

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

$O_3^{3-}$ , or it may belong to some other chemical species present in low concentration.

The three bond-stretching fundamentals of  $HOXeO_3^{3-}$  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.<sup>13-16</sup> The extrapolation shown predicts 735  $cm^{-1}$  for six oxygen atoms, to be compared to 685  $cm^{-1}$ , the most intense Raman band of  $HOXeO_3^{3-}$ . 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.

(13) H. H. Claassen, C. L. Chernick, and J. G. Malm, "Noble Gas Compounds," H. H. Hyman, Ed., University of Chicago Press, Chicago, Ill., 1963, p 287.

(14) H. H. Claassen, E. L. Gasner, H. Kim, and J. L. Huston, *J. Chem. Phys.*, **49**, 253 (1968).

(15) J. L. Huston and H. H. Claassen, *ibid.*, in press.

(16) J. L. Huston and H. H. Claassen, *ibid.*, **62**, 5646 (1970).

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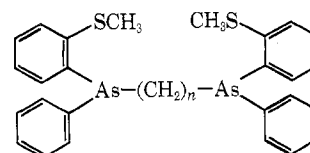
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In continuation of our studies<sup>2</sup> on the chelating properties of the potentially quadridentate arsenic-sulfur ligands bis[phenyl(*o*-thiomethylphenyl)arsino]propane ( $C_3$ ; structure Ia) and bis[phenyl(*o*-thiomethylphenyl)arsino]ethane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

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 at-

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



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

tempts 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  $Pt(\text{demethylated } C_2)$  and  $Pt(\text{demethylated } C_3)$ . 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 ( $\Lambda_M \approx 70 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  at  $5 \times 10^{-4} M$ ) but a dilution study in acetonitrile gives an Onsager slope of 980 (Table I), which is reasonable for a di-univalent electrolyte.<sup>2-4</sup> Like its palladium-

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

(4) F. A. Cotton, W. R. Robinson, R. A. Walton, and R. Whyman, *ibid.*, **6**, 931 (1967).

TABLE I  
MOLAR CONDUCTIVITIES FOR THE PLATINUM(II) COMPLEXES

Complex	Solvent	Concn $\times 10^4, M$	$\Delta_M, \text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$
Pt(C <sub>3</sub> )I <sub>2</sub>	DMF	2.5	70
	CH <sub>3</sub> NO <sub>2</sub>	5.0	70
[Pt(C <sub>3</sub> )Cl][B(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> ]	CH <sub>3</sub> NO <sub>2</sub>	5.0	65 <sup>a</sup>
Pt(C <sub>2</sub> )I <sub>2</sub>	CH <sub>3</sub> NO <sub>2</sub>	2.5	10
Pt(demethylated C <sub>3</sub> )	DMF	5.0	5

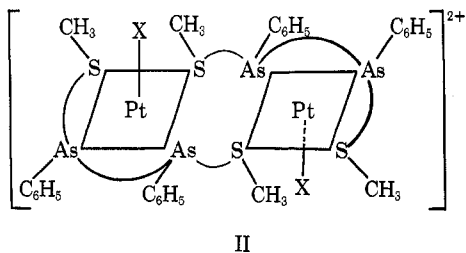
<sup>a</sup> This complex gave an Onsager slope of 980 in acetonitrile.

(II) analog, the platinum(II) complex [Pt(C<sub>3</sub>)Cl][B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>] gives a molecular weight in chloroform that is appreciably higher than the monomeric formula weight (Table II). We interpret the molecular weight data to

TABLE II  
MOLECULAR WEIGHTS OF THE PLATINUM(II) COMPLEXES IN CHLOROFORM

Complex	Concn, g/l.	Mol wt (found)	Formula wt
Pt(C <sub>3</sub> )I <sub>2</sub>	2.25	1023	1041
	6.75	1050	
Pt(C <sub>2</sub> )I <sub>2</sub>	2.40	1080	1027
	3.50	1070	
[Pt(C <sub>3</sub> )Cl][B(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> ]	2.80	1400	1142
	6.05	1450	
Pt(demethylated C <sub>3</sub> )	2.55	1500	757
	3.70	1450	
Pt(dias)I <sub>2</sub>	4.10	1490	
	2.50	900	945
	3.75	910	

