Predictions for possible new, doubly and triply bridged oxides and peroxides of C, N, P, and S

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By regarding the $X^{2-,3-}$ oxoanions of main group elements as pseudochalcogenides or pseudopnicogenides, and possibly cutting the peroxide bridges to oxide bridges, one arrives at a series of so far experimentally unknown oxides and peroxides, X_2, having high, but not exceedingly high energies.

Pseudohalides, such as CN^-, are known to form corresponding pseudohalogens, like NC–CN. Similarly, certain divalent and trivalent polyatomic anions, $X^{2-,3-}$, can be regarded as pseudochalcogenides and pseudopnicogenides. They can in principle form the corresponding neutral molecules X_2.[1] Now, consider an oxoanion, such as $X^{2-} = CO_3^{2-}$ from this point of view. The corresponding neutral X_2 dimer is $(CO_3)_2$, for which we consider the structure {O=C(–O–O–)$_2$C=O} **1**. If the peroxide bridges are shortened to oxide ones, the structure O=C(μ-O)$_2$C=O **2** is obtained. We here point out the possible existence of an entire class of such compounds. Further variations on the theme are obtained by replacing some or all of the oxygens by sulfurs, by adding or omitting terminal oxygens, by replacing them with halogen atoms, or by varying the total charge.

Related singly bridged peroxide systems are known. Peroxodisulfate, $S_2O_8^{2-}$, is one of the most powerful oxidizing agents.[2] Note that below we discuss the neutral S_2O_8. The peroxydicarbonate, $C_2O_6^{2-}$ is known. We here discuss the neutral C_2O_6. The diphosphate **9** is six electrons short of $2PO_4^{3-}$. These proposed oxidized oxoanion dimer molecules, if they can be made, are likely to be even stronger oxidants than the known peroxo compounds.

Triply bridged, 'confacial tetrahedral geometries' are rare.[3,4] We are not aware of experimentally known molecules with (–O–)$_3$ bridges.

The second-order Møller-Plesset or B3LYP density functional calculations were performed using GAUSSIAN 94. The obtained structures are reported in Table 1 and shown in Fig. 1. It was checked that all geometries correspond to local minima. The vibrational frequencies for species **1**–**5** are shown in Fig. 2. The pseudochalcogen corresponding to carbonate **1** is found to have a relatively low energy, Table 2. In the calculated structure the two coaxial carbonate planes are rotated through 37.8°. Double peroxide bridges are previously known in the cyclic peroxides of type $R_2C(–OO–)_2CR_2$.[5] We now replace the $–CR_2$ groups by –C=O groups.

Perhaps the most interesting result is that carbon dioxide would be able to form the metastable planar dimer **2** only about 200 kJ mol^{-1} above two monomers. Both this dimer and a $(CO_2)_3$ trimer have been recently discussed by Lewars.[6] He finds for the dimer **2** at the MP2/6-31G* level a barrier of 41 kJ mol^{-1}, which would make it a possible low-temperature species, that merits further studies. The structure of **2** does not offend chemical intuition, although the four-ring is strained. Furthermore the structures, vibrational frequencies and heats of formation are very similar at the four levels [(a)–(d)] of approximation. Four-rings with two opposite $>$C=O groups and two opposite $>$N–Ph groups are known.[7] If the ring oxygens are replaced with sulfur atoms, the resulting dimers **3** and **5** are only *ca.* 100 kJ mol^{-1} above two carbonyl sulfide or carbon disulfide monomers, respectively. The alternative $C_2O_2S_2$ structure **4** lies higher.

Of the present ten species, one is experimentally known. High-pressure experiments on CS_2 are thought to yield **5**, identified on the basis of an IR band at 1150 cm^{-1}.[8] The present calculations find a b_{1u} vibration with large intensity (814 km mol^{-1}) at 1125 cm^{-1} at the B3LYP/6-31G* level (c). The corresponding frequency for **2** and **3** is predicted to occur at

Table 1 Calculated geometries for the peroxide-bridged dimers X_2 corresponding to anions $X = EO_n^{q-}$. The geometries of the corresponding oxygen-bridged species are also given. E–O$_t$ is the terminal and E–O$_b$ the bridging distance, respectively. α is the dihedral E–O–O–E angle. Some sulfur analogues are included

