Review Article

Synthesis, Properties and Chemistry of Xenon(II) Fluoride

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Abstract

This paper presents a brief review of the basic information regarding xenon(II) fluoride such as the synthesis of a pure compound, its physical and chemical properties, its solubility in major inorganic solvents, safe handling and the use of spectroscopic methods (IR, Raman, NMR) for the characterization of its compounds. The use of XeF_2 as fluorinating and oxidizing agent is shown. The reactions of XeF_2 with different Lewis acids and the formation of XeF^+ and $Xe_2F_3^+$ salts are briefly described. The major part of this review is the presentation of XeF_2 as a ligand to metal ions. Different synthetic routes for the preparation of new coordination compounds of the type $[M^{n+}(XeF_2)_p](AF_6^-)_n$ are given together with the influence of the cation and the anion on the structural features of these compounds. The possibility of predicting the structure of these new compounds, knowing only the properties of the cation and the anion, is analyzed.

Keywords: Xe(II) fluoride, oxidizer, fluorinating agent, ligand, Lewis base

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1. Introduction

In the year 1962 the first noble gas compound $XePtF_6$[1] was synthesized and the era of the noble gas chemistry began. In the years that followed much has been written on this subject, e.g. books and review papers[2-8], if we mention just a few. The recent review paper clearly shows that the interest in this fascinating subject has not diminished; on the contrary, we can even talk about the renaissance of the noble gas chemistry.[9] Xenon(II) fluoride is one of the most easily handled noble gas compounds - therefore its chemistry is the most extensive. Its synthesis is relatively simple and there is no danger of the formation of explosive xenon oxides or oxide fluorides in higher oxidation states.

The main purpose of this brief review paper is to give some basic information about the synthesis of XeF_2, its properties and to show a great variety of possibilities this reagent offers to the synthetic chemists. We had no intention of giving a complete overview of all that has been done in this field due to the limitations of space, as well as bearing in mind that this was not the purpose of this review. The review is intended for readers without or with very limited knowledge of noble gas chemistry. Our idea was firstly to make readers aware of the noble gas chemistry, especially of the chemistry of xenon(II), which is an extensive one, and secondly that XeF_2 is a versatile reagent whose use is much more extensive than it is generally thought.

The main part of this review is devoted to the XeF_2 molecule acting as a ligand to the metal ions – this is where the contribution of our department is the most comprehensive and we can really furnish the information from the first hand.

2. Synthesis and properties of XeF_2

2.1. Synthesis of XeF_2

Xenon(II) fluoride was first reported independently by two laboratories.[10,11] XeF_2 can be prepared from gaseous mixture of xenon and fluorine using different kinds of energy, e.g. heat, UV light, sun light, electric discharge, high density γ radiation, irradiation by electrons from a van de Graff accelerator, irradiation by 10 MeV protons etc. If thermal methods of the preparation are used a large excess of xenon over fluorine should be employed in order to minimize formation of higher fluorides.[4]

One of the most elegant syntheses of XeF_2 yielding a pure product is a photochemical reaction of a gaseous mixture of xenon and fluorine with excess of xenon. The reaction can be performed in a Pyrex flask. The mixture is exposed to direct sunlight (Figure 1) or to UV light from a mercury lamp. Very pure XeF_2 in a greater quantity (up to 1 kg) can be best prepared by UV irradiation of xenon – fluorine gaseous mixture in the mole ratio xenon:fluorine is 2:1 with addition of about 1 mol % of HF in the fluorine as a catalyst.[12]

The thermal reaction between xenon and fluorine to form xenon difluoride is heterogeneous and takes place on the prefluorinated walls of the reaction vessel or on the surface of the added fluoride.[13] During the

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Melita Tramšek *finished her B.Sc. study in 1993 at the Faculty of Chemistry and Chemical Technology at the University of Ljubljana. After being employed at IMPOL d.d. in Slovenska Bistrica for a year and a half she joined Prof. Dr. Boris Žemva's group at the Jožef Stefan Institute, Department of Inorganic Chemistry and Technology in 1994. She received M.Sc. degree in 1997 and completed her PhD thesis in 2001 at the University of Ljubljana. Her research interests are in the area of syntheses and characterization of new inorganic fluorides. The majority of her scientific work is devoted to coordination compounds, especially those with noble gas fluorides as ligands to metal cations.*

Prof. Dr. Boris Žemva *received his PhD in Chemistry in 1971 from the University of Ljubljana, Slovenia. Afterwards he spent one year as a post-doctoral fellow with Professor Neil Bartlett at the University of California, Berkeley, U.S.A. He was the head of the Department of Inorganic Chemistry and Technology at the Jožef Stefan Institute from 1983 to 2006. His main research interests are in inorganic fluorine chemistry especially noble gas chemistry and in the syntheses of thermodynamically unstable fluorides. These compounds and their cationic species represent the strongest oxidizers known up to now. Recently he has been studying new coordination compounds with noble gas fluorides as ligands to metal ions. His achievements in science were recognized by Boris Kidrič Award in 1989, Humboldt Research Award in 1999 and the Award of American Chemical Society for creative work in fluorine chemistry in 2006. He was a Miller Visiting Professor at the University of California, Berkeley in 1993 and a Visiting Professor at Institut de Chimie de la matière condensée de Bordeaux, France in 1997. In 2001 he was appointed Ambassador of the Republic of Slovenia in Science. He is a full member of the Engineering Academy of Slovenia.*

Figure 1. Photochemical synthesis of XeF_2

study of the catalytic effect of some binary fluorides of the transition metals on the reaction between xenon and fluorine it was found out that NiF_2 is the strongest catalyst. In the presence of NiF_2 (surface about100 m^2) it is possible to synthesize XeF_6 even at 393 K from the gaseous mixture of xenon and fluorine in the mole ratio as low as 1:5. Of course, the reaction between xenon and fluorine can proceed also as homogeneous reaction if enough fluorine radicals are formed momentarily in the mixture of xenon and fluorine by a very exothermic side reaction.

