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Iron Trichloride–Phosphine Adducts with Tetrahedral Geometry and Their Reaction with Ethanol. Structure and Magnetic Properties of $[PH(t\text{-}Bu)_3]_2[Fe_2(\mu\text{-}OEt)_2Cl_6]$

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The reaction of $FeCl_3$ and the bulky phosphine ligands PR_3 [R = cyclohexyl (Cy), *tert*-butyl (*t*-Bu)] afforded stable mononuclear, 4-coordinate, pseudotetrahedral 1:1 adducts, $FeCl_3(PR_3)$. These red crystalline solids have been characterized by low-energy IR spectroscopy, magnetic susceptibility, and an X-ray crystallographic study for R = *t*-Bu. The reactions of these compounds with ethanol produces phosphonium salts. For R = Cy, only $[PHCy_3][FeCl_4]$ has been isolated. For R = *t*-Bu, the salt of the novel dianion $[Fe_2(\mu\text{-}OEt)_2Cl_6]^{2-}$ has been isolated and characterized by IR spectroscopy, variable-temperature magnetic susceptibility, and X-ray crystallography. Crystal data: monoclinic, space group $P2_1/c$, $a = 8.6243$ (6) Å, $b = 12.3849$ (7) Å, $c = 19.103$ (1) Å, $\beta = 94.594$ (6)°, $V = 2033.9$ (4) Å^3, $Z = 2$, $d_c = 1.34$ g/cm^3, $R = 0.065$, $R_w = 0.090$ for 181 parameters and 1604 observations with $F_o > 3\sigma(F_o^2)$. The dinuclear dianion exhibits 5-coordination around the two nonbonded (Fe···Fe = 3.177 Å) metal atoms, which are antiferromagnetically coupled with a coupling constant $J = -24.6$ (1) cm^{-1}.

Introduction

We recently became interested in the formation of $FeCl_3$ adducts with monodentate tertiary phosphines.[1,2] In spite of the simplicity of the system and the widespread use of both anhydrous $FeCl_3$ and phosphine ligands, the field had been relatively little explored, although it offers potential interest in terms of the study of the weak interactions between hard metal centers and soft donor ligands and the effect that these interactions might have on the chemical reactivity of Fe(III).

Prior to our studies, only few monodentate phosphine adducts of $FeCl_3$ had been reported. Naldini[3] described the synthesis of $FeCl_3(PPh_3)_2$ from $FeCl_3$ and PPh_3 in ether. In the absence of a structural investigation, a dinuclear, halide-bridged structure was proposed for this compound.[3] Singh and Rivest[4] reported the preparation of yellow $FeCl_3(PPh_3)$ from $Fe_3(CO)_{12}$ and PPh_3 in refluxing chloroform and final workup in ethanol. The formulation of the product was based on analytical, IR, and Mössbauer[5] data. The yellow complex $FeCl_3(PCy_3)$ (Cy = c-C_6H_{11}) was also reported to be obtained from $FeCl_3$ and PCy_3 in ethanol, but no characterization details other than color and melting point were given.[6]

We have recently investigated in greater depth the interaction between $FeCl_3$ and PPh_3 and other monodentate phosphines,[1] and have shown that the 1:2 adducts $FeCl_3(PR_3)_2$ (R = Ph, Me, Cy) adopt a monomeric, trigonal-bipyramidal structure with the phosphine ligands in the axial positions. The Fe–P distances vary from >2.6 Å for R = Ph to ca. 2.33 Å for R = Me. The compounds also exhibit different optical and magnetic properties. These results have been interpreted in terms of the influence of the phosphine on the ligand field splitting in the tbp geometry.[1]

We have also suggested,[1] on the basis of combined EPR and chemical reactivity studies, that the interaction between $FeCl_3$ and PR_3 (R = Me, Ph) in a 1:1 ratio produces solutions of the 4-coordinate, 13-electron $FeCl_3(PR_3)$ adducts, presumably with a pseudotetrahedral arrangement of the ligands around the metal center. These solutions are extremely unstable at room temperature. The interaction of $FeCl_3$ and PPh_3 in a 1:1 ratio does not yield[1,2] a yellow, stable compound similar to that reported by Singh and Rivest.[4]

Four coordination is common for Fe(III),[7] but the best characterized complexes are homoleptic species with halide or other anionic ligands and bear a negative charge [e.g. $FeCl_4^-$, $FeBr_4^-$, $Fe(OR)_4^-$, $Fe(SR)_4^-$; R = alkyl, aryl]. Neutral, 4-coordinate Fe(III) molecular complexes have been reported [examples are $FeCl_3(THF)$ (THF = tetrahydrofuran),[8,37] $FeCl_3(R_2O)$ (R = Me, Et),[9] $FeCl_3(POCl_3)$,[10] $2FeCl_3{\cdot}MeSe(CH_2)_3SeMe$,[11] $FeI_3SC(NMe_2)_2$,[38] and the above mentioned $FeCl_3(PR_3)$ (R = Ph,[4] Cy[6]) compounds], and two have been crystallographically characterized.[37,38] 4-Coordinate Fe(III) centers are also present in the solid-state Fe_3O_4 material.[12] Positively charged 4-coordinate Fe(III) species, to the best of our knowledge, have never been reported.

