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Xenon in oxide frameworks: at the crossroads between inorganic chemistry and planetary science

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The chemistry of noble gases was for a long time dominated by fluoride-bearing compounds of xenon. However, the last two decades have brought new insights into the chemistry of xenon oxides and oxysalts, including insights involving a novel type of non-covalent interaction (aerogen bonding), discoveries of new xenon oxides, oxide perovskite frameworks and evidence for an abrupt increase of xenon reactivity under extreme pressure-temperature conditions. The complex implementation of these findings could facilitate the development of explanations for long-standing interdisciplinary problems, such as the depletion of heavy noble gases in contemporary planetary atmospheres – the cosmochemical enigma known as the "missing xenon" paradox.

Introduction

After the first discovery of $XePtF_6$ and XeF_2 in 1962,[1] fluoro compounds of xenon and, to a lesser extent, of krypton were the drivers of noble gas chemistry for almost 40 years.[2] In contrast, the discoveries of xenon oxides and evidence for the octavalent state of this element in XeO_4 and perxenate anion, $[XeO_6]^{4-}$ (ref. 3) were striking but relatively short-lasting events in inorganic chemistry.[2] Xenon oxides and perxenates were considered to form a promising class of strong oxidants and were thoroughly studied in a few laboratories worldwide.[2–4] However, the experimental difficulties accompanying the multi-step syntheses of Xe(VI) and Xe(VIII) oxide compounds ruled out their wide-scale applicability, and the studies were largely stopped within ten years of the first reports. Meanwhile, the recent achievements in structural, computational and extreme-condition chemistry have brought about substantially new insights into the still exotic chemistry of xenon oxides. The few snapshots presented herein are aimed at outlining these frontiers and providing a linkage to the status of xenon oxides in resolving the problems of contemporary planetary and space science.

Aerogen bonding

The progress in computational chemistry in the 21st century has led to many discoveries and insights in the field of supramolecular interactions.[5] Aerogen bonding, a novel type of weak attractive linkage, was discovered[6] as a result of computational studies of the molecular structure of solid xenon(VI) trioxide, XeO_3 – a hazardous but unavoidable intermediate in the syntheses of higher-valence xenon(VIII) oxide compounds.[3] Whereas the intramolecular Xe=O bonds in XeO_3 are "classic" covalent bonds,[8] the overall integrity of its crystal structure is maintained *via* noble gas (aerogen) bonding (NgB) (Fig. 1), defined by IUPAC as an "attractive interaction between an electron rich atom or group of atoms and any element of Group-18
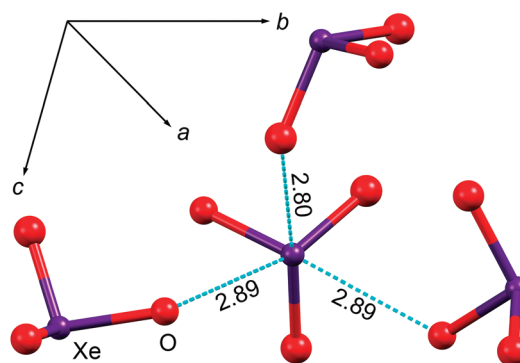

Fig. 1 Aerogen bonding[6] (dashed lines) in the crystal structure of solid XeO_3. Drawn using CCDC Mercury[7] on the basis of crystallographic data reported by Templeton *et al.* (1963).[8] Bond lengths in Å.

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acting as electron acceptor".[9] XeO_3 is a highly explosive substance,[8] and its detonation sensitivity is apparently related to an inferred weakness of aerogen bonding linkages between the neighbouring molecules. Aerogen bonding is currently a well-established type of interaction in noble gas chemistry,[9] and it plays an important role in novel xenon-based perovskite frameworks.[10]