2.2. Properties of XeF_2

XeF_2 is colourless as a solid, liquid or gas.The vapour pressure of the solid at 298 K is $6.0x10^2$ Pa,[14] which makes it possible that XeF_2 is sublimed under vacuum at room temperature. The melting point of XeF_2 is 402.18 K. Large crystals of XeF_2 are usually formed at room temperature (Figure 2). A linear and centro-symmetric structure ($D_{\infty h}$) of XeF_2 was deduced from vibrational spectra.[15] The most reliable value for the Xe-F bond length in the vapour phase is 197.73±0.15 pm.[15] The neutron diffraction study of the solid XeF_2 gave the value of 200 pm for the bond length of Xe-F.[16] In a solid XeF_2 each xenon atom has two fluorine atoms at the distance of 200 pm and eight fluorine atoms at the distance of 342 pm from eight neighbouring XeF_2 molecules.[17] There are strong electrostatic interactions between XeF_2 molecules. Such structural arrangement is in agreement with the high enthalpy of sublimation (55.71 kJ/mol) and assumed charge distribution in each molecule ($^{-0.5}F\text{-}Xe^{+1}\text{-}F^{-0.5}$).[18]

It is further evident from the packing arrangement that the equatorial region of each XeF_2 molecule is avoided by fluorine ligands of neighbouring molecules because the non-bonding valence electrons of xenon atom effectively shield the positive charge on the xenon.

Figure 2. Crystals of XeF_2

XeF_2 dissolves in a variety of solvents without oxidation or reduction, as for example in BrF_5, BrF_3, IF_5, anhydrous HF, CH_3CN, etc. [2] The solubility in anhydrous HF is rather high, amounting to 167 g/100g HF at 29.95 °C.[19] In the study of the interaction of XeF_2 with a variety of "inert" solvents, which are used in organic chemistry, it was found that both hydrogen- and chlorine-fluorine exchange was observed over a relatively short time scale with chloroform, dichloromethane and dibromomethane. XeF_2 reacts slowly with tetrachloromethane and fluorotrichlormethane, while in the acetonitrile the rate of the reaction is negligible.[20]

The vibrational bands of XeF_2 in the solid and in the vapour are: a.) in the solid: ν_1 is at 496 cm^{-1} (1.0), R; ν_3 is at 547 cm^{-1} (vs), IR; and lattice mode is at 108 cm^{-1} (0.33), R. b.) in the vapour: ν_1 is at 516.5 cm^{-1} (1.0), R; ν_2 is at 213.2 cm^{-1} (vs), IR; ν_3 is at 560.1 cm^{-1} (vs), IR and $\nu_1 + \nu_3$ is at 1070 cm^{-1} (w), IR.[21,22] Raman studies of molecular dynamics of XeF_2 in anhydrous HF instead of one ν_1 band showed several distinct peaks at 475 cm^{-1}, 516 cm^{-1} and 545 cm^{-1}. It was concluded that vibrational band near 475 cm^{-1} is referred to the vibration of Xe···F bridging bond of the solvated system of the xenon(II) fluoride ($FXe^{\delta+}\cdots FHF^{\delta-}$). The band at 545 cm^{-1} can be referred to the ν_3 mode of the distorted linear configuration of XeF_2. The band at 516 cm^{-1} is attributed to a totally symmetric Xe-F mode ν_1 of XeF_2 molecule.[23]

NMR spectroscopy became an extremely powerful tool in the structural characterization of xenon species

in solution and lately also in the solid state. NMR spectroscopic data for XeF_2 are: $\delta(^{129}Xe)$ (ppm): -2074 (gas phase, 90 ºC), from -2009 to -1592 (in various solvents), -1604±10 (solid state at 0 ºC); $\delta(^{19}F)$ (ppm): -183.4 (gas phase, 90 ºC), from -181.8 to -199.6 (in various solvents), 169±1 (solid state 0 ºC); $^1J(^{129}Xe\text{-}^{19}F)$ (Hz): 5627 (gas phase, 90 ºC), from -5579 to -5652 (in various solvents) -5550±50 (solid state at 0 °C).[24,25]

2.3. Bonding in XeF_2

The synthesis of the first true chemical compound with noble gas element, $XePtF_6$, immediately triggered the question whether the previous models of the bonding are still valid. The answer was positive. It was immediately clear that the same models can be applied both for interhalogen and halogen oxy species. Two approaches of bonding were applied: a.) molecular orbital model and b.) valence shell electron pair repulsion scheme. Here follows the application of both models in the case of XeF_2.

a.) Molecular orbital model.

This model does not involve the "outer", or higher valence-shell, orbitals of xenon atom, at least not to an extent which could significantly affect the bond energy. The simple molecular orbital approach describes the bonding in terms of three-centre molecular orbitals, derived from a *p*-orbital from each of the participating atoms. Combination of the three atomic orbitals provides three molecular orbitals: one bonding, one non-bonding and one anti-bonding. Since xenon atom contributes two electrons and each of the fluorine ligands only one electron to this pσ molecular orbital system, thus yielding four electrons to populate these orbitals. The bonding orbital with the lowest energy receives two electrons. The non-bonding orbital with the intermediate energy receives also two electrons. The molecular orbital with the highest energy remains empty. Consequently there is net bonding which is the best when the arrangement of the three atoms is centro-symmetric. The observed $D_{\infty h}$ molecular symmetry of XeF_2 is in harmony with these requirements. The non-bonding orbital is largely concentrated on the fluorine ligands thus restoring the fluorine ligand electron density. The bonding pair of electrons is responsible for the binding together of all three atoms. The delocalization of the electron pair is best described by the presentation $^{-0.5}F\text{-}Xe^{+1}\text{-}F^{-0.5}$. This assignment fits most of the physical and chemical properties of XeF_2. It should be noted, however, that *the xenon-fluorine bonds in XeF_2 are, in effect, single-electron bonds.*[26,27,28,29,30]

It can be concluded that it remains true that the noble-gas electron arrangement is especially stable arrangement, which all non-transitional-element atoms attain or retain. Xenon is not exceptional to this rule. *The octet is of paramount importance, the electron-pair bond is not.*

b.) Valence shell electron pair repulsion theory.

Coulson[29] has favoured the valence bond scheme which could be presented as the resonance between two canonical forms $F\text{-}Xe^+\ F^-$ and $F^-\ Xe^+\text{-}F$. In this ionic model each atom is surrounded by an octet of electrons. It assumes that each bond between the ligand F and Xe atom involves an electron pair. Further it assumes that all nonbonding valence electrons have a steric effect. Using this model Gillespie[31,32] predicted the shape of all at that time unknown species and his predictions were later confirmed when these species were isolated.