indicate a dimeric cation which undergoes appreciable ion association in chloroform. The pmr spectrum shows two resonances centered at approximately  $\tau$  7.40 (broad; CH<sub>3</sub> protons) and 7.90 (CH<sub>2</sub> protons). The spectrum is similar<sup>2</sup> to that of [Pd(C<sub>3</sub>)Cl][B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>] and, in accordance with our previous arguments, we believe the -SCH<sub>3</sub> groups in the complex are exchanging between coordinated and uncoordinated positions. The conductance value for [Pd(C<sub>3</sub>)I]I is also typical of a 1:1 electrolyte in nitromethane and in dimethylformamide (Table I), but in view of the above dilution study with the tetraphenylborate salt, the iodide complex has also been formulated as a dimeric Pt<sub>2</sub>(C<sub>3</sub>)<sub>2</sub>I<sub>2</sub><sup>2+</sup> species in polar solvents. These dimeric cations are tentatively assigned structure II. On the other hand, Pt(C<sub>2</sub>)I<sub>2</sub> is only weakly ionized in nitromethane ( $\Delta_M \approx 10 \text{ ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$ ; Table I). Both Pt(C<sub>3</sub>)I<sub>2</sub> and Pt(C<sub>2</sub>)I<sub>2</sub> exhibit monomeric molecular weights in chloroform (Table II). These results are comparable with our earlier observations on the palladium(II) complexes Pd(C<sub>3</sub>)I<sub>2</sub> and Pd(C<sub>2</sub>)I<sub>2</sub>.



II

The complex Pt(C<sub>3</sub>)I<sub>2</sub> has pmr resonances in deuteriochloroform at  $\tau$  7.03 (CH<sub>3</sub> protons; broad base) and 7.85 (CH<sub>2</sub> protons). However, the analogous palladium(II) complex, Pd(C<sub>2</sub>)I<sub>2</sub>, gave no signal downfield from the position of the thiomethyl resonance of the

free ligand ( $\tau \sim 7.75$ ). The position of the thiomethyl resonance in the platinum(II) complex indicates that one of the -SCH<sub>3</sub> groups is coordinated to platinum, but the two -SCH<sub>3</sub> groups become equivalent by a rapid exchange process.

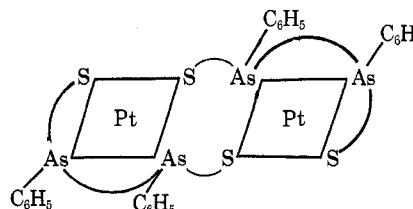
In order to compare the electronic spectra of Pt(C<sub>3</sub>)I<sub>2</sub> and Pt(C<sub>2</sub>)I<sub>2</sub>, with a reference compound, Pt(dias)I<sub>2</sub> (dias = 1,2-bis(diphenylarsino)ethane) was prepared. The latter complex is a nonelectrolyte in dimethylformamide and a monomer in chloroform; thus, it has a planar four-coordinate structure with two iodide and two arsenic atoms as ligands. The first absorption band of Pt(dias)I<sub>2</sub> (mull: 370 m $\mu$ ; 27.0 kK) occurs at 1.2 times the energy of Pd(dias)I<sub>2</sub>,<sup>2</sup> which is also monomeric and a nonelectrolyte (mull: 440 m $\mu$ ; 22.7 kK). This agrees with literature reports<sup>5,6</sup> on the relative ligand field splittings of similar platinum(II) and palladium(II) complexes. Although the pmr spectrum shows that the C<sub>2</sub> ligand functions differently with platinum(II) than with palladium(II), the electronic spectra are not distinctive enough to reveal a dissimilar structure in these two cases. Thus, the absorption bands of the platinum(II) complexes are  $\sim 1.17$ - $1.20$  times the energies of the corresponding palladium(II) complexes (Table III).

TABLE III  
ELECTRONIC SPECTRA OF THE PLATINUM(II) COMPLEXES<sup>a</sup>

Complex	Nujol mull	Solvents	
		CH <sub>2</sub> Cl <sub>2</sub>	CHCl <sub>3</sub>
Pt(C <sub>3</sub> )I <sub>2</sub>	375	330-340 sh	330-340 sh
Pt(C <sub>2</sub> )I <sub>2</sub>	370-380	...	...
Pt(demethylated C <sub>3</sub> )	340-380	378 (3350)	372 (3250)
Pt(demethylated C <sub>2</sub> )	360-380	...	...
Pt(dias)I <sub>2</sub>	370		

<sup>a</sup>  $\lambda_{\text{max}}$  (m $\mu$ ) and extinction coefficients, in parentheses, are presented.

The molecular weight of Pt(demethylated C<sub>3</sub>) in chloroform corresponds to a dimeric formula (Table II). This is consistent with the results reported earlier for the palladium(II) complexes of C<sub>2</sub> and C<sub>3</sub>.<sup>2</sup> The platinum(II) complexes also undergo S-alkylation with methyl iodide to furnish pure Pt(C<sub>3</sub>)I<sub>2</sub> and Pt(C<sub>2</sub>)I<sub>2</sub>; such reactions suggest that the dimeric complexes do not contain bridging mercapto groups. This is consistent with proposed structure III for the demethylated complex.



