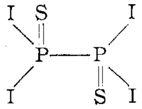
Correspondence

Some Evidence for a New Thioiodide of Phosphorus

Sir:

We wish to report the first structural information on a new[1] unstable thioiodide of phosphorus, $P_2I_4S_2$. The compound is best prepared by prolonged (65 hr.) stirring of a CS_2 solution of the elements in the ratio P:S:2I at room temperature, but it can also be prepared by shaking a CS_2 solution of P_2I_4 with the appropriate quantity of sulfur in a sealed tube until the uptake of sulfur is complete. Both reactions were done in the dark under a dry helium atmosphere, as were subsequent operations such as isolation of the compound, melting point determination, and Nujol mull preparation. Freshly prepared, the compound consists of orange crystals, m.p. 93–94° with decomposition. *Anal.* Calcd. for $P_2I_4S_2$: I, 80.11; S, 10.12. Found (Carius): I, 80.31; S, 10.01. The infrared spectra of Nujol mulls of the freshly prepared compound showed two peaks of approximately equal intensity at 300 and 329 cm.$^{-1}$. We assign the 300 and 329 cm.$^{-1}$ peaks to symmetric and antisymmetric P–I stretching on the basis that the infrared spectrum of P_2I_4, also previously unreported, shows two such peaks at 301 and 329 cm.$^{-1}$ in accord with its C_{2h} molecular symmetry in the solid state.[2] The 725 cm.$^{-1}$ absorption is assigned to P═S stretching by analogy with molecules like $Cl_3P(S)$ and $Br_3P(S)$ which have P═S vibrations[3,4] in the range 718 to 751 cm.$^{-1}$. In conjunction with the analytical data, the infrared spectral evidence indicates the presence of the $P(S)I_2$ group and valence considerations lead to the conclusion that the structure shown below is the most reasonable one.



Supporting evidence comes from the P^{31} n.m.r. spectrum of a CS_2 solution of the freshly prepared thioiodide which shows a singlet at -106 p.p.m. relative to 85% phosphoric acid. This chemical shift is close to the range of -50 to -100 p.p.m. which has been observed for thiophosphoryl compounds,[5,6] and the singlet peak demonstrates that only one type of phosphorus atom is present.

Infrared spectral examination of the thioiodide after storage in the dark in a helium-filled drybox indicated that decomposition had taken place in 2 days or less. After 25 days storage under these conditions the 300 and 329 cm.$^{-1}$ peaks were replaced by a very broad absorption covering the range 294 to 328 cm.$^{-1}$, and new peaks appeared at 228, 243, 387, 404, 413, 428, 441, 465, 481, 522, 545, 669, 678, and 690 cm.$^{-1}$. We have found that PI_3 exhibits a single broad absorption in the range 292 to 328 cm.$^{-1}$, and the remaining peaks have been identified as due to P_4S_7. The infrared spectra of the crystalline phosphorus sulfides, also previously unreported, will be the subject of a future paper. The X-ray powder pattern of the 25-day old material was identical with that of PI_3, and its ultraviolet spectrum in cyclohexane solution showed a band at 5180 Å. characteristic of molecular iodine. The most likely equation representing decomposition is therefore

$$7P_2I_4S_2 \longrightarrow 2P_4S_7 + 6PI_3 + 5I_2$$

The compound is sensitive to ultraviolet and visible light. For instance, irradiation of CS_2 solutions of the thioiodide for 1 hr. with a 20-watt fluorescent daylight lamp caused them to change in color from orange to dark brown (molecular iodine was detected in their ultraviolet spectra), and irradiation of the solid thioiodide for 0.5 hr. caused considerable intensification of the peaks due to decomposition in the infrared spectra.

The thioiodide is hydrolyzed by water with the evolution of H_2S and HI. We are currently investigating this reaction.

Acknowledgment.—The authors wish to thank Dr. J. C. Davis for the n.m.r. data.

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Received February 17, 1964

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[1] While this work was in progress a short note appeared by M. Baudler, G. Fricke, K. Fichtner, and G. Wetter, *Naturwissenschaften*, **50**, 548 (1963), describing the preparation of this compound, but structural data were not given.

[2] Y. C. Leung and J. Waser, *J. Phys. Chem.*, **60**, 539 (1956).

[3] G. Cilento, D. A. Ramsay, and R. N. Jones, *J. Am. Chem. Soc.*, **71**, 2753 (1949).

[4] M. L. Delwaule and F. Francios, *J. chim. phys.*, **46**, 87 (1949).

[5] J. R. Van Wazer, C. F. Callis, J. N. Shoolery, and R. C. Jones, *J. Am. Chem. Soc.*, **78**, 5715 (1956).

[6] R. A. Y. Jones and A. R. Katritzky, *Angew. Chem. Intern. Ed. Engl.*, **1**, 32 (1962).

