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Tetrachloroferrate(III) and Bromotrichloroferrate(III) Complexes of Copper(I)

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Compounds of the formula $[(C_6H_5)_3P]_3CuFeCl_3X$ (X = Cl, Br) are prepared by the reaction of the halotris(triphenylphosphine)copper(I), $[(C_6H_5)_3P]_3CuX$, with iron(III) chloride and include examples of the rarely reported three-coordinate Cu(I) cation. The nature of the products shows a unique solvent dependence. From chloroform–ethanol solvent, complexes designated as α-$[(C_6H_5)_3P]_3CuFeCl_3X$ result. Far-infrared, Mossbauer, and conductivity data for the isomorphous α complexes are in agreement with the ionic formulation $[(C_6H_5)_3P]_3Cu^+FeCl_3X^-$. Exclusive use of chloroform as solvent results in the formation of the β-$[(C_6H_5)_3P]_3CuFeCl_3X$ complexes. The isomorphous β complexes give different powder patterns from their isomeric α complexes. Far-infrared and Mossbauer data for the β complexes, in contrast to the corresponding data for the α complexes, indicate coordination of halogen on the tetrahaloferrate anion to the potentially vacant site on tris(triphenylphosphine)copper(I) *via* a single halide bridge. The two forms are interconvertible with solvent

$$\underset{\alpha\text{ form}}{[(C_6H_5)P]_3Cu^+FeCl_3X^-}\ \underset{CH_3NO_3\text{ or ethanol}}{\overset{CHCl_3}{\rightleftarrows}}\ \underset{\beta\text{ form}}{[(C_6H_5)_3P]_3CuXFeCl_3}$$

The α form converts to the β form in the presence of chloroform. The reverse conversion of β form to α form occurs in the presence of the more strongly ionizing solvents ethanol or nitromethane. Osmometric molecular weights and electronic spectra are also presented for the β complexes.

Introduction

Tris(triphenylphosphine)copper(I) is known to assume tetrahedral geometry through coordination of a number of anions[1-5] including F^-, Cl^-, Br^-, I^-, BH_3CN^-, NO_3^-, and quite remarkably BF_4^- and ClO_4^-.

In the present study, tetrachloroferrate(III) and bromotrichloroferrate(III) complexes of tris(triphenylphosphine)copper(I) were prepared. Of the structural changes which may occur in the region of the copper in such complexes, there is particular interest in three-coordination of a Cu(I) cation. Distortion of the tetrahedral geometry around iron would occur upon coordination of the halogen on tetrahaloferrate(III) to the potentially vacant site on three-coordinate copper. As part of a program to study the distortion of the tetrahedral geometry around iron, we have been investigating systems such as these. In addition to the distortion about iron, the potential bridging of a halogen between dissimilar metals is of interest, as well as the stabilization of a Cu(I) species in the presence of Fe(III).

Experimental Section

Materials. Triphenylphosphine was recrystallized from absolute ethanol. Anhydrous cuprous chloride (98%) and cuprous bromide (99%) were from Research Organic/Inorganic Chemical Corp. The chloride was further purified by the standard technique.[6] Anhydrous iron(III) chloride was prepared from iron wire and chlorine gas[7] and was sublimed twice. The iron(III) chloride was stored in sealed ampoules until use. Chlorotris(triphenylphosphine)copper(I),[2] bromotris(triphenylphosphine)copper(I),[8] and tetraethylammonium tetrachloroferrate(III)[9] were prepared as previously reported. Reagent grade chloroform, benzene, and hexane were dried over molecular sieves. Spectrograde methylene chloride was used for electronic spectra. USP absolute alcohol was used without further purification.

Analyses. Chemical analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. The analytical data are presented in Table I.