It was therefore of interest to study the 1:1 adducts of $FeCl_3$ with monodentate phosphine ligands in more detail. In view of the thermal instability observed by us for solutions of $FeCl_3(PR_3)$ when R = Me, Ph,[1] we turned our attention to bulkier phosphines. We report here the successful synthesis and characterization of the compounds $FeCl_3(PR_3)$ (R = Cy, *t*-Bu) and studies of their decomposition reaction in ethanol.

Experimental Section

Unless otherwise stated, all operations were carried out under a dinitrogen atmosphere by standard Schlenk-line techniques. Solvents were dried by conventional methods and distilled under dinitrogen prior to use. Instruments used were as follows: FTIR, Nicolet 5DXC and Perkin-Elmer 1800; EPR, Bruker ER200; room-temperature magnetic susceptibility (modified Gouy method), Johnson Matthey; UV/vis, Schimadzu UV-240. Elemental analyses were by Midwest Microlab, Indianapolis, IN. The effective magnetic moments were calculated from the molar susceptibilities after correction for the diamagnetism of the ligands with Pascal constants.

$FeCl_3$ was dehydrated by treatment in $SOCl_2$. PCy_3 and $P(t\text{-}Bu)_3$ were purchased from Strem Chemicals and used without further purification.

Preparation of $FeCl_3(PCy_3)$. Anhydrous $FeCl_3$ (0.369 g, 2.27 mmol) was dissolved in 10 mL of Et_2O and filtered onto a solution of PCy_3 (0.618 g, 2.20 mmol) in 15 mL of toluene, rapidly producing a red solution and a small amount of dark solid. The solution was filtered, layered with 20 mL of *n*-heptane, and stored at −20 °C for 3 days. A brick red microcrystalline material formed, which was filtered off and dried in vacuo to yield 0.714 g (73%) of analytically pure product. Anal. Calcd for $C_{18}H_{33}Cl_3FeP$: C, 48.8; H, 7.5; Cl, 24.0. Found: C, 49.0; H, 7.5; Cl, 24.1. Magnetic susceptibility: $\chi_g = 30.92 \times 10^{-6}$ cgsu; $\mu_{eff} = 5.76\ \mu_B$ (molar diamagnetic correction -274.4×10^{-6} cgsu). IR (Nujol mull/cm^{-1}): 1350 w, 1325 w, 1295 w, 1270 w, 1195 w, 1180 w, 1175 m, 1115 w, 1075 w, 1035 w, 1005 m, 915 w, 890 w, 880 w, 850 m, 750

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Table I. Crystal Data for $[PH(t\text{-}Bu)_3]_2[Fe_2(\mu\text{-}OEt)_2Cl_6]$

formula	$C_{28}H_{66}Cl_6Fe_2O_2P_2$	V, Å^3	2033.99 (4)
fw	821.19	Z	2
space group	$P2_1/c$	d_{calc}, g/cm^3	1.34
a, Å	8.6243 (6)	μ(Cu Kα), cm^{-1}	103.65
b, Å	12.3849 (6)	radiation (monochromated in incident beam)	Cu Kα (λ = 1.541 78 Å)
c, Å	19.103 (1)	temp, °C	23
α, deg	90	transm factors: max, min	1.000, 0.4147
β, deg	94.594 (6)	R^a	0.065
γ, deg	90	$R_w{}^b$	0.090

$^a R = \sum||F_o| - |F_c||/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$.

w, 730 w, 515 w, 470 w, 395 s, 380 sh, 345 m. UV/visible [$CHCl_3$, room temperature/nm (ϵ/L·mol^{-1}·cm^{-1})]: 245 (13 600), 270 sh (6800), 313 (9100), 362 (8600).

