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Crystal Structure of $[XeF_5^+]_2[PdF_6^{2-}]$

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Received December 18, 1972

Crystals of $[XeF_5^+]_2[PdF_6^{2-}]$ are yellow needles. The unit cell is orthorhombic with $a = 9.346$ (6), $b = 12.786$ (7), $c = 9.397$ (6) Å, $V = 1122.9$ Å^3, $Z = 4$, and $d_c = 3.91$ g cm^{-3}. Structure refinement has proceeded satisfactorily in space group $Pca2_1$ (No. 29) using three-dimensional graphite-monochromatized X-ray Mo Kα data. With anisotropic temperature factors for all atoms, a final conventional R factor of 0.0256 (including zero weight data) for 1464 independent reflections was obtained. The asymmetric structural unit contains two crystallographically distinct XeF_5^+ ions and a PdF_6^{2-} ion. The PdF_6^{2-} ion is almost octahedral and only one Pd–F interatomic distance (1.860 (6) Å) departs significantly from the average Pd–F distance of 1.893 Å. The XeF_5^+ ions each approximate to C_{4v} symmetry and are not significantly different in size, shape, or coordination. The cations are characterized by F_{ax}–Xe–F_{eq} angles of ~79° and average axial and equatorial bond lengths of 1.81 and 1.84 Å, respectively. The individual Xe–F distances of the same type (axial or equatorial) do not depart significantly from the average values for the type. The coordination of the XeF_5^+ ions (by the F atoms of anions) in this structure is similar to the cation coordination observed in $[XeF_5^+][AsF_6^-]$.

Introduction

In the course of experiments[1] aimed at a more convenient synthesis of palladium tetrafluoride[2] we obtained the XeF_6 adducts of PdF_4, $2XeF_6 \cdot PdF_4$ and $4XeF_6 \cdot PdF_4$. These stoichiometries are similar to those reported previously by Pullen and Cady[3] for the XeF_6 adducts of the germanium and tin tetrafluorides. Although Raman data[1] indicated that the PdF_4 adducts were $[XeF_5^+]_2[PdF_6^{2-}]$ and $[Xe_2F_{11}^+]_2$-$[PdF_6^{2-}]$, respectively, full structural investigations were desirable. Such ionic formulations are consistent with XeF_6 being a good base.[4] Comparison of the geometry of the cation in a doubly charged anion environment with that of the cation in singly charged anion salts[4-6] was also of interest. Suitable single crystals of the 2:1 adduct for high-quality X-ray structural investigation proved to be readily preparable. The structure has been determined and is reported in this paper.

Experimental Section

$2XeF_6 \cdot PdF_4$ was prepared as described in a forthcoming paper.[1] Suitable crystalline samples were obtained by heating the compound in a Monel bomb to 400° under fluorine pressure (1000 psi). The bomb was cooled slowly to room temperature (~20°/hr). Yellow, needle-shaped crystals were found adhering to the walls of the bomb. Suitably sized specimens were loaded into 0.2-mm o.d. quartz capillaries, which had been drawn down to smaller diameter at the sealed end. Crystals were wedged into the drawn-down capillary ends with the aid of Pyrex push rods. All manipulations were carried out in a Vacuum Atmospheres Corp. Dri-Lab provided with a nitrogen atmosphere. The capillaries were temporarily sealed with a plug of Kel-F grease and then removed from the drybox and sealed by drawing down in a small flame.

Crystal Data. The crystal chosen for data collection was a yellow needle with dimensions 0.3 × 0.2 × 0.1 mm. Weissenberg photographs showed $F_{16}PdXe_2$ (mol wt 673.0) to be orthorhombic, with $a = 9.346$ (6), $b = 12.786$ (7), $c = 9.397$ (6) Å, $V = 1122.9$ Å^3, $Z = 4$, and $d_c = 3.91$ g cm^{-3}. The unit cell volume satisfies Zachariasen's criterion[7] for close-packed fluoride lattices, the effective volume per fluorine atom being 17.6 Å^3. The systematic absences $0kl$, $l = 2n + 1$, and $h0l$, $h = 2n + 1$, indicated the space group[8] to be either $Pca2_1$ (No. 29) or $Pcam$ (No. 57).

