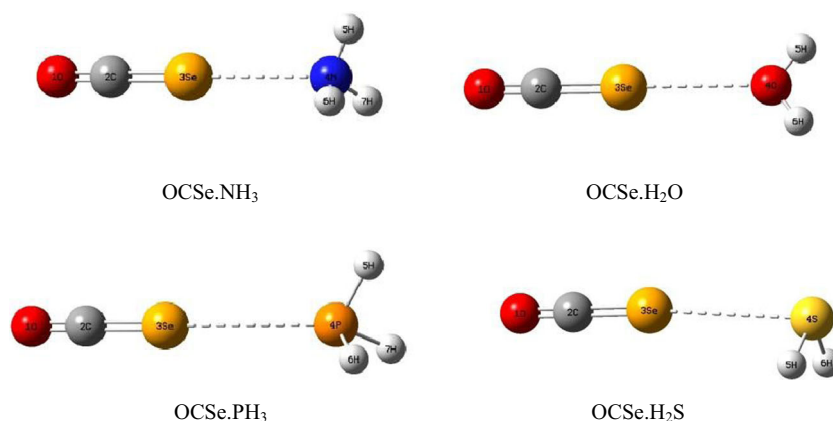
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Introduction

Since the first recognition that covalently-bonded chalcogen atoms (O, S, Se, Te), could take part in attractive interactions with other chalcogen atoms [1], or indeed with other electronegative atoms, like N and P, a number of important papers have been published detailing the properties of this type of non-covalent interaction (see, e.g., refs. [2–34]). In some of these publications the term chalcogen bond has been explicitly used to describe such interactions [18, 19, 24, 25, 27–32, 34]. The chalcogen bond is superficially unusual in that it involves a close approach of two electronegative atoms, e.g., sulfur or selenium on the one hand and nitrogen, oxygen, phosphorus or sulfur on the other, which results in an attractive interaction. Non-covalent interactions have been thoroughly reviewed recently [35], and include the hydrogen bond [36], the lithium bond [37], and the halogen bond [38]. Close inspection of such interactions, however, reveals the electronic nature of the association: a lone pair of electrons on a N, O, P or S atom donates charge to a σ^* orbital associated with a CS or CSe bond, for example. The halogen-bonded and chalcogen-bonded interactions are members of the generic group of associations described as σ -hole bonding [11–15, 17–19, 21, 24, 25, 30–32, 34, 39, 40], the σ -hole being a region of positive charge situated on the extension of a terminal C-halogen or C-chalcogen bond, for example, which provides a site of attraction for an approaching lone pair orbital. This interpretation accounts for the high directionality of halogen and chalcogen bonds. We have recently examined the series of complexes formed between NH_3 , H_2O , PH_3 , and H_2S as electron donors and CO_2 , OCS , and OCSe as electron acceptors, bound through the oxygen atom of the acid partner [41], and those between the same four bases and OCS , CS_2 , and SeCS as electron acceptors, with the interaction occurring through the sulfur atom [42]. This second series of aggregates constitutes a set of 12 related complexes, whose structural,

Fig. 1 Optimized structures of the OCSe.NH₃, OCSe.H₂O, OCSe.PH₃, and OCSe.H₂S complexes



energetic, and vibrational spectroscopic properties vary in a systematic fashion as the acid and the base are permuted. Where experimental structural data are available, our computed results compared favorably with them. These 12 complexes were all found to be of the chalcogen-bonded type. We now turn to complexes containing the next member of the group 16 elements, selenium, as electron acceptor. We have computed the properties of the selenium analogues of the 12 sulfur-bound complexes which constituted the subject of our previous paper [42], and we discuss the systematic variations within the Se-bound group, and between corresponding members of the S-bound and Se-bound aggregates. We have been unable to find any reference to experimental studies of this set of adducts.

Computational details

The calculations were performed using the Gaussian-09 program [43], at the second order level of Møller-Plesset perturbation theory (MP2) [44] and with the augmented correlation-consistent polarized valence triple-zeta basis sets of Dunning (aug-cc-pVTZ) [45–49]. Stationary points were identified as true minima through harmonic vibrational analysis by the absence of any imaginary normal modes of vibration. This analysis also yielded the full vibrational assignments of the complexes, and enabled the complex-monomer wavenumber shifts to be determined. The interaction energies were corrected for basis set superposition error (BSSE) [50] by the Boys-Bernardi full counterpoise procedure [51], and for vibrational zero-point energy differences.