Preparation of $FeCl_3[P(t\text{-}Bu)_3]$. Anhydrous $FeCl_3$ (1.19 g, 7.35 mmol) was dissolved in 20 mL of Et_2O and filtered onto a solution of $P(t\text{-}Bu)_3$ (1.49 g, 7.35 mmol) in 7 mL of toluene, immediately producing a clear red solution and some red precipitate. The solution was concentrated to ca. 15 mL under reduced pressure, producing more solid, which was filtered out, washed with 15 mL of Et_2O, and dried in vacuo. Yield: 2.16 g (81%) of brown-red microcrystalline material. Anal. Calcd for $C_{12}H_{27}Cl_3FeP$: C, 39.5; H, 7.5; Cl 29.2. Found: C, 39.4; H, 7.5; Cl, 30.1. Magnetic susceptibility: $\chi_g = 37.9 \times 10^{-6}$ cgsu. $\mu_{eff} = 5.73\ \mu_B$ (molar diamagnetic correction -221.4×10^{-6} cgsu). IR (Nujol mull/cm^{-1}): 1395 s, 1365 s, 1195 w, 1170 s, br, 1020 s, 930 m, 880 w, 800 m, 725 w, br, 620 m, 595 m, 565 w, 505 m, 470 m, 395 vs, 350 s. UV/visible [$CHCl_3$, room temperature/nm (ϵ/L·mol^{-1}·cm^{-1})]: 228 (10 100), 245 sh (7600), 270 sh (2900), 314 (4800), 363 (5200). A single crystal for an X-ray study was obtained by layering a small amount of the unconcentrated solution described above with *n*-heptane and storing at −20 °C. Both $FeCl_3(PR_3)$ (R = Cy, *t*-Bu) compounds slowly decompose (over a few weeks), as shown by the fading of their color, under dinitrogen at room temperature in the solid state.

Decomposition Reactions of $FeCl_3(PR_3)$ in Ethanol: (A) R = Cy. Formation of $[PHCy_3][FeCl_4]$. $FeCl_3(PCy_3)$ (0.316 g, 0.714 mmol) was placed in a Schlenk tube and treated with ethanol (10 mL). An immediate change was observed: the red insoluble solid turned yellow and at the same time partially dissolved to afford a suspension of a yellow solid in a yellow solution. Subsequent warming of the suspension to the reflux temperature yielded a yellow clear solution, from which yellow crystalline $[PHCy_3][FeCl_4]$ was obtained upon cooling. Yield: 99 mg. Anal. Calcd for $C_{18}H_{34}Cl_4FeP$: C, 45.1; H, 7.2; Cl, 29.6; P, 6.5. Found: C, 45.3; H, 7.4; Cl, 29.0; P, 5.4. IR (Nujol mull in a CsI plate/cm^{-1}): 380 s. $\chi_g = 31.3 \times 10^{-6}$ cgsu; $\mu_{eff} = 6.03\ \mu_B$ (molar diamagnetic correction -297.2×10^{-6} cgsu).

(B) R = *t*-Bu. Preparation of $[PH(t\text{-}Bu)_3]_2[Fe_2(\mu\text{-}OEt)_2Cl_6]$. $FeCl_3[P(t\text{-}Bu)_3]$ (1.098 g, 3.01 mmol) was placed in a Schlenk tube and treated with ethanol (35 mL). The solid partially dissolved at room temperature to afford a yellowish solution. Warming to the reflux temperature caused the complete dissolution of the red solid to afford a yellow-orange solution. Cooling to room temperature resulted in the extensive formation of yellow-orange crystals. A single crystal for the X-ray analysis was selected from this batch. After the crystals were isolated and dried in vacuo, another crop of product was obtained by layering the mother liquor with *n*-heptane at room temperature. A total of 0.712 g (65%) of air-stable, crystalline product was obtained. Anal. Calcd for $C_{14}H_{33}Cl_3FeOP$: C, 41.0; H, 8.1; Cl, 25.9. Found: C, 41.0; H, 8.1; Cl, 25.9. IR (Nujol mull in a CsI plate/cm^{-1}): 2400 m, 1405 m, 1350 w, 1260 w, 1210 w, 1180 m, 1155 w, 1090 m, 1030 s, 945 and 935 w, 875 s, 810 m, 720 w, 615 w, 530 s, 495 m, 475 m, 340 s, 300 s. UV/visible [$CHCl_3$, room temperature/nm (ϵ/cm^{-1}·mol^{-1}·L)]: 213 (16 800), 242 (15 400), 312 (12 000), 361 (9700). χ_g (25 °C) = 16.3×10^{-6} cgsu; μ_{eff} (per iron) = 4.07 μ_B (diamagnetic correction for a half-molecule -255.0×10^{-6} cgsu).

X-ray Crystallography for $[PH(t\text{-}Bu)_3]_2[Fe_2(\mu\text{-}OEt)_2Cl_6]$. A single crystal was glued onto the tip of a glass fiber, which was mounted on the diffractometer. Cell determination and data collection and reduction were routine. An empirical absorption correction was applied to the data.[13] Relevant crystal data are assembled in Table I. The structure was solved by direct methods, which revealed the position of the iron and chlorine atoms, and refined by alternate full-matrix least-squares cycles and difference Fourier maps. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and assigned an isotropic thermal parameter equal to 1.2 times the equivalent isotropic thermal parameter of the neighboring carbon or phosphorus atom. They were used for structure factor calculations but not refined. Final positional parameters are reported in Table II, whereas selected bond distances and angles are listed in Table III.

