

[CONTRIBUTION FROM ARGONNE NATIONAL LABORATORY, ARGONNE, ILL.]

Raman Spectrum of Xenic Acid¹BY HOWARD H. CLAASSEN² AND GERALDINE KNAPP

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The Raman spectrum of a 2.0 *M* aqueous solution of XeO₃ has been obtained. Intense bands at 780, 344, 833, and 317 cm.⁻¹ are assigned as ν_1 , ν_2 , ν_3 , and ν_4 , respectively, of un-ionized XeO₃ molecules of symmetry C_{3v}. Several much weaker bands are assigned to a low concentration of an unknown species.

The dangerously explosive white solid that is often the result of exposure of xenon fluorides to moist air was first identified by Smith³ as XeO₃. Whereas this material will detonate from slight mechanical shock when dry, it has been found to be quite safe when wet. It can be prepared by hydrolysis of XeF₆ in water and concentrated by evaporation of the water to a molarity of approximately four before crystallization begins. In view of the high solubility of this material, Raman spectroscopy seemed a good tool for obtaining structural information.

The solution was prepared by neutral hydrolysis of XeF₆ in the presence of MgO. The water was added to a glass vessel containing XeF₆ and powdered MgO at -195°. The mixture was allowed to warm slowly to 0° with frequent shaking. It was then filtered at 0° and the filtrate passed successively through columns of zirconium phosphate and zirconium oxide to remove the magnesium and fluoride ions. The resulting solution was slightly acid and contained essentially all the original xenon. The use of radioactive xenon permitted determination of the concentration by γ -counting. Iodometric titration was used to check the concentration and also established the valence of xenon as +6. Further details on the method of hydrolysis and titrimetric analysis will be given elsewhere.⁴

The Raman spectrum of the solution was obtained with a Cary 81 photoelectric instrument using the standard 7-mm. sample tube. Qualitative information about polarization was obtained by use of Polaroid cylinders around the sample tube. The infrared spectrum of the solution was studied around 800 cm.⁻¹ by pressing a drop between two silver chloride plates. A Perkin-Elmer 421 spectrophotometer was used.

The Raman spectrum obtained for a 2 *M* solution is reproduced in Fig. 1. Polarization scans showed that the 780 cm.⁻¹ band is highly polarized but could detect no polarization of the other strong bands at 833, 344, and 317 cm.⁻¹. The two stretching frequencies were also observed in the infrared at 779 and 829 cm.⁻¹. The latter was more intense than the former.

The Raman spectrum has four intense bands and several much weaker ones. It seems plausible to assume that the intense ones represent fundamentals of the same, predominant molecular species and the weak ones are due to another species of very low concentration. The question of interest is to determine at least the nature of the predominant species. Either un-ionized molecules, XeO₃, of pyramidal shape, or tetrahedral [XeO₄]²⁻ ions would have four Raman-active fundamentals. For the former all four would also be

infrared active but for the tetrahedral ion only one of the high and one of the low frequency fundamentals would be active in the infrared. The fact that both high frequency bands are observed in the infrared indicates XeO₃ molecules. On the other hand, for the pyramidal XeO₃ molecules, one of the two low-frequency fundamentals should be polarized in the Raman spectrum, but no evidence for polarization could be obtained experimentally for either of these two bands. This latter is evidence of a negative sort: there may be a slight polarization that our method was unable to detect. The polarization data for the 317 cm.⁻¹ band are much more precise than for the one at 344 because the latter is a shoulder. This may be taken as evidence that the 317 cm.⁻¹ band should be assigned as ν_4 , a depolarized band, and that 344 is the polarized symmetric vibration.

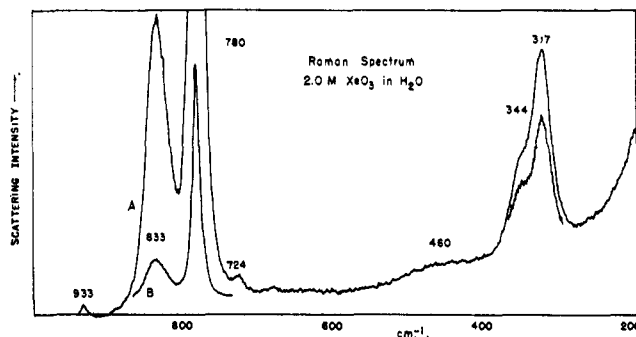


Fig. 1.—Raman spectrum of 2.0 *M* XeO₃ in H₂O: A, slit width of 7 cm.⁻¹; B, slit width of 2.5 cm.⁻¹.