				Distance/pm			Angle/°	
X	Species	No.	Symmetry	E–O$_t$	E–O$_b$	O–O	O$_t$–E–O$_b$	α
CO_3^{2-}	O=C(–O–O–)$_2$C=O	**1**^{a}	D_2	119.9	137.4	147.8	123.3	65.7
	O=C(–O–)$_2$C=O	**2**^{a}	D_{2h}	118.4	140.2	—	133.0	
	O=C(–O–)$_2$C=O	**2**^{b}	D_{2h}	117.3	139.5	—	132.9	
	O=C(–O–)$_2$C=O	**2**^{c}	D_{2h}	117.6	139.6	—	133.2	
	O=C(–O–)$_2$C=O	**2**^{d}	D_{2h}	116.7	139.3	—	133.2	
	O=C(–S–)$_2$C=O	**3**^{c}	D_{2h}	118.7	182.6	—	130.1	
	S=C(–O–)$_2$C=S	**4**^{c}	D_{2h}	159.3	138.9	—	133.5	
	S=C(–S–)$_2$C=S	**5**^{c}	D_{2h}	161.3	179.2	—	131.2	
	F–C(–O–)$_3$C–F	**6**^{a}	D_{3h}	129.2	145.0	—	123.5	
NO_3^-	N(–O–)$_3$N	**7**^{a}	D_{3h}	—	150.1	—	127.2	
NO_4^{3-}	O=N(–O–)$_3$N=O	**8**^{a}	D_{3h}	116.4	161.7	—	126.1	
PO_4^{3-}	O=P(–O–O–)$_3$P=O	**9**^{c}	D_3	146.0	165.0	148.7	115.9	36.4
SO_4^{2-}	O_2S(–O–O–)$_2SO_2$	**10**^{c}	C_{2h}	143.8^e	169.2	146.2	103.8, 110.7	76.3

^{a} MP2/6-31G*. ^{b} MP2/cc-pVTZ. ^{c} DFT B3LYP/6-31G*. ^{d} DFT B3LYP/cc-pVTZ. ^{e} Both equal.

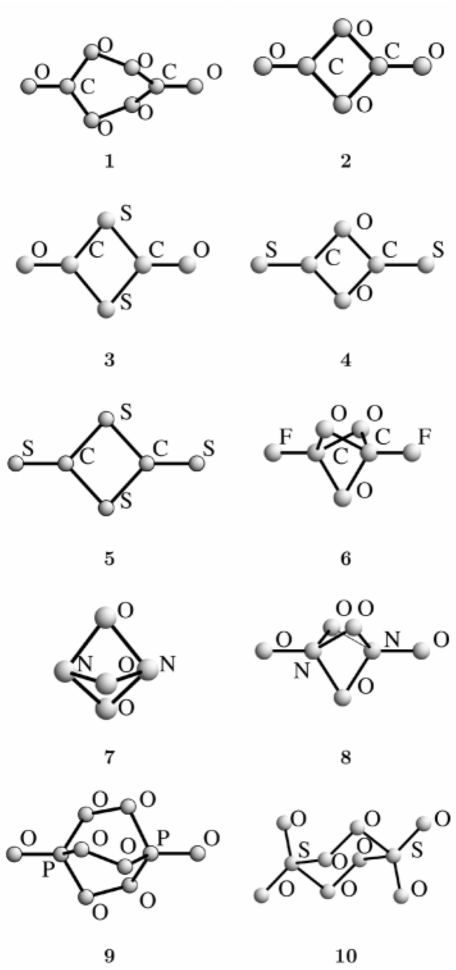

Fig. 1 The calculated structures of species **1**–**10**

Table 2 Calculated heats of formation, ΔH (kJ mol^{-1}), with respect to the reference compounds given, without zero-point energy corrections. For footnotes, see Table 1

Molecule	Reference	ΔH
1[a]	$2CO + H_2O_2 - 2H_2$	−9
2[a]	$2CO_2$	206
2[b]	$2CO_2$	196
2[c]	$2CO_2$	174
2[d]	$2CO_2$	202
3[c]	2OCS	111
4[c]	2OCS	225
5[c]	$2CS_2$	115
6[a]	$CO + CO_2 + F_2$	−19
7[a]	$N_2 + \frac{3}{2}O_2$	653
	$ON–NO_2$	552

1951 (a) or 1950 (d) and 1863 (c) cm^{-1}, respectively, Fig. 2. As the dimerisation energies for **3** and **5** are comparable, compression of OCS should result in **3**.