Results

Molecular structures and interaction energies

The Se-bound complexes of OCSe, SCSe, and CSe₂ with NH₃, H₂O, and PH₃ optimized in C_{3v}, C_{2v}, and C_{3v} symmetry

respectively, with linear XCSe...Y fragments (X=O, S, Se, Y=N, O, P), consistent with our findings in respect of the corresponding S-bound complexes of OCS, CS₂, and SeCS [42]. By contrast, the complexes with H₂S were found to contain an almost linear XCSe...S chain, but with the XCSe molecule approaching the H₂S plane virtually perpendicularly, in C_s symmetry, again in common with the results for OCS.H₂S, CS₂.H₂S, and SeCS.H₂S [42]. This observation is consistent with the HOMOs of the NH₃, H₂O, and PH₃ monomers being the a₁ lone pair orbitals (*sp*^{3.3}, *sp*^{0.9}, and *sp*^{0.9} hybridized respectively), directed along the symmetry axes, while that of the H₂S monomer is the b₁ lone pair (essentially a pure 3*p* orbital normal to the symmetry axis). The optimized structures of OCSe.NH₃, OCSe.H₂O, OCSe.PH₃, and OCSe.H₂S, as examples, are illustrated in Fig. 1. The structures of the SCSe and CSe₂ counterparts are very similar.

The interaction energies, corrected for BSSE and for zero-point energy differences, are collected in Table 1. Reflecting the results for the S-bound series [42], these binding energies are all less than 10 kJ mol⁻¹. However, while the interaction energies of the S-bound set were up to 24 % lower than those of their O-bound counterparts [41], the Se-bound adducts were from 28 to 55 % more stable than the S-bound analogues. The reason for the variations from O to S is that, in the O-bound cases there are two interactions present, a n(Y)→π*(CO) primary attraction and a n(O)→σ*(YH) back donation, which reinforce one another, while in the S-bound cases the only interaction is a n(Y)→σ*(CS) attraction. In

Table 1 Interaction energies of the Se-bound complexes of OCSe, SCSe, and CSe₂ with NH₃, H₂O, PH₃, and H₂S, corrected for basis set superposition energy and zero-point energy differences

Base	Interaction energy (kJ mol ⁻¹)		
	OCSe	SCSe	CSe ₂
NH ₃	-9.97	-8.03	-7.84
H ₂ O	-8.01	-6.59	-6.43
PH ₃	-5.71	-4.96	-4.97
H ₂ S	-5.50	-4.91	-4.93

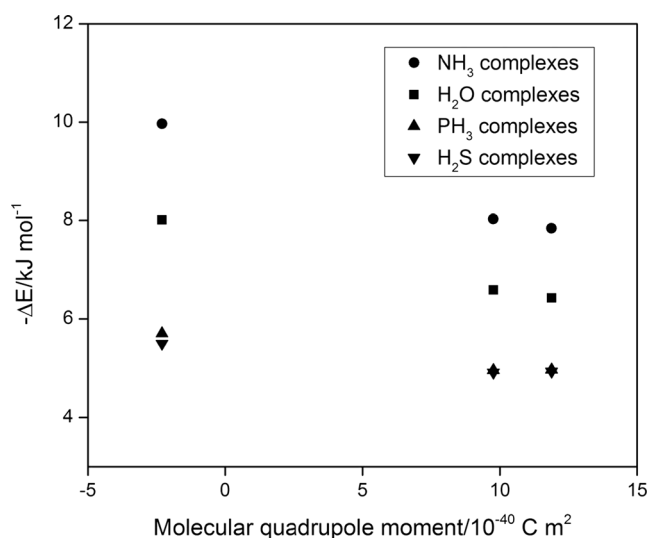


Fig. 2 Plots of the interaction energies of the Se-bound complexes of OCS_e, SCSe, and CSe₂ with NH₃, H₂O, PH₃, and H₂S versus the molecular quadrupole moments of the acids