Novel xenon oxides

The developments in the chemistry of xenon oxides and perxenates in the 1960s were expected to be accompanied by structural studies of newly synthesized compounds.[8,11] However, the rudimentary quality of research equipment and limited computational resources imposed serious constraints on characterization of xenon compounds at that time. The gap between computational resources and characterization needs was bridged during the first two decades of the current century, when both the long-known XeO_3[12] and newly discovered XeO_2 and $[XeOXeOXe]^{2+}$ (Fig. 2)[13] were synthesized and studied using modern methods of structural science. Although pure XeO_2 could not be isolated in a state allowing its direct X-ray structural examination, its molecular structure was proposed on the basis of spectroscopic data.[13] Shortly thereafter, the results of a computational study were reported, explaining the Raman spectral features of XeO_2 on the basis of a crystallographically reliable structural model.[14] The xenon atom in XeO_2 was modelled to be coordinated by four oxygen atoms, resulting in a distorted-square-planar coordination similar to that previously proposed for fluoride-bearing compounds XeF_4, $Xe(OTeF_5)_4$, $XeOF_2$ and $[XeOF_3]^-$ (ref. 15). On a separate subject matter, several mechanisms have been proposed to explain the presence and retention of XeO_2 in quartz, the Earth's most common silicon oxide.[16]

