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Chalcogen-bonded complexes of some carbon dioxide analogues

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HIGHLIGHTS

- The properties of a series of chalcogen-bonded complexes containing OCS, CS_2 and SeCS have been investigated.
- The interaction energies and the perturbations of the monomer structures correlate with the quadrupole moments of the acids.
- The vibrational spectral changes also vary regularly with the natures of the acids and bases.

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ABSTRACT

Ab initio calculations have been carried out on the sulphur-bonded van der Waals complexes formed between the carbon dioxide analogues carbonyl sulphide, carbon disulphide and thiocarbonyl selenide, and the common electron donors ammonia, water, phosphine and hydrogen sulphide. The structures of these twelve complexes are all similar, and involve an approximately linear XCS···Y fragment (X = O, S, Se; Y = N, O, P, S). These structures contrast with those of the oxygen-bound complexes of carbon dioxide, carbonyl sulphide and carbonyl selenide reported earlier which, with the exception of the hydrogen sulphide species, are characterized by four-membered rings with varying orientations involving the C, O, H and Y atoms. The molecular structures, interaction energies and vibrational spectra have been studied, and the variations in these properties have been correlated with the complex structures and with the molecular quadrupole moments of the acid monomers.

Introduction

The chalcogen bond is a member of the family of non-covalent interactions, which has recently enjoyed a good deal of attention, both experimentally and theoretically [1]. In this type of interaction, a chalcogen atom (e.g. sulphur or selenium) acts as a site of acceptance of electronic charge from an electron-rich region such as a lone pair of electrons on the donor atom of a base. The receptor region of the acid (the electron acceptor, in this case OCS, CS_2 or SeCS) is believed to be a σ^* antibonding orbital located on the sulphur or selenium atom [2,3]. An analogy between chalcogen bonds, hydrogen bonds [4] and halogen bonds [5,6] is thus apparent. In a recent publication we reported some *ab initio* studies of the series of van der Waals complexes formed between the acid molecules carbon dioxide, carbonyl sulphide and carbonyl selenide and the bases ammonia, water, phosphine and hydrogen sulphide [7]. We found that the complexes with NH_3, H_2O and PH_3 involved a primary C···N (O, P) interaction and a secondary attraction between a H atom of the base and the O atom of CO_2, OCS or OCSe in a four-membered cyclic structure. The complexes of CO_2, OCS and OCSe with H_2S adopted three different structures, a C···S bonded species in which the C_2 axis of the H_2S molecule was virtually perpendicular to the OCO direction (in $CO_2{\cdot}H_2S$), an adduct with a C···S and an O···H interaction (in $OCS{\cdot}H_2S$) and a cyclic doubly hydrogen-bonded complex (SH···O and SH···Se) (in $OCSe{\cdot}H_2S$). We have now extended the range of acids in this set of complexes to include the S-bound adducts between OCS, CS_2 and SeCS and the standard bases NH_3, H_2O, PH_3 and H_2S. We anticipate the existence of complexes containing CS···N (O, P, S) interactions, and we explore the changes in the properties of these twelve species as the base and acid are systematically varied.

Computational details

The calculations were performed using the Gaussian-09 program [8], at the second order level of Møller–Plesset perturbation theory (MP2) [9] and with Dunning's augmented correlation-consistent polarized valence triple-zeta basis set (aug-cc-pVTZ) [10–14]. Optimizations were carried out at the TIGHT level of

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convergence [8] and the complexes were confirmed as genuine minima on the potential energy surfaces by harmonic vibrational analysis; none of the converged structures yielded any imaginary normal modes of vibration. The interaction energies were computed relative to those of the relaxed monomers, i.e. in their geometries in the complex structures, and corrected for basis set superposition error (BSSE) [15], using the full counterpoise procedure of Boys and Bernardi [16], and for vibrational zero-point energy differences.

Results – molecular structures and interaction energies

All the complexes containing NH_3, H_2O and PH_3 were characterized by a linear XCS···Y fragment (X = O, S, Se; Y = N, O, P); the interactions were directed along the C_3 axes of NH_3 and PH_3 and the C_2 axis of H_2O, resulting in complexes of C_{3v} (NH_3 and PH_3) or C_{2v} (H_2O) symmetry. The complexes with H_2S featured an essentially linear XCS···S moiety, but with the C_2 axis of H_2S approximately perpendicular to the XCS line (C_s symmetry). Optimizations using other starting structures invariably relaxed to the structures reported here, except for the cases of the OCS complexes, where the O-bound isomers were found to be stationary points, as reported in Ref. [7]. The optimized structures of OCS·NH_3, OCS·H_2O, OCS·PH_3 and OCS·H_2S are illustrated in Fig. 1; the structures of the corresponding adducts with CS_2 and SeCS are qualitatively similar.

