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The Structure of Octavalent Xenon in Aqueous Solution[1]

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The Raman spectrum of aqueous octavalent xenon—the perxenate ion—has been studied as a function of concentration and pH. The results indicate that XeO_6^{4-} is never a principal species. The spectra instead show that the ion $HXeO_6^{3-}$ is the predominant species in the most alkaline solutions.

Introduction

Octavalent xenon forms perxenate salts with a variety of metals. The alkali metal perxenates have the stoichiometry $M_4XeO_6 \cdot xH_2O$. The particular salts $Na_4XeO_6 \cdot 6H_2O$, $Na_4XeO_6 \cdot 8H_2O$, and $K_4XeO_6 \cdot 9H_2O$ have been characterized by X-ray diffraction studies, which have shown the presence of octahedral XeO_6^{4-} ions in the crystals.[3-5] The infrared and Raman spectra of solid perxenates have also been found to be consistent with the presence of such ions.[6,7]

The structure of the perxenate ion in aqueous solution is less clear, however. Appelman and Malm[8] studied dilute solutions of sodium perxenate both by ultraviolet absorption spectroscopy and by potentiometric titration. They were able to determine the charge on the perxenate ions but not the degree of hydration. They interpreted their results in terms of the anion $H_2XeO_6^{2-}$, predominant at pH 7–10, and the anion $HXeO_6^{3-}$, predominant at higher pH. They found no evidence for ions of charge 4−, and they set an upper limit of 3 for the equilibrium constant of the reaction

$$HXeO_6^{3-} + OH^- = XeO_6^{4-} + H_2O \qquad (1)$$

Peterson, Claassen, and Appelman[7] observed the infrared and Raman spectra of 1.8 *M* aqueous cesium perxenate, and they tentatively interpreted the spectra in terms of a symmetrical XeO_6^{4-} ion as the predominant species. Since no evidence had been found for this ion in more dilute solutions, however, they suggested that further Raman studies should be undertaken when a more powerful red laser was available that would permit observation of Raman spectra as functions of concentration and of pH. These further studies are the subject of the present paper. Because Xe(VIII) on acidification oxidizes water and forms Xe(VI), the Raman spectrum of a pure solution of sodium xenate(VI) has been measured for comparison. This spectrum has also been studied by Peterson, *et al.*,[7] who assigned it to the ion $HXeO_4^-$.

Experimental Section

Preparation of Cesium Perxenate.—A 0.02 *M* sodium perxenate solution was prepared by methods described elsewhere.[8] This solution was passed through a column containing the cation-exchange resin Bio-Rad AG50X8, 50–100 mesh, which had been converted to the cesium form by treatment with 0.1 *M* CsOH. The effluent cesium perxenate solution was evaporated to dryness in a rotary evaporator at room temperature under vacuum. The residue, a hygroscopic yellow solid, was crushed and dried in a vacuum desiccator over anhydrous magnesium perchlorate. The xenon content and total oxidizing power of the cesium perxenate were determined iodometrically,[8] and the cation content was determined by acidimetry.[8] The salt contained 15.63% Xe, and it was found to have 7.90 equiv of oxidizing power and 4.02 equiv of cation per mole of xenon. These values are probably within experimental uncertainty of the theoretical values of 8.00 and 4.00, respectively. If the unaccounted-for mass is water, the salt approximates the composition $Cs_4XeO_6 \cdot 4.5H_2O$.

Sodium Xenate(VI).—A *ca.* 1.5 *M* solution of sodium xenate(VI) was prepared by precisely neutralizing an XeO_3 solution with NaOH according to the reaction $XeO_3 + OH^- = HXeO_4^-$. The XeO_3 was synthesized by methods described elsewhere.[8]

Spectral Measurements.—A Coherent Radiation krypton laser was used for excitation of Raman spectra. It provided 0.5 W of CW power at 6471 Å. The instrumentation included a Spex 1401 double monochromator, linear in wave number, an ITT FW-130-S20 detector, a Victoreen 1001 dc amplifier, and a TI recorder. The frequency counter of the monochromator was periodically calibrated by emission lines from a small neon lamp.