Xenon in oxide perovskite frameworks

The poor ability to characterize substances greatly diminished the early knowledge of the crystal chemistry of perxenates (the salts of perxenic acid, H_4XeO_6) – perhaps, the most unusual class of xenon oxide compounds.[2] Xenon, along with osmium and ruthenium, belongs to a very narrow group of elements that are able to attain the highest possible oxidation state, *i.e.*, +8.[2] In contrast to the pristine Xe(VIII) oxide XeO_4 (the anhy-
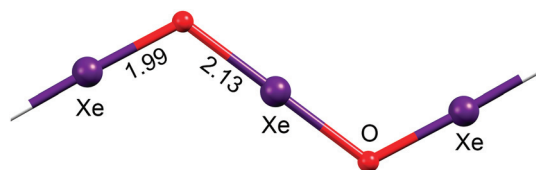
dride of perxenic acid), which has been isolated but is extremely unstable,[3,17] the salts of the perxenate(VIII) anion $[XeO_6]^{4-}$ are generally very stable both in the solid state and in aqueous alkaline solutions.[11] The perxenate anion forms a nearly perfect octahedron (Fig. 3),[11,18] with Xe–O bond lengths very similar to those in the majority of octahedral building units of inorganic oxysalts.[19] This observation implies that almost any known type of octahedral oxide framework could be formed by perxenate units. However, due to experimental limitations, only the three simplest perxenate salts (hydrates) were structurally characterized in the 20th century.[11] The latest studies of both newly discovered and long-known xenon(VIII) compounds have shown that this noble gas can be incorporated into stable and rigid oxide perovskite frameworks.[10,18] Therefore, the group 18 elements of the periodic table (noble gases) have become the last ones to be shown to be able to be accommodated by the perovskite structure.[20] Here, the first representatives were the classic "double" perovskites $KM(NaXeO_6)$ (M = Ca, Sr, Ba)[18] (Fig. 3), followed by the discovery of an unexpectedly elegant framework of the "yellow potassium salt" $K_4Xe_3O_{12}$,[10] a compound first synthesized almost 60 years ago.[3,21] $K_4Xe_3O_{12}$ has a layered perovskite structure whose 3D
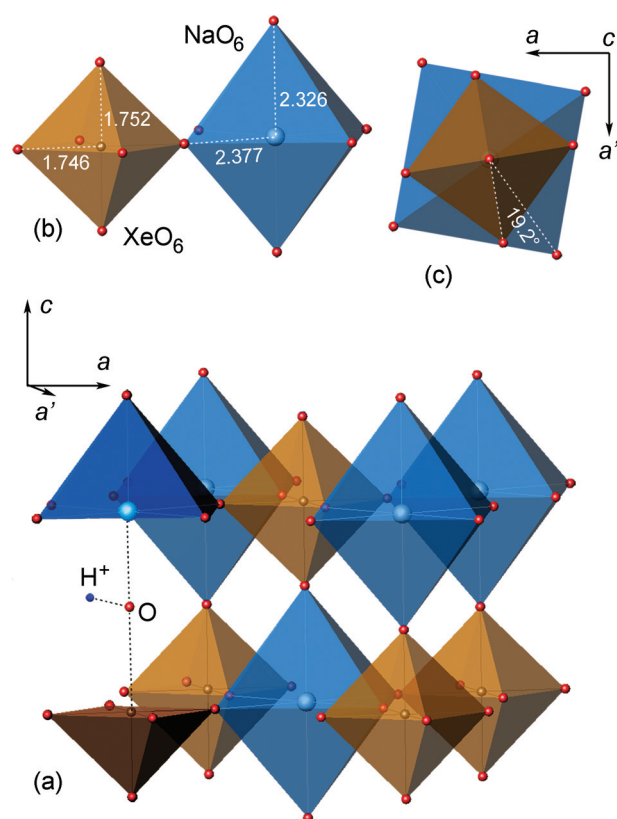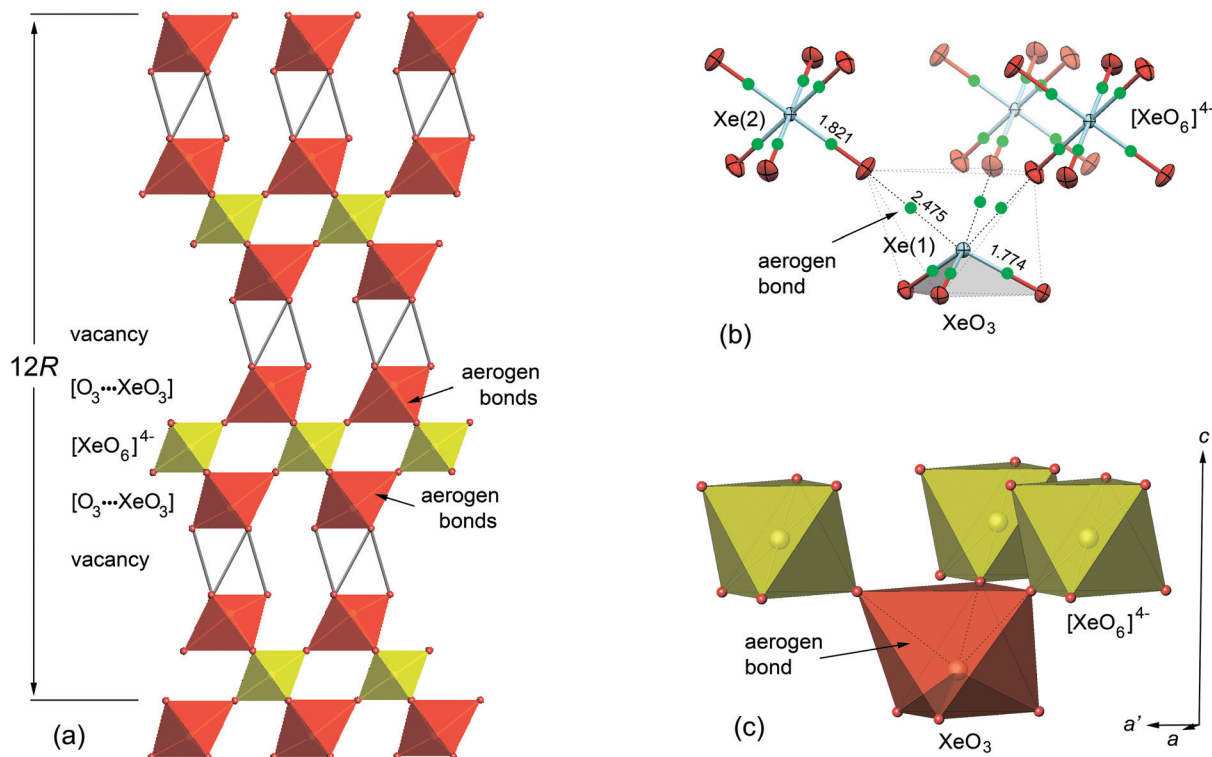

Fig. 3 Crystal structure of $KCa(XeNaO_6)$, the first Xe-bearing perovskite. (a) General view of the double perovskite framework. (b) A fragment showing corner-sharing octahedra XeO_6 and NaO_6. (c) XeO_6 and NaO_6 octahedra tilted around the four-fold axis of the perovskite structure. Bond lengths in Å. Adapted with permission from ref. 18, copyright (2015) Gesellschaft Deutscher Chemiker.


Fig. 2 Molecular geometry of the $[XeOXeOXe]^{2+}$ cation. Drawn using CCDC Mercury[7] based on crystallographic data reported by Ivanova *et al.* (2015).[13] Bond lengths in Å.

