tronic absorption spectrum which was measured from 9090 to 37,800 cm^{-1}. Benzene was used in the visible region since this solvent was used for all other solution measurements. 1,2-Dichloroethane was used to record the entire spectrum. Table II summarizes

TABLE II

ELECTRONIC ABSORPTION SPECTRA OF FeCl$_3 \cdot$C$_4$H$_8$O

Solvent	Concn,^{a} M	$\bar{\nu}_{max}$, cm^{-1}	ϵ_{max},^{b} M^{-1} cm^{-1}
Benzene	7.21 × 10^{-2}	14,900	2.38
		16,700 sh	
		17,100	2.74
1,2-Dichloroethane	5.95 × 10^{-2}	14,900	1.64
		16,700 sh	
		17,100	
		18,300 sh	
		19,400	1.83
		21,000 sh^c	
1,2-Dichloroethane	3.22 × 10^{-5}	28,900	6880

^{a} These are formal concentrations of iron(III). ^{b} The ϵ values were calculated without consideration of the increasing absorption due to a charge-transfer band on which all the d–d transitions are superimposed. ^{c} The 21,000-cm^{-1} shoulder was observed for a solution qualitatively diluted to a concentration between 4 × 10^{-3} and 1 × 10^{-2} M.

these data. All bands found between 9090 and 21,000 cm^{-1} are believed to be La Porte and spin-forbidden transitions from the sextet ground state of the spin-free d^5 configuration to excited quartet states. Assignments on the basis of a four-coordinate structure of C_{3v} symmetry are not made in more detail due to the fact that the complex is involved in concentration-dependent association. If it is assumed that only monomers and dimers are present in solution, the molecular weight data indicate that at 5.95 × 10^{-2} m, the mole fraction of monomer is 0.92. This would give a ratio of [Fe]$_{mon}$/[Fe]$_{dim}$ = 6.0, where [Fe]$_{mon}$ is the formal concentration of Fe in monomer and [Fe]$_{dim}$ is the formal concentration of Fe in dimer. Thus, assuming equimolar absorptivities for Fe in each form, the ratio of absorbances A_{mon}/A_{dim} is ~6.0. Therefore, some of the observed shoulders in the absorption spectrum could be due to dimer absorption. It should be noted that there are no data which rule out association beyond the dimeric form. Calculation assuming the presence of only monomers and trimers gives an absorbance ratio of ~7.4 monomers to 1 trimer, assuming equal molar absorptivities. Thus, the greater the degree of association in solution, the more likely it is that the bands are due to monomer. An intense charge-transfer band is observed at 28,900 cm^{-1} in 1,2-dichloroethane. The benzene solution shows the beginning of a charge-transfer band at considerably lower energy than the 1,2-dichloroethane solution, thus making observation of the ligand field bands difficult. The coincidence of the bands at 14,900, 16,700, and 17,100 cm^{-1} may indicate that the same solute structure exists in both solvents. A sketch of the 1,2-dichloroethane spectrum is shown in Figure 2.

Magnetic susceptibility measurements made in a benzene–cyclohexane solution show that at low concentrations the iron(III) has a spin-free d^5 ground state. Seven measurements over a concentration range of 1.90 × 10^{-2}–4.81 × 10^{-2} M give an average value for μ_{eff} of 5.79 ± 0.03 BM.

In summary, the complex FeCl$_3 \cdot$C$_4$H$_8$O has been

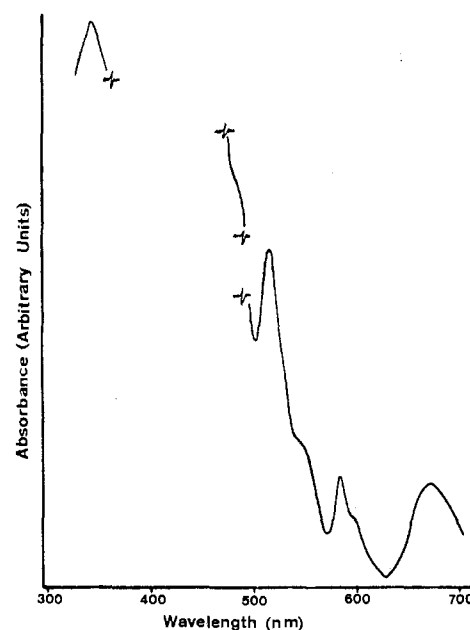

Figure 2.—Electronic spectrum of FeCl$_3 \cdot$C$_4$H$_8$O in 1,2-dichloroethane showing six d–d transitions and one charge-transfer transition.

prepared and shown to contain O-coordinated THF. The complex is monomeric in benzene at low concentrations but associates as the concentration increases. The structure appears to be the same in benzene and 1,2-dichloroethane solutions, and all measurements are consistent with a four-coordinate, high-spin iron(III) complex.

