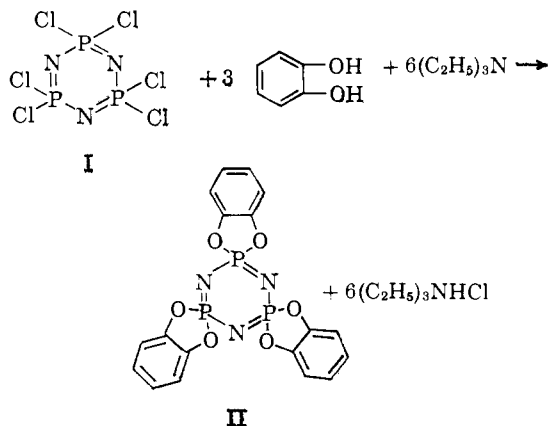in tetrahydrofuran to yield tris(o-phenylenedioxy)-phosphonitrile trimer (II). Polymers and an unusual salt-like by-product (III) were also formed in this reaction.

I

II

The arylphosphonitrilate (II) is a white, crystalline solid, m.p. 244–245°, which sublimes without appreciable decomposition at 230° (0.05 mm.). *Anal.* Calcd. for $C_{18}H_{12}N_3O_6P_3$: C, 47.0; H, 2.63; N, 9.15; P, 20.3. Found: C, 46.85; H, 2.85; N, 9.16; P, 20.3. The molecular weight was shown by mass spectrometry to be 459. This compound appears to be less stable to thermal rearrangement than the hexaphenoxy analog, $[NP(OC_6H_5)_2]_3$,[6] and this behavior undoubtedly reflects a release of steric strain in ring cleavage reactions of II.

The by-product (III) was also formed quantitatively when II was treated with 6 equivalents of catechol and 3 equivalents of triethylamine in toluene. The evolution of ammonia in this reaction indicated an unusual cleavage of the phosphorus–nitrogen ring system. Treatment of III with strong base yielded triethylamine and phenolic residues. *Anal.* Calcd. for $C_{24}H_{28}NO_6P$ (III) after purification by sublimation: C, 63.0; H, 6.17; N, 3.06; P, 6.79. Found: C, 62.8; H, 6.32; N, 3.16; P, 6.95. Infrared spectra of the solid indicated the presence of the groups: NH (3200 cm.[-1]), o-substituted aryl (1600, 1500, 1100, 1060, 1040, and 750 cm.[-1]), O-aryl (1250 cm.[-1]), and O–P–O (830 and 735 cm.[-1]). The ultraviolet spectrum of this material in acetonitrile solution was similar to that of II but was displaced 15 mμ toward the visible. The λ_{max} and log ε values (in parentheses) for III were 290 mμ (sh) (4.07), 284 mμ (4.17), 280 mμ (sh) (4.14), and 227 mμ (sh) (4.17). A mass spectrum of this product at 300° showed considerable fragmentation, but triethylamine was identified as one of the species formed. X-Ray powder diffraction patterns were consistent with a hexagonal, two-molecule unit cell, in which each unit had a molecular weight of 457. The n.m.r. spectra of this material in dimethylformamide indicated a methyl to phenyl proton ratio of 3 to 4.

This evidence suggests that possible structures for this compound are those depicted in IIIa and IIIb.

IIIa　　　　　　　　　　　　IIIb
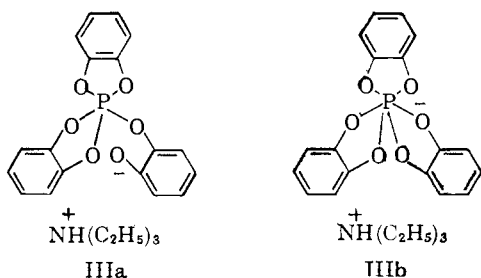
The ultraviolet spectrum indicates that structure IIIa predominates in solution. However, structure IIIb appears to exist in the crystalline state. The X-ray and infrared evidence can be correlated with the high symmetry of this form. The strong, sharp NH peak (3200 cm.[-1]) is indicative of a larger charge separation than would be expected for structure IIIa. This is consistent with steric shielding of the negatively charged site in a similar manner to that demonstrated for the tetraphenylborate ion.[11] The observed stability of the solid salt is also more compatible with structure IIIb than with the triethylamine salt of a phenol.