On the Question of the Hexachlororhenate(III) Ion

Sir:

It has been shown[1-3] that a chlororhenate(III) with empirical formula $CsReCl_4$ actually contains a polynuclear anion, $[Re_3Cl_{12}]^{3-}$, with a cluster of rhenium atoms, whereas Chatt and Rowe[4] have provided indirect but persuasive evidence for the existence

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[1] J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *J. Am. Chem. Soc.*, **85**, 1349 (1963).

[2] W. T. Robinson, J. E. Ferguson, and B. R. Penfold, *Proc. Chem. Soc.*, 116 (1963).

[3] J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *Inorg. Chem.*, **2**, 1166 (1963).

[4] J. Chatt and G. A. Rowe, *J. Chem. Soc.*, 4019 (1962).

TABLE I

ANALYTICAL DATA[a]

Description of substance	K	N	H	Re	Cl	Formulas Proposed in ref. 5	This work
Green octahedra	16.6	...	...	39.3	44.4	K_2ReCl_6	K_2ReCl_6
Yellow crystals	...	...	...	...	43.7	K_3ReCl_6	K_2ReCl_6
K_2ReCl_6 (calcd.)	16.40	...	...	39.0	44.60	...	...
K_3ReCl_6 (calcd.)	22.73	...	...	36.07	41.20	...	...
Green octahedra	...	6.43	1.88	42.9	48.9	$(NH_4)_2ReCl_6$	$(NH_4)_2ReCl_6$
Yellow crystals	...	6.61	1.84	43.1	49.0	$(NH_4)_3ReCl_6$	$(NH_4)_2ReCl_6$
Reddish crystals	...	6.51	1.71	42.6	48.8	...[b]	$(NH_4)_2ReCl_6$
$(NH_4)_2ReCl_6$ (calcd.)	...	6.40	1.84	42.80	48.93	...	...
$(NH_4)_3ReCl_6$ (calcd.)	...	9.26	2.65	41.10	46.99	...	...

[a] All data from Galbraith Analytical Laboratories, Knoxville, Tenn., to whom we are grateful for excellent cooperation. [b] Not mentioned in ref. 5.

of *trans*-$[Re(P(C_2H_5)_2C_6H_5)_3Cl_3]$. It was, therefore, with great interest that we read of the preparation[5] of K_3ReCl_6 and $(NH_4)_3ReCl_6$, since this might be taken to suggest that the polynuclear anion is stable only with larger cations ($r \geqslant r_{Cs}$), while $ReCl_6^{3-}$ is preferred with smaller ones ($r \leqslant r_K$). However, the reported preparations appear to be erroneous.

Using the reaction conditions summarized below, we obtained mixtures of crystals of different colors and habits in good general agreement with the observations of the Russian workers. We believe it safe to assume that we have reproduced the preparative part of their work. We have, however, conclusively established that the crystals which they describe as being the Re(III) complexes K_3ReCl_6 and $(NH_4)_3ReCl_6$ are, in fact, the Re(IV) complexes K_2ReCl_6 and $(NH_4)_2ReCl_6$. Analyses (see Table I) agree much better with these formulas than with those for Re(III) complexes; in the case of the ammonium salt, the nitrogen analysis is conclusively in favor of $(NH_4)_2ReCl_6$.

However, analysis of rhenium complexes is difficult and the results possibly are open to uncertainty. Therefore, other evidence has been obtained. Reflectance spectra (see Fig. 1) of all the compounds are essentially identical with one another and with that of an authentic sample[6] of K_2ReCl_6.

Finally, X-ray powder data on the putative "K_3ReCl_3" and "$(NH_4)_3ReCl_6$" are identical with those for the substances identified as K_2ReCl_6 and $(NH_4)_2ReCl_6$, respectively. In both cases, the patterns can be indexed as cubic and correspond to space group Fm3m with $z = 4$ (the same as $(NH_4)_2PtCl_6$ and K_2PtCl_6). The unit cell edges are 9.82 ± 0.02 and 9.98 ± 0.02 Å. for the K and NH_4 compounds of Re, respectively; these are in good agreement with the values of 9.840[7] and 9.978[8] for the authentic K_2ReCl_6 and $(NH_4)_2ReCl_6$. It would be expected that the analogous Re(III) compounds, having additional cations in the cells, would have appreciably larger lattice parameters, as in the case of Cs_2CoF_6 (a_0 = 8.905 Å.) and Cs_3CoF_6 (a_0 = 9.22 Å.).[9]