Instrumentation and Experimental Methods. Molecular weights were determined on a Mechrolab vapor pressure osmometer calibrated with benzil. Conductivity measurements were obtained with a Yellow Springs Instrument Co. Model 31 conductivity bridge. The cell constant was determined as 0.843 cm^{-1} using potassium chloride. The specific conductance of the nitromethane was measured as 5.85×10^{-6} ohm^{-1} cm^{-1}. Nujol mull infrared spectra were recorded on a Perkin-Elmer 457 spectrophotometer in the region 4000–400 cm^{-1} using a KBr disk and on a Beckman IR-11 spectrophotometer in the region 780–55 cm^{-1} using polyethylene film windows. Electronic spectra were recorded on a Cary 14 spectrophotometer. X-Ray diffraction equipment consisted of a Debye–Scherrer camera with an effective diameter of 11.46 cm. Nickel-filtered Cu Kα radiation was used. Line intensities were estimated visually. All melting points are corrected. The Mossbauer spectra were taken in transmission geometry using a constant-acceleration transducer described elsewhere[10] with data collected from a gas-filled proportional counter by a 400-channel analyzer operating in the multiscale mode and phase-locked to the transducer. The source was ~10-mCi ^{57}Co diffused into palladium and was maintained at room temperature. Aluminum sample cells were fitted with Mylar windows and sealed with O rings; powdered sample thicknesses varied from 0.5 to 0.1 mm. Measurements at 4.2°K were taken using a Janis Model 8DT liquid helium research dewar fitted with a beryllium window Mossbauer tail. The results were least squares fitted to lorentzian line shapes with correction for source–absorber distance using a Sigma 7 computer. The velocity scale was calibrated frequently against NBS 0.8-mil iron foil Standard Reference Material SRM 1541.

Preparation of Complexes. General Data. Precautions were taken to prevent hydrolysis of the iron(III) chloride starting material in all of the preparations by weighing the material in a nitrogen drybox at a dew point less than −75° and performing the initial steps of the reaction under prepurified, dry nitrogen. All of the tris(triphenylphosphine)copper(I) tetrahaloferrates(III) prepared were found to be stable in air with no signs of decomposition after several months.

α-Tris(triphenylphosphine)copper(I) Tetrachloroferrate(III), α-$[(C_6H_5)_3P]_3CuFeCl_4$. To a solution of iron(III) chloride (1.41 g, 8.7 mmol) in 130 ml of chloroform and 100 ml of absolute ethanol was added chlorotris(triphenylphosphine)copper(I) (6.62 g, 7.5 mmol). The reaction mixture immediately turned dark brown. After gently refluxing for 1 hr, the mixture was filtered in the ambient atmosphere and 500 ml of hexane was added to the filtrate. The precipated yellow needles were filterered and washed three times with 50 ml of hexane. The product was dried in a vacuum system overnight at a pressure of 10^{-3} Torr; yield 5.5 g (71%); mp 151.5–152.5° dec. Attempts to recrystallize the product from chloroform–ethanol led to a heterogeneous mixture of yellow and white crystals melting over

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Table I. Analytical Data for $[(C_6H_5)_3P]_3CuFeXCl_3$ Complexes

	% C		% H		% P		% Fe		mequiv of halide/ 10 mg of sample	
Compd	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
α-$[(C_6H_5)_3P]_3CuFeCl_4$	61.88	61.95	4.33	4.36	8.87	8.76	5.33	5.31	0.0382	0.0387
β-$[(C_6H_5)_3P]_3CuFeCl_4$	61.88	62.15	4.33	4.30	8.87	8.91	5.33	5.30	0.0382	0.0390
α-$[(C_6H_5)_3P]_3CuFeCl_3Br$	59.37	59.48	4.16	4.22	8.51	8.75	5.11	5.03	0.0366	0.0375
β-$[(C_6H_5)_3P]_3CuFeCl_3Br$	59.37	59.14	4.16	4.27	8.51	8.47	5.11	5.09	0.0366	0.0378

Table II. X-Ray Powder Pattern Data for $[(C_6H_5)_3P]_3CuFeCl_3X$ Complexes (*d*, Å)

α-$[(C_6H_5)_3P]_3$-$CuFeCl_4$	α-$[(C_6H_5)_3P]_3$-$CuFeCl_3Br$	β-$[(C_6H_5)_3$-$P]_3CuFeCl_4$	β-$[(C_6H_5)_3$-$P]_3CuFeCl_3Br$
10.35 w	10.37 w	10.85 s	10.85 s
9.90 w	9.96 w	9.83 s	9.83 s
9.33 s	9.38 s	9.00 s	9.00 s
8.23 w	8.21 w	7.87 vw	7.92 vw
7.83 w	7.83 w	7.17 w	7.17 w
6.43 s	6.50 s	6.56 m	6.56 m
5.57 w	5.61 w	6.27 w	6.27 w
5.11 m	5.15 m	5.91 w	5.91 w
4.91 vw	4.93 vw	5.53 w	5.53 w
4.75 m	4.75 m	4.86 vw	4.87 vw
4.46 w	4.53 w	4.69 w	4.69 w
4.33 s	4.34 s	4.50 w	4.50 w
4.07 w	4.10 w	4.35 m	4.35 m
3.92 m	3.93 m	4.19 m	4.16 m
3.63 w	3.64 w	3.97 w	3.97 w
3.47 w	3.48 w	3.86 w	3.86 w
3.30 mw	3.30 mw	3.53 vw	3.53 vw
3.11 vw	3.11 vw	3.27 w	3.27 w
2.95 w	2.95 w	3.11 w	3.11 w
2.83 w	2.84 w	3.05 vw	3.05 vw
		2.89 w	2.89 w
		2.86 w	2.86 w