Solutions were contained in Pyrex tubes of 5-mm i.d. with optical windows on one end for transmission of the focused laser beam from below. Polarization measurements were made by method IV of those described by Claassen, *et al.*[9] In the description of the spectra "$\perp$" means that the electric vector of the incident light was perpendicular to the plane containing the slit length and the incident laser beam, while "$\|$" means that the electric vector was parallel to this plane. The value of *f*, the ratio of monochromator efficiency for horizontally polarized light to that for vertically polarized light, varied from 3.0 at a 300-cm^{-1} shift to 3.3 at a 800-cm^{-1} shift.

To slow down the oxidation of water by perxenate, the samples were cooled to near 0° by blowing cold nitrogen gas over the container. Raman spectra were obtained of cesium perxenate solutions of concentrations 1.7, 1.0, and 0.48 *M*. Some of the solutions were partially acidified with 10.8 *M* aqueous HF, and Raman spectra were recorded after amounts between 0.25 and 2.2 equiv of H^+ had been added per mole of xenon. Inasmuch as precipitation occurred on acidification of concentrated solutions, such solutions were prepared in centrifuge tubes, and the Raman measurements were made on the supernatant liquid after centrifugation. A few samples were acidified with $HClO_4$ instead of HF, and the precipitated $CsClO_4$ was removed by centrifugation.

A Du Pont 310 curve resolver was used to analyze the Raman spectra.

Ultraviolet spectra of perxenate solutions were measured on a Cary 14 spectrophotometer. Quartz cells of 1-mm path length were used for 0.003 *M* solutions. The spectra of 1 *M* perxenate solutions were obtained by pressing a drop between two sapphire plates, thereby producing a thin layer of indeterminate thickness.

Results and Discussion

Figure 1 shows the Raman spectrum of concentrated cesium perxenate. The $\perp$ trace A is essentially like that shown by Peterson, *et al.*,[7] but the $\|$ trace B is significantly different because polarization measure-

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[2] Summer Student Training Program, 1970.

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[7] J. L. Peterson, H. H. Claassen, and E. H. Appelman, *Inorg. Chem.*, **9**, 619 (1970).

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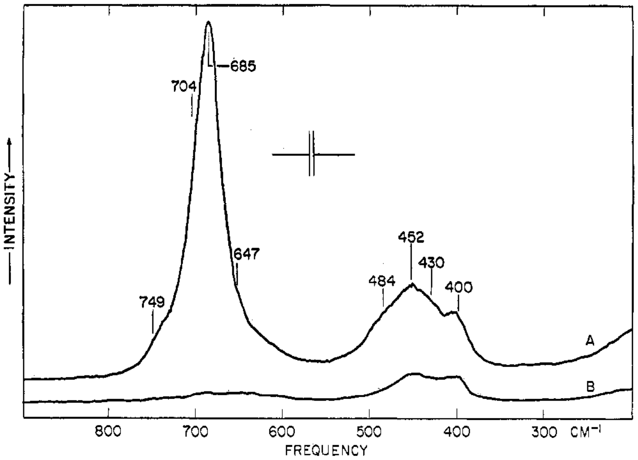

Figure 1.—Raman spectrum of 1.7 *M* cesium perxenate at ~0°. Curve A is ⊥ and B is || (see text). Spectral slit width was 5 cm^{-1}.

ments are made more precisely in the present study. The important new information is that part of the scattering in the bond-bending region from 400 to 500 cm^{-1} is definitely polarized, whereas the less accurate earlier data indicated only depolarized bands in this region. The observation of a polarized band in the bond-bending frequency region clearly rules out O_h symmetry and therefore would seem to exclude the XeO_6^{4-} ion postulated in the earlier study.