Other examples of hexavalent phosphorus anions have been restricted to the $(PF_6)^-$ ion and the $(PCl_6)^-$ ion in phosphorus pentachloride.[12] The unique structure and stability of IIIb in the solid state can be attributed to the fact that the sterically hindered counter-ions are separated in the crystal lattice. Under these circumstances, the negative charge can be stabilized more readily on phosphorus than on oxygen.

(11) P. Chevalier and C. Sandorfy, *Can. J. Chem.*, **38**, 2524 (1960).

(12) J. R. Van Wazer, "Phosphorus and Its Compounds," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1958, pp. 238 and 805.

CHEMICAL DEPARTMENT　　　　　　　　　　　H. R. ALLCOCK
CENTRAL RESEARCH DIVISION
AMERICAN CYANAMID COMPANY
STAMFORD, CONNECTICUT

Tetrahedral Tetrachlorocopper(II) Complex in Molten Salt Solutions

Sir:

The absorption spectra of solutions of copper(II) chloride in melts of cesium chloride and tributyl-2,4-dichlorobenzylphosphonium chloride (Phosphon[1]) indicate the presence of tetrahedral, or mildly distorted tetrahedral, $CuCl_4{}^{2-}$ complexes. The importance of this result lies in the fact that only a few examples of tetrahedral, or distorted tetrahedral, copper(II) complexes are known,[2,3] and of these only the distorted bromo complex has been found previously[3] in liquid solutions. Tetracoordinated chlorocopper(II) complexes have been reported to occur in liquid solvents with excess chloride ions,[4] but a comparison of their spectra with those reported below shows that they are not tetrahedral.

Measurements were made with a Cary Model 14H spectrophotometer over the wave number range of 4000–27,000 cm.[-1]. Copper(II) chloride when dissolved in molten Phosphon at 128° was found to have a d–d band at 8000 cm.[-1] with a molar extinction coefficient, ε, of 79 l./mole-cm. and the lowest energy charge-transfer band at 22,200 cm.[-1] (ε = 732 l./mole-cm.). In molten cesium chloride as solvent the d–d band was also at 8000 cm.[-1] (ε = l./mole-cm.), while the lowest-energy charge-transfer band was a shoulder

(1) Kindly donated by the Virginia-Carolina Chemical Co.

(2) (a) L. Helmholz and R. F. Kruh, *J. Am. Chem. Soc.*, **74**, 1176 (1952); (b) E. Prince, *Acta Cryst.*, **13**, 544 (1957); (c) B. Morosin and E. C. Lingafelter, *ibid.*, **13**, 807 (1960); (d) B. Morosin and E. C. Lingafelter, *J. Phys. Chem.*, **65**, 50 (1961); (e) D. M. Adams, J. Chatt, J. M. Davidson, and J. Gerratt, *J. Chem. Soc.*, 2189 (1963).

(3) J. C. Barnes and D. N. Hume, *Inorg. Chem.*, **2**, 444 (1963).

(4) See, for example: (a) J. Bjerrum, *Dan. Mat. Fys. Med.*, **22**, No. 18 (1946); (b) J. Bjerrum, C. J. Ballhausen, and C. K. Jørgensen, *Acta Chem. Scand.*, **8**, 1275 (1954); (c) C. J. Ballhausen, *Dan. Mat. Fys. Med.*, **29**, No. 4 (1954); (d) N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

near 24,600 cm.$^{-1}$ ($\epsilon \sim 775$ l./mole-cm.). No other maxima or shoulders indicative of other d–d bands were found, but the 8000-cm.$^{-1}$ band was broad and could possibly encompass unresolved components.

