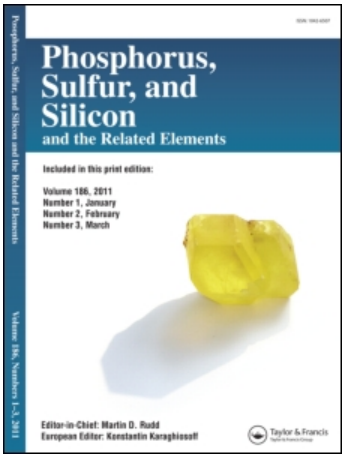


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

I.R. INVESTIGATIONS ON SOME HYDROGEN BONDED COMPLEXES OF PLATINUM(II) INVOLVING P-F LIGANDS

Alfred Kolbe[a]; Reinhard Schmutzler[b]; Lutz Heuer[b]
[a] Sektion Chemie der Martin Luther-Universität, [b] Institut für Anorganische und Analytische Chemie der Technischen Universität, Braunschweig, Germany

To cite this Article Kolbe, Alfred , Schmutzler, Reinhard and Heuer, Lutz(1991) 'I.R. INVESTIGATIONS ON SOME HYDROGEN BONDED COMPLEXES OF PLATINUM(II) INVOLVING P-F LIGANDS', Phosphorus, Sulfur, and Silicon and the Related Elements, 61: 1, 27 — 30
To link to this Article: DOI: 10.1080/10426509108027333
URL: http://dx.doi.org/10.1080/10426509108027333

Phosphorus, Sulfur, and Silicon, 1991, Vol. 61, pp. 27–30
Reprints available directly from the publisher
Photocopying permitted by license only

I.R. INVESTIGATIONS ON SOME HYDROGEN BONDED COMPLEXES OF PLATINUM(II) INVOLVING P-F LIGANDS

ALFRED KOLBE
Sektion Chemie der Martin Luther-Universität, O 4010 Halle an der Saale

and

REINHARD SCHMUTZLER* and LUTZ HEUER
Institut für Anorganische und Analytische Chemie der Technischen Universität, W 3300 Braunschweig, Germany

(Received January 3, 1991; in final form January 16, 1991)

I.R.-spectroscopic investigations of two hydrogen-bonded platinum(II) complexes involving arylphosphonofluoridous acids and their anions (**1** and **2**) are reported. The hydrogen bonds observed were found to differ significantly, depending on the substituents on the phenyl ring: whereas compound **1**, involving unsubstituted phenyl rings, corresponds to Speakman's A type, the xylyl-substituted compound **2** is of type B in the Speakman terminology. All the characteristics of a hydrogen bond were found to disappear upon replacing hydrogen by a bridging BF_2 group.

Key words: I.R. Investigations; hydrogen bonds; Platinum(II).

In the course of a study of fluorophosphine complexes of platinum the formation of the unusual platinum(II) complexes, $[Pt\{ArP(F)O\}_2\{ArP(F)OH\}_2]$, **1** (Ar = Ph) and **2** (Ar = 2.5-$Me_2C_6H_3$) was noted.[1]

These complexes were found to involve coordination of two units of arylphosphonofluoridous acid and two units of arylphosphonofluoridite to Pt(II). The characterization of **1** and **2** was by n.m.r. spectroscopy, and, in the case of **2**, by single crystal X-ray diffraction.[1] Because of the presumed hydrogen-bonded system in **1** and **2** a study of the vibrational spectra of the compounds was initiated. The results are presented and discussed in the following.

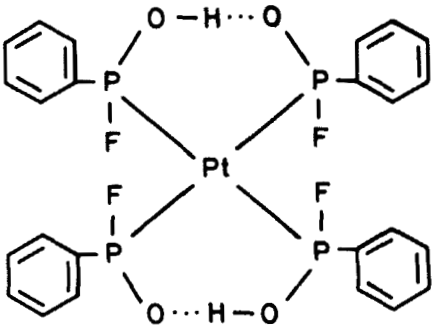
At the same time a phosphonofluoridous acid, 2.6-$(PhO)_2C_6H_3P(F)(:O)H$, **3** was synthesized.[1] This compound is of a type previously reported by Falius.[2] Its I.R. spectrum reveals a strong, sharp absorption at 2400 cm^{-1}. An intermolecular interaction via a hydrogen bond is ruled out in this case. The I.R. spectrum of **3** is in accord with the suggestion[3] that the equilibrium

$$R_2POH \rightleftharpoons R_2P(:O)H$$

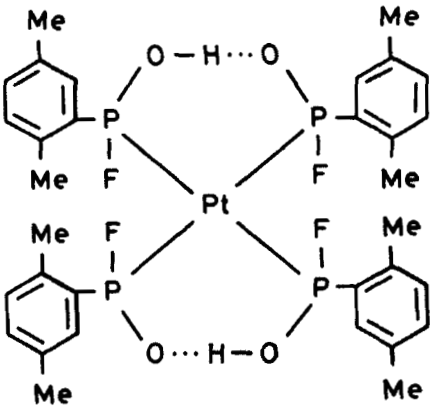
lies completely on the right in the case of electronegative groups, R. The absorptions at 1234 and 1209 cm^{-1} are assigned to the antisymmetric stretching vibration of the ether group and to the PO stretching vibration, respectively.

* To whom correspondence should be addressed.