The Raman spectrum of cesium perxenate is unaffected by dilution from 1.7 to 0.48 *M*, nor is it altered significantly by acidification until 1 equiv of acid has been added per mole of xenon (except for some formation of Xe(VI)).

Furthermore, the ultraviolet absorption spectrum of a 1 *M* cesium perxenate solution is virtually the same as that of a 0.003 *M* solution, and both spectra show the characteristic absorption peak at *ca.* 240 nm that Appelman and Malm attributed to $HXeO_6^{3-}$.[6] These observations indicate that if Appelman and Malm's limit for the equilibrium constant of reaction 1 is correct, the ion XeO_6^{4-} cannot be a principal species in any of these solutions, inasmuch as reaction 1 would be substantially reversed by dilution or partial acidification.

Thus both spectral and "chemical" evidences lead to the rejection of XeO_6^{4-} as a predominant species, and we may conclude that the anion present in perxenate solutions of high pH has a charge of 3−. The question remains whether the spectral data can be satisfactorily interpreted in terms of the six-coordinated ion $HXeO_6^{3-}$ or whether a more highly hydrated ion must be postulated.

Most of the Raman spectra obtained showed a weak, sharp, and highly polarized band at about 1065 cm^{-1}, which was also observed by Peterson, *et al.*[7] We believe this to be the most intense band of a small CO_3^{2-} impurity. The other carbonate bands are weaker and so are not observable in the spectra. Since the scattering due to hydrogen bending motions around 1600 cm^{-1} and hydrogen stretching motions around 3400 cm^{-1} are in the regions where the solvent water scatters and since no bands were observed between 800 and 1265 cm^{-1}, we show in our figures only the region from 200 to 900 cm^{-1}.

The approximate curve envelopes of Figure 1 in the 400–500-cm^{-1} region are shown in Figure 2 as drawn by the curve analyzer. Four component bands are required to fit the observed envelope, and one of them, at 484 cm^{-1}, is definitely polarized. The depolarization values determined from the curve areas of the component bands in Figure 2 are as follows: 484 cm^{-1}, 0.2; 452 cm^{-1}, 0.5; 430 cm^{-1}, 0.5; 400 cm^{-1}, 0.6. The last three values are rather lower than the theoretical 0.75 for a depolarized band, but the ratio one gets depends on how one draws the background line under the bands, and this is rather subjective. The 484-cm^{-1} band is definitely polarized, and it seems reasonable, in view of the uncertainties, to list the other three as depolarized.

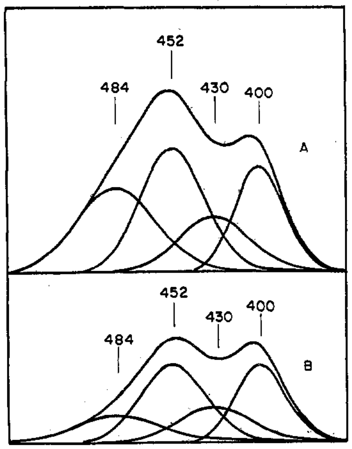

Figure 2.—Analysis of the low-frequency region of Figure 1. A is ⊥ and B is ||.

Figure 3 shows an analysis of the higher frequency region of curve A of Figure 1. Four bands are required to fit the observed trace, and all of them are definitely polarized.

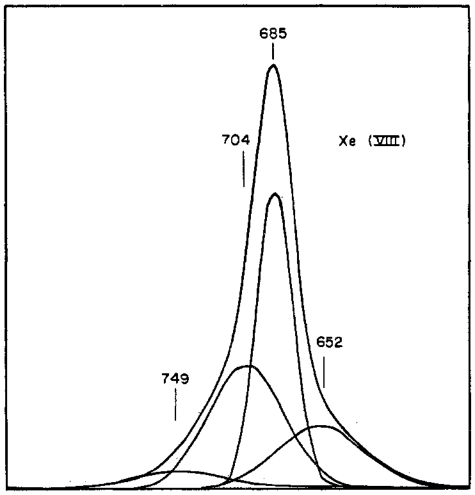

Figure 3.—Analysis of the high-frequency region of Figure 1.