These spectra are attributed to tetrahedral, or mildly distorted tetrahedral, $CuCl_4{}^{2-}$ on the basis of a comparison of the position of the d–d band with the d–d band of crystalline $Cs_2CuCl_4{}^5$ at 9000 cm.$^{-1}$ and that of copper(II)-doped $Cs_2ZnCl_4{}^5$ at 8300 cm.$^{-1}$. The band energy shifts toward lower values with decreasing distortion of the $CuCl_4{}^{2-}$ complex, and presumably the $CuCl_4{}^{2-}$ complex in the melts is less distorted than in the crystals.

These results may be rationalized in terms of ligand field theory.[6] In the limit of no distortion from T_d symmetry, the 8000-cm.$^{-1}$ band of $CuCl_4{}^{2-}$ would be assigned to the $\Gamma_7(^2D_{5/2}) \rightarrow \Gamma_8(^2D_{3/2})$ transition with a Dq value of about 700 cm.$^{-1}$ when the spin–orbit coupling parameter is chosen to have the free-ion value of -830 cm.$^{-1}$. Only one other d–d band is expected for T_d symmetry, $\Gamma_7(^2D_{5/2}) \rightarrow \Gamma_8(^2D_{5/2})$. This band will occur far into the infrared region at about $-(3/2)\lambda - (3/20)\lambda^2/Dq$. The above tetrahedral Dq value of 700 cm.$^{-1}$ may be compared with the Dq for octahedral $CuCl_6{}^{4-}$ in copper(II)-doped $CsCdCl_3$.[7] The latter substance has a broad absorption at about 12,400 cm.$^{-1}$ which, in terms of octahedral symmetry, is reasonably assigned to the $\Gamma_8(^2D_{5/2}) \rightarrow \Gamma_7(^2D_{5/2})$, $\Gamma_8(^2D_{3/2})$ transitions with a Dq of -1250 cm.$^{-1}$. This gives $|Dq_{tet}/Dq_{oct}| = 0.56$ for chlorocopper(II) complexes. The corresponding ratio for chloronickel(II) complexes[8] is about 0.6. The $CuCl_4{}^{2-}$ complex observed in CsCl and Phosphon melts may be somewhat distorted from regular tetrahedral symmetry so that the above assignment and numerical value of the ligand field parameters have only an approximate significance. Karipides and Piper[9] have assigned the spectrum of Cs_2CuBr_4 in terms of subcubic symmetry species, but $CuCl_4{}^{2-}$ in melts is almost certainly much less distorted than $CuBr_4{}^{2-}$ in Cs_2CuBr_4.

The lowest energy charge-transfer band in crystalline Cs_2CuCl_4 is reported[2a] at about 24,000 cm.$^{-1}$, in agreement with the molten salt spectra. A similar band of $CuBr_4{}^{2-}$ has been assigned by Braterman[10] in a reasonable way to an electron jump from a nonbonding ligand orbital into a d-type orbital. Assignments of higher energy charge-transfer bands using Braterman's model are open to question, since he neglects electron jumps which originate in d-orbitals and terminate in antibonding orbitals.

Previous studies have been made of the spectrum of $CuCl_2$ dissolved in the LiCl–KCl eutectic melt[7,11,12] and it was proposed that this spectrum is that of tetrahedral $CuCl_4{}^{2-}$. However, the maximum of the d–d absorption was found at 9500 cm.$^{-1}$ so that if the tetrachloro complex is present in this system, it must be extremely distorted.

(5) W. E. Hatfield and T. S. Piper, to be published.

(6) A. D. Liehr, J. Phys. Chem., 64, 43 (1960).

(7) D. M. Gruen and R. L. McBeth, "Coordination Chemistry," Butterworth and Co., London, 1963, pp 23–47.

(8) Based on an analysis of the spectrum of Ni(II)-doped CsCdCl₃ in reference 7 and the Dq value for Ni(II)-doped Cs₂ZnCl₄ from H. A. Weakliem, J. Chem. Phys., 36, 2117 (1962).

(9) A. G. Karipides and T. S. Piper, Inorg. Chem., 1, 970 (1962).