Table II. Positional Parameters for $[PH(t\text{-}Bu)_3]_2[Fe_2(\mu\text{-}OEt)_2Cl_6]$

atom	x	y	z
Fe	0.9457 (2)	0.1014 (1)	0.95339 (8)
Cl(1)	0.7789 (7)	0.0712 (3)	0.8593 (2)
Cl(2)	1.0901 (4)	0.2122 (4)	0.8883 (3)
Cl(3)	0.8433 (4)	0.2260 (2)	1.0200 (2)
P	1.2679 (3)	0.6043 (2)	1.1772 (1)
O	1.1284 (7)	0.0310 (5)	0.9983 (3)
C(1)	1.170 (1)	0.4811 (8)	1.1392 (6)
C(2)	1.222 (2)	0.378 (1)	1.1750 (8)
C(3)	0.996 (2)	0.492 (1)	1.141 (1)
C(4)	1.195 (2)	0.472 (1)	1.0610 (7)
C(5)	1.228 (1)	0.6306 (8)	1.2704 (5)
C(6)	1.307 (2)	0.547 (1)	1.3195 (7)
C(7)	1.056 (2)	0.631 (2)	1.2765 (8)
C(8)	1.285 (2)	0.741 (1)	1.2926 (7)
C(9)	1.478 (1)	0.618 (1)	1.1587 (6)
C(10)	1.570 (2)	0.524 (2)	1.187 (2)
C(11)	1.541 (2)	0.714 (2)	1.190 (2)
C(12)	1.494 (2)	0.624 (2)	1.0840 (8)
C(13)	1.291 (1)	0.061 (1)	0.9987 (6)
C(14)	1.328 (1)	0.155 (1)	1.0458 (7)

Table III. Selected Intramolecular Distances (Å) and Angles (deg) for $[PH(t\text{-}Bu)_3]_2[Fe_2(\mu\text{-}OEt)_2Cl_6]$

	Distances		
Fe–O	1.940 (6)	O–C(13)	1.44 (1)
Fe–O′	2.011 (6)	C(13)–C(14)	1.49 (2)
Fe–Cl(1)	2.242 (4)	P–C(1)	1.86 (1)
Fe–Cl(2)	2.287 (4)	P–C(5)	1.87 (1)
Fe–Cl(3)	2.227 (3)	P–C(9)	1.88 (1)
	Angles		
Cl(1)–Fe–Cl(2)	90.3 (2)	Cl(3)–Fe–O′	98.5 (2)
Cl(1)–Fe–Cl(3)	108.4 (2)	O–Fe–O′	73.0 (3)
Cl(1)–Fe–O	136.6 (2)	Fe–O–Fe′	107.0 (3)
Cl(1)–Fe–O′	91.4 (2)	Fe–O–C(13)	129.8 (6)
Cl(2)–Fe–Cl(3)	98.8 (2)	Fe′–O–C(13)	123.2 (6)
Cl(2)–Fe–O	93.0 (2)	C(1)–P–C(5)	113.7 (5)
Cl(2)–Fe–O′	161.1 (2)	C(1)–P–C(9)	114.4 (5)
Cl(3)–Fe–O	113.8 (2)	C(5)–P–C(9)	114.7 (5)

Results

The 1:1 interaction between anhydrous $FeCl_3$ and PCy_3 or $P(t\text{-}Bu)_3$ ligands (eq 1) is rapid at room temperature in toluene or ether with formation of red crystalline precipitates of the 1:1 adducts.

$$FeCl_3 + PR_3 \rightarrow FeCl_3(PR_3) \qquad (R = Cy,\ t\text{-}Bu) \qquad (1)$$

The best results are obtained when ether is used to dissolve $FeCl_3$, since the product crystallyzes without unreacted $FeCl_3$ as a contaminant.[14] Supposedly, ether forms soluble adducts with $FeCl_3$,[9] but its donor properties are inferior to those of the

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(14) For related syntheses carried out in toluene, we occasionally observed effective magnetic moments considerably higher than the expected theoretical value. This result can only be explained by the presence of a paramagnetic (for five unpaired electrons) impurity with a lower molecular weight.

phosphine ligands. The two products are thermally sensitive both in solution and in the solid state, and they become less intensely colored upon prolonged storage at room temperature under dinitrogen, although they can be stored for longer periods of time under dinitrogen at −20 °C.