comparing the S-bound with the Se-bound species, the natural bond orbital (NBO) [52] charges on the selenium atoms are uniformly more positive than those on the sulfur atoms of the corresponding complexes, and the Se...Y electrostatic attraction is substantially stronger than the S...Y. We found that, for both the O-bound [41] and the S-bound complexes [42], the interaction energies correlated with the molecular quadrupole moments of the electron acceptors. This is the lowest non-zero multipole moment which is common to all three electron acceptors. For the OCS_e, SCSe, and CSe₂ monomers, an experimental value for the quadrupole moment is available only for OCS_e [53], but calculated values have been obtained for all three acids [54]. Our computed interaction energies correlate reasonably well with the computed quadrupole moments for the NH₃ and H₂O complexes, as shown in Fig. 2, with separate relationships for each family. For the PH₃ and H₂S complexes, the interaction energies are fairly insensitive to the nature of the acid and the base. The polarizabilities of the interacting bases are also

Table 2 Intermolecular structural parameters of the Se-bound complexes of OCS_e, SCSe, and CSe₂ with NH₃, H₂O, PH₃, and H₂S

Base	Parameter	OCS _e	SCSe	CSe ₂
NH ₃	R (Se...N)/pm	313.05	322.93	323.30
	∠Se...NH/deg	112.17	112.21	112.21
H ₂ O	R (Se...O)/pm	304.74	311.39	311.76
	∠Se...OH/deg	127.84	127.89	127.90
PH ₃	R (Se...P)/pm	367.26	373.99	373.91
	∠Se...PH/deg	122.33	122.41	122.42
H ₂ S	R (Se...S)/pm	359.60	366.29	366.13
	∠Se...SH/deg	88.72	84.92	83.50

important factors in determining the interaction energies of the complexes [32, 55–57]. The polarizabilities increase as 1.45, 2.81, 3.782, and 4.84 × 10⁻³⁰ m³ for H₂O, NH₃, H₂S, and PH₃ respectively [58], and the computed interaction energies follow this trend, allowing for the discontinuity between the first row and second row bases.

The intermonomer Se...Y separations of the various complexes, as well as the Se...YH bond angles, are presented in Table 2. The Se...Y distances are shorter for the OCS_e complexes than for the other two sets, and the values for the SCSe and CSe₂ adducts are virtually identical. The separations are substantially larger for the complexes containing second row donor atoms, PH₃ and H₂S, and predictably, for all four series, they diminish with increasing interaction energy. The dependencies of the Se...Y distances on the interaction energies are illustrated in Fig. 3; again the values for each set are governed by separate relationships. The intermolecular Se...YH angles are essentially independent of the electron acceptor, and their variation with the base is dominated by the very minor changes in the intramolecular HYH angles.

The changes in the internal bond lengths and angles of the base molecules are gathered in Table 3. In keeping with the weakness of the interactions these changes are minimal, and no trends are apparent. The near constancy of the angle changes is responsible for the lack of variation in the values of the Se...YH angles referred to above. Table 4 lists the changes in the bond lengths of the XCSe fragments on complexation. The bound CSe bond lengths increase almost linearly with increasing binding energy, and in this case the results for the first row base complexes, NH₃ and H₂O, lie on a single trend line, and those for the second row base set, PH₃ and H₂S, on a second line, as shown in Fig. 4. The broad trends in the perturbations of the CX bond lengths are an increase with the

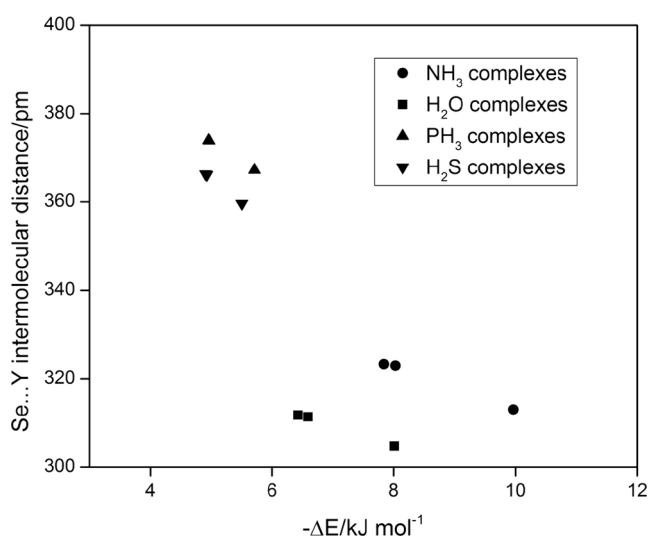


Fig. 3 Plots of the Se...Y intermolecular distance of the Se-bound complexes of OCS_e, SCSe, and CSe₂ with NH₃, H₂O, PH₃, and H₂S versus the interaction energies of the complexes (Y = N, O, P, S)