The interaction energies of the complexes are presented in Table 1. These energies are all less than 10 kJ mol^{-1}, and cover a remarkably narrow spread of values. The order of strengths of binding with respect to the bases is $NH_3 > H_2O > PH_3 \approx H_2S$, and with respect to the acids $OCS > CS_2 \approx SeCS$, at least for the NH_3 and H_2O complexes; for the complexes with PH_3 and H_2S the interaction energies are virtually constant. Since CS_2 does not possess a permanent dipole moment, the lowest non-zero multipole moment common to all three of these electron acceptors, which may be regarded as a measure of the extent of electrostatic interaction, is the quadrupole moment. Within the NH_3 and H_2O sets of adducts the strengths of interaction fall off as the quadrupole moments of the acids vary from -3.558 (OCS) through 7.112 (CS_2) to 9.763×10^{-40} C m^2 (SeCS) [17], as shown in Fig. 2, and as we found for the CO_2/OCS/OCSe series [7]. The more negative is the quadrupole moment of the electron acceptor, the stronger is the interaction. There is no discernible relationship between the interaction energies and the dipole moments of the bases. Clearly the complexes in this series are all extremely weakly bound and, with the exception of the first row electron donor atoms, N and O, are almost independent of the acid or the base. The differences in the properties of compounds of the first row *versus* those of the second and third rows have been well known for many years [18]. It is interesting to note that Tatamitani and Ogata found experimentally that the preferred structure of OCS·H_2O in the gas phase was an S···O bound model of C_{2v} symmetry [19]. For the O-bound OCS·NH_3 complex the interaction energy is slightly higher (12%) than that of the S-bound variant, while for the H_2O, PH_3 and H_2S adducts the S-bound counterparts have the higher interaction energies, by 4.5%, 17% and 17% respectively [7]. Our finding that the S-bound OCS·H_2O complex is more stable than the O-bound is in agreement with experiment and with the calculations of Garden and co-workers [20]. The infrared experiments of Fraser et al. on OCS·NH_3 were not able to determine its structure unambiguously [21], but the CS_2·H_2O complex was shown by Ogata and Lovas to be planar with C_{2v} symmetry [22], consistent with our result and that of Garden et al. [20].

Table 1
Interaction energies of the S-bound complexes of OCS, CS_2 and SeCS with NH_3, H_2O, PH_3 and H_2S, corrected for basis set superposition energy and zero-point energy differences.

Base	Interaction energy/kJ mol^{-1}		
	OCS	CS_2	SeCS
NH_3	−6.438	−5.575	−5.563
H_2O	−5.412	−4.720	−4.676
PH_3	−3.758	−3.715	−3.808
H_2S	−3.785	−3.743	−3.843

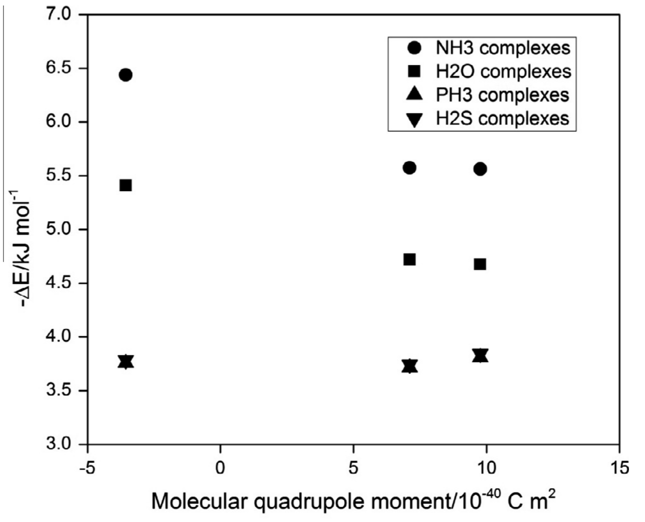

Fig. 2. Plots of the interaction energies of the complexes *versus* the molecular quadrupole moments of the electron acceptors.

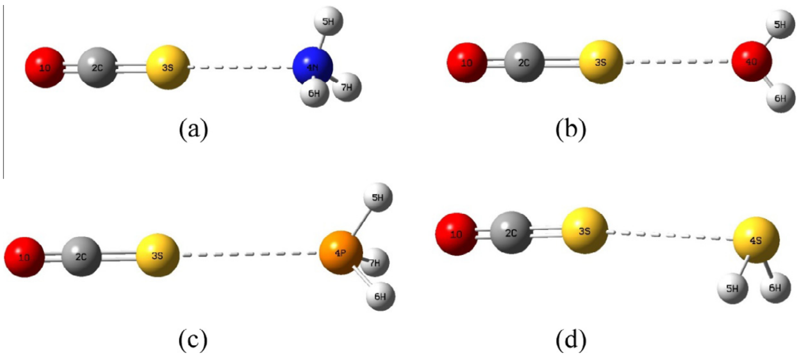

Fig. 1. Optimized structures of the (a) OCS·NH_3, (b) OCS·H_2O, (c) OCS·PH_3 and (d) OCS·H_2S complexes.