Bonding models and calculations of physical and spectroscopic properties of XeF_2 are the subject of some recently published papers.[33,34]

3. XeF_2 as a fluorinating and oxidizing agent

XeF_2 has considerable potential in oxidative fluorination because of its low average bond energy (133.9 kJ/mol) and because of the inertness of its reduction product xenon. However it has been shown that XeF_2 has considerable kinetic stability, e.g. it might be recovered from aqueous solution, in which it is thermodynamically unstable towards hydrolysis, by extraction with CCl_4 or by fractional destillation.[4]

The formation of cationic Xe(II) species e.g. XeF^+, $Xe_2F_3^+$ in anhydrous HF as a solvent and in the presence of Lewis acids, makes XeF_2 even stronger oxidizing and fluorinating agent. Electron affinity of XeF^+ and $Xe_2F_3^+$ is greater than that of XeF_2 and the transfer of an electron to either of these cations would generate the $XeF^\bullet$ radical, as an effective fluorine atom source.[35] Elements, lower fluorides, halides and halo complexes, oxides and carbonyls of several elements can be oxidized with XeF_2 in anhydrous HF. For example elements such as Ni, Hg, Mo, Nb, Os can be oxidized either to binary fluorides (NiF_2, HgF_2) or XeF_2 adducts (NbF_5, OsF_5). Lower fluorides like TlF, SnF_2, AsF_3, MnF_2, CoF_2, MoF_4, CrF_2 are oxidized to TlF_3, SnF_4, AsF_5, MnF_3, CoF_3, MoF_6, CrF_4. Products of the oxidation of halides and halo complexes $MoBr_4$, $RuCl_3$, $OsBr_4$, KWF_6 and K_3RhF_6 are MoF_6, RuF_5, OsF_5, WF_6 and K_2RhF_6.[36]

Oxyfluorides or fluorides are main products of the oxidation of some oxides like SO_2, ReO_2, RuO_2.[36] At room temperature XeF_2 does not react with UO_2, U_3O_8 or ZrO_2 powders. Reaction can be induced to proceed in the air without heating by addition of a drop of water. After initial slow reaction a violent reaction followed. The products of the reaction were either metal fluorides or oxyfluorides.[37] XeF_2-HF system is useful

for preparation of transition metal carbonyl fluorides either by direct oxidation of carbonyls (e.g. $Mo(CO)_6$ to $Mo(CO)_3F_3$, $Os_3(CO)_{12}$ to *cis*-$[Os(CO)_4F_2]$, $Ru_3(CO)_{12}$ to *cis*-$[RuF_2(CO)_4]$ or by halogen exchange (e.g. $Ru(CO)_3Cl_2$ to $Ru(CO)_3F_2$ and $Ru(CO)_2F_3$).[36,38,39]

We should not leave out the oxidizing properties of XeF_2 in aqueous solution. Chlorate, bromate and iodate can be oxidized to the respective perhalates.[40] It is also capable oxidizing chloride to chlorine, iodide and iodate to periodate, Ce(III) to Ce(IV), Ag(I) to Ag(II), etc.[2] In acidic solutions XeF_2 is capable of oxidizing Pu(III) to Pu(IV) and further to Pu(VI).[41]

XeF_2 can be used as fluorinating agent for fullerenes. It was demonstrated, that fluorination of T_h-$C_{60}Br$ with XeF_2 in anhydrous HF at room temperature resulted in the formation of T_h-$C_{60}F_{24}$.[42]

Besides the use of XeF_2 for the fluorinations of inorganic materials, we should also mention its wide use in organic chemistry. It is an excellent reagent for the introduction of fluorine atom into organic molecules. This is not the purpose of this review therefore we will not go into details. Besides, several excellent reviews were written covering this subject.[43,44,45]

We would like briefly to mention another example of XeF_2 oxidizing ability that is its use as etching reagent for silicon.[46] XeF_2 etches silicon in a gas phase at room temperature with extremely high selectivity to numerous materials including silicon dioxide, many metals including aluminium, copper and gold and many polymers. The advantage of XeF_2 as etching reagent is that the final products of etching process are gases SiF_4 and Xe which can be pumped off. Now commercial equipment for etching by XeF_2 is available.

The purpose of this chapter is to give the reader an idea how extensive is the field of XeF_2 acting as an oxidizing and fluorinating agent.

4. XeF_2 as a medium strong Lewis base

XeF_2 is a reasonably good fluoride ion donor. The fluoride ion donor ability among the binary fluorides of xenon is: $XeF_6 > XeF_2 >> XeF_4$. This finding is in agreement with the enthalpies of ionization[47] (XeF_x (g) $\rightarrow XeF_{x-1}^+$ (g) + F^- (g); ΔH^0 for XeF_2 = 9.45 eV, ΔH^0 for XeF_4 = 9.66 eV and ΔH^0 for XeF_6 = 9.24 eV). Strong fluoride ion acceptors, e.g. AsF_5, SbF_5, BiF_5 can withdraw a fluoride ion from XeF_2 forming XeF^+ species and in the case of excess XeF_2 over Lewis acid, also $Xe_2F_3^+$ species. In the free XeF_2 molecule the bond between xenon and fluorine is one electron bond.[30] If one fluoride ion is abstracted from XeF_2, the bond between Xe and remaining F^- becomes stronger, that is two electrons bond. The increase in the Xe-F bond energy in the cation formation (133.9 kJ/mol in XeF_2 to 195.9 kJ/mol in the cation)[4] contributes to the fluoride ion donor ability of the difluoride. XeF_2 also forms compounds in which the abstraction of the fluoride ion from XeF_2 molecule is at the beginning of its ionization pathway $XeF_2 \rightarrow XeF^+ + F^-$.[48] In these compounds the covalent contribution to the bonding is substantial. XeF_2 also forms molecular adducts in which the negatively charged F ligands of XeF_2 are attracted by the positive centre of the partner molecule.

Xe(II) compounds can be prepared by fusing together stoichiometric amounts of the component fluorides in an inert atmosphere or dissolving them in an appropriate solvent (non-oxidizing or reducing solvent). One component can be also in excess.

The intention of the review of the compounds with XeF_2 is to show the wealth of the possibilities. The emphasis is on the compounds, which were isolated and characterized in our group.