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## An Adduct of Tetracyanoethylene and Triphenylphosphine

BY JOHN E. DOUGLAS

Tetracyanoethylene (TCNE) is a well-known electron acceptor and triphenylphosphine (TPP) is a well-known donor. It would appear reasonable that adduct formation should occur between them. However, as Shine and Gordon[1] have pointed out, "in studies of complexes between TCNE and heteroatomic donors by spectral methods most workers report other reactions which make complex detection difficult." Our experience with the TCNE–TPP system has been no different. Reported here is the preparation and characterization of a solid TCNE–TPP adduct and also a brief account of the solution behavior of these substances and other bases related to TPP.

A 2:1 TCNE–TPP adduct has been prepared by Reddy and Weis[2] for which they propose the structure

(1) H. J. Shine and R. J. Gordon, *J. Org. Chem.*, **35**, 949 (1970).
(2) G. S. Reddy and C. D. Weis, *ibid.*, **28**, 1822 (1963).

I. The compound which we report will be shown to be (TCNE·TPP)$_2$ and is distinctly different from I.


I
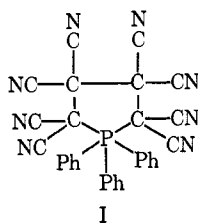
Preparation and Characterization

The adduct is a dark red solid prepared by mixing TPP and TCNE in ether under the conditions specified in the Experimental Section. The visible spectrum shows an intense maximum at 495 nm.

Elemental analysis of the product corresponds closely to that of an equimolar TCNE–TPP adduct. The experimental molecular weight of 758 compares to 781 calculated for (TCNE·TPP)$_2$, which is taken to be the molecular formula of the compound.

Infrared Spectrum and Structure.—TCNE has been shown to interact with electron donors in several different ways and the infrared spectrum provides a useful diagnostic test. This is discussed by Stanley, *et al.*,[3] and by Baddley.[4] Uncomplexed TCNE shows two C≡N frequencies, reported at 2237 and 2250 cm^{-1} [5] or at 2228 and 2260 cm^{-1}.[6] In our adduct ν(C≡N) appears as a single frequency at 2189 cm^{-1}. Rettig and Wing[7] pointed out that a single C≡N stretching vibration is observed at 2220 cm^{-1} in adducts of TCNE with certain organometallic compounds of Pt, Pd, Rh, Cr, and Ir. These all have a structure of the type II. They stated that the exhibition of this

II
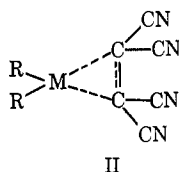
single C≡N vibration is diagnostic of this type structure. This leads us to believe that our adduct also has this structure. Cobaltocene[8] and dibenzenechromium[9] form compounds with TCNE that also show a single C≡N frequency at 2190 cm^{-1}, essentially identical with that in our adduct. Other evidence suggests that these compounds contain the TCNE$^-$ anion radical. The single C≡N frequency which is observed in our compound is evidence for a structure like II, while its appearance at a lower frequency is consistent with that expected if there is a large shift of negative charge to TCNE.

Other modes of TCNE interaction lead to a different behavior for ν(C≡N) and can thereby be discounted as possibilities for our adduct. In K$^+$TCNE$^-$ ν(C≡N)

(3) J. Stanley, D. Smith, B. Latimer, and J. P. Devlin, *J. Phys. Chem.*, **70**, 2011 (1966).
(4) W. H. Baddley, *Inorg. Chim. Acta Rev.*, 7 (1968).
(5) T. Takenaka and S. Hayashi, *Bull. Chem. Soc. Jap.*, **37**, 1216 (1964).
(6) F. A. Miller, O. Sala, P. Devlin, J. Overend, E. Lippett, W. Lueder, H. Moser, and J. Varchmin, *Spectrochim. Acta*, **20**, 1233 (1964).
(7) M. F. Rettig and R. M. Wing, *Inorg. Chem.*, **8**, 2685 (1969).
(8) R. L. Brandon, J. H. Osiecki, and A. Ottenberg, *J. Org. Chem.*, **31**, 1214 (1966).
(9) J. W. Fitch III and J. J. Lagowski, *Inorg. Chem.*, **4**, 864 (1965).