X-Ray Measurements. Diffraction data were collected at room temperature (24.5 ± 1.5°) on a Picker automatic four-circle diffractometer using Mo Kα radiation (λ 0.7107 Å). Accurate cell dimensions were obtained by measuring the 2θ angle for the Mo Kα_1 peak for the highest angle reflection observable along each of the principal axes. The c axis was oriented along ϕ.

A full description of the methods used in collection and treatment of intensity data has been previously described.[9] The absorption coefficient μ(Mo Kα) = 78.7 cm^{-1}. Although the crystal was larger than the optimum size, no absorption correction was applied because the crystal was irregularly shaped and had no well-defined faces. We believe that our neglect of absorption is not likely to have resulted in significant error in the positional parameters. Coppens has pointed out[10] that absorption error can result in quite large changes in the positional parameters, but these changes are usually within the standard deviations. He further points out that correction for absorption has its major effect in reduction of the standard deviations, rather than shifts in atomic position. It is probable that the values of the anisotropic thermal parameters to some extent reflect our neglect of absorption. Therefore, we caution that these parameters may not properly represent the thermal motion. The only other difference from the previously described procedure for the data treatment[9] was in the choice for the value of q, the arbitrary factor employed to prevent the relative errors for large counts becoming unrealistically small. A value $q = 0.04$ was assumed here. Three standards were measured every 200 reflections. The intensities of the (600) and (060) reflections increased by 2.4% during the period of data collection; the intensity of the (002) reflection increased by 10.0%. All of the intensity data were corrected by linear interpolation, assuming a 2.4% increase.

Scattering factors for neutral F, Xe, and Pd were taken from Doyle and Turner[11a] and Cromer and Waber.[11b] Cromer and Liberman's values[12] of $\Delta f'$ and $\Delta f''$ were used for anomalous dispersion corrections.

Complete sets of hkl and $hk\bar{l}$ data were collected for $2\theta \leqslant 45°$ and amounted to 1464 unique reflections. In the least-squares refinements 1410 data which satisfied the condition $I \geqslant 3\sigma(I)$ were given nonzero weight.

Structure Refinement. At the outset, it was assumed that the structure would be centric, so the two acentric data sets were averaged to give a single centric data set. A three-dimensional Patterson synthesis revealed the positions of two of the three heavy atoms, but it also indicated that the non-centric group ($Pca2_1$, No.

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Table I. Positional and Thermal Parameters for $[XeF_5^+]_2[PdF_6^{2-}]$ with Estimated Standard Deviations in Parentheses[a]

ATOM	X	Y	Z	B11	B22	B33	B12	B13	B23
PD	.17525(7)	.24185(6)	.250*	2.70(3)	2.53(3)	1.13(2)	-.25(3)	-.02(3)	.22(3)
XE(1)	.53535(7)	.12057(5)	.0332(1)	3.11(3)	3.24(3)	1.75(3)	.75(2)	-.10(2)	.29(3)
XE(2)	.51278(7)	.38670(6)	.4738(1)	2.85(3)	3.20(3)	1.82(3)	-.58(3)	-.20(2)	.49(3)
F(1)	.0394(6)	.2865(5)	.3880(8)	4.0(3)	3.1(3)	1.3(3)	.9(2)	.5(2)	-.2(3)
F(2)	.0268(6)	.2145(5)	.1235(8)	3.8(3)	2.5(3)	1.5(3)	-.1(2)	-.5(2)	-.0(2)
F(3)	.3261(7)	.2720(6)	.3796(8)	3.8(3)	5.4(4)	1.7(3)	-1.7(3)	-.9(2)	1.1(3)
F(4)	.3101(6)	.1917(6)	.1150(8)	3.5(3)	6.8(4)	1.8(3)	1.7(3)	.9(2)	1.0(3)
F(5)	.1555(7)	.1085(5)	.3352(7)	4.1(3)	2.4(3)	2.0(3)	.1(2)	.4(2)	.7(2)
F(6)	.1809(7)	.3767(5)	.1659(8)	4.6(3)	2.6(3)	2.4(3)	-.8(2)	-.2(2)	.9(2)
F(7)	.4920(9)	-.0171(5)	-.001(1)	8.7(4)	2.2(3)	4.9(5)	.6(3)	-1.6(3)	.8(3)
F(8)	.7048(8)	.0634(7)	.0830(9)	4.7(4)	8.6(5)	5.0(5)	3.6(4)	-1.1(3)	.3(4)
F(9)	.6348(8)	.1241(6)	-.1368(8)	4.2(3)	5.8(4)	2.9(3)	1.7(3)	1.7(3)	.4(3)
F(10)	.6289(9)	.2376(6)	.0990(8)	5.5(4)	6.5(4)	2.7(4)	-1.5(3)	-1.7(3)	-.5(3)
F(11)	.5049(9)	.0869(8)	.2209(9)	7.3(5)	8.9(5)	1.9(4)	3.5(4)	.7(3)	2.6(4)
F(12)	.6658(8)	.4658(6)	.4212(9)	4.9(4)	6.8(5)	4.9(5)	-2.6(3)	-.1(3)	1.7(4)
F(13)	.4460(8)	.5180(5)	.519(1)	6.5(4)	2.9(3)	5.3(5)	-.1(3)	.2(4)	.9(3)
F(14)	.6301(8)	.2836(7)	.4013(9)	5.0(4)	6.0(4)	3.8(4)	-.2(4)	1.6(3)	-.9(3)
F(15)	.4669(9)	.4216(7)	.288(1)	8.2(5)	7.1(5)	2.6(4)	-4.0(4)	-1.7(3)	2.6(4)
F(16)	.6188(8)	.3897(6)	.6381(8)	4.2(3)	4.4(3)	2.4(3)	-.7(3)	-1.4(2)	-.1(3)

