71. *Preparation and Electronic Spectra of some Tetrahedral Complexes of Iron*(II).

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The preparations of the complexes FeL_2X_2, where L = Ph_3AsO or quinoline and X = Cl or Br, are reported. Tetraethylammonium tetraisocyanatoferrate(II) has also been made, but could not be obtained pure. *X*-Ray isomorphism studies show that the neutral complexes, and also the previously known analogous compounds with triphenylphosphine oxide, have essentially tetrahedral structures. The electronic spectra of both the anionic and neutral complexes show a strong band in the region 4500—5500 cm.$^{-1}$. These results are discussed in terms of ligand fields of C_{2v} symmetry for the neutral complexes, and of T_d symmetry for the tetraisocyanatoferrate(II) ion.

ALTHOUGH there has recently been considerable interest in tetrahedral complexes of first-row transition metals, those of iron(II) have received very little attention. Tetrahedral structures have been reported for the tetrahalogenoferrate(II) ions [1] and the tetraisothiocyanatoferrate(II) ion.[2] The compounds $Fe(Ph_3P)_2X_2$, where X = Cl, Br, or I, have been described,[3] and it was suggested that these compounds also contained tetrahedrally co-ordinated iron(II), although no firm evidence to support this conclusion was adduced. In order to provide more information about the readiness of iron(II) to form tetrahedral complexes, we have prepared and studied several compounds with a tetrahedral structure. These are listed in Table 1, together with values for their electronic spectra. Most of the complexes are of the type FeL_2X_2, where L = Ph_3AsO, Ph_3PO, or quinoline, and X = Cl or Br, and we shall discuss these compounds first.

TABLE 1.

Electronic absorption spectra of tetrahedral complexes of iron(II).

Compound	State	Absorption max. (cm.$^{-1}$) (ε_{molar} for soln.)	Compound	State	Absorption max. (cm.$^{-1}$) (ε_{molar} for soln.)
$[Et_4N]_2[FeBr_4]$	Solid † (mull)	~3000	$Fe(Ph_2MeAsO)_2Br_2$	Solid	5100
$[Et_4N]_2[Fe(NCO)_4]$	Solid	~5000br *	$Fe(Ph_3PO)_2Cl_2$	Solid	4550
$Fe(Ph_3AsO)_2Cl_2$ ...	Solid	5000	$Fe(Ph_3PO)_2Br_2$	Solid	4500
$Fe(Ph_3AsO)_2Br_2$ ...	Solid	4700	$Fe(C_9H_7N)_2Cl_2$	Solid	5500
	$CHCl_3$ (0·106M)	5000 (48)	$Fe(C_9H_7N)_2Br_2$	Solid	~5100br

* Obscured to a certain extent by C–N vibrational overtones. † By reflectance unless stated otherwise.

On mixing solutions of ferrous chloride, or ferrous bromide, and triphenylarsine oxide in solvents such as acetone or ethanol, crystalline complexes of the composition $Fe(Ph_3AsO)_2X_2$ were readily formed. The solvents used were de-oxygenated and the preparations were carried out under nitrogen, but the solid complexes appear to be quite stable to aerial oxidation; the chloro-complex was unchanged after two years' storage. It was found that the presence of water interfered with the preparation of the bromo-complex. Unless precautions were taken to remove the water, the solid products showed inconsistent analyses, and spectral properties that were quite different from those of dibromobis(triphenylarsine oxide)iron(II), although they were very similar to this compound in appearance.

The analogous complexes with triphenylphosphine oxide have been reported previously,[4]

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[1] Gill, *J.*, 1961, 3512.

[2] Forster and Goodgame, *J.*, 1965, 268.

[3] Naldini, *Gazzetta*, 1960, **90**, 391.

[4] (*a*) Frazer, Gerrard, and Twaits, *J. Inorg. Nuclear Chem.*, 1963, **25**, 637; (*b*) Sheldon and Tyree, *J. Amer. Chem. Soc.*, 1958, **80**, 4775.

and we have prepared them again in order to study their spectra. Quinoline also forms 2 : 1 complexes with ferrous chloride and bromide; these compounds are more readily oxidised than are the tertiary phosphine oxide or arsine oxide complexes.

The molar electrolytic conductances of these compounds in nitrobenzene at room temperature are all very small (4—8 ohm^{-1} cm.^{2}), and are in agreement with their formulation as neutral complexes, FeL_2X_2; the small values observed probably arise from some solvolysis.