4.1. Reactions of XeF_2 with pentafluorides

The compounds of XeF_2 with pentafluorides are the most common. So far three types of the compounds were found: $2XeF_2 \cdot MF_5$, $XeF_2 \cdot MF_5$ and $XeF_2 \cdot (MF_5)_2$. Two types of bonding were suggested for these compounds: salt-like (e.g. $XeF^+MF_6^-$ or $Xe_2F_3^+MF_6^-$) formulation and the cases where covalent contribution is very important and XeF_2 molecule is coordinated to MF_5 via fluorine bridge. The type of bonding is strongly dependent upon the pentafluoride used. The degree of ionic character in these compounds varies depending on the Lewis acidity of the pentafluoride. More ionic character of the XeF_2 bonding is expected in the cases with very strong Lewis acids like SbF_5 and BiF_5.

In the reactions of different pentafluorides with excessive XeF_2 the compounds of the composition $2XeF_2 \cdot MF_5$ (M = As, Sb, Bi, Ta, Ru, Os, Rh, Ir, Pt, Au)[49,50,51,52,5] were isolated. These compounds readily lose XeF_2 in a dynamic vacuum yielding 1:1 and 1:2 compounds. Most of them were characterized by Raman spectroscopy. The bands, characteristic for $Xe_2F_3^+$ vibrations (Xe-F stretching) are usually very intense. The characteristic doublet is found in the region from approximately 580 to 600 cm^{-1}. Xe-F stretching is found at about 100 cm^{-1} higher frequency as in the solid XeF_2 and it is related to the vibrations of the shorter (terminal) Xe-F bond in the cation. In more extensive Raman study of some of these compounds (M = As, Sb) more bands were assigned to the vibrations of the cation, including the weak bands for the stretching of the longer Xe···F bonds.[53] In some cases the salt formulation is also proved by single crystal analysis ($Xe_2F_3AsF_6$; two modifications: monoclinic[54] and trigonal, and monoclinic $Xe_2F_3SbF_6$ [55], and $Xe_2F_3RuF_6$ [56]). In all cases $Xe_2F_3^+$ cations are planar V shaped species (Figure 3), symmetrical about the bridging fluorine

atom. The terminal Xe-F distances range from to 190.7 to 192.9 pm, whereas the bridging Xe···F_b distances range from 209 to 226 pm. The most striking structural difference for $Xe_2F_3^+$ cation in these structures is the large variation of the Xe···F_b···Xe bridging angle ranging from 139.8° to 160.3°.[54, 55, 56]

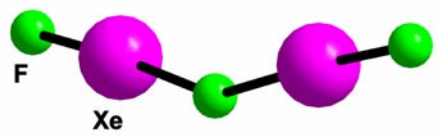

Figure 3. V-shaped cation $Xe_2F_3^+$ in the compounds $Xe_2F_3AF_6$ (A = As , Sb, Ru)

The compounds with the mole ratio XeF_2: MF_5 is 1:1 ($XeF^+MF_6^-$) and with the mole ratio XeF_2: MF_5 is 1:2 ($XeF^+M_2F_{11}^-$) were obtained for the most of the metals mentioned above.[49,50,51,4] Free XeF_2 molecule is linear and symmetrical, while in the cases of the compounds with Lewis acids MF_5 (M= As, Sb, Bi, Ta, Ru), XeF_2 molecule is distorted. Xe···F bridging distance is strongly elongated showing that XeF_2 donated fluoride ion to MF_5 acceptor to generate MF_6^- and $M_2F_{11}^-$ anions. The elongation of the Xe-F bond on one side of XeF_2 molecule results in the shortening of the bond between Xe and non-bridging F^- on the other side. In the case of compounds with the strong Lewis acids (e.g. AsF_5, SbF_5, BiF_5, TaF_5, RuF_5.) bands assigned to the symmetrical stretching vibration of the shorter, non-bridging Xe-F bond are found in the region from 596 to 619 cm^{-1}. The most distorted XeF_2 molecule among these compounds is in $XeFSb_2F_{11}$ with Raman band of ν(Xe-F) at 620 cm^1.[53] Crystal structures of $XeFAsF_6$[57] and $XeFRuF_6$[58] can be mentioned here (Figure 4). Short Xe-F distances are 187.2 pm (Ru) and 187.3 pm (As), while the elongated Xe···F distances are 218.2 (Ru) and 221.2 pm (As). These cases clearly demonstrate that XeF_2 molecule in these compounds is at the end of its ionization pathway: $XeF_2 \rightarrow XeF^+ + F^-$.[48]

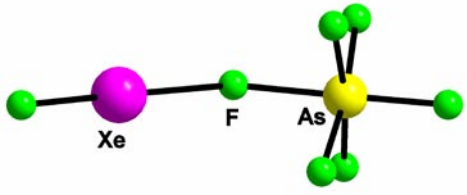

Figure 4. Structure of $XeFAsF_6$ [57]

Molecular adducts of XeF_2 with pentafluorides are also known. One of the first examples is $XeF_2 \cdot IF_5$ which was characterized by Raman spectroscopy, band for XeF_2 was found at 493 cm^{-1}, showing that only undistorted XeF_2 was present in the compound.[59] An other such example is $XeF_2 \cdot VF_5$.[60] The interaction between XeF_2 and VF_5 is so weak that even IR beam can decompose $XeF_2 \cdot VF_5$ in its components in the vapour phase. The molecular adducts $XeF_2 \cdot 2BrF_5$ and $XeF_2 \cdot 9BrF_5$ were postulated on the basis of the melting point composition diagram.[5]

4.2. Reactions of XeF_2 with tetrafluorides

A number of the compounds with tetrafluorides is not as high as in the case of pentafluorides. The variety of the mole ratios between XeF_2 and MF_4 ranges from 4:1 to 1:2 compounds. Tetrafluorides of Ti, Cr, Mn, Rh, Pd, Pt, Sn and even XeF_4 form compounds with XeF_2.[61,62,63,64,4,5] Tetrafluorides are weaker Lewis acids as pentafluorides therefore the compounds with Xe-F^+ or $Xe_2F_3^+$ cations and MF_5^- or MF_6^{2-} anions are not so common. In the system XeF_2/CrF_4 two structurally characterized compounds were found: $XeF_2 \cdot CrF_4$ (Figure 5) and $XeF_2 \cdot 2CrF_4$.[63, 64] The compounds can be prepared by the reaction between CrF_5 and excess XeF_2 at 323-333K. CrF_5 is reduced to CrF_4, while XeF_2 is oxidized to XeF_4, the final product is blue $XeF_2 \cdot CrF_4$. This product is also the starting compound for the preparation of the single crystals of $XeF_2 \cdot 2CrF_4$, by heating the sample in a thermal gradient or by recrystallizing it in a supercritical SF_6. In both structures the XeF_2 molecules are distorted with non-bridging Xe-F distances ranging from 190.3 to 193 pm and bridging Xe-F distances ranging from 212.7 to 218.6. Non-bridging Xe-F distances and Raman spectra (ν(Xe-F) at 574 cm^{-1} for $XeF_2 \cdot CrF_4$) indicate that XeF_2 is at beginning of the ionization pathway mentioned earlier. XeF_2 forms molecular adduct with XeF_4 which makes the purification of XeF_4 even more difficult.[65]