Both $FeCl_3(PR_3)$ (R = Cy, *t*-Bu) compounds are *red* solids. This contrasts with the report of a yellow $FeCl_3(PCy_3)$ compound by Issleib and Brack,[6] obtained from $FeCl_3$ and the phosphine in alcoholic solvent. A 1:1 adduct with PPh_3, $FeCl_3(PPh_3)$, was also reported to be yellow.[4] The latter derivative was obtained[4] from $Fe_3(CO)_{12}$ and PPh_3 in $CHCl_3$ and final workup in ethanol. It is reported to display the correct C, H, Cl, and Fe analyses, and a Mössbauer study was later described as consistent with the formulation of this molecule as a 4-coordinate complex with a pseudotetrahedral geometry.[5] We have not been able to obtain this yellow solid by direct interaction of $FeCl_3$ and PPh_3 in a 1:1 ratio in either ethanol, chloroform, or other solvents.[1,2]

We do not know the relationship between these yellow solids and our red solids, but we have conclusive evidence that our red solids are 4-coordinate mononuclear complexes with pseudotetrahedral coordination geometry. The evidence is the following: These two compounds are soluble in nonpolar organic solvents (e.g. toluene), therefore suggesting that they are neutral. Both compounds exhibit two low-energy IR absorptions in the typical region of Fe–Cl stretching vibrations (395 s, 345 m cm^{-1} for R = Cy; 395 vs, 350 s cm^{-1} for R = *t*-Bu). For the C_{3v} symmetry of the tetrahedrally coordinated $FeCl_3(PR_3)$ molecules, two bands of A_1 and E types are expected. An examination of the relative intensity of the two bands suggests that the higher energy absorption is due to the asymmetric, E type stretching vibration, whereas the lower energy absorption is due to the symmetric, A_1 type mode. Although most pyramidal XY_3 halogeno compounds show $\nu(A_1) > \nu(E)$,[15] matrix-stabilized pyramidal $FeCl_3$ has a more energetic E mode (460.2 cm^{-1}) and a less energetic A_1 mode (363.0 cm^{-1}).[16] The above mentioned yellow $FeCl_3(PPh_3)$ has been reported[4] to exhibit absorptions at 370 s and 320 w cm^{-1}, assigned to Fe–Cl stretching vibrations. Other claimed tetrahedrally coordinated $FeCl_3L$ compounds[8-11] have not been investigated by far-IR spectroscopy.

We have not been able to obtain a crystal structure for $FeCl_3(PCy_3)$. The crystals were poor diffractors, probably because of extensive orientational disorder of the cyclohexyl groups. Nor have we been able to successfully complete an X-ray structural analysis on the $FeCl_3[P(t\text{-}Bu)_3]$ compound. The selected crystals had a triclinic cell very close to being monoclinic [$\alpha = 90.15\ (2)°$, $\gamma = 89.91\ (1)°$]. Data collection was first attempted in the monoclinic system. The structure was solved, and the expected pseudotetrahedral arrangement of three chlorine atoms and one $P(t\text{-}Bu)_3$ ligand around the Fe center was obtained. However, refinement of the structure stopped at $R = 0.15$; not all the carbon atoms were located, and a few of the identified carbon atoms showed severe stability problems. This phenomenon could be due to either extensive disorder of the *t*-Bu groups or wrong choice of the crystal system. A second data set was collected in the triclinic system, but similar final results were obtained. The crystal data clearly show $FeCl_3P(t\text{-}Bu)_3$ to be a neutral, mononuclear tetrahedral complex, although the bad quality of the data or the inherent thermal activity/disorder of the molecules in the crystal makes an accurate determination of bond distances and angles impossible. A more detailed description of the experimental crystallography for $FeCl_3[P(t\text{-}Bu)_3]$ is given in the supplementary material.

The two $FeCl_3(PR_3)$ compounds (R = Cy, *t*-Bu) have the same color and nearly identical UV/visible and far-IR spectra. We therefore conclude that they have the same structure. They also exhibit the same magnetic moment, close to the expected value for five unpaired electrons (5.76 μ_B for R = Cy; 5.73 μ_B for R = *t*-Bu).

Addition of a second equivalent of the phosphine to a toluene solution of $FeCl_3(PCy_3)$ did not show the formation of the 1:2 adduct, but it rather led to decomposition by unknown routes, as indicated by the precipitation of a yellow-orange solid. The $FeCl_3(PCy_3)_2$ derivative has been described[1] and was prepared in low yields by interaction of $FeCl_3$ and 2 equiv of PCy_3 in toluene. On the other hand, it has been shown that $FeCl_3(PR_3)_n$ compounds (R = Me, Ph) undergo thermal decomposition faster for $n = 1$ than for $n = 2$.[1] No evidence was found for the existence of a 1:2 adduct with $P(t\text{-}Bu)_3$. This could be ascribed to the larger cone angle for this ligand (cone angles[17] are 170° for PCy_3 and 182° for $P(t\text{-}Bu)_3$).