The $HXeO_6^{3-}$ ion may be designated as $HOXeO_5^{3-}$ and characterized approximately as having C_{4v} symmetry, with five O ligands and one OH ligand, the latter being considered as a single mass. The vibrations then factor into symmetry species designated as

4 a_1 + 2 b_1 + b_2 + 4 e, with all eleven fundamentals Raman active and the four a_1 and four e fundamentals also infrared active. Four Raman bands must be polarized, three in the bond-stretching and one in the bond-bending region. The observed data fit these expectations rather well. Table I gives a tentative assignment of observed frequencies. The four a_1 fundamentals are uniquely assigned on the basis of Raman polarization, but the other assignments are less certain. They are based on relative intensities and frequencies and are guided by comparisons with other molecules of the same symmetry: IOF_5, $ReOF_5$, and $OsOF_5$.[10-12] The two b_1 fundamentals are not observed, while the unassigned band at 749 cm^{-1} is quite weak. The agreement is as good as can reasonably be expected, so the postulate that $HOXeO_5^{3-}$ is the predominant ion seems firmly supported by the vibrational data.

TABLE I

ASSIGNMENT OF OBSERVED VIBRATIONAL BANDS OF AQUEOUS CESIUM PERXENATE TO AN $HOXeO_5^{3-}$ ION OF C_{4v} SYMMETRY

Freq, cm^{-1}	Intens	Polarizn	Assignment
		Raman	
400	m	dp	ν_{11} e
430	w	dp	ν_{10} e
452	m	dp	ν_7 b_2
484	m	p	ν_4 a_1
652	m	p	ν_3 a_1
685	vs	p	ν_2 a_1
704	s	p	ν_1 a_1
749	w	p	?
		Infrared[a]	
425	m	. . .	ν_{10} e
443	s	. . .	ν_9 e
605	vs	. . .	ν_8 e

[a] From ref 7.

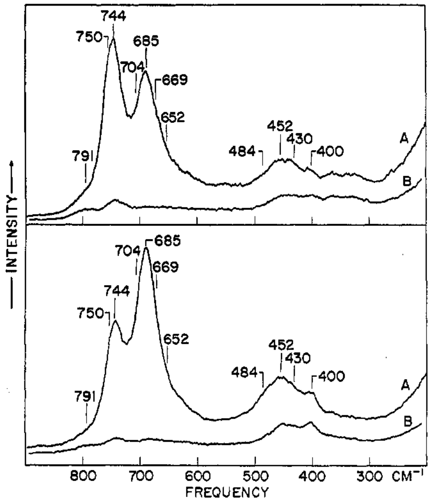

Figure 4.—Raman spectra of 1.7 *M* cesium perxenate after acidification with 1.1 (lower) and with 1.5 (upper) equiv of HF per mole of xenon. Curves A are ⊥ and B are ||. Spectral slit width was 5 cm^{-1}.

Figure 4 presents the Raman spectra of the 1.7 *M* perxenate solution after 1.1 and 1.5 equiv of HF have been added per mole of xenon. Virtually the same spectra are obtained when $HClO_4$ is used instead of HF. The new peak near 750 cm^{-1} that grows with progressive acidification belongs to Xe(VI) (see Figure 5). By the time 2 equiv of acid has been added per mole of xenon, the perxenate is essentially completely reduced to xenate(VI).