(10) P. S. Braterman, ibid., 2, 448 (1963).

(11) G. Harrington and B. R. Sundheim, Ann. N. Y. Acad. Sci., 79, 950 (1960).

(12) D. M. Gruen and R. L. McBeth, Nature, 194, 468 (1962).

(13) Operated for the U. S. Atomic Energy Commission by Union Carbide Corp.

METALS AND CERAMICS DIVISION   G. PEDRO SMITH
OAK RIDGE NATIONAL LABORATORY[13]   TREVOR R. GRIFFITHS
OAK RIDGE, TENNESSEE

Spin Exchange in Solutions of Potassium Naphthalenide

Sir:

We have studied the spin exchange interaction as a function of radical concentration and temperature in dilute solutions of potassium naphthalenide in tetrahydrofuran (THF) through observation of the breadths of hyperfine components in the electron spin resonance (e.s.r.) absorption spectrum. At relatively high concentrations of free radical and temperatures the line breadths vary nearly linearly with radical concentration. In contrast to the case of $K_2NO(SO_3)_2$ dissolved in water,[1] this linear relationship extrapolates through the origin without application of a correction factor. It seems likely that the contributions of spin exchange and other factors to the line breadth are not simply additive in the naphthalenide–THF system. As for $K_2NO(SO_3)_2$ in water we observe that line shapes deviate from Lorentzian at low concentrations of radicals. The lower the temperature, the higher the concentration at which deviation from the Lorentzian shape is first noticed. At 0.39×10^{-3} M the lines observed are nearly gaussian even at room temperature.

The second-order rate constants derived from the slopes of the line width vs. concentration plots vary from 2.8×10^9 l. mole^{-1} sec.$^{-1}$ at 20° to 1.1×10^9 l. mole^{-1} sec.$^{-1}$ at $-60°$. The rate constant varies linearly with kT/η, where η is the viscosity of the solvent above $-30°$, and the plot extrapolates through the origin within experimental uncertainty. This indicates that exchange takes place at every appropriate collision.[2] Thus, the rate constants given above are approximately half the rate constants for bimolecular encounters between the free-radical molecules.

If spin exchange is the dominant mechanism of line broadening, different hyperfine lines should broaden at different rates as in the case of electron exchange between radical ion and parent hydrocarbons.[3] A sensitive method of detecting line breadth changes within a spectrum is to compare the amplitudes of the derivative curves of the lines. A variation in line breadth shows up as a deviation of the ratio of amplitudes from that calculated on the basis of equal breadths.

A comparison between experimental and theoretical amplitude ratios is given in Table I for a 1.35×10^{-3} M solution at 40 and 0°. The agreement between experimental and theoretical values is seen to be excellent at 40° while at 0° considerable deviation is noted. We interpret this to mean that spin exchange almost completely determines the line width at 40°, but only contributes to the breadth at 0° in this solution.

TABLE I

DERIVATIVE CURVE AMPLITUDE RATIOS[a]

2	9[b]	11.77[c]	11.8[d]	10.3[e]
3	6[b]	7.75[c]	7.87[d]	6.77[e]
11	1.5[b]	1.67[c]	1.65[d]	1.53[e]

[a] The ratios are of the amplitude of the line 13 in the naphthalenide spectrum to that of the line whose number is given in the first column. The lines are numbered in succession from high field to low field. [b] Ratios calculated on the basis of equal line widths. [c] Ratios calculated on the basis that spin exchange determines the line widths completely. [d] Experimental ratios at 40° for a 1.35×10^{-3} M solution. [e] Same as footnote d except at 0°

(1) M. T. Jones, J. Chem. Phys., 38, 2892 (1963).

(2) (a) J. D. Currin, Phys. Rev., 126, 1995 (1962); (b) D. Kivelson, J. Chem. Phys., 33, 1094 (1960); (c) G. E. Pake and T. R. Tuttle, Jr., Phys. Rev. Letters, 3, 423 (1959).

(3) P. J. Zandstra and S. I. Weissman, J. Chem. Phys., 35, 757 (1961).