With the objective in mind of finding a relationship between our red $FeCl_3(PR_3)$ compounds and the yellow $FeCl_3(PCy_3)$ complex reported in the literature,[6] which was obtained by interaction of $FeCl_3$ and PCy_3 in ethanol, we subjected the red $FeCl_3(PR_3)$ derivatives to treatment in ethanol. For both compounds (R = Cy, *t*-Bu), yellow solutions are obtained, but the products of the two reactions are different, and none of these correspond to an $FeCl_3(PR_3)$ formulation. The PCy_3 compound decomposes according to eq 2, whereas the $P(t\text{-}Bu)_3$ compound follows the path described in eq 3 to produce the novel $[Fe_2(\mu\text{-}OEt)_2Cl_6]^{2-}$ dianion.

$$2FeCl_3(PCy_3) + 2EtOH \rightarrow [PHCy_3][FeCl_4] + \text{unidentified products} \quad (2)$$

$$2FeCl_3[P(t\text{-}Bu)_3] + 2EtOH \rightarrow [PH(t\text{-}Bu)_3]_2[Fe_2(\mu\text{-}OEt)_2Cl_6] \quad (3)$$

The $[PHCy_3][FeCl_4]$ salt has been identified by elemental analysis and IR spectroscopy (P–H stretching vibration at 2360 cm^{-1}, Fe–Cl T-mode stretching vibration at 380 cm^{-1}). We were unable to isolate other products from the reaction mixture of eq 2.

The product of reaction 3 analyzes correctly for $FeCl_3[P(t\text{-}Bu)_3]\cdot EtOH$. It shows the characteristic P–H stretching vibration at 2400 cm^{-1}, indicating an ionic formulation. A room-temperature magnetic susceptibility measurement shows a reduced magnetic moment with respect to a high-spin configuration ($\mu_{eff} = 4.07\ \mu_B$ per Fe center), which appears to be consistent with the formation of a dinuclear species in which the iron centers are antiferromagnetically coupled. The above hypotheses are fully confirmed by an X-ray structural analysis and by a variable-temperature magnetic susceptibility study.

Views of the $[PH(t\text{-}Bu)_3]^+$ cation and $[Fe_2(\mu\text{-}OEt)_2Cl_6]^{2-}$ dianion are shown in Figure 1. The asymmetric unit contains one full cation and half of the dianion, which sits on a crystallographic inversion center. Selected bond distances and angles are given in Table III. The dianion consists of two 5-coordinate Fe(III) centers bridged by two ethoxide groups and bearing three terminal chloro ligands each. The coordination geometry around each iron atom can be described either as distorted trigonal-bipyramidal, the Cl(2) and O′ atoms occupying the pseudoaxial positions, or as distorted square-pyramidal, the Cl(3) atom being the apical ligand. The actual coordination geometry, in fact, can be viewed to lie along the Berry pseudorotation coordinate between the two ideal tbp and sp geometries, the Cl(2)–Fe–O′ angle closing up and the Cl(1)–Fe–O angle opening up on going from tbp to sp.

The observed distortion might be brought about by the reduction of the O–Fe–O′ angle to the observed value of 73.0 (3)°, probably due to the constriction required for the oxygen atoms to bind both Fe centers to form the Fe_2O_2 ring. The Fe–Fe separation of 3.177 Å indicates no bonding and is slightly longer than most Fe–Fe distances for related bis(alkoxo-bridged) compounds, which are all 5- or 6-coordinate neutral molecules. Examples are 3.144 (1) Å for $Fe_2L(OEt)_2Cl_2$ and 3.106 (7) Å for $Fe_2L(OMe)_2Cl_2$ (L = dianion of 1,4-piperazinediylbis(*N*-ethylenesalicylaldimine)),[18,19]

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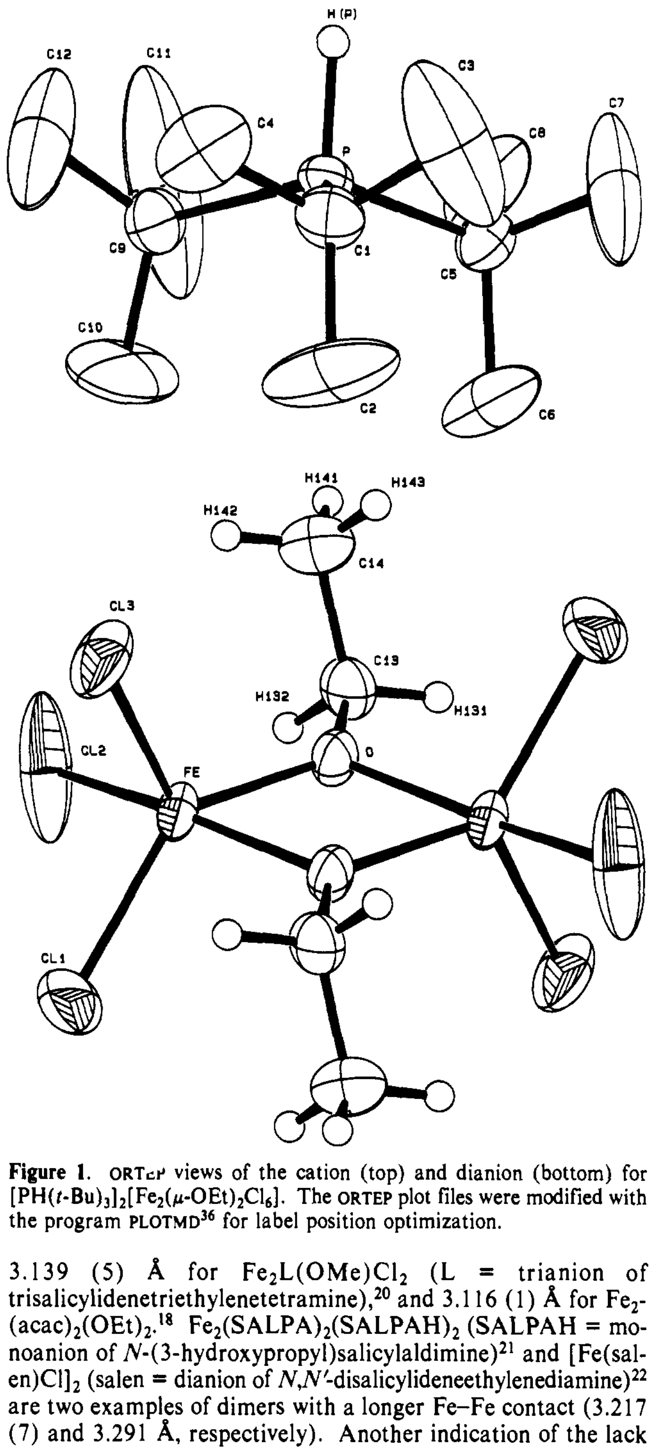