[a] The asterisk signifies a fixed parameter. Reference 9 describes the form of the thermal parameters.

Table III. Interatomic Distances (Å) and Angles (deg) within the $[XeF_5^+]_2[PdF_6^{2-}]$ Asymmetric Structural Unit

Distances		Angles			
Xe(1)-F(8)	1.806 (7)	F(8)-Xe(1)-F(1)	134.21 (42)	F(12)-Xe(2)-F(2)	135.92 (39)
F(7)	1.836 (7)	F(4)	146.39 (44)	F(3)	142.70 (45)
F(9)	1.849 (7)	F(5)	140.21 (40)	F(6)	140.82 (42)
F(10)	1.841 (7)	F(7)	81.45 (40)	F(13)	79.79 (39)
F(11)	1.838 (8)	F(9)	78.06 (35)	F(14)	80.20 (42)
F(4)	2.418 (6)	F(10)	79.93 (40)	F(15)	77.98 (39)
F(5)	2.582 (6)	F(11)	78.02 (38)	F(16)	78.02 (37)
F(1)	2.617 (7)	F(7)-Xe(1)-F(9)	88.93 (52)	F(13)-Xe(2)-F(15)	85.40 (46)
Xe(2)-F(12)	1.820 (7)	F(11)	84.93 (48)	F(16)	88.25 (49)
F(13)	1.842 (7)	F(10)-Xe(1)-F(9)	91.82 (41)	F(14)-Xe(2)-F(15)	87.80 (49)
F(14)	1.845 (8)	F(11)	86.63 (48)	F(16)	90.28 (41)
F(15)	1.855 (8)	F(1)-Pd-F(2)	89.66 (33)	F(3)-Pd-F(4)	90.23 (36)
F(16)	1.835 (7)	F(3)	89.85 (37)	F(5)	89.10 (35)
F(3)	2.445 (7)	F(5)	85.25 (34)	F(4)	93.53 (35)
F(6)	2.559 (7)	F(6)	91.70 (34)	F(4)-Pd-F(5)	92.45 (37)
F(2)	2.639 (7)	F(2)-Pd-F(4)	90.28 (36)	F(6)	90.59 (36)
Pd-F(1)	1.902 (6)	F(5)	91.59 (32)		
F(2)	1.860 (6)	F(6)	85.75 (35)		
F(3)	1.902 (7)				
F(4)	1.900 (7)				
F(5)	1.893 (6)				
F(6)	1.898 (6)				