X-Ray powder photographs show that all these complexes have essentially tetrahedral structures. The complexes $Fe(Ph_3PO)_2Cl_2$ and $Fe(Ph_3AsO)_2Cl_2$ are both isomorphous with $Co(Ph_3AsO)_2Cl_2$, which is known to be tetrahedral,[5] and the corresponding bromo-complexes are both isomorphous with $Mn(Ph_3PO)_2Br_2$, which has also been shown to be tetrahedral.[6] Dichlorodiquinolineiron(II) is isomorphous with its tetrahedral cobalt(II) analogue, and dibromodiquinolineiron(II) is isomorphous with the corresponding nickel(II) complex.[7]

TABLE 2.

Comparison of Δ values (cm.$^{-1}$) for some tetrahedral complexes of iron(II) and cobalt(II).

	Fe	Co		Fe	Co
$M(Ph_3AsO)_2Cl_2$	5000	3300 [d]	$M(C_9H_7N)_2Br_2$	5100	4250
$M(Ph_3AsO)_2Br_2$	~4850 *	3250 [d]	MCl_4^{2-}..................	4000 [a]	~3150 [e]
$M(Ph_3PO)_2Cl_2$............	4550	3300 [d]	MBr_4^{2-}	3000 [b]	~2850 [e]
$M(Ph_3PO)_2Br_2$	4500	3200 [d]	$M(NCS)_4^{2-}$	~5200 [c]	4550 [e]
$M(C_9H_7N)_2Cl_2$............	5500	4350	$M(NCO)_4^{2-}$	~5000	4150 [e]

* Averaged from solution and solid-state values.

Ref. 8. [b] Ref. 9 and this work. [c] Ref. 2. [d] Ref. 5. [e] Ref. 12.

The electronic spectra of the solid complexes and also that of the tetrahedral compound $Fe(Ph_2MeAsO)_2Br_2$,* have been obtained by the reflectance technique in the range 4000—20,000 cm.$^{-1}$. Now, under the influence of a ligand field of T_d symmetry the ^5D free-ion ground state of iron(II) splits into two levels ^5E and $^5T_2$ with the orbital doublet lying lower in energy. Thus, the electronic spectrum of a tetrahedral iron(II) complex should consist, to a first approximation, of a single spin-allowed band due to $^5E \longrightarrow {}^5T_2$, the energy of which will depend only upon the value of Δ, the ligand field strength parameter. For tetrahedral iron(II), values of Δ in the range 3000—6000 cm.$^{-1}$ would be expected, and therefore the electronic transition would be observed in the near-infrared region. Moreover, it is well established experimentally that the electronic bands of tetrahedral complexes of bivalent first-series transition-metal ions are usually about one hundred times more intense than those of octahedral complexes. The available experimental evidence for tetrahedral iron(II) complexes is in agreement with theory. Thus, the energies and extinction coefficients for the $^5E \longrightarrow {}^5T_2$ transition for the FeX_4^{2-} ions are reported to be: $X = Cl^-$ at ~4000 cm.$^{-1}$ (ε = 60—80),[8] Br^- at ~3000 cm.$^{-1}$ (ε = 90),[9] and NCS^- at ~5200 cm.$^{-1}$ (ε = 142),[2] and iron(II) doped into the zinc sulphide sphalerite lattice shows [10] a strong, broad absorption centred at about 3300 cm.$^{-1}$.

The electronic spectra of the complexes that we have studied are in accord with the essentially tetrahedral structures postulated on the basis of the *X*-ray diffraction photographs. All the compounds have a strong band in the region 4000—6000 cm.$^{-1}$. The numerical results are given in Table 1, and the spectra obtained for the complexes of

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* Kindly supplied by Dr. G. A. Rodley, University College, London.

[5] Goodgame, Goodgame, and Cotton, *Inorg. Chem.*, 1962, **1**, 239.

[6] Goodgame and Cotton, *J.*, 1961, 3735.

[7] Goodgame and Goodgame, *J.*, 1963, 207.

[8] Furlani, Cervone, and Valenti, *J. Inorg. Nuclear Chem.*, 1963, **25**, 159.

[9] Hamer, *Mol. Phys.*, 1963, **6**, 257.