Compound **6** has a favourable heat of formation, as seen from Table 2. Its e′ and a_2'' frequencies at 1187 and 1419 cm^{-1} have intensities of 320 and 820 km mol^{-1}, respectively, at MP2/6-311G* level.

The trigonal bipyramidal, D_{3h}, structure **7** of N_2O_3 is calculated to lie at very high energy, 552 kJ mol^{-1} above the experimentally known $ON–NO_2$ structure. The vibrational frequencies of the high-energy form are, however, all positive and quite large (e″ 525, e′ 648 (42), 732(3), a_2'' 722(41), a_1' 848, 1120 cm^{-1}). It is a possible high-energy species. The IR intensities (in parentheses) are quite low and the static dipole moment is zero. For the valence isoelectronic P_2S_3, the D_{3h} structure is calculated to lie only slightly above the lowest 'W' one.[9]

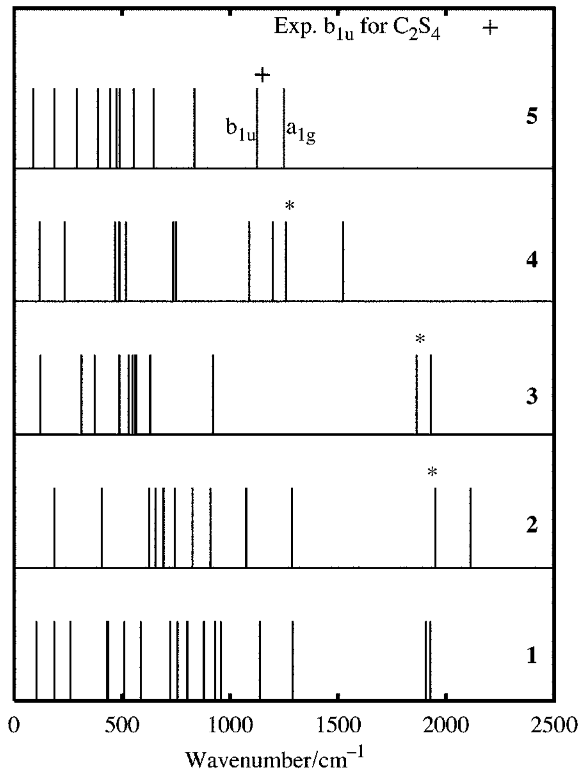

Fig. 2 The calculated vibrational frequencies of species **1**–**5**. The predicted, intensive b_{1u} vibration frequencies of **2**–**4** are marked with a star.

The structure of **8** is of the same type as that calculated for $[O{=}Si(–O–)_3Si{=}O]^{2-}$ by Cederbaum and coworkers.[10] The corresponding $C_2O_5{}^{2-}$ was here found to be unstable, having two negative frequencies.

Concluding, we suggest that the carbonyl sulfide dimer **3** is likely and the carbon dioxide dimer **2** conceivable as a synthetic goal. The latter has already been proposed by Lewars[6] as a possible low-temperature species.

The proposed molecules might have applications as strong oxidants or as high-energy species.

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Notes and references

1 A. M. Golub, H. Köhler and V.V. Skopenko, *Chemistry of Pseudohalides*, Elsevier, Amsterdam, 1986, p. 469.

2 F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Wiley, New York, 1988, p. 524.

3 C. Zheng, R. Hoffmann and D. R. Nelson, *J. Am. Chem. Soc.*, 1990, **112**, 3784.

4 C. Horn, I. Dance, D. Craig, M. Scudder and G. Bowmaker, *J. Am. Chem. Soc.*, 1998, **120**, 10 549.

5 *Houben-Weyl, Methoden der organischen Chemie, 4:e Auflage, Band VIII, Sauerstoffbindungen III*, ed. E. Müller, Georg Thieme Verlag, Stuttgart, 1952, p. 31.

6 E. Lewars, *J. Mol. Struct. (THEOCHEM)*, 1996, **363**, 1.

7 Ref. 5, p. 221.

8 S. F. Agnew, R. E. Mischke and B. I. Swanson, *J. Phys. Chem.* 1988, **92**, 4201.

9 L. L. Lohr and D. Sundholm, *J. Mol. Struct.*, 1997, **413–414**, 495.

10 T. Sommerfeld, M. K. Scheller and L. Cederbaum, *J. Chem. Phys.*, 1996, **104**, 1464.

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