Table 3 Intramolecular bond length and bond angle changes of the NH₃, H₂O, PH₃, and H₂S fragments of the complexes with OCSe, SCSe, and CSe₂

Base	Bond	Change/pm			Angle	Change/deg		
		OCSe	SCSe	CSe ₂		OCSe	SCSe	CSe ₂
NH ₃	NH	0.07	0.07	0.07	HNH	-0.13	-0.17	-0.17
H ₂ O	OH	0.05	0.06	0.06	HOH	0.20	0.10	0.09
PH ₃	PH	-0.08	-0.06	-0.05	HPH	0.44	0.33	0.32
H ₂ S	SH	0.06	0.06	0.06	HSH	0.00	-0.03	-0.04

base in the order H₂S < PH₃ < H₂O < NH₃ and an increase with the acid in the order CO < CS ≈ CSe.

Vibrational spectra

The extent to which the molecular interaction perturbs the vibrational spectra of the interacting molecules is reflected in the intramolecular wavenumber shifts. Table 5 lists the changes of the wavenumbers of the electron acceptor molecules and Table 6 lists the same information for the electron donor species. The stretching wavenumber shifts of the acid fragment molecules are consistently to the red and those of the bending vibrations to the blue (Table 5), in common with normal experience. These shifts correlate broadly with the interaction energies, as shown in Fig. 5. For the base fragments (Table 6) the stretching wavenumber shifts are all to the red, as anticipated, with the exception of the PH₃ complexes, where the behavior is reversed. The reason for the anomalous behavior of the PH₃ complexes has been discussed before [41, 42, 59–62]. The symmetric bending modes of the NH₃ and the bending vibrations of the H₂O complexes shift to the blue, and all the other bending vibrations are perturbed to lower wavenumbers. However, only for the symmetric bending vibrations of the NH₃ complexes do the shifts exceed 5 cm⁻¹, while those for the remaining bending modes are negligible, so the information provided by these wavenumber shifts in respect of the strength of interaction is limited.

One of the more reliable vibrational spectroscopic properties as an indicator of the extent of interaction is the intermonomer Se...Y stretching wavenumber. The values of this property are shown in Table 7. Increasing binding energy results in an increase of the intermolecular stretching force constant and hence leads to a higher stretching wavenumber. The dependence of these wavenumbers on the strength of interaction is displayed in Fig. 6; for all four series a sensible dependence is observed, again with separate fit lines for the first row and for the second row base groups. The tight clustering of the values for the PH₃ and H₂S complexes is once again evident.

Discussion

The structures of the Se-bound complexes of OCSe, SCSe, and CSe₂ with NH₃, H₂O, PH₃, and H₂S are similar to those of the corresponding S-bound analogues [42], with the complexes containing NH₃, H₂O, and PH₃ featuring a linear XCSe...Y fragment and those with H₂S having the electron acceptor molecule lying virtually perpendicular to the H₂S plane. The interaction energies of the Se-bound complexes are all small, but those of the NH₃ and H₂O adducts decrease regularly with increasing quadrupole moment of the electron acceptor. The energies of the PH₃ and H₂S complexes are

Table 4 Intramolecular bond length changes of the OCSe, SCSe, and CSe₂ fragments of the complexes with NH₃, H₂O, PH₃, and H₂S

Base	OCSe		SCSe		CSe ₂	
	Bond	Bond length change/pm	Bond	Bond length change/pm	Bond	Bond length change/pm
NH ₃	CO	0.18	CS	0.35	CSe (free)	0.35
	CSe	0.74	CSe	0.34	CSe (bonded)	0.29
H ₂ O	CO	0.18	CS	0.30	CSe (free)	0.30
	CSe	0.34	CSe	0.14	CSe (bonded)	0.10
PH ₃	CO	0.07	CS	0.15	CSe (free)	0.13
	CSe	0.40	CSe	0.21	CSe (bonded)	0.19
H ₂ S	CO	0.06	CS	0.12	CSe (free)	0.10
	CSe	0.41	CSe	0.23	CSe (bonded)	0.21