Fig. 4 Crystal structure of layered perovskite $K_4Xe_3O_{12}$. (a) General view of the structure showing the stacking sequence of perxenate $[XeO_6]$ octahedra (yellow) and $[O_3{\cdots}XeO_3]$ octahedra (orange-brown) formed by aerogen bonding of XeO_3 molecules to oxygen atoms of adjacent perxenate anions. (b) An ellipsoid view of the covalent and aerogen bonding. Calculated positions of the critical points are marked by green balls. (c) Polyhedral representation of a fragment shown in b. Bond lengths in Å. Adapted with permission from ref. 10, copyright (2016) American Chemical Society.

integrity is maintained *via* a combination of covalent, ionic, and – most strikingly – the above-mentioned aerogen bonds (Fig. 4). This salt displays a tendency to be highly explosive, a property inherited from the parent XeO_3,[3,21] and the weak aerogen linkages serve as trigger bonds responsible for the detonation sensitivity of both compounds.[10]

Xenon chemistry under extreme conditions

The enhanced reactivity of xenon towards oxygen under a high-pressure and high-temperature environment was predicted on the basis of computational studies.[14,22] Later on, many of these predictions for xenon oxides[22] were not confirmed by experiments. However, the suboxide Xe_3O_2, was shown to be stable at pressures greater than 75 GPa,[14] and was successfully synthesized at 83 GPa.[23] The discovery of Xe_3O_2, along with another (unpredicted) high-pressure phase, that of Xe_2O_5,[23] opened a new branch of xenon oxide chemistry. It is noteworthy that aerogen bonding, which was discovered almost simultaneously in solid XeO_3 (ref. 6) and predicted to be a special type of weak interaction in the structural model of Xe_3O_2 (ref. 14), was subsequently revealed in the structures of Xe_3O_2 and Xe_2O_5 experimentally determined in high-pressure conditions (ref. 23) (Fig. 5). The data on high-pressure xenon
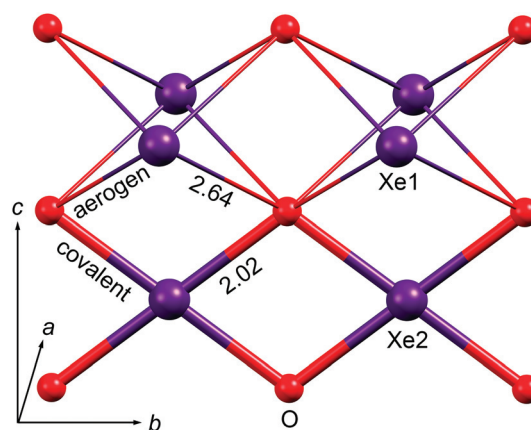
Fig. 5 Covalent Xe–O bonds (thick lines) and aerogen bonds (thin lines) in the crystal structure of Xe_3O_2 determined at 83 GPa. Drawn using CCDC Mercury based on crystallographic data reported by Dewaele *et al.* (2016).[23] Xe–Xe bonds were omitted for clarity. Bond lengths in Å.

reactivity,[23,24] crystal–chemical and physical–chemical considerations[13,14,16,18] could now be gathered together, inspiring the development of new ways to incorporate this element into oxygen-based silicate compounds at the conditions characteristic of the deep interior of the Earth.[25] The latest experimental studies on the chemistry of xenon under

extreme conditions has led to a solution for the long-standing cosmochemical enigma – the observed depletion in contemporary planetary atmospheres of xenon relative to argon, as compared to the overall percentages of these elements in the Solar System. This phenomenon is known in planetary science as "the missing xenon" paradox.[26] That xenon is noble but not inert was first revealed almost 60 years ago. The new discoveries show that this strange gas can be hidden from us as a constituent of solid oxide frameworks beneath the Earth's crust.

Conclusions

Since the discovery of xenon reactivity, the chemistry of this element has always been considered to be sort of exotic. And the chemistry of xenon oxides could be regarded as an "exotic of exotics". However, the latest discoveries in the world of xenon have shown that investigations of pure chemistry, seemingly distant from direct practical applications, can bring unexpected and valuable results at the crossroads of multidisciplinary problems.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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