III

### Experimental Section

Potassium tetrachloroplatinate(II) was prepared by a standard procedure.<sup>7</sup> Preparations of the ligands were described earlier.<sup>2</sup>

[Pt(C<sub>3</sub>)Cl][B(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>].—The C<sub>3</sub> ligand (0.3 g; 0.5 mmol) was dissolved in acetone (20 ml) and to this was added potassium

(5) H. P. Fritz, I. R. Gordon, K. E. Schwarzshams, and L. M. Venanzi, *J. Chem. Soc.*, 5210 (1965).

(6) R. C. Taylor, G. R. Dobson, and R. A. Kolodny, *Inorg. Chem.*, **7**, 1886 (1968).

(7) G. B. Kauffman and D. O. Cowan, *Inorg. Syn.*, **7**, 239 (1963).

tetrachloroplatinate(II) (0.2 g; 0.5 mmol dissolved in 2–3 ml of water). The mixture was refluxed for 10 hr. The bright yellow solution was filtered from the potassium chloride and the filtrate was treated with an ethanol solution of sodium tetraphenylborate. The resulting granular, cream-colored material was collected on a filter, washed with ethanol, and finally recrystallized from an ethanol–acetone mixture. *Anal.* Calcd for  $C_{53}H_{50}As_2BClPtS_2$ : C, 55.72; H, 4.41; Cl, 3.10. Found: C, 55.58; H, 4.31; Cl, 3.29.

**Pt(demethylated  $C_3$ ).**—The bright yellow solution that resulted from the reaction of the  $C_3$  ligand and potassium tetrachloroplatinate(II) (as described above) was treated with ether to precipitate a yellow solid. This material was collected on a filter, dissolved in DMF (10 ml), and the solution was refluxed for 10 hr. The solution was concentrated until some yellow crystals separated. Ethanol (20 ml) was added and the mixture was stored overnight at 5°. The crystals were collected, washed with ethanol, and dried. *Anal.* Calcd for  $C_{27}H_{24}As_2PtS_2$ : C, 42.81; H, 3.19; S, 8.46. Found: C, 42.60; H, 3.13; S, 8.39.

**Pt(demethylated  $C_2$ ).**—This complex was obtained by a procedure similar to that given above for Pt(demethylated  $C_3$ ). *Anal.* Calcd for  $C_{26}H_{22}As_2PtS_2$ : C, 41.97; H, 2.98; S, 8.62. Found: C, 41.79; H, 3.05; S, 8.50.

**Pt( $C_3$ ) $I_2$ .**—The Pt(demethylated  $C_3$ ) complex was treated with excess methyl iodide and allowed to stand at room temperature overnight. The methyl iodide was then removed and the residue was recrystallized twice from dichloromethane. *Anal.* Calcd for  $C_{29}H_{30}As_2I_2PtS_2$ : C, 33.44; H, 2.90; I, 24.38. Found: C, 33.27; H, 2.71; I, 24.26.

**Pt( $C_2$ ) $I_2$ .**—This compound was prepared by treatment of Pt(demethylated  $C_2$ ) with methyl iodide as described above for Pt( $C_3$ ) $I_2$ . *Anal.* Calcd for  $C_{28}H_{28}As_2I_2PtS_2$ : C, 32.73; H, 2.75; I, 24.70. Found: C, 32.04; H, 2.65; I, 25.02.

**Pt(dias) $I_2$ .**—1,2-Bis(diphenylarsino)ethane (Strem Chemicals) (0.25 g; 0.5 mmol) was dissolved in a hot ethanol–chloroform mixture and to this was added an aqueous ethanol solution of potassium tetrachloroplatinate(II) (0.2 g; 0.5 mmol). The pinkish white precipitate was collected on a filter, washed with water and ethanol, and then digested with hot concentrated HCl–ethanol (1:1 volume ratio) for 2 hr. The solid was collected on a filter, washed with ethanol, suspended in ethanol–chloroform (1:1), and then stirred with ethanolic sodium iodide for 1 hr. The yellow material was recrystallized from a chloroform–ethanol mixture. *Anal.* Calcd for  $C_{26}H_{24}As_2I_2Pt$ : C, 33.01; H, 2.54; I, 26.88. Found: C, 32.88; H, 2.57; I, 26.98.