[a] Key: s, strong; m, medium; w, weak; vw, very weak.

a wide range. Dissolving the α-$[(C_6H_5)_3P]_3CuFeCl_4$ in alcohol resulted in disproportionation to starting materials. The white chlorotris(triphenylphosphine)copper(I) resulting from the disproportionation was identified by comparison of its melting point to that of an authentic sample (mp 164–165°). The yellow solution was shown to contain iron(III) chloride by addition of tetraethylammonium chloride which resulted in the formation of yellow needles of tetraethylammonium tetrachloroferrate(III). These recrystallized yellow needles gave the same room-temperature Mossbauer spectrum and melting point (270–271°) as those of an authentic sample of tetraethylammonium tetrachloroferrate(III). The molar conductance (Λ_M) of α-$[(C_6H_5)_3P]_3CuFeCl_4$ in nitromethane indicates a 1:1 electrolyte: 59.3 ohm^{-1} cm^2 mol^{-1} (10.94 × 10^{-3} *M*) at 24.1°. The Λ_M values (10^{-3} *M* in parentheses) in nitromethane for related compounds are as follows: $[(C_2H_5)_4N][FeCl_4]$, 84.2 (9.08) at 24.1°; $[Ti(acac)_3][FeCl_4]$,[11] 93.5 (10.8) at 30°; $[Ge(acac)_3][FeCl_4]$,[12] 69.0 (10.0) at 30°; $[Si(acac)_3][FeCl_4]$,[12] 70.4 (10.0) at 30°.

α-Tris(triphenylphosphine)copper(I) Bromotrichloroferrate(III), α-$[(C_6H_5)_3P]_3CuFeCl_3Br$. The reaction was performed in a manner similar to that for α-tris(triphenylphosphine)copper(I) tetrachloroferrate(III). Iron(III) chloride (2.22 g, 13.7 mmol) was allowed to react with bromotris(triphenylphosphine)copper(I) (10.37 g, 11.3 mmol) in 130 ml of chloroform and 100 ml of absolute ethanol. The stirred dark brown solution was warmed but not refluxed for 1 hr. The mixture was filtered in the atmosphere; 500 ml of hexane which was added slowly precipitated orange crystals of product from the filtrate. The product was filtered, washed three times with 50 ml of hexane, and then was dried on the vacuum system; yield 6.9 g (57%); mp 151.0–151.5° dec. The molar conductance for α-$[(C_6H_5)_3P]_3CuFeCl_3Br$ also indicated a 1:1 electrolyte: 58.7 ohm^{-1} cm^2 mol^{-1} (9.38 × 10^{-3} *M*) at 24.4°.

β-Tris(triphenylphosphine)copper(I) Tetrachloroferrate(III), β-$[(C_6H_5)_3P]_3CuFeCl_4$. Iron(III) chloride (1.09 g, 6.7 mmol) was dissolved in 85 ml of chloroform. Chlorotris(triphenylphosphine)copper(I) (6.03 g, 6.8 mmol) was added whereupon the solution turned dark brown. The reaction mixture was stirred for 1 hr at room temperature and then filtered. To the filtrate was added 150 ml of hexane. Yellow green crystals formed which upon filtering and washing with hexane turned dark brown. The sample was dried on the vacuum system. The yield (6.27 g) was 86% based on the iron(III) chloride used. Exposure of the brown sample to chloroform vapor caused a color change from brown to yellow-green because of weak coordination of chloroform. Reevacuation turned the compound brown. The compound changed from brown to yellow above 100° and melted at 151.5–152.5° dec. The molecular weight determined by osmometry in benzene and chloroform indicates dissociation: calcd for $C_{54}H_{45}P_3CuFeCl_4$, 1048; in benzene found, 541 (2.96 × 10^{-3} *M*) and 528 (2.09 × 10^{-3} *M*); in chloroform found, 547 (0.93 × 10^{-3} *M*). The electronic spectrum was taken in dichloromethane. λ_{max} in nm (ϵ_{max} × 10^{-3} in parentheses); 257 (37.7), 275 (sh), 312 (sh), 363 (6.0).