29) was the correct space group. Full-matrix least-squares[13] and a subsequent Fourier synthesis yielded the positions of the third heavy atom and several of the fluorine atoms. The refinement proceeded routinely down to $R = 0.075$ with all 19 atoms placed and the heavy atoms assigned anisotropic thermal parameters. At this point, the structure seemed to have settled into a false minimum, since bond lengths and angles gave very poor agreement with previous structures of this type. After much experimentation involving location of atoms across symmetry elements (and pseudosymmetry elements), to generate a chemically acceptable arrangement, the R value dropped to 0.060. Subsequent least-squares refinement with all atoms anisotropic, but using the data appropriate for the centric space group, yielded an R value of 0.020. At this point the data were reordered to satisfy the noncentric symmetry and to take advantage of anomalous dispersion. Two polarities must be considered. Least-squares refinement yielded $R = 0.0260$ (including zero weight data), $R = 0.0241$ (excluding zero weight data), and $R_w = 0.0274$ for the polarity with mostly negative z coordinates. For the polarity with mostly positive z coordinates, $R = 0.0256$ (including zero weight data), $R = 0.0237$ (excluding zero weight data), and $R_w = 0.0267$. The magnitudes of the z parameters of the two forms did not differ by more than one standard deviation. We describe here the arbitrarily chosen structure with the mostly positive z atomic parameters. A final difference Fourier showed that the largest residual electron density was -1.7 e/Å^3. The standard deviation of an observation of unit weight was 0.994. The largest shift of any parameter divided by the estimated standard deviation on the last cycle of least-squares refinement was less than 0.003. Table I gives the final positional and thermal parameters for this refinement. The F_o, standard deviations, and ΔF data are given in the microfilm version of this paper in Table II.[14]

Description of the Structure

The asymmetric structural unit contains two crystallographically distinct XeF_5 groups and a PdF_6 group. The structural unit is illustrated in Figures 1 and 2.

The PdF_6 group is almost octahedral. As may be determined from Table III, only one Pd-F distance [Pd-F(2) = 1.860 Å] departs significantly from the average Pd-F distance of 1.893 Å. All cis F-Pd-F angles are within 5° of 90°.

The two XeF_5 groups are similar, each being an approximately C_{4v} symmetry species, with an F_{ax}-Xe-F_{eq} angle of ~79°. The average Xe-F axial interatomic distance of the two crystallographically distinct species is 1.813 Å and the axial Xe-F distance for each species does not depart significantly from this mean. The mean of all Xe-F equatorial interatomic distances is 1.843 Å. Again there is no significant departure from this mean value for the Xe-F equatorial distances in each species.

Each Xe atom of each XeF_5 group makes one short contact with one PdF_6 group [*i.e.*, Xe(2)-F(3), Xe(1)-F(4)] and two somewhat longer contacts to a second PdF_6 group. These Xe· · ·F contacts link XeF_5 and PdF_6 groups into "rings"

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(13) All calculations were done on a CDC-6600 computer, using unpublished versions of least-squares, FORDAP, and other programs written and revised by A. Zalkin. All drawings were done using ORTEP, by C. K. Johnson, Oak Ridge National Laboratory, June 1965.

(14) Table II, a listing of observed structure factors, will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-73-1726.

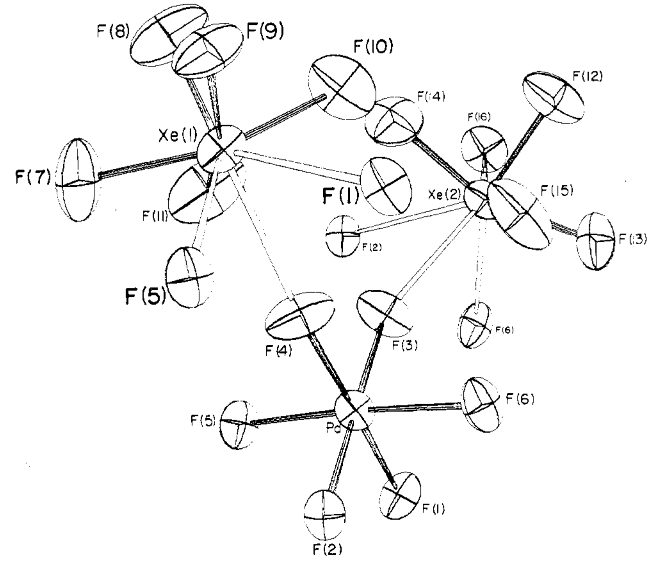

Figure 1. The formula unit in $[XeF_5^+]_2[PdF_6^{2-}]$.

containing two species of each kind as shown in Figures 3-5. These "rings" are linked by the further involvement of the PdF_6 groups in adjoining "rings." There is a striking resemblance of the four-membered "ring" in this structure to that previously observed in $[XeF_5^+][AsF_6^-]$.[6]

It should be noted that the three F ligands of the PdF_6 groups which make close approach to the Xe atom do so more or less symmetrically with respect to the pseudo-fourfold axis of each XeF_5 group. Thus the F_{ax}-Xe· · ·F (close contact) angles all lie within the range 135-146°. The manner in which the XeF_5 and PdF_6 groups are arranged in the crystal is illustrated in the stereogram which is Figure 5.