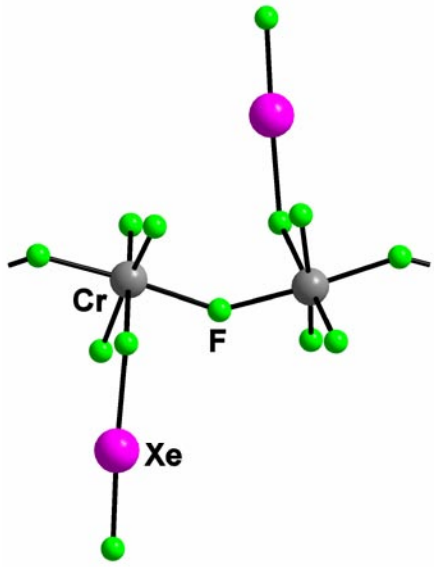

Figure 5. Structure of the $XeF_2 \cdot CrF_4$ [63]

4.3 XeF_2 in the compounds with weak fluoride ion acceptors

Adducts with weak fluoride ion acceptors $MoOF_4$ and WOF_4 are also known. In these adducts XeF_2 interacts with the metal centre. In the crystal structure of $XeF_2 \cdot WOF_4$, bond distances in XeF_2 (189 pm and 204 pm) indicate, that the XeF_2 molecule is distorted but the covalent contribution to the bonding is essential. Raman frequencies (ν(Xe-F)) for these two compounds are 575cm^{-1} (Mo) and 585cm^{-1} (W).[8,66] In $(XeF_2)_2 \cdot XeF_5^+AsF_6$, $XeF_2 \cdot XeF_5^+AsF_6^-$ and $XeF_2 \cdot 2(XeF_5^+AsF_6^-)$ the negatively charged F ligand of the XeF_2 molecules interact with positively charged Xe atoms of the XeF_5^+ cations.[48] Structural and Raman data show that the interaction of XeF_2 is considerably weaker as in the cases of stronger Lewis acid. In $XeF_2 \cdot 2(XeF_5^+AsF_6^-)$ the XeF_2 molecule bridges two $XeF_5^+AsF_6^-$ units and it is almost undistorted (Xe-F distance 203 pm, ν(Xe-F) at 496 cm^{-1}). In the other two cases XeF_2 molecules are non-bridging and therefore distorted ($(XeF_2)_2 \cdot XeF_5^+AsF_6^-$: Xe-F distances: 205 pm, 199 pm and 201 pm, ν(Xe-F) 550 and 542 cm^{-1}; $XeF_2 \cdot XeF_5^+AsF_6^-$: Xe-F distances: 200 pm, 197 pm, ν(Xe-F) 559 cm^{-1}.[48]

Several adducts have been prepared in which the XeF_2 molecule is indistinguishable from the molecule in crystalline XeF_2, e.g. $XeF_2 \cdot XeF_4$,[65] $XeF_2 \cdot IF_5$,[59] $XeF_2 \cdot XeOF_4$.[67] In the system XeF_2/MF_6 (M = Mo, W, U) the compounds of the type $XeF_2 \cdot MF_6$ were claimed on the basis of the melting point – composition diagrams.[4]

5. XeF_2 as a ligand in coordination compounds

In the recent years a new series of the compounds with XeF_2 as a ligand to the metal ions was synthesized. The first compound in which XeF_2 was bound directly to the metal centre was $[Ag(XeF_2)_2](AsF_6)$.[68] Later the systematic investigation of the reactions of $M^{n+}(AF_6^-)_n$ (M is the metal in oxidation state n, A = As, Sb, Bi, P, Ta, Ru) with XeF_2 in anhydrous HF as a solvent was performed. Details about the syntheses and structural features of the coordination compounds with the univalent central atom M^+ (M = Ag[68,69], Li), with alkaline earth metals (Mg-Ba)[70-74], with other M^{2+} metals (M = Cd, Cu, Zn, Pb)[75-78] and lanthanide metals Ln^{3+} [79-81] can be found in the literature. The compound of Cd with BF_4^- anion $[Cd(XeF_2)](BF_4)_2$ should be also mentioned.[82]

There are two facts, which should be taken into account in order to synthesize new coordination compounds with XeF_2 as a ligand to metal ions:

1.) metal cations should be relatively weak Lewis acids to prevent the withdrawal of F^- from XeF_2 molecule and thus make possible the generation of $Xe_2F_3^+AF_6^-$ or $XeF^+AF_6^-$ salts.

2.) XeF_2 dissolved in anhydrous HF is relatively strong oxidizing agent; therefore it is essential that metal cations are resistant towards further oxidation. If metal cations are oxidized they are converted to stronger Lewis acids and the possibility that they will withdraw F^- from XeF_2 molecule is even greater.

5.1. Synthetic routes for the preparation of the compounds $[M^{n+}(XeF_2)_p](AF_6^-)_n$

The following synthetic routes could be applied for the preparation of the coordination compounds of the type $[M^{n+}(XeF_2)_p](AF_6^-)_n$:

1.) The reaction between $M^{n+}(AF_6^-)_n$ and excess of XeF_2 in anhydrous HF as a solvent.