[10] Low and Weger, *Phys. Rev.*, 1960, **118**, 1119.

triphenylarsine oxide and of quinoline are shown in Figs. 1 and 2. A solution spectrum could be obtained only for dibromobis(triphenylarsine oxide)iron(II). The other complexes were not sufficiently soluble in, or were decomposed by, the usual organic solvents; even the compound $Fe(Ph_3AsO)_2Br_2$ decomposed quite quickly in solution. The molar extinction coefficient for the $^5E \longrightarrow {}^5T_2$ band for this compound is 48 compared with values of 60—90 for the analogous bands in the spectra of the FeX_4^{2-} ions (where X = Cl or Br),[8,9] and with $\varepsilon = 1{\cdot}6$ for the $^5T_{2g} \longrightarrow {}^5E_g$ band for the hexa-aquoiron(II) ion.[11] The extinction coefficients of the electronic bands of $Co(Ph_3AsO)_2Br_2$ are also smaller [5,12] than are those of $CoBr_4^{2-}$.

The Δ values obtained from the energies of the near-infrared bands for the compounds we have studied, and also some other tetrahedral iron(II) complexes, are listed in Table 2, together with the Δ values for the analogous complexes of cobalt(II). The values for the FeX_4^{2-} ions appear to be some 5—25% greater than those of the analogous cobalt(II) species. One point of interest is that there is a proportionately larger difference between the values of Δ for the ions $FeCl_4^{2-}$ and $FeBr_4^{2-}$ than between $CoCl_4^{2-}$ and $CoBr_4^{2-}$. The value reported by Hamer [9] for tetraethylammonium tetrabromoferrate(II) in acetonitrile seems to be rather low in comparison with the other FeX_4^{2-} species. However, we find that the $^5E \longrightarrow {}^5T_2$ transition for this compound in the solid state occurs in virtually the same position as it does in solution (Table 1 and Fig. 2).

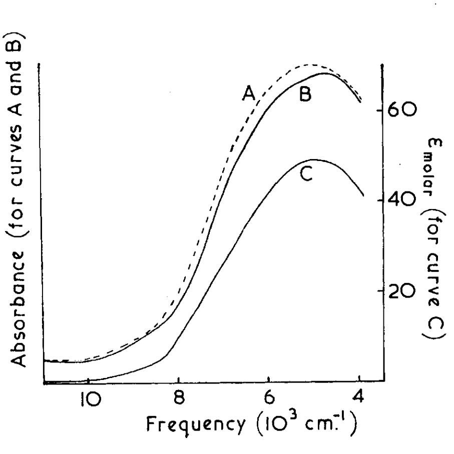

FIG. 1. Electronic spectra of the complexes $Fe(Ph_3AsO)_2X_2$:
A, X = Cl, solid by reflectance;
B, X = Br, solid by reflectance;
C, X = Br, 0·106M in chloroform.

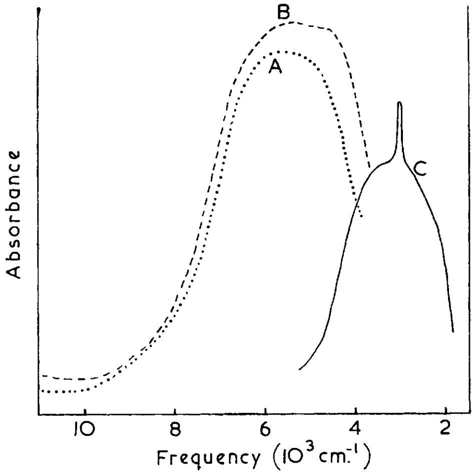

FIG. 2. Electronic spectra of some tetrahedral complexes of iron(II):
A, $Fe(C_9H_7N)_2Cl_2$, solid by reflectance;
B, $Fe(C_9H_7N)_2Br_2$, solid by reflectance;
C, $(Et_4N)_2(FeBr_4)$ solid, mull.

The energies of the electronic bands of the complexes FeL_2X_2 are all greater than those of the $FeCl_4^{2-}$ and $FeBr_4^{2-}$ ions, and they increase in the order L = $Ph_3PO < Ph_3AsO <$ quinoline. This behaviour is expected from the order of these ligands in the spectrochemical series. However, the actual band energies for the complexes FeL_2X_2 are rather higher than expected. The apparent Δ values calculated from the positions of the electronic bands

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[11] Jørgensen, *Acta Chem. Scand.*, 1954, **8**, 1502.
[12] Cotton, Goodgame, and Goodgame, *J. Amer. Chem. Soc.*, 1961, **83**, 4690.

for the triphenylphosphine oxide and triphenylarsine oxide complexes are some 40—50% greater than those of the corresponding cobalt(II) compounds. Unfortunately, we have been unable to prepare a compound containing a tetrahedral FeL_4^{2+} ion, where L = Ph_3PO or Ph_3AsO, and we could not, therefore, obtain a direct measure of the Δ values of these ligands when tetrahedrally co-ordinated to iron(II).