Discussion

Structure Analysis. The analysis was hampered by the fact that the structure deviates only a little from space group *Pcan* (No. 60, with an unconventional setting).[8] The coordinates of Xe and F listed in Table I can be grouped as pairs related by the transformation x, $\frac{1}{2} - y$, $\frac{1}{2} - z$ with discrepancies no greater than 0.046 for F and 0.023 for Xe, while Pd would be related to itself by this operation if its y were increased by 0.008. If this correspondence were exact, the symmetry would be *Pcan*, a centric space group. This pseudosymmetry escaped notice at first because there are clear violations of the extinction rule for the n glide. The structure consisting of Xe(2) atoms is nearly the inverse of that of the Xe(1) atoms and thus has the same Patterson vectors. As a result, it was easy to find vectors for two sets of four heavy atoms per unit cell in the Patterson maps, but a third set could not be found. If one tries to interpret these vectors in space group *Pcam* (the centric group consistent with the extinction rules), either set of four atoms can be placed on the mirror planes, but then the other must be in a general set of positions. This interpretation was definitely ruled out by the absence of vectors for such atoms related by the mirror. It should be emphasized that, while the structure does not deviate far from the centric symmetry of space group *Pcan*, it is nowhere near the symmetry of *Pcam*. Had the similarity to space group *Pcan* been noticed, it would have been easy to assign four Pd atoms to a special position (on the twofold axis) and eight Xe atoms to a general position.

The next complication is that Pd hardly contributes to the phasing of any reflection with $h + k$ odd, nor Xe to any reflection with $l = 0$ and $h + k$ odd. For other reflections the heavy atoms give good phasing for the centric pseudostructure, but the deviations from this symmetry will be controlled by the accident of the slight displacements of the trial structure. Thus the heavy-atom positions are not a very helpful guide to the correct positions of the F atoms, and false minima with relative good agreement indices are possible. A similar situation was encountered in the refinement of the structure of $Na_4XeO_6 \cdot 6H_2O$.[15]

Table IV. The XeF_5^+ Ion

	Xe-F_{ax},Å	Av Xe-F_{eq}, Å	Av F_{ax}-Xe-F_{eq}, deg	Ref
XeF_6 (t)[f]	1.84 (4)[g]	1.86 (3)	77.2 (18)	*a*
XeF_6 (h)	1.76 (3)	1.92 (2)	80.0 (6)	
$[XeF_5^+][AsF_6^-]$	1.76 (2)	1.82 (3)	80.4 (15)	*b*
$[XeF_5^+][RuF_6^-]$	1.79 (1)	1.85 (1)	79.0 (6)	*c*
$[XeF_5^+][PtF_6^-]$	1.81 (8)	1.88 (8)	79.5 (40)	*d*
$[XeF_5^+]_2[PdF_6^{2-}]$	1.81 (1)	1.84 (1)	79.2 (4)	*e*

[a] Reference 21. [b] Reference 6. [c] Reference 5b. [d] Reference 5a. [e] Present work. [f] (t) indicates tetramer and (h) hexamer. [g] Numbers in parentheses are the estimated standard deviations for the least significant digits.

A third difficulty is the question of absolute polarity. The structure is too nearly centric for there to be any dramatic differences in the Bijvoet pairs, and the differences in agreement indices are not very decisive. It is even more difficult to exclude the possibility of two orientations mixed by twinning. Had the measurements been confined to one octant, as is often the custom, the polar dispersion effect[16,17] would have caused a serious uncertainty. With full data that effect disappears, and nearly the same results are obtained with either assumption of polarity.