Comparisons of frequencies with other similar molecules and ions lend strong support for the pyramidal, C_{3v} molecule, XeO₃. Table I lists frequencies that have been published for the two isoelectronic ions [Te-

TABLE I
FREQUENCIES FOR COMPARISON

Molecule or ion	Method of observation	ν_1	ν_2	ν_3	ν_4	Ref.
[TeO ₃] ²⁻	Raman of solution	758	364	703	326	^a
[IO ₃] ⁻	Raman of solution	779	390	826	330	^b
XeO ₃	Raman of solution	780	344	833	317	This work
XeO ₃	Infrared of solid	770	311	820	298	^c
[IO ₄] ⁻	Raman of solution	791	256	853	325	^d

^a H. Siebert, *Z. anorg. allgem. Chem.*, **275**, 225 (1955). ^b S. T. Shen, Y. T. Yao, and T. Wu, *Phys. Rev.*, **51**, 235 (1937). ^c D. F. Smith, ref. 3. ^d H. Siebert, *Z. anorg. allgem. Chem.*, **273**, 211 (1953).

O₃]²⁻ and [IO₃]⁻, for solid XeO₃, and for the tetrahedral ion [IO₄]⁻. The frequency correspondences between our data and those of the two isoelectronic ions and those of solid XeO₃ are much better than between our data and those of [IO₄]⁻. Thus we may conclude from the spectra that the predominant molecular species in the 2 *M* solution is the un-ionized molecule,

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission.

(2) Wheaton College, Wheaton, Ill.

(3) D. F. Smith, *J. Am. Chem. Soc.*, **85**, 816 (1963).

(4) E. H. Appelman and J. G. Malm, *ibid.*, **86**, 2141 (1964).

XeO₃. Further support for this is given by the observation⁴ that the electrical conductivity of the solution is very low.

The very weak Raman bands at 933, 524, and around 460 cm.⁻¹ must then be assigned to another molecular species of low concentration, that is, as yet, unknown.

[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY, UNIVERSITY OF CHICAGO, CHICAGO 37, ILL.]

Crystal and Molecular Structures of Some Metal Tetraphenylporphines¹

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The crystal and molecular structures of copper tetraphenylporphine, palladium tetraphenylporphine, zinc tetraphenylporphine dihydrate, and ferric hydroxide tetraphenylporphine monohydrate were determined from three-dimensional X-ray diffraction data. These structures are all tetragonal. The space group of both copper tetraphenylporphine and palladium tetraphenylporphine is $I\bar{4}2d$ with four molecules per unit cell. The other two porphyrins have two molecules per unit cell. The space group of the zinc porphyrin is $I4/m$ and the molecular symmetry is $4/m$. The iron porphyrin has space group $I4$ and a molecular symmetry of 4. The molecular configuration changes from a planar to a buckled, nonplanar one depending on the crystal packing and on the substituents attached to the porphine nucleus. Copper and palladium tetraphenylporphine are very nonplanar, while the porphine nucleus of the zinc compound is planar. The iron porphyrin is nearly planar except that the iron atom is 0.2 Å. above the plane of the four nitrogen atoms in the porphyrin ring.

Introduction

Previous structural determinations have shown that although some phthalocyanines are planar,³ nickel etioporphyrin I⁴ and tetraphenylporphine⁵ are nonplanar. We reported in a previous communication⁶ that copper tetraphenylporphine is also nonplanar; this paper includes the details of this structure determination. Nickel etioporphyrin II⁷ appears to be planar, but disorder in the crystal makes it impossible to detect suspected slight deviations from planarity.

A summary of some porphyrin crystal forms found by us and others⁸⁻¹⁰ is given in Table I. The large number of different crystal forms can be partially explained by the wide variety of solutions from which the crystals were grown.

Experimental

The metal tetraphenylporphines were prepared by the usual methods.¹¹ The PdTPP sample was kindly supplied by A. Martell.