The positions of the electronic bands for the complexes FeL_2X_2 can be explained more readily if the true symmetry (C_{2v}) of the ligand field is taken into account. The lowering of symmetry from T_d to C_{2v} will raise the degeneracies of the ^5E and $^5T_2$ states thus: ^5E becomes $^5A_1 + {}^5A_2$ and $^5T_2$ becomes $^5A_1 + {}^5B_1 + {}^5B_2$. Although one cannot say *a priori* whether $^5A_1$ or $^5A_2$ becomes the ground state in a given complex, the effect of this splitting will be to lower the ground state with respect to the unsplit ^5E level, and therefore to increase the energies of all electronic transitions. Thus the band energies we observe for the compounds FeL_2X_2 are not unreasonable. Moreover the splitting of the $^5T_2$ level will cause a broadening or outright splitting of the near-infrared band. The electronic bands are in fact somewhat broader than those of the $FeCl_4^{2-}$ and $FeBr_4^{2-}$ ions, but comparisons of this nature for solid-state spectra in this region are probably not very reliable.

In the absence of magnetic interactions, the magnetic behaviour of tetrahedral iron(II) complexes should be relatively straightforward. For complexes that are little distorted from T_d symmetry, a small orbital contribution to the spin-only magnetic moment (4·90 B.M.) is expected because of the mixing-in of the $^5T_2$ level under the influence of spin-orbit coupling. With reasonable values of Δ and λ, the spin-orbit coupling constant, values of $\mu_{\text{eff.}} = 5{\cdot}1$—$5{\cdot}2$ B.M. are predicted. However, moments in the range 5·33—5·46 B.M. have been reported for complexes containing the ions FeX_4^{2-}, where X = Cl,[1,8] Br,[1] I,[1] and NCS.[2] We have measured the moment of tetramethylammonium tetrachloroferrate(II) and find it to be 5·44 B.M. at 297°K.

The magnetic moments of the two neutral complexes that appeared to be the most stable towards oxidation, namely those with triphenylarsine oxide, were determined at room temperature. The magnetic moments, 5·24 B.M. for the chloro complex and 5·10 B.M. for the bromo complex, are both lower than those of the FeX_4^{2-} ions. This may well be associated with the lowering of the symmetry of the ligand field from T_d to C_{2v}. It may be noted that the magnetic moments of the complexes $Fe(Ph_3P)_2X_2$ (X = Cl, Br, or I), where low-symmetry components of the ligand fields are probably appreciable, are reported to be in the range 4·77—5·28 B.M. However, with the triphenylphosphine complexes, it is difficult to understand why the moment of the iodo-complex (5·28 B.M.) should be so much larger than that of the chloro-complex (4·88 B.M.). In general, it appears from the available data that the magnetic properties of tetrahedral or pseudotetrahedral complexes of iron(II) are somewhat more complicated than would have been expected.

The Tetraisocyanatoferrate(II) *Ion*.—Tetraethylammonium tetraisocyanatoferrate(II) has been prepared by the general method described in a previous communication.[13] The compound is exceedingly hygroscopic, as well as being rather easily oxidised, and all attempts to obtain an analytically pure specimen were unsuccessful. However, there is little doubt that the $Fe(NCO)_4^{2-}$ ion has a tetrahedral structure, since the reflectance spectrum shows the characteristic, strong band, due to $^5E \longrightarrow {}^5T_2$, in the near-infrared region (Table 1). The band centre could not be determined very accurately because of the presence of vibrational overtone bands of the cyanate groups (at ~4400 cm.$^{-1}$). However, it appears to be at a slightly lower energy than that found for the tetraisothiocyanatoferrate(II) ion.[2] The vibrational spectrum of tetraethylammonium tetraisocyanatoferrate(II) is also in accord with the suggested tetrahedral structure for the anion.[13]

It appears from the results of this and previously published work that iron(II) is intermediate between cobalt(II) and nickel(II) in its tendency to form complexes with a tetrahedral structure.

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[13] Forster and Goodgame, *J.*, 1965, 262.