Stepwise Preparation of α-$[(C_6H_5)_3P]_3CuFeCl_4$. The reaction was performed in a manner identical with that described for β-tris(triphenylphosphine)copper(I) tetrachloroferrate(III) in chloroform. Two-thirds of the reaction mixture was removed and the brown β complex was isolated and identified by its X-ray powder pattern. To the remaining solution of β-$[(C_6H_5)_3P]_3CuFeCl_4$ was added an equal volume of ethanol. The mixture was mildly refluxed for 1 hr. Addition of hexane precipitated yellow needles of α-$[(C_6H_5)_3P]_3CuFeCl_4$ which were identified by their powder pattern and far-infrared spectrum.

β-Tris(triphenylphosphine)copper(I) Bromotrichloroferrate(III), β-$[(C_6H_5)_3P]_3CuFeCl_3Br$. Iron(III) chloride (1.09 g, 6.17 mmol) was allowed to react with bromotris(triphenylphosphine)copper(I) (6.30 g, 6.18 mmol) in 80 ml of chloroform. The dark brown solution was stirred for 1 hr at room temperature and filtered. A 200-ml quantity of hexane was added to the filtrate, and orange crystals precipitated. The crystals were washed three times with 50 ml of hexane. The material changed in color from orange to dark brown. The last traces of solvent were removed on the vacuum system to give 6.0 g of solid corresponding to a yield of 82%. It turned from dark brown to orange when exposed to chloroform vapor in the vacuum system. Reevacuation changed the color back to brown indicating that again the color change was associated with weak coordination of the solvent. The compound changed in color from brown to orange above 100° and melted at 151.0–151.5° dec. The osmometric molecular weight determined in benzene and chloroform indicated dissociation: calcd for $C_{54}H_{45}P_3CuFeCl_3Br$, 1092; found in benzene, 559 (3.29 × 10^{-3} *M*), 576 (2.73 × 10^{-3} *M*), and 577 (2.60 × 10^{-3} *M*); found in chloroform, 535 (1.25 × 10^{-3} *M*). The electronic spectrum was taken in dichloromethane. λ_{max} in nm (ϵ_{max} × 10^{-3} in parentheses): 257 (39.1), 276 (sh), 314 (sh), 363 (6.2).

Interconversion Reactions. Conversion of the yellow α-$[(C_6H_5)_3P]_3CuFeCl_4$ and orange α-$[(C_6H_5)_3P]_3CuFeCl_3Br$ complexes to their corresponding dark brown β complexes took place in pure chloroform. The α-$[(C_6H_5)_3P]_3CuFeCl_4$ was dissolved in chloroform containing a large molar excess of triphenylphosphine used to minimize dissociation of triphenylphosphine from the complex. To the solution was added ligroin until crystals began to form and then a slight excess was added. The crystals were filtered and washed with ligroin. The β-$[(C_6H_5)_3P]_3CuFeCl_4$ was identified by X-ray powder diffraction. In the identical manner, α-$[(C_6H_5)_3P]_3CuFeCl_3Br$ was converted to the corresponding β complex which was identified by powder X-ray diffraction and far-infrared spectroscopy. The brown β complexes β-$[(C_6H_5)_3P]_3CuFeCl_4$ and β-$[(C_6H_5)_3P]_3CuFeCl_3Br$ converted to their corresponding α complexes when exposed to ethanol or nitromethane vapor on the vacuum system. The conversion was evidenced visually over several days by a color change from brown to yellow for the tetrachloroferrate(III) complex and from brown to orange for the bromotrichloroferrate(III) complex. An X-ray powder pattern of the salt in each case confirmed the conversion to the α complex.

Results and Discussion

Powder Pattern X-Ray. In Table II, the powder pattern data show that two different crystalline forms exist for both

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Table III. Far-Infrared-Active Bands (400–55 cm^{-1}) for $[(C_6H_5)_3P]_3CuFeCl_3X$ and Related Compounds

$[(C_6H_5)_3P]_3CuFeCl_4$		$[(C_6H_5)_3P]_3CuFeCl_3Br$		$[(C_2H_5)_4N]$-$[FeCl_4]$[a]	$[(C_2H_5)_4N][Fe$-$Cl_3Br]$[a]
α form	β form	α form	β form		
388 vs	387 vs, 370 sh	384 vs, 356 s	382 vs, 366 s, 347 s	388 vs	391 vs, 350 s
	328 w				
	299 w				
		298 s, 264 m	298 vw,[b] 264 vvw[b]		296 s, 268 m
			253 w		
					245 sh
	233 w				
			202 w		
180 w		180 w			
		~150 w			
137 m	137 w	137 w	136 w	137 m	135 w
					117 sh

[a] Data from ref 9. [b] Trace impurity of corresponding α form.