Chemical Aspects. Hexafluoropalladates(IV) have long been known[18] and a regular octahedral PdF_6^{2-} geometry was indicated by the isomorphism of the alkali fluoropalladates with the fluoroplatinates, of which the crystal structure of K_2PtF_6 was known from X-ray single-crystal structure analysis.[19] Hitherto, however, the only structure determination reported for a PdF_6^{2-} salt was that of Bartlett and Quail,[20] derived for K_2PdF_6 from X-ray powder data. Although the precision of their structure is uncertain, the quoted Pd-F bond length of 1.86 Å is roughly compatible with the Pd-F bond lengths observed in the $[XeF_5]_2[PdF_6]$ structure (see Figures 1 and 2 and Table III). It is not known to what extent the unsymmetrical strongly polarizing cations of the xenon salt perturb the anion from ideality. A bond length of 1.86 Å in the alkali salts is quite plausible and a value between 1.86 and 1.90 Å seems certain.

The structure of $[XeF_5]_2[PdF_6]$ is of most interest at this time for the geometry of the cation and the cation coordination. The cation has previously been established by X-ray single-crystal analysis in the salts $[XeF_5^+][MF_6^-]$ (M = Pt,[5] Ru,[5], As[6]) and crystalline XeF_6 itself has been formulated[21] as $[XeF_5^+]F^-$. Table IV gives the bond lengths and angles for the various structures examined so far. It can be seen that within the quoted standard deviations, there are barely

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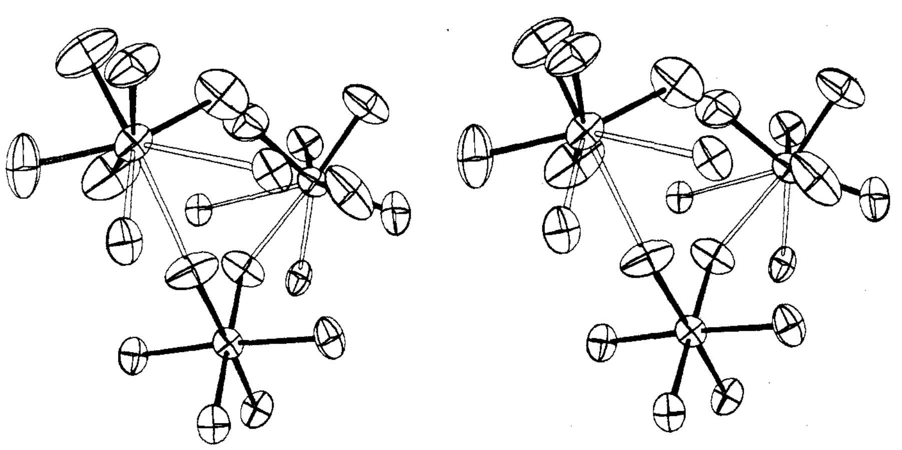

Figure 2. Stereogram of the formula unit in $[XeF_5^+]_2[PdF_6^{2-}]$.

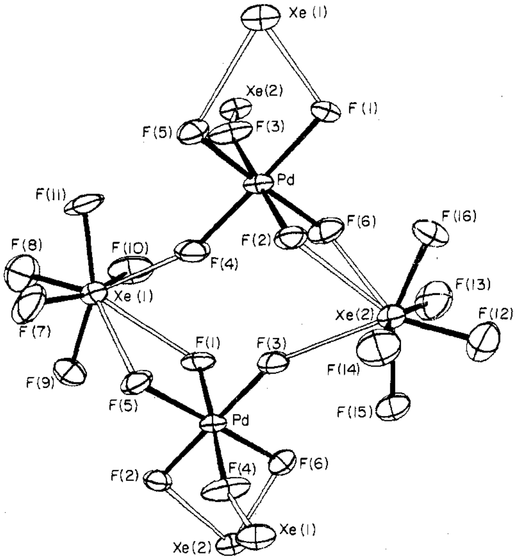

Figure 3. The $[XeF_5^+][AsF_6^-]$-like rings in $[XeF_5^+]_2[PdF_6^{2-}]$.