After the reaction was completed the excess XeF_2 and the solvent were pumped away. The reaction product was monitored in situ by Raman spectroscopy. In this way also at room temperature unstable products were detected. When totally symmetric stretching vibration (ν_1) of the free XeF_2 molecule at 497 cm^{-1} was absent it was clear that the rest of the XeF_2 is bounded. In the case of magnesium the ν_1 of the free XeF_2 molecule disappeared at the composition $[Mg(XeF_2)_6](AsF_6)_2$. This coordination compound is not stable at room temperature but it was slowly losing XeF_2 finally yielding the compound $[Mg(XeF_2)_4](AsF_6)_2$ which was possible to isolate at room temperature and even grow single crystals. This compound was also slowly losing XeF_2 yielding at room temperature stable $[Mg(XeF_2)_2](AsF_6)_2$.[73]

2.) The reaction between $M^{n+}(AF_6^-)_n$ and stoichiometric amounts of XeF_2 in anhydrous HF.

This synthetic route is used in the cases where the isolated compound is still having some decomposition vapour pressure of XeF_2 at room temperature and it could partly decompose while excess XeF_2 is pumped away. By using stoichometric amounts of both reagents a purer product is obtained.

3.) Direct synthetic route

In the cases of phosphates or borates a direct synthetic route could be applied because PF_5 and BF_3 are not strong enough Lewis acids to form stable XeF^+ salts. In the direct synthesis the reaction is performed between MF_n and XeF_2 in anhydrous HF acidified with excess of PF_5 or BF_3.[72, 82]

5.2. The types of XeF_2 as a ligand

XeF_2 molecule as a ligand in the coordination compounds of the type $[M^{n+}(XeF_2)_p](AF_6^-)_n$ is acting either as a non-bridging ligand interacting only with one metal centre, or as a bridging ligand, connecting

two metal centres. In the first case XeF_2 is donating one fluoride ion to the metal centre. The symmetric environment of the xenon atom is distorted. The bond distance between xenon atom and fluoride ion donated to the metal cation increases and the distance between terminal (non-bridging) fluoride ion and xenon atom decreases. The Raman stretching band of the shorter Xe-F bond is in the range from 544 to 584 cm^{-1}. In the bridging XeF_2 molecule both fluoride ions interact with two different metal centres. The Xe-F bond distances change only slightly but the Raman stretching band of the Xe-F bond is in the range from 500 to 535 cm^{-1}. The enhancement of this stretching frequency from 496 cm^{-1} to 535 cm^{-1} is associated (1) with the interactions between metal centres and XeF_2 molecule and (2) with high Coulomb field which these metal centres are placed in. The transformation of the free XeF_2 molecule through the phase in which XeF_2 molecule is acting as a ligand to the complete ionization of XeF_2 in XeF^+ and F^- is shown in the Figure 6.

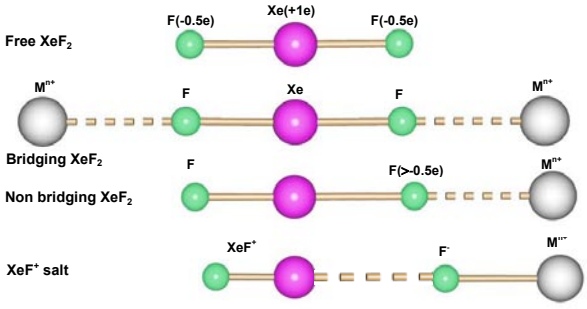

Figure 6. XeF_2 on the ionization pathway from "free" molecule to the XeF^+ cation

The number of XeF_2 molecules (bridging and non-bridging) around one metal centre can range from one non-bridging XeF_2 molecule in $[Cd(XeF_2)](BF_4)_2$ [82] to up to nine XeF_2 molecules (5 non-bridging and 4 bridging) around one Ca atom in $[Ca_2(XeF_2)_9](AsF_6)_4$.[74]

5.3. The influence of the central atom on the possibility of the formation and on the structural diversity of the coordination compounds $[M^{n+}(XeF_2)_p](AF_6^-)_n$

During the reaction between $M^{n+}(AF_6^-)_n$ and XeF_2 in anhydrous HF is the influence of the cation M^{n+} and its Lewis acidity essential for the course of the reaction. The coordination compounds of the type $[M^{n+}(XeF_2)_p](AF_6^-)_n$ will be formed only in the cases when Lewis acidity of M^{n+} is not high enough to withdraw fluoride ion from XeF_2 forming MF_n and $Xe_2F_3^+AF_6^-$. For example in the cases of the compounds $Ni(AsF_6)_2$ and $Mn(AsF_6)_2$ the Lewis acidity of Ni^{2+} is high enough to withdraw fluoride ion from XeF_2 forming NiF_2 and $Xe_2F_3^+AsF_6^-$, while in the case of manganese, Mn^{2+} is oxidized to Mn^{3+} which is even stronger Lewis acid. [75] Even more interesting is the situation in the lanthanide series. In the beginning of the series from La to Gd the Ln^{3+} are weak Lewis acids and the coordination compounds $[Ln(XeF_2)_p](AsF_6)_3$ are formed. The exceptions are Ce, Pr and Tb which are oxidized to Ln^{4+} thus forming stronger Lewis acids than Ln^{3+} and the final products are LnF_4 and $Xe_2F_3^+AsF_6^-$. In the middle of the Ln series (Dy, Ho) the Lewis acidity of the cation is "on the border"; both reactions took place: LnF_3 and $[Ln(XeF_2)_p](AsF_6)_3$ are formed simultaneously. Further along the series from Er to Lu the isolated products are only LnF_3 and $Xe_2F_3^+AsF_6^-$.[81]

The impact of the cation on the structural diversity (see section 5.5) of these coordination compounds is determined by some of its properties e.g. electron affinity, effective nuclear charge, effective volume, Lewis acidity of the cation, covalency of the M-F bond, coordination number etc. The influence of the cation is clearly seen in the case of the compounds $[M(XeF_2)_4](AsF_6)_2$ with M = Mg[73], Ca[71], Cd[76]. The anion and the number of XeF_2 molecules per central atom are the same in all three cases. The crystal structure of $[Mg(XeF_2)_4](AsF_6)_2$ represents the first molecular structural type with only non-bridging XeF_2 ligands. The type of the structure is a consequence of a small Mg^{2+} ion and therefore a low coordination number of Mg (CN=6) and the covalency of the Mg-F bond. The electron charge transfer from the XeF_2 molecule to the cation due to the covalent character of the Mg-F bond renders the XeF_2 molecule less capable of bridging two magnesium cations. Here it should be emphasized that also in the case of the compound $[Mg(XeF_2)_2](AsF_6)_2$ (Figure 7) where less XeF_2 molecules are available, again only non-bridging XeF_2 molecules are present. The coordination around the metal centre is achieved by *cis* bridging of the anion forming a chain.