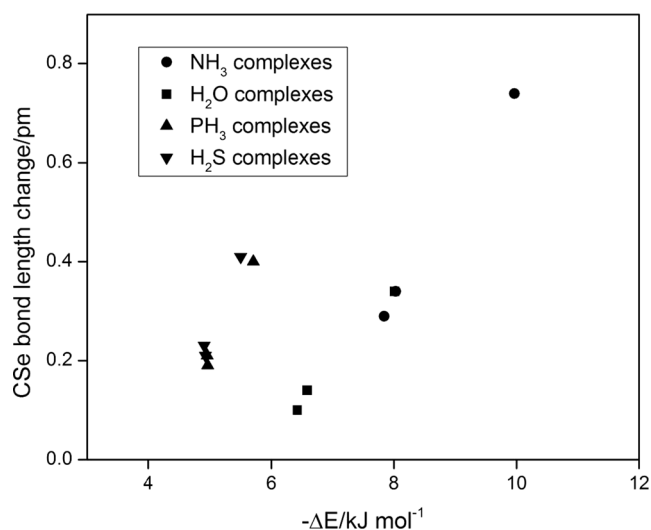


Fig. 4 Plots of the changes in the CSe bond lengths of the electron acceptor molecules of the Se-bound complexes of OCSe, SCSe, and CSe₂ with NH₃, H₂O, PH₃, and H₂S versus the interaction energies of the complexes

almost independent of the quadrupole moments, and are virtually indistinguishable from one another. The intermonomer separations fall off with the strength of interaction, as expected, and this is true for all four sets of complexes, although once again the properties of the corresponding PH₃ and H₂S complexes are fairly similar. The bonded CSe bond length is the intramolecular geometrical parameter which is most sensitive to the extent of interaction. This bond length increases by an amount which correlates with the interaction energy; one trend line is observed for the NH₃ and H₂O complexes and a second one for those with PH₃ and H₂S.

Table 5 Intramolecular wavenumber shifts of the electron acceptor molecules of the Se-bound complexes of OCSe, SCSe, and CSe₂ with NH₃, H₂O, PH₃, and H₂S

Electron acceptor	Monomer mode	Wavenumber shift/cm ⁻¹			
		NH ₃	H ₂ O	PH ₃	H ₂ S
OCSe	ν_1	-16.4	-7.6	-9.4	-9.0
	ν_2	15.1	9.7	7.3	7.1
SCSe			11.1		7.3
	ν_3	-18.8	-12.9	-9.5	-9.4
	ν_1	-6.2	-3.3	-3.5	-3.5
CSe ₂	ν_2	12.9	8.0	6.0	5.9
			9.2		6.3
	ν_3	-13.6	-8.8	-6.7	-6.6
CSe ₂	ν_1	-4.3	-2.1	-2.3	-2.2
	ν_2	13.8	8.2	6.9	6.6
			9.9		7.1
	ν_3	-12.8	-7.9	-6.4	-6.2

Table 6 Intramolecular wavenumber shifts of the electron donor molecules of the Se-bound complexes of OCSe, SCSe, and CSe₂ with NH₃, H₂O, PH₃, and H₂S

Electron donor	Monomer mode	Wavenumber shift/cm ⁻¹		
		OCSe	SCSe	CSe ₂
NH ₃	ν_1	-7.3	-7.3	-7.2
	ν_2	30.6	26.8	27.1
	ν_3	-9.0	-8.9	-8.8
	ν_4	-1.0	-0.7	-0.5
H ₂ O	ν_1	-6.5	-7.5	-7.7
	ν_2	0.9	1.4	1.5
	ν_3	-7.9	-8.8	-9.1
PH ₃	ν_1	3.9	2.2	1.9
	ν_2	-4.3	-4.2	-4.7
	ν_3	5.4	3.4	3.0
	ν_4	-1.9	-1.7	-1.9
H ₂ S	ν_1	-4.6	-4.3	-4.5
	ν_2	-1.3	-1.1	-1.0
	ν_3	-4.7	-4.5	-4.7

The effects of interaction on the vibrational spectra are most clearly manifested in the wavenumber shifts of the modes of the electron acceptors, and the wavenumbers of the intermolecular stretching vibrations. The CX and CSe stretching modes are uniformly red-shifted, while the bending modes shift to the blue. The magnitudes of the shifts are broadly governed by the strengths of interaction, and the same dependence is observed for the Se...Y stretching wavenumbers. These wavenumbers are significantly higher