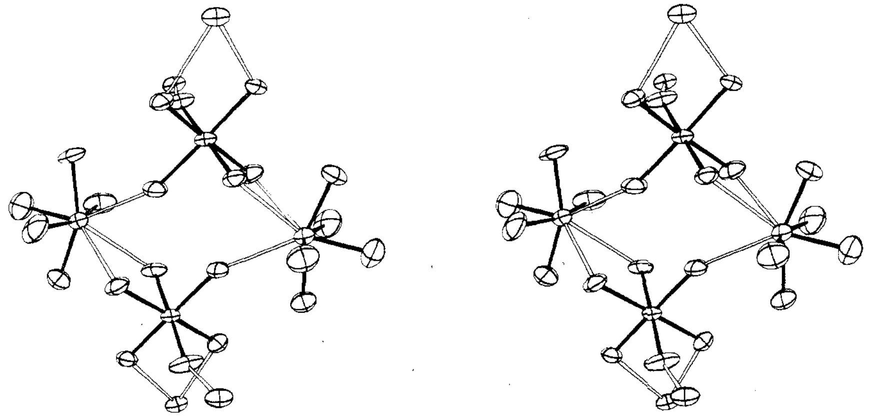

Figure 4. Stereogram of the $[XeF_5^+][AsF_6^-]$-like rings in $[XeF_5^+]_2[PdF_6^{2-}]$.

any significant differences between XeF_5^+ species in different lattices, including XeF_5^+ in crystalline XeF_6. As has already been pointed out above, the two crystallographically distinguishable XeF_5^+ species in $[XeF_5]_2[PdF_6]$ are not significantly different. The common geometry of the XeF_5 moiety in all of the quoted structures and its close similarity[5,22] to the geometry of the neutral molecule IF_5 provide compelling evidence for the cation XeF_5^+. As we have discussed in an earlier paper[9] the strictly isoelectronic relatives of XeF_5^+ are remarkably similar in shape to it. Table V presents the data. This highlights, even more dramatically than before, the constancy of the bond angle F_{ax}-E-F_{eq}.[9]

Table V. Distances (Å) and F_{ax}-E-F_{eq} Angles (deg) for the Isoelectronic Species EF_5 (E = Sb, Te, I, Xe), Averaged to C_{4v} Symmetry for Comparison

	SbF_5^{2-} [a]	TeF_5^- [b]	IF_5 [c]	XeF_5^+
E-F_{ax}	1.916 (4)	1.862 (4)	1.817 (10)	1.813 (7)
E-F_{eq}	2.075 (3)	1.952 (4)	1.873 (5)	1.843 (8)
F_{ax}-E-F_{eq}	97.4 (1)	78.8 (2)	80.9 (2)	79.2 (4)

[a] R. R. Ryan and D. T. Cromer, *Inorg. Chem.*, **11**, 2322 (1972).
[b] S. H. Mastin, R. R. Ryan, and L. B. Asprey, *ibid.*, **9**, 2100 (1970).
[c] G. R. Jones, R. D. Burbank, and N. Bartlett, *ibid.*, **9**, 2264 (1970).

The coordination behavior of the XeF_5^+ species not only supports the discrete nature of the species but also provides evidence of steric activity of the Xe(VI) nonbonding valence-electron pair. Figures 1-5 show that each XeF_5 species in $[XeF_5]_2[PdF_6]$ is coordinated to three F ligands of two PdF_6 groups such that the three F ligands lie approximately on a conical surface, the axis of which is coincident with the symmetry axis of the XeF_5. But if we describe XeF_5^+ as a pseudooctahedral species in which the nonbonding valence-electron pair occupies the Xe coordination site trans to the axial bond, the position of the F ligands "on the conical surface" is seen to be appropriate; since then the Xe valence "pair" is avoided, and the positive charge of the cation (which we can anticipate will be centered essentially at the xenon atom) is least shielded. This model does not, of course, allow us to predict that three F ligands would coordinate to each XeF_5^+ and indeed in $[XeF_5^+][PtF_6^-]$ and $[XeF_5^+]$-

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[22] G. R. Jones, R. D. Burbank, and N. Bartlett, *Inorg. Chem.*, 9, 2264 (1970).