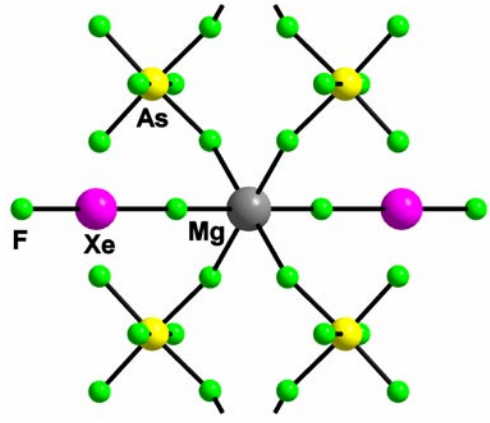

Figure 7. Example of the metal coordinated by non-bridging molecules of XeF_2; $[Mg(XeF_2)_2](AsF_6)_2$ [73]

The cations Ca^{2+} and Cd^{2+} are bigger and the coordination number (CN = 8 (Ca), 9 (Cd)) increases in comparison with Mg^{2+}. Although the size of Ca^{2+} (126 pm) and Cd^{2+} (124 pm) are similar, electron affinities are not (Ca^{2+}: 11.87 eV; Cd^{2+}: 16.91 eV).[83] In accordance with the much higher electron affinity of Cd^{2+} a higher charge transfer from XeF_2 molecule to the metal ion, and therefore a higher degree of covalency in the M-F bond, is expected in the case of Cd compound than in the case of Ca compound. This makes bridging interactions in the Cd structure less favourable. In the compound $[Cd(XeF_2)_4](AsF_6)_2$ there are only two bridging XeF_2 molecules, resulting in the chain arrangement of crystal packing, while in $[Ca(XeF_2)_4](AsF_6)_2$ there are four bridging XeF_2 molecules yielding a layer structure (Figure 8).[71, 76]

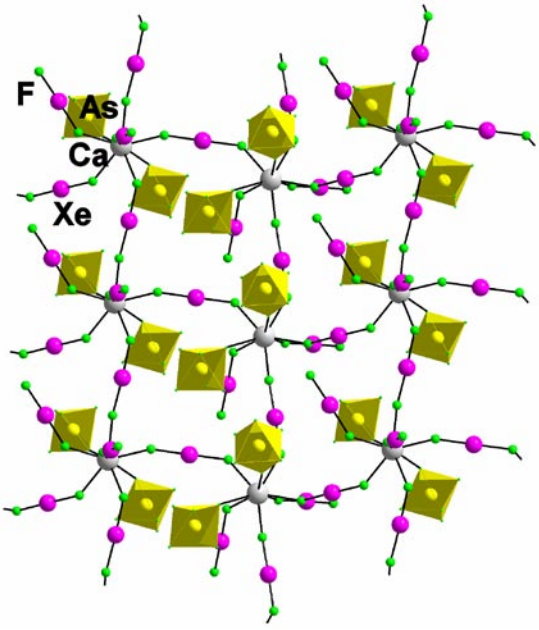

Figure 8. Layer structure in the $[Ca(XeF_2)_4](AsF_6)_2$[71]

It is evident that with changing only the cation three different crystal structures were obtained: molecular, chain and layer structure. In all three structures only XeF_2 molecules are connecting the metal centres. Along the alkaline earth metals Mg cation have only non-bridging XeF_2 molecules, in the compounds with Ca^{2+} both types are present (non-bridging and bridging XeF_2) (Figure 9), while XeF_2 in the cases of Sr and Ba (Figure 10) is more capable of bridging interactions. The reason for these structural features is that along the alkaline earth metals the effective nuclear charge on the central atom is diminishing and as a consequence of this the charge transfer from XeF_2 molecule to the metal ion is smaller thus making XeF_2 molecules more capable for the bridging.

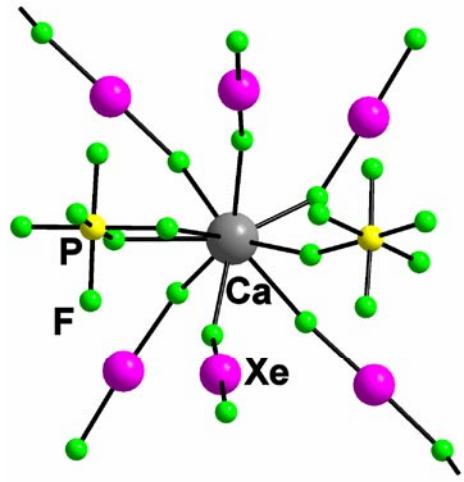

Figure 9. Example of the metal coordinated by non-bridging and bridging molecules of XeF_2; $[Ca(XeF_2)_5](PF_6)_2$ [72]

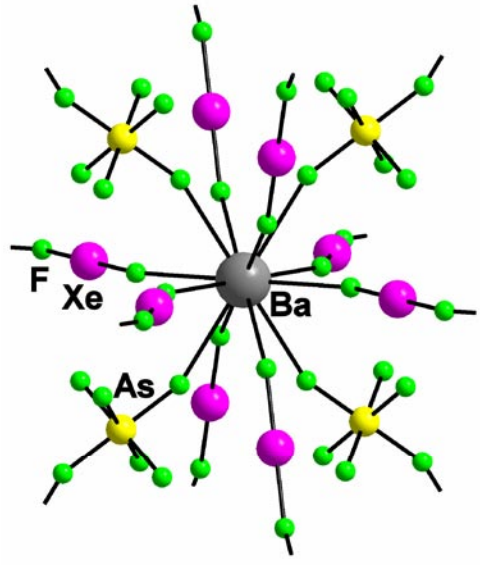

Figure 10. Example of the metal coordinated by bridging molecules of XeF_2; $[Ba(XeF_2)_5](AsF_6)_2$

5.4. Influence of the anion in the compounds of the type $[M^{n+}(XeF_2)_p](AF_6^-)_n$ on their structures

The impact of the anion AF_6^- on the structural diversity of these coordination compounds is less important as the influence of the cation. The following properties of the AF_6^- anion should be taken into account: Lewis basicity of AF_6^-, the charge on the F-ligands of AF_6^-, size of the anion etc. The differences in the properties of the determined cation and anion which govern the structural behaviour of these coordination compounds are sometimes very subtle and therefore it is difficult if not impossible to predict what kind of the structure new isolated coordination compounds would adopt.