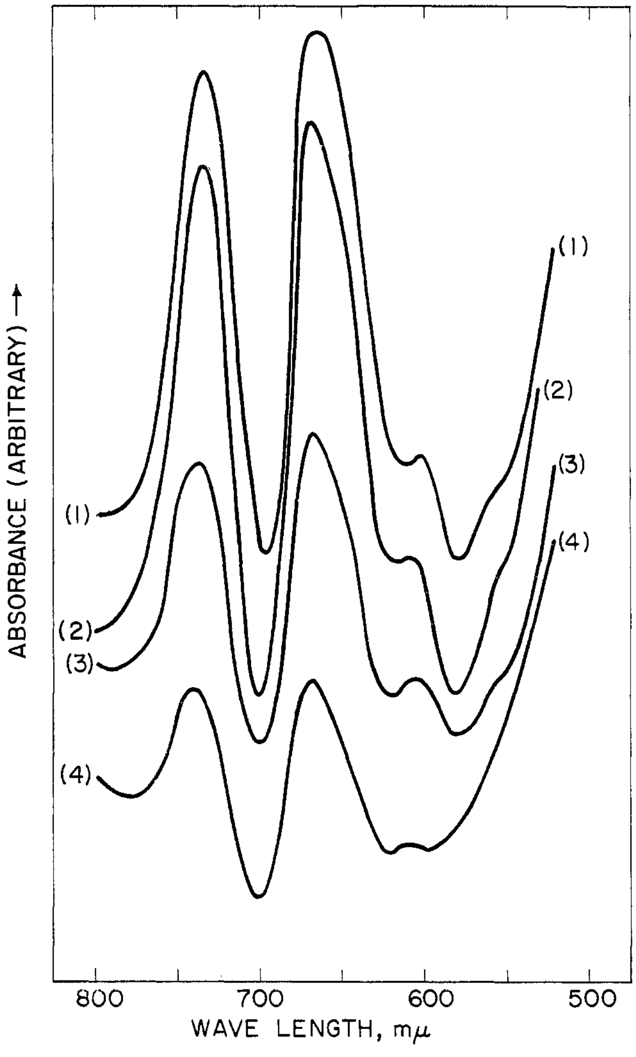

Fig. 1.—Reflectance spectra of $[ReCl_6]^{2-}$ salts from various sources. (1) Authentic sample of K_2ReCl_6. (2) Yellow crystals of $(NH_4)_2ReCl_6$ [identified previously as $(NH_4)_3ReCl_6$]. (3) Green octahedral crystals of $(NH_4)_2ReCl_6$. (4) Large reddish crystals of $(NH_4)_2ReCl_6$.

The growth of K_2ReCl_6 and $(NH_4)_2ReCl_6$ in different habits and different colors in the same reaction vessel is somewhat surprising, but can probably be attributed to growth occurring at different times and hence under different physical and chemical conditions during the preparative procedure.

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(5) V. G. Tronev and S. M. Bondin, *Khim. Redkikh Elementov, Akad. Nauk SSSR*, **1**, 40 (1954).

(6) L. C Hurd and V. A. Reinders, *Inorg. Syn.*, **1**, 178 (1939).

(7) N.B.S. Monograph 25, Section 2, U. S. Department of Commerce, National Bureau of Standards, Washington, D. C., 1963, p. 28.

(8) Measured in this laboratory by J. T. Mague.

(9) R. Hoppe, *Rec. Trav. Chim. Pay Bas*, **75**, 569 (1956).

We conclude that although it may be possible to prepare salts of $[ReCl_6]^{3-}$ under suitable conditions, the existing claim[5] to such a preparation is invalid.

All pressure reactions were carried out in Pyrex glass tubes contained in steel bombs using an autoclave rocking unit.

Ammonium perrhenate (0.02 M) and ammonium chloride (0.04 M) in concentrated hydrochloric acid (40 ml.) were heated for 1.5 hr. with hydrogen at 150° and an initial pressure of 100 atm. The products, large green octahedra, red-brown octahedra, and small yellow crystals, were filtered, washed with concentrated hydrochloric acid and ethanol, and dried under vacuum.

Using identical conditions, potassium perrhenate (0.002 M) and potassium chloride (0.004 M) in concentrated hydrochloric acid (5 ml.) yielded large green octahedra and small yellow crystals.

Acknowledgment. —We are grateful to the U. S. Atomic Energy Commission for financial support.

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RECEIVED FEBRUARY 6, 1964

The Infrared Spectra of Ammines of Cobalt(III) Chloride

Sir:

Use of infrared spectra in the 700–200 cm.$^{-1}$ region to establish the identity of certain thermal decomposition products of $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_5Cl]Cl_2$, and *trans*-$[Co(NH_3)_4Cl_2]Cl$[1] has led to a re-examination of the spectra of these three ammines[2] and a re-evaluation of the assignments previously proposed for absorptions in the CsI region.[3] While our spectral data are in generally good agreement with those of Shimanouchi and Nakagawa,[4] we believe that their conclusions with regard to the Co–X and Co–N stretching vibrations require reconsideration.