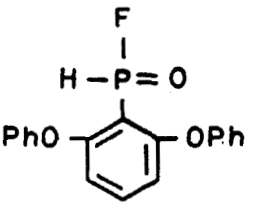
Compounds **1** and **2** were of particular interest because of the pronounced intramolecular hydrogen bond system, which is reflected, in the case of **2**, in a short O . . . O distance (235 pm). In a review published in 1978 Hadzi and Detoni[4] have quoted a value of 239 pm as the shortest O . . . O distance in a hydrogen-bonded system previously known. More recently, shorter O . . . O bond lengths have been reported only by Raymond,[5] and by Willett,[6] and their coworkers, decreasing to



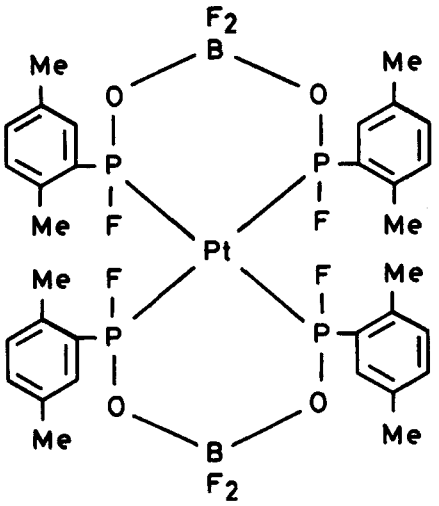
1



2



3



4

as little as 229 pm in the extreme case of the anion $[H_3O_2]^-$[6]. According to a classification put forward by Speakman[7] the strong hydrogen bond present in **2** could be expected to correspond to type A whereby the proton was assumed to be symmetrically placed between the two oxygen atoms. The spectroscopic data are not, however, in agreement with this assumption. In the background of the I.R. spectrum of **2** two broad bands, at 1280 and 760 cm^{-1}, are observed. Upon cooling down to $-150°C$ a strong increase of the intensity of these bands is noted; this is considered unambiguous proof of hydrogen bonding. The observation of two bands is believed to be due to the presence of an asymmetric hydrogen bond. This suggested asymmetry is supported by the observation of a clearly split PO absorption at 1080 cm^{-1}. This splitting is thought to arise from two PO groups interacting unequally with a proton.

The I.R. spectrum of the phenyl compound, **1**, cannot be discussed merely by analogy to that of **2**. Even at low temperature only one broad hydrogen bond absorption at 950 cm^{-1} (also observed at room temperature) is seen. Therefore, it is suggested that the proton in this hydrogen bond is placed completely symmetrically, corresponding to Speakman's type A hydrogen bond.[7] The O . . . O distance in the case of **1** is not known. Because of the symmetry of the hydrogen bond the O . . . O distance is believed to be shorter than 235 pm. The observation that the PO band at 1118 cm^{-1} is not split is in agreement with the assumption of a highly symmetrical hydrogen bond, suggesting equivalent PO bonds.

The substituents of the phenyl ring in **2** apparently give rise to a hydrogen-bond system known for acid salts corresponding to Speakman's type B while the hydrogen bond in **1** would seem to correspond to Speakman's type A. Thus, the effect of the electronegativity of fluorine upon oxygen is apparently less pronounced in **2** than in **1**, in which the aromatic ring exerts a marked $-I$ effect. The acidity could, consequently, be higher and, in agreement with observation, the hydrogen atom would tend more to assume a symmetric position.

In our I.R. investigations of compounds **1** and **2** no bands corresponding to the bending vibration, $O \ldots \overset{\uparrow}{\underset{\downarrow}{H}} \ldots O$, were noted.

The different position of the PO absorption in **1** and **2** may also be rationalized. If the influence of the electronic effects is correctly interpreted, a larger partial moment of this bond and, consequently, lower frequencies should be observed in the case of **2** while the opposite situation would obtain in the case of **1**, involving an unsubstituted phenyl group. The PF frequency in the hydrogen-bonded systems, due to overlap with other bands, cannot be assigned with certainty.

In the I.R. spectrum of the BF_2-bridged complex, **4**, in which hydrogen bonds are absent, only sharp bands were observed. No significant changes in the appearance of the I.R. spectrum of **4** with temperature were noted.

EXPERIMENTAL

The synthesis of compounds, **1–4** is described in literature.[1]

I.R. spectra were recorded on KBr pellets of the compounds, **1** and **4**, on the I.R. spectrometer SPECORD M 80 (CARL ZEISS JENA).

ACKNOWLEDGEMENTS

We are grateful to BASF AG, BAYER AG, CHEMETALL GmbH, and HOECHST AG, for generous supplies of chemicals, and to Fonds der Chemischen Industrie, Frankfurt am Main, for financial support. L. Heuer is indebted to Land Niedersachsen for a maintenance grant.

REFERENCES

1. L. Heuer, P. G. Jones, R. Schmutzler, and D. Schomburg, *New. J. Chem.*, **14,** 891 (1990).
2. U. Ahrens and H. Falius, *Chem. Ber.*, **105,** 3317 (1972).
3. M. W. Smith and M. S. Gordon, *J. Am. Chem. Soc.*, **107,** 1922 (1985).
4. D. Hadzi and S. Detoni, in "Intramolecular Interactions from Diatomics to Biopolymers," ed. B. Pullman; Wiley, Chichester, 1978, p. 224.
5. K. Abu-Dari, K. N. Raymond, and D. P. Freyberg, *J. Am. Chem. Soc.*, **101,** 3688 (1979).
6. K. E. Halvorson, R. D. Willet, and A. C. Massabni, *Chem. Comm.*, **1990,** 346.
7. J. C. Speakman, *Structure and Bonding*, **12,** 141 (1972); Springer Verlag, Berlin.