In the row PF_6^-, AsF_6^-, SbF_6^-, BiF_6^- the F ligands in these AF_6^- anions have different negative charge. In the PF_6^- the negative charge on F ligands is the highest and in the SbF_6^- and BiF_6^- the negative charge on F ligands is the lowest. This is important because in the coordination compounds of the type $[M^{n+}(XeF_2)_p](AF_6^-)_n$, XeF_2 is competing with AF_6^- in the coordination of the metal centre. This can be shown in the following examples. In the compound $[Cd(XeF_2)](BF_4^-)_2$ the negative charge on F ligands of BF_4^- anion is higher as in the case of AF_6^- anions, because of the lower number of F ligands. Therefore the competition of XeF_2 with BF_4^- is very difficult and up to now only the above mentioned compound was isolated in an environment very rich with XeF_2.[82] Other examples are homoleptic compounds that are compounds with only XeF_2 molecules coordinating the central atom. The pure homoleptic compounds ($[M(XeF_2)_6](SbF_6)_2$ M = Zn, Cu)[78] were up to now isolated only with SbF_6^- as an anion because the negative charge on the F ligands of SbF_6^- is the lowest and therefore the competition of the XeF_2 molecule for the coordination of the metal centre is the most efficient.

5.5. Structural diversity in this new class of the coordination compounds

The coordination sphere of the metal cations is usually composed of XeF_2 molecules (only bridging or non-bridging or both types of XeF_2) and AF_6^- anions (they can act as monodentate ligand, bidentate ligand or bridging ligand). The rare examples of cation coordinated only by XeF_2 molecules are: $[Ca_2(XeF_2)_9](AsF_6)_4$ (one homoleptic Ca atom, Figure 11)[74] and $[M(XeF_2)_6](SbF_6)_2$ (M= Zn, Cu).[78] The metal centres can be connected: (a) only by XeF_2 molecules, (b) by XeF_2 and AF_6^- anions, (c) only by AF_6^- anions.

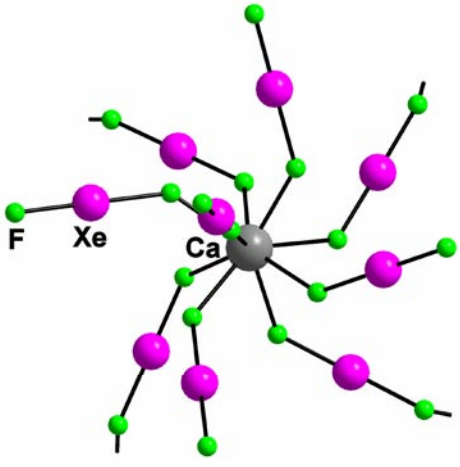

Figure 11. Example of the metal coordinated only by XeF_2 (bridging and non-bridging); one Ca^{2+} centre in $[Ca_2(XeF_2)_9](AsF_6)_4$.[74]

The coordination compounds of the type $[M^{n+}(XeF_2)_p](AF_6^-)_n$ exhibit various structural types: molecular structure ($[Mg(XeF_2)_4](AsF_6)_2$[73]), dimeric structure ($[Cd_2(XeF_2)_{10}](SbF_6)_4$[77]), chain structure (e.g. $[Ca(XeF_2)_5](PF_6)_2$, [72] $[Cd(XeF_2)_4](AsF_6)_2$ [76]), double chain structure ($[Nd(XeF_2)_{2.5}](AsF_6)_3$[79]), layer structure (e.g. $[Ca(XeF_2)_4](AsF_6)_2$ [71]), double layer structure ($[Pb(XeF_2)_3](AsF_6)_2$, $[Sr(XeF_2)_3](AF_6)_2$ (A = As,[75] P)), 3D network ($[Ca(XeF_2)_{2.5}](AsF_6)_2$,[71] $[Ag(XeF_2)_2](PF_6)$[69]) or structure with homoleptically coordinated centre and isolated SbF_6^- units ($[Zn(XeF_2)_6](SbF_6)_2$), $[Cu(XeF_2)_6](SbF_6)_2$ [78]).

6. Conclusions

XeF_2 is a versatile and useful reagent in the synthetic inorganic chemistry. Its synthesis is relatively simple and accessible also for less sophisticatedly equipped inorganic laboratories. XeF_2 is a relatively strong oxidizing and fluorinating agent. XeF^+ and $Xe_2F_3^+$ cations formed in acidic anhydrous HF or XeF^+ and $Xe_2F_3^+$ salts represent even stronger oxidizers than neutral XeF_2 molecule. A brief review of the reactions of XeF_2 with different Lewis acids and the formation of adducts with XeF_2 is also given. One of its major uses in the synthetic work over the past decade is the preparation of a whole series of new coordination compounds with XeF_2 as a ligand to the metal ion. XeF_2 is an excellent ligand because of its semi ionic character and its small size (65 $Å^3$). Recently over thirty new coordination compounds were synthesized and structurally characterized. The influence of the cation and of the anion in these interesting compounds is elucidated.

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Povzetek

V prispevku podajamo kratek pregled osnovnih podatkov o ksenonovem difluoridu, kot so metoda za sintezo čiste spojine, fizikalne in kemijske lastnosti, topnost v pogostejših anorganskih topilih, varno ravnanje s XeF_2 in uporaba spektroskopskih metod za karakterizacijo (infrardeča spektroskopija, Ramanska spektroskopija, NMR spektroskopija). Predstavljena je tudi uporaba XeF_2 kot oksidacijskega in fluorirnega sredstva. Na kratko so predstavljene reakcije XeF_2 z različnimi Lewisovimi kislinami in tvorba XeF^+ in $Xe_2F_3^+$ soli. Velik del prispevka je namenjen predstavitvi novih koordinacijskih spojin tipa $[M^{n+}(XeF_2)_p](AF_6^-)_n$ v katerih XeF_2 nastopa kot ligand kovinskega kationa. Opisane so različne sintezne poti za pripravo teh spojin in vpliv kationa ter aniona na strukturne značilnosti teh spojin. Na osnovi poznavanja lastnosti kationa in aniona smo analizirali možnost predvidevanja struktur teh novih spojin.