EXPERIMENTAL

Dichlorobis(triphenylarsine oxide)iron(II).—Iron(II) chloride tetrahydrate (1·25 g.) was dissolved in de-oxygenated ethanol (15 ml.) under nitrogen, and triphenylarsine oxide [14] (4·0 g.) was then added. The mixture was refluxed for 15 min. and then cooled. Pale yellow *crystals* formed, which were filtered off and washed with ethanol and acetone before being dried *in vacuo* (75% yield; m. p. 182°) (Found: C, 55·7; H, 3·9; Fe, 7·1. $C_{36}H_{30}As_2Cl_2FeO_2$ requires C, 56·05; H, 3·9; Fe, 7·25%); Λ_M in $PhNO_2$ (10^{-3}M) = 4·6 ohm^{-1} cm.^{2}; $\mu_{eff.}$ = 5·24 B.M. at 298°K. The solid is stable in air.

Dibromobis(triphenylarsine oxide)iron(II).—Hydrated iron(II) bromide was dissolved in de-oxygenated acetone and the solution kept over molecular sieves (4 A) for 10 min. The solution was then filtered into an acetone solution of triphenylarsine oxide (in slight excess), which had also been dried with molecular sieves. Yellow crystals separated. The *complex* was filtered off, washed with acetone and ether, and dried *in vacuo* (53% yield; m. p. 185°) (Found: C, 50·5; H, 3·6; Br, 18·0. $C_{36}H_{30}As_2Br_2FeO_2$ requires C, 50·2; H, 3·6; Br, 18·6%); Λ_M in $PhNO_2$ (10^{-3}M) = 3·8 ohm^{-1} cm.^{2}; $\mu_{eff.}$ = 5·10 B.M. at 294°K. The solid is fairly stable in air, and is very soluble in chloroform, but the resulting yellow solution decomposes very readily.

Dibromobis(diphenylmethylarsine oxide)iron(II).—A specimen of this compound was kindly supplied by Dr. G. A. Rodley, University College, London.

Dichlorodiquinolineiron(II).—This yellow *complex* was prepared by adding a slight excess of quinoline to a solution of iron(II) chloride tetrahydrate in ethanol. No precautions against oxidation were necessary if the preparation was carried out rapidly. The compound crystallised from the mixture rapidly and was filtered off, washed with ethanol and ether, and dried *in vacuo* (54% yield; m. p. 142°) (Found: C, 55·5; H, 3·9; Cl, 18·3. $C_{18}H_{14}Cl_2FeN_2$ requires C, 56·1; H, 3·6; Cl, 18·4%); Λ_M in $PhNO_2$ (10^{-3}M) = 5·0 ohm^{-1} cm.^{2}. The compound is slightly unstable in air.

Dibromodiquinolineiron(II).—Hydrated iron(II) bromide was dissolved in de-oxygenated acetone under nitrogen. The solution was filtered into an excess of quinoline. Scratching the sides of the flask caused yellow crystals to separate rapidly. The *complex* was filtered off and washed with acetone and ether (60% yield; m. p. 151°) (Found: C, 45·0; H, 3·1; Br, 33·2. $C_{18}H_{14}Br_2FeN_2$ requires C, 45·6; H, 3·0; Br, 33·7%); Λ_M in $PhNO_2$ (10^{-3}M) = 7·9 ohm^{-1} cm.^{2}. The compound is unstable in air, becoming brown after a few days' exposure.

Tetraethylammonium Tetraisocyanatoferrate(II).—This *complex* has been prepared impure by the method described previously [13] for other tetraisocyanatometallate(II) complexes. Dry de-oxygenated solvents are necessary. The pale brown *complex* is very readily oxidised in air, is extremely hygroscopic, and cannot be recrystallised without extensive decomposition (Found: C, 47·3; H, 7·9; N, 17·5. $C_{20}H_{40}FeN_6O_4$ requires C, 49·6; H, 8·3; N, 17·4%).

Other complexes prepared as described were $Fe(Ph_3PO)_2Cl_2$,[4a] $Fe(Ph_3PO)_2Br_2$,[4b] $(Et_4N)_2FeBr_4$.[1]

Physical Measurements.—The reflectance spectra were obtained with a Beckman D.K. 2 recording spectrometer, and the spectrum of $[Et_4N]_2[FeBr_4]$ in a hexachlorobutadiene mull was obtained with a Grubb–Parsons Spectromaster infrared spectrometer. Other physical measurements were carried out as described previously.[15]

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[14] Shriner and Woolf, *Org. Synth.*, 1950, **30**, 97.

[15] Forster and Goodgame, *J.*, 1964, 2790.