Figure 1. ORTEP views of the cation (top) and dianion (bottom) for $[PH(t\text{-}Bu)_3]_2[Fe_2(\mu\text{-}OEt)_2Cl_6]$. The ORTEP plot files were modified with the program PLOTMD[36] for label position optimization.

3.139 (5) Å for $Fe_2L(OMe)Cl_2$ (L = trianion of trisalicylidenetriethylenetetramine),[20] and 3.116 (1) Å for $Fe_2(acac)_2(OEt)_2$.[18] $Fe_2(SALPA)_2(SALPAH)_2$ (SALPAH = monoanion of *N*-(3-hydroxypropyl)salicylaldimine)[21] and $[Fe(salen)Cl]_2$ (salen = dianion of *N,N'*-disalicylideneethylenediamine)[22] are two examples of dimers with a longer Fe–Fe contact (3.217 (7) and 3.291 Å, respectively). Another indication of the lack of Fe–Fe bonding is the relatively open Fe–O–Fe′ angle, 107.0 (3)°.

The sum of the bond angles at the O atom is 360°, indicating an sp^2 hybridization for the O atom, which would seem to indicate some degree of π-donation into the Fe_2 system by the O atoms. Fe–O distances are 1.940 (6) Å (Fe–O) and 2.011 (6) Å (Fe–O′). The inequivalency could be explained by the trans-labilizing effect of Cl(2) on the Fe–O′ distance. The O atom (pseudoequatorial in the distorted tbp structure) does not have ligands close to its trans position. A longer axial bond has been observed previously in $Fe(N_3)_5^{2-}$ (2.041 (15) Å vs 1.96 (4) Å for the equatorial bond), which is the only known homoleptic Fe(III) compound of tbp geometry.[23] However, whether the axial or the equatorial bond should be longer in a transition-metal tbp complex seems to be a delicate function of the electron count.[24] The Fe–Cl bond distances in the $[Fe_2(\mu\text{-}OEt)_2Cl_6]^{2-}$ dianion vary in the range 2.227–2.287 Å. Again, the distance depends on the relative position of the Cl atom in the structure: the pseudoaxial Fe–Cl(2) bond is the longest. These Fe–Cl distances are longer than those found in $FeCl_4^-$ (in the 2.175–2.185 Å range).[25] This lengthening could be due to a decrease of effective positive charge on Fe(III) in the dinuclear dianion with respect to $FeCl_4^-$, because of the increase in coordination number from 4 to 5, and possibly also because of the π-donation from the bridging oxygen atoms, which is suggested by the bond angles at O (see above). In agreement with the above reasoning, the chloride-containing 6-coordinate bis(alkoxo)-bridged dimers mentioned above[18–20,22] show even longer Fe–Cl bonds (in the 2.30–2.36 Å range) than those found in the $[Fe_2(\mu\text{-}OEt)_2Cl_6]^{2-}$ species. Also, the Fe–Cl bonds in the 5-coordinate dianion are slightly longer than those found in the 5-coordinate neutral $FeCl_3(PR_3)_2$ (R = Ph, Me) compounds (in the 2.19–2.23 Å range).[1]

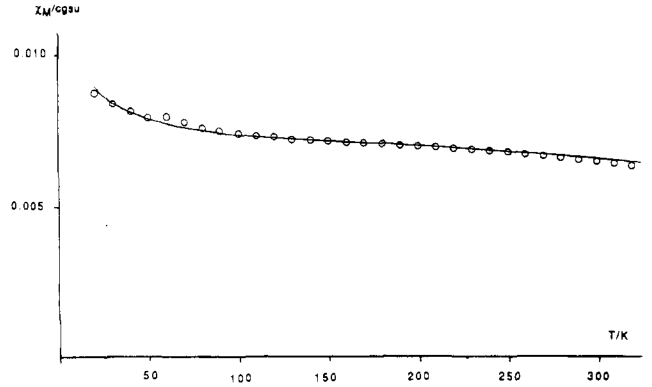

Figure 2. Temperature dependence of the magnetic susceptibility of $[PH(t\text{-}Bu)_3]_2[Fe_2(\mu\text{-}OEt)_2Cl_6]$. The circles are the experimental points, whereas the solid line represents the best fit.