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## A Novel Criterion for Carbonyl Stretching Band Assignment and Its Application to the Infrared Spectrum of ( $\pi$ -Cyclopentadienyl)(methyldichlorosilyl)-dicarbonyliron<sup>1,2</sup>

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Cyclohexane solutions of the complex<sup>3</sup> ( $\pi$ - $C_5H_5$ )Fe(CO)<sub>2</sub>SiCl<sub>2</sub>CH<sub>3</sub> show four strong infrared absorptions in the region of CO stretching vibrations. The expected

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(1) Work performed in the laboratories of Professor F. G. A. Stone, Bristol, U. K., whom I thank for facilities and encouragement.

(2) After this work was completed, a similar criterion was suggested by J. D. Warren and R. J. Clark, *Inorg. Chem.*, **9**, 373 (1970). However the present work represents, to my knowledge, the first time that such a splitting has actually been observed and measured.

(3) W. Jetz and W. A. G. Graham, *J. Amer. Chem. Soc.*, **89**, 2773 (1967).

number is 2, both of roughly equal intensity.<sup>4</sup> The extra bands were attributed to the presence of rotational isomers I and II,<sup>5</sup> which differ by rotation through 120° about the Si–Fe bond.

Accordingly, the bands may be grouped into two pairs on the basis of their relative intensities. Thus the weaker pair (at<sup>3</sup> 2031 and 1983 cm<sup>-1</sup>) arise from the less abundant isomer, while the pair at<sup>3</sup> 2022 and 1973 cm<sup>-1</sup> arise from the more abundant one. However, none of the usual criteria allows the band pairs to be assigned to the individual isomers I and II. Therefore the following method was employed.

The two CO environments of isomer I are symmetrically identical since they are interchanged by a molecular symmetry element, the mirror plane.<sup>5</sup> Thus substitution of either position by <sup>13</sup>C<sup>16</sup>O will produce identical satellite bands having about 2% of the intensity of the isotopically normal species in natural abundance. In contrast, the two CO environments of isomer II, which has no nontrivial symmetry elements,<sup>5</sup> will in principle be different from each other. Substitution of either position by <sup>13</sup>C<sup>16</sup>O should produce a different spectrum in each case. This would cause a splitting of the <sup>13</sup>C<sup>16</sup>O satellite bands of isomer II, but not of isomer I, and provide a basis for distinguishing their spectra.

The previously published spectrum of the complex<sup>3</sup> reveals the expected splitting in the satellite of the 1983-cm<sup>-1</sup> band but not in those accompanying the bands at 1973 and 2022 cm<sup>-1</sup>. The latter absorption obscures the satellite of the 2031-cm<sup>-1</sup> band. A sample of the complex was prepared by the method of Jetz and Graham.<sup>3</sup> Its infrared spectrum in cyclohexane solution agreed closely with that reported by those authors. In particular, the measured value of the splitting in the satellite of the 1983-cm<sup>-1</sup> band was 4.2 ± 0.5 cm<sup>-1</sup>. No splitting was observed in the satellites of the 2022- and 1973-cm<sup>-1</sup> absorptions.

These observations confirm the original interpretation<sup>3</sup> of the spectrum, on which the present treatment is based, and allow the bands observed in this region to be fully assigned. In addition, the size of the splitting may be used as the third parameter necessary to evaluate all three approximate<sup>4</sup> CO force constants for isomer II. Those for isomer I may be calculated from the two CO frequencies of isotopically normal molecules (Table I).

TABLE I  
ASSIGNMENTS OF CO STRETCHING FREQUENCIES AND APPROXIMATE CO FORCE CONSTANTS

	Isomer <sup>a</sup>	
	I	II
Assumed point symmetry	$C_s$	$C_1$
In-phase CO stretch, cm <sup>-1</sup>	2022	2031
In-phase <sup>13</sup> CO stretch, cm <sup>-1</sup>	2008	...
Out-of-phase CO stretch, cm <sup>-1</sup>	1973	1983
Out-of-phase <sup>13</sup> CO stretch, cm <sup>-1</sup>	1942	1959, 1954.5
$k_{1,b}$ mdyn/Å	0.40	0.38
$k$ (transoid to Cl), mdyn/Å	16.24	16.35
$k$ (transoid to CH <sub>3</sub> ), mdyn/Å	...	16.45

<sup>a</sup> Reference 5. <sup>b</sup> I thank Dr. R. C. Dougherty for the use of a PDP8 computer to calculate the force constants.

The CO groups of isomer II may be transoid<sup>5</sup> to either a methyl group or a chlorine atom. The latter case

(4) J. Dalton, I. Paul, and F. G. A. Stone, *J. Chem. Soc. A*, 2744 (1969), and references therein.

(5) Newman projections of the isomers, numbered as above, are reproduced in ref 3. Isomer I has the mirror plane of symmetry.