In their study of the spectra of $[Co(NH_3)_6]X_3$ ($X = Br^-, I^-$), $[Co(NH_3)_5X]^{2+}$ ($X = F^-, Cl^-, Br^-, I^-$), and *trans*-$[Co(NH_3)_4X_2]^+$ ($X = Cl^-, Br^-$), Shimanouchi and Nakagawa assumed that the NH_3 ligand behaved as a dynamic group. This permitted a normal coordinate analysis of these systems and allowed the mathematical treatment to be that of a seven-body problem. As a result, interactions (coupling) between the low frequency (below 900 cm.$^{-1}$) vibrations of NH_3 and the Co–N skeleton had to be ignored or assumed negligible; this would appear to be an unsupported condition.

With regard to the Co–X stretching mode, Shimanouchi and Nakagawa calculated the following stretching force constants (mdynes/Å.): K(Co–F), 2.00; K(Co–Cl), 1.97; K(Co–Br), 2.53; and K(Co–I), 2.00. For $[Co(NH_3)_5X]^{2+}$ these data require assignment of the Co–X stretching mode as follows: F^-, 504 and 493 cm.$^{-1}$; Cl^-, 487 and 479 cm.$^{-1}$; Br^-, 487 cm.$^{-1}$; and I^-, 428 cm.$^{-1}$. That the Co–X bond order should follow the trend Co–Br, Co–I, Co–Cl[5] is subject to question on the basis of a simple electronegativity argument that is supported by recent nuclear quadrupole resonance studies of metal–halogen complexes[6] and a far-infrared spectral study of tetrahalometalates.[7] Data from the latter reference show that the bond order is not Co–Br, Co–I, Co–Cl, but rather Co–Cl, Co–Br, Co–I as expected. Also, there is no apparent reason for two absorption bands for the single nondegenerate Co–X stretching motion in $[Co(NH_3)_5X]^{2+}$, except the possibility of lattice coupling, in view of the reported crystal structure[8] of $[Co(NH_3)_5Cl]Cl_2$.[9] Recent work[7,10,11] on the Co–Cl stretching mode in $[CoCl_4]^{2-}$ led to assignments which, together with data on Pd–Cl and Pt–Cl stretching motions,[12] lead us to the conclusion that the 290 cm.$^{-1}$ band in $[Co(NH_3)_4Cl_2]Cl$, and the 283 cm.$^{-1}$ band in $[Co(NH_3)_5Cl]Br_2$ and $[Co(NH_3)_5Cl](NO_3)_2$, are due to the Co–Cl stretching vibration. Accordingly, it must follow that the Co–Br and Co–I modes lie below 250 cm.$^{-1}$, which is supported by the recent work of Sabatini and Sacconi.[7]

With regard to the Co–N stretching vibrations, Shimanouchi and Nakagawa assigned the (Co–N) F_{1u} stretching mode in $[Co(NH_3)_6]^{3+}$ at 464 cm.$^{-1}$. Both they and Nakamoto, *et al.*, have published spectra for $[Co(NH_3)_6]I_3$ that are somewhat different,[4,13] and the spectra obtained by the latter for $[Co(NH_3)_6]Cl_3$, $[Co(NH_3)_6]Br_3$, and $[Co(NH_3)_6]I_3$ focus attention on the crystal structure of each complex and the three weak bands at 450–500 cm.$^{-1}$. The chloride and bromide are monoclinic and the iodide is cubic.[14] The space group for the iodide is O_h^5-$F4/m\bar{3}2/m$, with $Z = 4$. Hence the Co^{3+} ion in $[Co(NH_3)_6]^{3+}$ resides at a lattice site of O_h symmetry, and therefore the selection rules operative are those associated with the O_h point group.[15–17] Thus, if the three weak bands observed for the chloride and bromide are the com-

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(1) G. W. Watt, *Inorg. Chem*, **3**, 325 (1964).

(2) Measured as Nujol mulls using a Beckman IR-7 infrared spectrophotometer in conjunction with a Beckman long wave length (CsI) interchange.

(3) For review and references see: K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, pp. 143–151.

(4) T. Shimanouchi and I. Nakagawa, *Spectrochim. Acta*, **18**, 89 (1962).

(5) The Co–F case is not compared in view of its recognized anomalous behavior.

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(8) Y. Shigeta, Y. Komiyama, and H. Kuroya, *Bull. Chem. Soc. Japan*, **36**, 1159 (1963).

(9) Crystalline $[Co(NH_3)_5Cl]Cl_2$ is orthorhombic, having a CaF_2-type lattice. The space group is Pnma-D_{2h}^{16}, with $Z = 4$, thus placing the $[Co(NH_3)_5Cl]^{2+}$ in general positions.

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