$[(C_6H_5)_3P]_3CuFeCl_4$ and $[(C_6H_5)_3P]_3CuFeCl_3Br$. Furthermore, the close similarity in the two complexes designated as α-$[(C_6H_5)_3P]_3CuFeCl_4$ and α-$[(C_6H_5)_3P]_3CuFeCl_3Br$ indicate that they are isomorphous while the powder pattern data for β-$[(C_6H_5)_3P]_3CuFeCl_4$ and β-$[(C_6H_5)_3P]_3CuFeCl_3$-Br establishes that these two compounds are isomorphous.

α Complexes. Tetrahedral $FeCl_4^-$ anion is characterized by the infrared-allowed asymmetric stretch (ν_3) and asymmetric bend (ν_4).[9,13-15] These bands appear at positions quite different from those of octahedral iron(III) chlorides[14] and the tetrahedral tetrachloro complex of iron(II).[14,16,17]

Far-infrared data[18] for the tris(triphenylphosphine)copper(I) tetrahaloferrate(III) complexes and for comparison purposes tetraethylammonium tetrachloroferrate and bromotrichloroferrate(III) are given in Table III. The iron-chlorine stretching bands for the tetrahaloferrate(III) complexes are illustrated in Figure 1. The α-$[(C_6H_5)_3P]_3CuFeCl_4$ and $[(C_2H_5)_4N][FeCl_4]$ complexes have the strong unsplit iron-chlorine asymmetric stretch at 388 cm^{-1} and the medium-intensity asymmetric bend at 137 cm^{-1} indicative of the undistorted tetrahedral $FeCl_4^-$ anion.

The far-infrared spectrum of α-$[(C_6H_5)_3P]_3CuFeCl_3Br$ shows a striking similarity to that of $[(C_2H_5)_4N][FeCl_3Br]$ indicating the presence of the C_{3v} $FeCl_3Br^-$ anion. In the α-$[(C_6H_5)_3P]_3FeCl_3Br$ the two predicted iron-chlorine stretching frequencies are present at 384 and 356 cm^{-1}. The iron-chlorine bend occurs at 137 cm^{-1}; the iron-bromine stretches are found at 298 and 264 cm^{-1}. These bands have been previously assigned[9] with certainty for $FeCl_3Br^-$ in $[(C_2H_5)_4N][FeCl_3Br]$ except for the 268-cm^{-1} peak which has been only tentatively assigned as an iron-bromine stretch because of other peaks in the area. Thus the far-infrared data indicate that the anions of the α complexes retain the T_d symmetry of the $FeCl_4^-$ and C_{3v} symmetry of the $FeCl_3Br^-$. These data agree with the ionic formulation of $[(C_6H_5)_3P]_3$-$Cu^+FeCl_4^-$ and $[(C_6H_5)_3Cu^+FeCl_3Br^-$ for the α complexes. Mossbauer isomer shifts and conductance measurements are in full agreement with this formulation.

The conductivity measurements show the α-$[(C_6H_5)_3P]_3$-$Cu^+FeCl_3X^-$ complexes to be 1:1 electrolytes in nitromethane, a solvent in which the α complex is known to predominate over the β complex. The β complexes convert to the α complexes in the presence of that solvent.

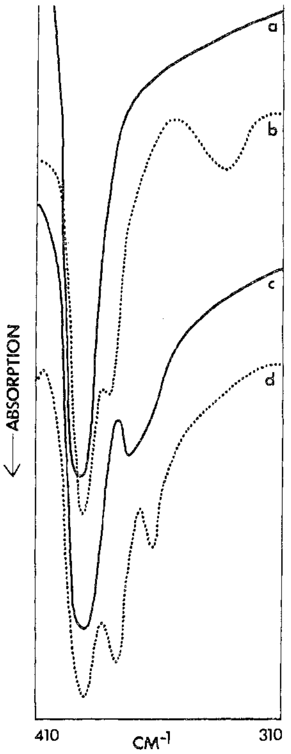

Figure 1. Nujol mull spectra in the iron-chlorine stretching region of (a) α-$[(C_6H_5)_3P]_3CuFeCl_4$, (b) β-$[(C_6H_5)_3P]_3CuFeCl_4$, (c) α-$[(C_6H_5)_3P]_3CuFeCl_3Br$, and (d) β-$[(C_6H_5)_3P]_3CuFeCl_3Br$.