appears as a doublet which is red shifted to 2180–2201 cm^{-1}.[3] When TCNE bonds *via* the nitrile nitrogen, ν(C≡N) appears either as three strong peaks and one weak peak[7] or as a single peak with a shoulder.[10] Coordination at a nitrile nitrogen might also be expected to cause the appearance of ν(C=C) which is absent for symmetry reasons in the spectrum of TCNE. This does appear in the spectrum of K$^+$TCNE$^-$ red shifted 198 cm^{-1} from its position in the Raman spectrum of TCNE[3] and has been attributed to coordination of K$^+$ with a nitrile nitrogen in TCNE$^-$.[7] In the spectrum of our adduct, nothing was observed in this region that could not reasonably be attributed to TPP.

The structural environment of the phosphorus can also be inferred from the infrared spectrum. Reddy and Weis[2] reported that a trio of bands from 13.3 to 14.5 μ is characteristic of five-coordinate aromatic phosphonium compounds. We observed such a trio at 685, 716, and 742 cm^{-1}. For comparison, the spectrum of cyclopropyltriphenylphosphonium bromide was run. It shows a trio quite similar in appearance at 683, 716, and 756 cm^{-1}.

Other Structural Information.—The conductivity in dichloromethane shows that the compound is nonionic. The nmr spectrum of the adduct in CDCl$_3$ shows that the fine structure of the phenyl hydrogen resonances is missing and there is a general broadening but no shifts or new resonances are observed. The visible spectrum of the solid adduct in dichloromethane shows an intense maximum at 495 nm, compared with that of 470 nm when dichloromethane solutions of TCNE and TPP are mixed directly, as will be described below.

Structural Conclusions.—The structure of the adduct must conform to the principal structural features proposed above. It is a nonionic compound with the formula (TCNE·TPP)$_2$. The phosphorus is five-coordinated across the carbons of the TCNE molecule and with transfer of charge to TCNE. A structure consistent with these characteristics is III.

III
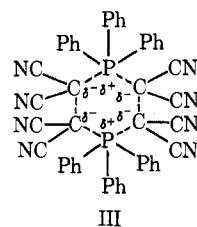
Other Related Bases.—We attempted to prepare a tetracyanoethylene–tributylphosphine adduct by the same technique which was used to prepare the TPP adduct. A heavy, noncrystallizable oil formed. The infrared spectrum shows a single (C≡N) frequency at 2205 cm^{-1} with a small shoulder at 2175 cm^{-1}. No product could be isolated from the interaction of TCNE with triphenylarsine or triphenylstibine although color changes in solution indicated an interaction of some sort.

Solution Behavior of the TCNE–TPP System

The TCNE–TPP system was studied extensively in

(10) J. S. Ricci, J. A. Ibers, M. S. Fraser, and W. H. Baddley, *J. Amer. Chem. Soc.*, **92**, 3489 (1970).

dichloromethane by spectrophotometric methods. The addition of a TPP solution to a dilute solution of TCNE leads to the formation of an intense absorption maximum at 470 nm which may take several minutes to reach its maximum value. (The initial rate is approximately first order in TPP and erratic with respect to TCNE.) The intensity then diminishes slowly and other maxima slowly appear. A peak is also formed at 420 nm when lower concentrations of both reagents are used; this peak is also favored when TCNE is used which has not been freshly resublimed. This species is identified as TCNE⁻ following the arguments of Isaacs.[11] The succession of spectral changes is similar to that observed for TCNE and aromatic amines by Rappoport,[12] who suggested initial complex formation followed by rearrangement. In our case, however, the slow rate of formation suggests that the product is not formed by a direct donor–acceptor interaction. The suggestion that the species absorbing at 420 nm must be a precursor to the species at 470 nm was disproved by study of the succession of spectral changes. Tri-*m*-tolylphosphine and tri-*p*-tolylphosphine displayed the same solution behavior as triphenylphosphine. Tri-*o*-tolylphosphine failed to react, suggesting steric inhibition from the ortho methyl group.