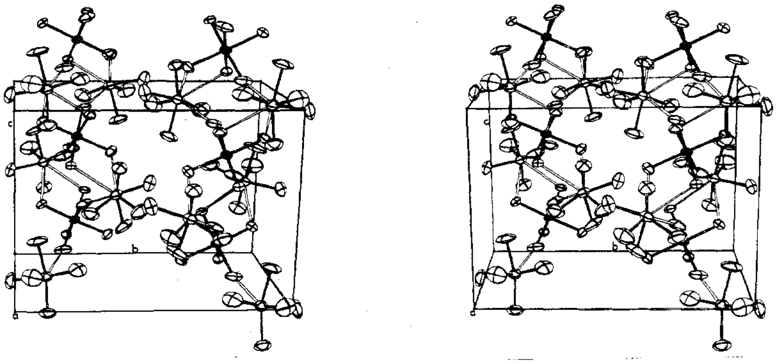

Figure 5. Stereogram of the $[XeF_5^+]_2[PdF_6^{2-}]$ unit cell, showing the packing of linked $[XeF_5^+][AsF_6^-]$-like rings.

$[RuF_6^-]$[5] the cation coordination in anion F ligands is four—not three.

It is not yet clear why certain anions (like PtF_6^- and RuF_6^-) provide four F ligands to coordinate to XeF_5^+, whereas PdF_6^{2-} and AsF_6^- [6] provide three. The similarity of the XeF_5^+ coordination in the PdF_6^{2-} and AsF_6^- salts is striking. As a consequence, essentially the same ring (shown for $[XeF_5]_2$-$[PdF_6]$ in Figure 3) of two XeF_5 groups linked to two MF_6 groups occurs in each structure. It is of relevance to the hypothesis of steric activity of the nonbonding Xe(VI) valence-electron "pairs" that the XeF_5 groups do not share a common axis in the ring but avoid one another (see the stereogram, Figure 4).

It appears probable that the $2XeF_6{\cdot}MF_4$ (M = Ge, Sn) complexes reported[3] by Pullen and Cady will prove to be structurally related to $[XeF_5^+]_2[PdF_6^{2-}]$. The ability of XeF_6 to donate F^- to a tetrafluoride to form $[XeF_5^+]_2$-$[PdF_6^{2-}]$ indicates that it is a moderately good base. It remains, however, to be seen if $[XeF_5^+]_3[MF_6^{3-}]$ salts can be derived from the metal trifluorides.

Registry No. $[XeF_5^+]_2[PdF_6^{2-}]$, 39797-61-0.

Acknowledgment. This work was supported by the Atomic Energy Commission under Contract No. W-7405-eng-48.

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Crystal and Molecular Structure of a Pentacoordinate Copper(II) Hippurate Dimer

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Received July 21, 1972

The crystal and molecular structure of tetraaquobis(μ-hippurato-*O*)-bis(hippurato-*O*)dicopper has been determined from a single-crystal X-ray diffraction study. The compound $Cu[(C_6H_5)CONHCH_2COO]_2{\cdot}4H_2O$ crystallizes in the monoclinic space group $P2_1/c$ with unit cell constants $a = 7.253$ (1), $b = 40.169$ (3), $c = 7.466$ (1) Å, and $\beta = 102.81$ (1)°. The structure was solved by the heavy-atom method and refined by block-diagonal least-squares methods to a final $R = 0.074$ for the 1693 reflections considered as observed. The compound exists as a dimer with each copper having distorted [4 + 1] tetragonal-pyramidal geometry and bridging is through two carboxyl oxygens with distances 1.93 and 2.37 Å. The hippurate ligands are unexpectedly monodentate.

Introduction

Authentic five-coordinate complexes of the first-row transition metals are known.[1,2] In general, they are formed with simple monatomic or diatomic ligands, such as halide or carbonyl, or they are formed by polydentate ligands which tend to force a particular geometry. Both types of coordination compounds are known for copper(II). The simple five-coordinate type is represented by $CuCl_5^{2-}$ which has been shown to have a trigonal-bipyramidal structure.[3] The more complex species are represented by $\{Cu[N,N'\text{-di-(3-aminopropyl)piperazine}]Cl\}\{ClO_4\}$ which has been found to have a square-pyramidal geometry with N atoms in the base and the chloride in the apical position.[4] In addition, copper(II) forms five-coordinate species with a variety of amino acids and peptide model compounds.[5] In these complexes, the geometry about the copper atom is approximately square pyramidal with amino or peptide nitrogens and carboxyl or peptide oxygens in the base and either a water molecule or a carboxyl oxygen (from a neighboring ligand) in the apical position. Only recently have examples of oxygen-bridged dimers been reported.[6]

In a recent communication,[7] we reported the preparation and characterization of a five-coordinate Cu(II) dimer of the hippurate anion. This report details the complete crystallographic study of this complex.

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