The observed ^{57}Fe Mossbauer data for the $[(C_6H_5)_3P]_3Cu$-$FeCl_3X$ complexes at 4.2°K are listed in Table IV together with the data observed for $[(C_2H_5)_4N][FeCl_4]$. A representative Mossbauer spectrum of β-$[(C_6H_5)_3P]_3CuFeCl_4$ at 4.2°K is shown in Figure 2. Total counts were 2 × 10^6. No Mossbauer absorptions could be observed for any of the $[(C_6H_5)_3P]_3CuFeCl_3X$ complexes at room temperature nor at 77°K; weak and broadened spectra were observed at 4.2°K. By contrast, $[(C_2H_5)_4N][FeCl_4]$ under the same conditions gave relatively sharp, more intense spectra as indicated by the smaller half-width (Γ) and higher per cent effect values (ε). The small per cent effect values for the $[(C_6H_5)_3P]_3$-$FeCl_3X$ complexes make it seem likely that intermolecular bonding is minimal in these complexes, since in ferrocene polymers[19] and in tin compounds with intermolecular

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Table IV. Mossbauer Parameters for $[(C_6H_5)_3P]_3CuFeCl_3X$ Complexes and for $[(C_2H_5)_4N][FeCl_4]$ at 4.2°K

Compd	mm/sec			
	δ^a	Δ^b	Γ^c	$\epsilon,^d$ %
$[(C_2H_5)_4N][FeCl_4]$	+0.34	0	0.55	9.1
α-$[(C_6H_5)_3P]_3CuFeCl_4$	+0.33	0	1.40	0.4
α-$[(C_6H_5)_3P]_3CuFeCl_3Br$	+0.33	0	1.73	0.5
β-$[(C_6H_5)_3P]_3CuFeCl_4$	+0.27	0.35^e	$0.28, 1.60^f$	0.6
β-$[(C_6H_5)_3P]_3CuFeCl_3Br$	+0.27	g	2.24	0.6

^{a} Isomer shift relative to iron foil as standard, ±0.01 mm/sec. ^{b} Quadrupole splitting. ^{c} Full width at half-maximum. ^{d} Per cent effect. ^{e} Measured relative to sodium nitroprusside. ^{f} Asymmetric doublet. ^{g} Not resolved.

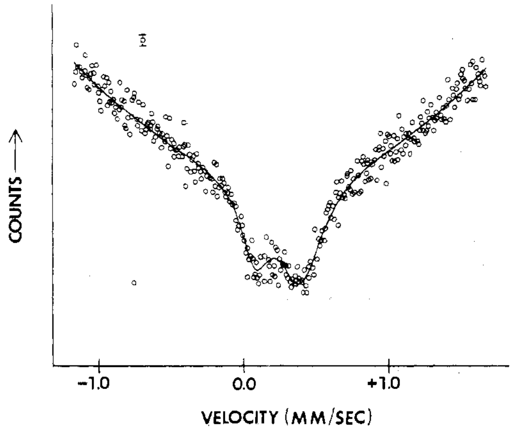

Figure 2. Mossbauer spectrum of β-$[(C_6H_5)_3P]_3CuFeCl_4$.

bonds[20,21] the *f* factor is sharply increased by comparison with similar compounds not having polymeric nature.

The similar Mossbauer isomer shift values for $FeCl_4^-$ in both α-$[(C_6H_5)_3P]_3Cu^+FeCl_4^-$ (+0.33 mm/sec) and $[(C_2H_5)_4N][FeCl_4]$ (+0.34 mm/sec) further evidence the ionic formulation for the α complex. Previous measurement of the isomer shift for the $FeCl_3Br^-$ anion at 77°K has shown it to be very close to that of the $FeCl_4^-$ anion.[9] Consequently, the isomer shift value of +0.33 mm/sec for α-$[(C_6H_5)_3P]_3Cu^+FeCl_3Br^-$ agrees with the presence of the $FeCl_3Br^-$ anion. [In direct contrast, the anion-coordinated β complexes show significantly decreased values for the isomer shift (*vide infra*).]

The α complexes are proposed to contain a trigonal Cu(I) cation. Three-coordinate copper(I), although much less common than the four-coordinate moiety, was found by structural determinations in the compounds of bis(thiourea)-copper(I)[22] and $[(C_6H_5)_3P]_3Cu_2Cl_2$.[23] The latter compound contains both a three-coordinate and a four-coordinate copper.