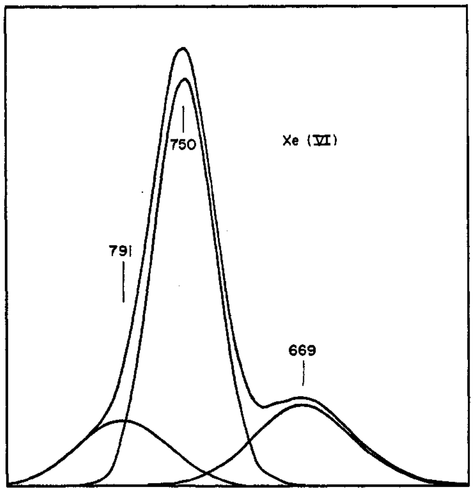

Figure 5.—Analysis of part of the Raman spectrum of aqueous sodium xenate(VI).

To look for evidence of a further protonated Xe(VIII) ion in the acidified samples, we attempted to fit the 600–800-cm^{-1} regions of Figure 4 as a linear combination of the spectrum of $HOXeO_5^{3-}$, shown in Figures 1 and 3, with that of $HXeO_4^-$, shown in Figure 5. The results appear in Figure 6. To obtain a satisfactory fit to the spectra of Figure 4, it is necessary to add a new band at 744 cm^{-1}. This band grows as acidification progresses, and it may be the most intense band of $H_2XeO_6^{2-}$ or some other 2− anion. The frequency of this band cannot be distinguished in our experiments from 749 cm^{-1}, the frequency of the very weak and unassigned band shown in Figure 3 and Table I. The latter, however, cannot be attributed to $H_2XeO_6^{2-}$ because the concentration of this ion should be quite negligible in an unacidified cesium perxenate solution. The unassigned 749-cm^{-1} band may represent an overtone of one of the unobserved fundamentals of HOXe-

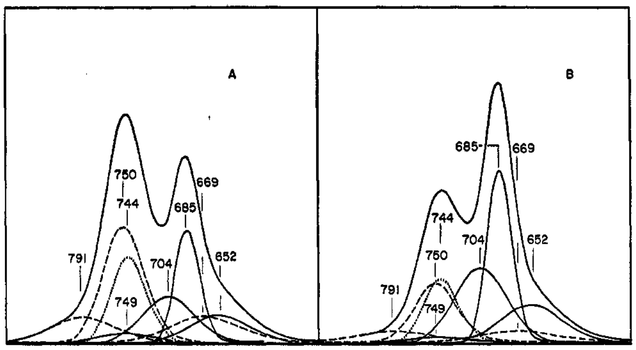

Figure 6.—Analysis of the 600–800-cm^{-1} regions of curves A of Figure 4: A, 1.5 equiv of HF; B, 1.1 equiv of HF; ——, curve envelope and bands of $HOXeO_5^{3-}$; - - - -, bands of $HXeO_4^-$; · · · ·, new band, possibly of $H_2XeO_6^{2-}$.

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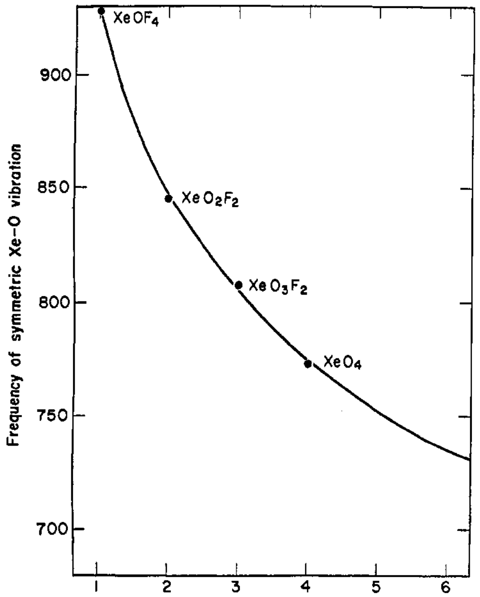

Figure 7.—Frequency of symmetric xenon–oxygen stretching vibrations of xenon oxide fluorides and xenon tetroxide.