Experimental Section

The adduct may be prepared by adding 1 ml of a saturated solution of TCNE in benzene to 50 ml of a rather concentrated solution of TPP in diethyl ether. The addition is carried out very slowly from a small syringe while stirring vigorously. A dark red solid forms within a few minutes. It is quite soluble in organic solvents, including dichloromethane and acetone. The method of adding TCNE is quite critical. If the preparation is done with solid TCNE present or by the rapid addition of TCNE solution, the product shows an additional pair of absorption maxima at 395 and 417 nm. These correspond to the maxima reported at 399 and 418 nm for the pentacyanopropenide ion.[13]

Tetracyanoethylene and phosphines were obtained from Eastman. Cyclopropyltriphenylphosphonium bromide was obtained from Aldrich Chemical Co. Purification of reagents and exclusion of the atmosphere appeared to be unimportant in preparation of the solid adduct. In solution studies TCNE was always freshly resublimed under vacuum and triphenylphosphine was recrystallized from ethanol. The solvent was freshly distilled under nitrogen. Solutions were used fresh, kept in stoppered vessels, and transferred *via* syringe, and contact with the atmosphere was minimized at all times. A few experiments done under a nitrogen blanket gave results that were unchanged.

Infrared spectra were obtained from KBr pellets and mineral oil mulls on a Beckman IR-20 spectrophotometer. Visible–uv spectra were obtained on Beckman DK-2 and Cary 14 instruments.

Anal. Calcd for (TCNE·TPP)₂: C, 73.8; H, 3.8; N, 14.4; P, 7.9. Found: C, 73.47; H, 3.95; N, 14.18; P, 7.74.

Molecular weight was determined by Galbraith Laboratories by vapor pressure osmometry in CHCl₃.

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(12) Z. Rappoport, *ibid.*, 4468 (1963); Z. Rappoport and A. Horowitz, *ibid.*, 1348 (1964).
(13) W. J. Middleton, E. L. Little, D. D. Coffmand, and V. A. Engelhardt, *J. Amer. Chem. Soc.*, **80**, 2778 (1958).

A Spectroscopic Study of IF₇ and IF₆ in Anhydrous Hydrogen Fluoride

BY MORLEY BROWNSTEIN AND HENRY SELIG*

The vibrational spectra of IF₇ were first examined by Lord, *et al.*,[1] but it was later shown that their samples contained IOF₅ impurity.[2] More recently Claassen, *et al.*, have carried out a detailed examination of the gas-phase vibrational spectra.[3] As the Raman spectrum of IF₅ showed considerable frequency shifts and intensity changes on going from the gas to liquid phase,[4] it was felt worth reinvestigating the liquid-phase spectra of IF₇ to compare with the gas-phase observations.

Adducts of IF₇ with fluoride acceptors were first prepared by Seel and Detmer, who proposed an ionic structure $IF_6{}^+MF_6{}^-$.[5] Christe and Sawodny confirmed the ionic nature of $IF_6{}^+AsF_6{}^-$ by vibrational spectroscopy and showed that the cation has octahedral symmetry.[6] Their assignments were recently supported by polarization measurements on the Raman spectrum of $IF_6{}^+AsF_6{}^-$ in anhydrous hydrogen fluoride.[7] A Mössbauer study of $^{129}IF_6{}^+AsF_6{}^-$ has also confirmed the octahedral symmetry of the cation.[8] No quadrupole coupling was observed in the Mössbauer spectrum at 90°K.

Two broad-line nmr studies of solid $IF_6{}^+AsF_6{}^-$ have also been reported. The ¹⁹F, ⁷⁵As, and ¹²⁷I resonances have all been observed at room temperature.[9] The ¹⁹F spectrum at a 4-kG field strength features two broad overlapping peaks. A more detailed study at frequencies up to 94.1 MHz showed resolved peaks for F in $AsF_6{}^-$ and F in $IF_6{}^+$.[10]

In this paper we present the results of a Raman study of IF₇, as a liquid and dissolved in HF, and the ¹⁹F nmr spectrum of $IF_6{}^+$ in HF. The Raman spectrum of $IF_6{}^+AsF_6{}^-$ in HF has already been reported,[7] so no further work was carried out on it. The nmr of IF₇ in HF was not investigated because of the extreme broadness of the IF₇ resonance (>5000 Hz).[11]

Experimental Procedures

The IF₇ was prepared as described previously.[3] Infrared spectra showed only traces of HF present with no other impurities. Arsenic pentafluoride (Ozark-Mahoning) was used without further purification. All manipulations were carried out in an all-Monel vacuum line seasoned with chlorine trifluoride except for handling of hydrogen fluoride which was transferred in a Kel-F line. Hydrogen fluoride was purified as previously described.[12]

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(12) J. Shamir and A. Netzer, *J. Sci. Instrum.*, **1**, 770 (1968).