β Complexes. In contrast to the α complexes where discrete ions are present, the β complexes belong to the more common class of copper(I) complexes in which copper(I) is four-coordinate, sp^3. Tris(triphenylphosphine)copper(I) is found to be four-coordinate with numerous anions, even those which are commonly noncoordinating.[1-5]

Structural determinations of the related compounds of $[(C_6H_5)_2CH_3P]_3CuCl$[24] and $[(C_6H_5)_3P]_2CuBH_4$[2] have established a tetrahedral geometry around copper(I).

Anion coordination to the copper(I) in the β complexes is evidenced by the reduced symmetry of the $FeCl_4^-$ and $FeCl_3Br^-$ anionic species in the far-infrared spectra. For β-$[(C_6H_5)_3P]_3CuFeCl_4$, the symmetry of the $FeCl_4^-$ anion is reduced from T_d found in the tetrachloro α complex and other ionic tetrachloroferrates(III) to C_{3v} or possibly some lower symmetry. Upon reducing to C_{3v} symmetry, the number of asymmetric stretching frequencies would increase to 2 and the symmetric stretch (ν_1), which is no longer infrared forbidden, would appear. The ν_1 for $FeCl_4^-$ previously observed[13,16] in the Raman spectrum is reported at 330 cm^{-1}. Far-infrared data given for β-$[(C_6H_5)_3P]_3CuFeCl_4$ in Table III and illustrated in Figure 1 show a splitting of the asymmetric stretch into two bands at 387 and 370 cm^{-1}. Accompanying the splitting of the asymmetric stretch is the appearance of the now infrared-allowed symmetric stretch at 328 cm^{-1}. The spectrum of the tetrachloro β complex is also characterized by the appearance of two weak bands at 299 and 233 cm^{-1} which were not present in the spectrum of the α-$[(C_6H_5)_3P]_3Cu^+[FeCl_4]^-$. These two bands are attributed to a chlorine bridge between copper and iron since, in general, bridging halide stretching frequencies are weaker and are present at lower wave numbers than their cooresponding terminal stretching frequencies. Also with the presence of two dissimilar metals one would expect two halide bridging stretches. The asymmetric bend for the tetrachloro β complex still appears at 137 cm^{-1} although it is weaker than for the corresponding α complex.

A reduction of the C_{3v} symmetry of the $FeCl_3Br^-$ anion in β-$[(C_6H_5)_3P]_3CuFeCl_3Br$ is evidenced by the additional splitting of the iron–chlorine asymmetric stretch to give three peaks at 382, 366, and 347 cm^{-1}; the latter two peaks arise from the splitting of the 356-cm^{-1} peak in the trichlorobromo α complex. The spectrum is also characterized by the disappearance of the strong- and medium-intensity iron–bromine asymmetric stretching frequencies at 298 and 264 cm^{-1} except for trace peaks which are attributed to a small amount of the α-$[(C_6H_5)_3P]_3Cu^+[FeCl_3Br]^-$ formed in the reaction. This disappearance of the iron–bromine stretching frequency indicates that a bromine atom remains in the bridge position rather than rearrangement to a chloro-bridged species. Apparently, the increased polarizability of bromide over that of chloride favors the bromo-bridged compound. The relative size of the halogen atom attached to copper is not an important factor as a dissociation study has pointed out for the related halotris(triphenylphosphine)copper(I) complexes.[8] In these complexes, phosphine dissociation increases in the series $I < Br < Cl$ which is contrary to that expected if steric factors were important. The weak bands appearing at 253 and 202 cm^{-1} in the β-trichlorobromo complex are assignable as bridging bromine stretching frequencies which, as expected, appear at lower frequencies than those observed for the chlorine bridge in β-$[(C_6H_5)_3P]_3CuClFeCl_3$ at 299 and 233 cm^{-1}. The ratios ν_{Br}/ν_{Cl} are 0.85 (253 cm^{-1}/299 cm^{-1}) and 0.87 (202 cm^{-1}/233 cm^{-1}).

The Mossbauer isomer shifts for β-$[(C_6H_5)_3P]_3CuClFeCl_3$ and β-$[(C_6H_5)_3P]_3CuBrFeCl_3$ are both +0.27 mm/sec. This significant decrease in the isomer shift values for the anion-coordinated tetrahaloferrates(III) from that of the ionic tetrahaloferrates(III) (Table IV) indicates an increase in s-electron density at the iron nucleus of the anion coordi-

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nated species. The increase in electron density corresponds to an increase of the covalent character of the iron–chlorine bonds of the molecular β complexes compared to that of the ionic tetrahaloferrates(III). In the latter case the negative charge of the anion resides more on the electronegative chlorine atoms.