O_5^{3-}, or it may belong to some other chemical species present in low concentration.

The three bond-stretching fundamentals of $HOXeO_5^{3-}$ at 652, 685, and 704 cm^{-1} are so close together that one must conclude that the force constant for the Xe–OH bond is not very much lower than for the Xe–O bond. This, together with the low value of these frequencies compared to 927 cm^{-1} for the Xe–O stretching motion in $XeOF_4$, might suggest a large amount of hydrogen bonding in the aqueous medium. Comparison with other oxygen-containing xenon compounds, however, indicates that the xenon–oxygen frequency is primarily a function of the number of oxygens bonded to the xenon. Figure 7 is a plot of symmetric stretching frequency against number of oxygen atoms for the four known relevant compounds that can be studied as isolated molecules.[13–16] The extrapolation shown predicts 735 cm^{-1} for six oxygen atoms, to be compared to 685 cm^{-1}, the most intense Raman band of $HOXeO_5^{3-}$. This difference of 50 cm^{-1} may reasonably be attributed partly to a somewhat weaker Xe–OH bond and partly to weakening of terminal oxygen bonds by hydrogen bonding with water molecules.

Our results, then, lead us to the conclusion that Xe(VIII) is octahedrally coordinated in aqueous solution but that the predominant species at high pH is $HOXeO_5^{3-}$, not XeO_6^{4-} as had been previously suggested.

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Notes

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Arsenic–Sulfur Polydentate Ligands. III. Platinum(II) Complexes of Bis[phenyl(*o*-thiomethylphenyl)arsino]propane and Bis[phenyl(*o*-thiomethylphenyl)arsino]ethane

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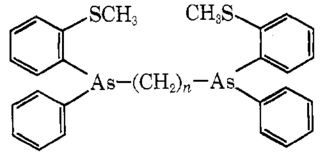
In continuation of our studies[2] on the chelating properties of the potentially quadridentate arsenic–sulfur ligands bis[phenyl(*o*-thiomethylphenyl)arsino]propane (C_3; structure Ia) and bis[phenyl(*o*-thiomethylphenyl)arsino]ethane (C_2; structure Ib), we now report some platinum(II) complexes of these two ligands.



Ia, $n = 3$; C_3
b, $n = 2$; C_2

The refluxing of a solution of potassium tetrachloroplatinate(II) with the C_3 ligand in aqueous acetone results in the formation of $Pt(C_3)Cl^+$, which has been isolated as the tetraphenylborate salt. Similar attempts with the C_2 ligand did not yield an identifiable pure product. Also, attempts to isolate the complexes $Pt(C_3)Cl_2$ and $Pt(C_2)Cl_2$ in reasonable purity were unsuccessful. Well-characterized iodo complexes $Pt(C_3)I_2$ and $Pt(C_2)I_2$, however, were obtained by *S*-methylation of the corresponding demethylated complexes Pt(demethylated C_2) and Pt(demethylated C_3). These demethylated complexes were prepared by refluxing in dimethylformamide the impure product obtained from the reaction of potassium tetrachloroplatinate(II) and the ligands.

The complex $[Pt(C_3)Cl][B(C_6H_5)_4]$ exhibits a conductance value appropriate for a uni-univalent electrolyte in nitromethane ($\Lambda_M \approx 70$ ohm^{-1} cm^2 mol^{-1} at 5×10^{-4} *M*) but a dilution study in acetonitrile gives an Onsager slope of 980 (Table I), which is reasonable for a di-univalent electrolyte.[2–4] Like its palladium-

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(1) On leave from the University of Burdwan, Burdwan, West Bengal, India.

(2) R. L. Dutta, D. W. Meek, and D. H. Busch, *Inorg. Chem.*, **9**, 1215 (1970).

(3) M. S. Elder, G. M. Prinz, P. Thornton, and D. H. Busch, *ibid.*, **7**, 2426 (1968).

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