TABLE I
FORMS OF PORPHYRIN CRYSTALS

Compound	Form	Dimensions, Å.			Oblique angles, deg.			Density		Z ^a	Space group	Reference
		a	b	c	α	β	γ	Obsd.	Calcd.			
Porphine	Monoclinic	12.35	12.35	10.30				1.336	1.339	4	P2 ₁ /a	8
TPP	Triclinic						102			1	P $\bar{1}$	d
TPP	Orthorhombic	12.0	19.2	14.7				1.26		4		9
TPP	Tetragonal	15.12	15.12	13.94						4	$I\bar{4}2d$	5
CuTPP	Tetragonal	15.04 ^c	15.04	13.993				1.40	1.43	4	$I\bar{4}2d$	b
PdTPP	Tetragonal	15.088	15.088	13.987				1.48	1.51	4	$I\bar{4}2d$	b
NiTPP	Tetragonal	15.04	15.04	13.92						4	$I\bar{4}2d$	b
ZnTPP	Triclinic	6.03	9.89	13.0	101	108	93	1.29		1	P1	9 ^b
ZnTPP	Orthorhombic	14.8	17.2	14.6				1.29		4	P2 ₁ 2 ₁ 2 ₁	b
ZnTPP·(H ₂ O) ₂	Tetragonal	13.440	13.440	9.715				1.30	1.35	2	I4/m	b
FeTPPOH·H ₂ O	Tetragonal	13.534	13.534	9.820				1.31	1.31	2	I4	b
Etio I	Monoclinic	10.3	19.5	6.75		98		1.17	1.17	2	P2 ₁ /c	9, 10
Ni Etio I	Tetragonal	14.61	14.61	12.38				1.35	1.35	4	I4 ₁ /amd	b
Ni Etio II	Tetragonal	14.68	14.68	12.51				1.5	1.37	4	I4 ₁ /amd	7

^a Molecules per unit cell. ^b This work. ^c Estimated uncertainties in Å. for a and c, respectively, are: CuTPP, 0.02 and 0.004; PdTPP, 0.002 and 0.001; FeTPPOH·H₂O, 0.006 and 0.006; ZnTPP·(H₂O)₂, 0.006 and 0.01. ^d A. Tulinsky, private communication.

The present work was undertaken to determine if all tetraphenylporphines are nonplanar. This was accomplished by varying the metal atom in order to study the influence of changing the coordination number of the metal. The effects of changes in crystal packing were also studied. Tetraphenylporphine will be denoted by TPP, palladium tetraphenylporphine by PdTPP, etc.

Deep purple CuTPP and PdTPP crystals were grown from benzene, dark red ZnTPP·(H₂O)₂ crystals from an acetone-ethanol solution, and dark red FeTPPOH·H₂O crystals from a chloroform-ethanol solution.¹² All of the crystals were well formed tetragonal bipyramids. The edges of the pyramid base varied from 0.1 to 0.3 mm. in length.

A triclinic form of ZnTPP, listed in Table I, was grown from benzene. This crystal form decomposes slowly. Precession photographs taken a few days after preparation of the crystals showed evidence of decomposition.

(1) This research was supported by a Public Health Service Grant and the Louis Block Fund.

(2) NASA Predoctoral Fellow.

(3) J. M. Robertson, *J. Chem. Soc.*, 615 (1935); 1195 (1936); J. M. Robertson and I. Woodward, *ibid.*, 219 (1937); 36 (1940).

(4) E. B. Fleischer, *J. Am. Chem. Soc.*, **85**, 146 (1963).

(5) J. L. Hoard, M. J. Hamor, and T. A. Hamor, *ibid.*, **85**, 2334 (1963).

(6) E. B. Fleischer, *ibid.*, **85**, 1353 (1963).

(7) M. B. Crute, *Acta Cryst.*, **12**, 24 (1959).

(8) C. Rimington, S. F. Mason, and O. Kennard, *Spectrochim. Acta*, **12**, 65 (1958).

(9) J. M. Goldstein, Ph.D. Dissertation, University of Pennsylvania, 1959.

(10) C. L. Christ and D. Harker, *Amer. Mineralogist*, **27**, 219 (1942).

(11) D. Thomas and A. Martell, *J. Am. Chem. Soc.*, **81**, 5111 (1959), and references given therein.

(12) We gratefully acknowledge the help of Mrs. S. Choi, who skillfully grew the ZnTPP·(H₂O)₂ and FeTPPOH·H₂O crystals.