An asymmetric Mossbauer doublet was resolved for β-$[(C_6H_5)_3P]_3CuClFeCl_3$ indicating distortion of the electronic environment around the iron nucleus. The β-$[(C_6H_5)_3P]_3CuBrFeCl_3$ could not be resolved into a doublet but an increased line width over that observed for the α complexes indicated possible splitting in that complex also. The tetrahedral distortion is attributed either to anion coordination or crystal lattice distortion. The lability of the complexes in solution made it impossible to rule out the latter. Based on the symmetry distortion of the anion observed in the far-infrared spectrum, tetrahedral distortion due to anion coordination is the more favored cause of the Mossbauer splitting in the β complex.

Solvent Dependency. The ability of $FeCl_4^-$ and $FeCl_3Br^-$ to coordinate to tris(triphenylphosphine)copper(I) is dependent upon the nature of the solvent. From reactions in the exclusive presence of chloroform, the anion-coordinated β complexes result. The β complexes can also be achieved by dissolving the α complexes in chloroform and precipitating with ligroin

$$\text{ionic } \alpha \text{ complexes} \xrightarrow{CHCl_3} \text{molecular } \beta \text{ complexes}$$

Ethanol and nitromethane with their significantly higher dielectric constants favor formation of the ionic α forms $[(C_6H_5)_3P]_3Cu^+FeCl_3X^-$. Adding ethanol to the reaction mixture or placing the β complexes in the presence of ethanol or nitromethane vapor causes conversion of the β complexes to the α complexes

$$\text{molecular } \beta \text{ complexes} \xrightarrow[\text{or ethanol}]{CH_3NO_3} \text{ionic } \alpha \text{ complexes}$$

Consequently, the anion-coordinated species (β complexes) are favored in solvents with lower dielectric constants such as chloroform while the ionic species (α complexes) are favored by solvents with higher dielectric constants as in the case of nitromethane and ethanol.

Dissociation of $FeCl_4^-$ and $FeCl_3Br^-$ can be ruled out as the cause for the low molecular weight values for the β complexes in chloroform solvent. The infrared spectra of the β complexes in chloroform show an additional splitting of the iron–chlorine stretching frequencies from that observed for uncoordinated $FeCl_4^-$ and $FeCl_3Br^-$ indicating that the anion remains coordinated. The nature of the solution species is not known but the significantly different splitting of the iron–chlorine bands from that of the previously described Nujol mull spectra of the β complexes seems to indicate that the solution species are complex as is indeed the case reported for chlorotris(triphenylphosphine)copper(I).[25] The observed molecular weights for the β complexes are similar to the results previously observed for the related halogen-coordinated tris(triphenylphosphine)copper(I) complexes. In the halogen-coordinated tris(triphenylphosphine)copper(I) compounds, the anion remains coordinated in solution[1,3] and low osmometric molecular weight values in chloroform and benzene are caused by dissociation of triphenylphosphine.[1,8] The osmometric molecular weight values for the β complexes in chloroform and benzene indicate approximately the same degree of dissociation previously reported for the halotris(triphenylphosphine)copper(I) compounds.

In the electronic spectra of the β complexes the two bands at the high-energy end of the spectrum are assigned as the $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions found in triphenylphosphine at 261 and 282 cm^{-1}, respectively.[26] The two bands at lower energy are metal–halogen charge-transfer bands typical for tetrachloroferrate(III)[9,27,28] and bromotrichloroferrate(III).[9] Two other reported charge-transfer bands are masked by the more intense triphenylphosphine bands.

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Registry No. α-$[(C_6H_5)_3P]_3CuFeCl_4$, 52699-09-9; β-$[(C_6H_5)_3P]_3CuFeCl_4$, 52699-19-1; α-$[(C_6H_5)_3P]_3CuFeCl_3Br$, 52699-10-2; β-$[(C_6H_5)_3P]_3CuFeCl_3Br$, 52699-41-9; $[(C_2H_5)_4N][FeCl_4]$, 14240-75-6; $[(C_6H_5)_3P]_3CuCl$, 15709-76-9; $[(C_6H_5)_3P]_3CuBr$, 15709-74-7.

Supplementary Material Available. Spectral data in the range of 1200–400 cm^{-1} will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (108 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-2914.

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