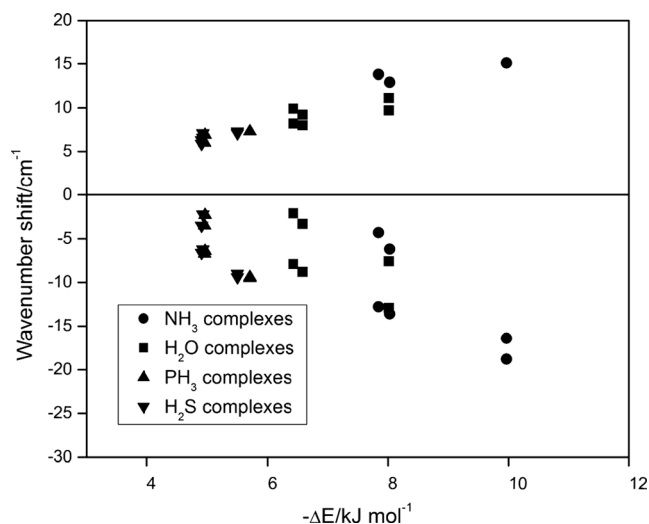


Fig. 5 Plots of the intramolecular wavenumber shifts of the electron acceptor molecules of the Se-bound complexes of OCSe, SCSe, and CSe₂ with NH₃, H₂O, PH₃, and H₂S versus the interaction energies of the complexes

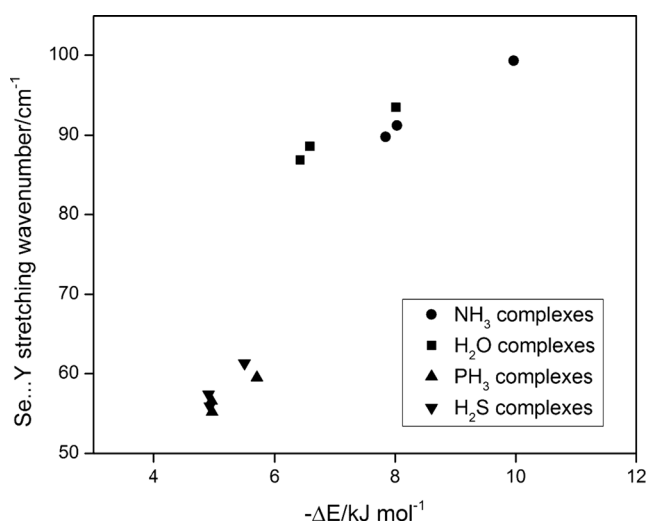
Table 7 Intermolecular Se...Y stretching wavenumbers of the Se-bound complexes of OCSe, SCSe, and CSe₂ with NH₃, H₂O, PH₃, and H₂S (Y=N, O, P, S)

Base	Se...Y stretching wavenumber/cm ⁻¹		
	OCSe	SCSe	CSe ₂
NH ₃	99.3	91.2	89.8
H ₂ O	93.5	88.6	86.9
PH ₃	59.5	56.6	55.2
H ₂ S	61.3	57.4	55.9

for the NH₃ and H₂O series than for the PH₃ and H₂S adducts, and again separate relationships are found for the two sets of complexes.

The results of the molecular structural and vibrational spectroscopic properties are all consistent with the strengths of interaction of the complexes, and the well-known distinction between the properties of complexes containing first row elements and those of the second and third rows [63] is confirmed.

We now plan to consolidate the data presented here for the selenium-bound complexes with those for the oxygen-bound [41] and sulfur-bound [42] analogues in a forthcoming publication, and include our results obtained using the NBO [52] and quantum theory of atoms in molecules (QTAIM) [64, 65] approaches to determine the properties of these adducts. These new results will incorporate our computations of the electrostatic potentials of the interacting monomers and are expected to provide further insight into the mechanism of formation of these series of complexes.

**Fig. 6** Plots of the intermolecular Se...Y stretching wavenumbers of the Se-bound complexes of OCSe, SCSe, and CSe₂ with NH₃, H₂O, PH₃, and H₂S versus the interaction energies of the complexes (Y=N, O, P, S)

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