Variable-temperature susceptibility studies confirm antiferromagnetic coupling between the two iron centers. The effective magnetic moment drops from 4.04 μ_B per Fe center at 320 K to 1.19 μ_B at 20 K. The data have been analyzed on the basis of the usual spin–spin interaction model based on the exchange Hamiltonian $H = -2JS_1 \cdot S_2$ with $S_1 = S_2 = {}^5/_2$, $g = 2.00$, and TIP = 0.[26] The magnetic susceptibility expression was

$$\chi_M \text{ (per iron)} = \frac{1.5007}{T} \times \frac{e^{2x} + 5e^{6x} + 14e^{12x} + 30e^{20x} + 55e^{30x}}{1 + 3e^{2x} + 5e^{6x} + 7e^{12x} + 9e^{20x} + 11e^{30x}}(1 - p) + \frac{4.376}{T}p$$

where $x = J/kT$, and p gauges the amount of a magnetically dilute ferric impurity. A nonlinear fitting routine that minimized the function $F = \sum_i(\chi_i^{obs} - \chi_i^{calcd})^2$ (unit weights) yielded $J = -24.6$ (1) cm^{-1} and $p = 0.032$ (3), with a minimum for the function F of 9.02×10^{-5} for 31 observations and a correlation coefficient of 0.9896. The fit is illustrated in Figure 2.

Discussion

After having synthesized trigonal-bipyramidal 1:2 adducts of $FeCl_3$ with phosphine ligands whose spin state is a function of the nature of the phosphine,[1] we have now shown that it is possible to prepare relatively stable 1:1 adducts, $FeCl_3(PR_3)$, by the use of bulky phosphine ligands (R = Cy, *t*-Bu). The preparation reactions were carried out in ethereal solvent. It is interesting to note that Fe(III) (a classical hard acid) prefers the softer phosphine to the harder ether, even though ether is present in large

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excess, being the solvent of the reaction. In order to understand this behavior, we have to abandon the qualitative hard and soft ideas and examine the thermodynamics of the acid–base interaction. We shall use Drago's semiempirical treatment of acid–base interactions.[27] To summarize the theory, the enthalpy of the acid–base interaction is described by the empirical formula $-\Delta H = E_AE_B + C_AC_B$, where E and C are parameters of the acid (A) or base (B). The best theoretical interpretation of these parameters is that the X_AX_B products ($X = E$ or C) are proportional to the extent of respectively the electrostatic (or ionic) contribution or the covalent contribution. The more elaborate treatment,[28] where an additional term is introduced to account for the electronegativity driven charge transfer, is not necessary in our case since both the acid and the bases are neutral species.[28] Usually, a softer acid or base has a larger C coefficient and a smaller E coefficient than a harder one, so that the C_AC_B product is large in a soft–soft interaction, whereas the E_AE_B product is large in a hard–hard interaction.

Unfortunately, E_A and C_A parameters for $FeCl_3$ are not available. The E_B and C_B parameters for tricyclohexylphosphine or tri-*tert*-butylphosphine are not known either, but those of other phosphine or phosphite ligands are known[27d] (PMe_3, $E_B = 1.11$ and $C_B = 6.51$; $C_2H_5C(CH_2O)_3P$, $E_B = 0.73$ and $C_B = 6.47$). Since PMe_3 and $C_2H_5C(CH_2O)_3P$ have quite different electronic properties[17,29] and their E and C parameters are nevertheless similar, we feel safe to conclude that PCy_3 and $P(t\text{-Bu})_3$ probably also have similar E and C parameters. The largest variation is in the E parameter; since PCy_3 and $P(t\text{-Bu})_3$ are electronically more similar to PMe_3, we anticipate that their E parameters will be close to 1.1. If we now compare these parameters to those of Et_2O ($E_B = 1.08$; $C_B = 3.08$),[27d] we conclude that the E_AE_B product remains substantially unchanged, whereas the C_AC_B term strongly favors the binding of the phosphine ligand. In conclusion, the application of Drago's semiempirical treatment of acid–base interactions shows that, under the assumptions discussed above, bonding of a phosphine ligand to a Lewis acid will be preferred over bonding of ether, no matter what the nature of the acid. This is a case where the application of the hard and soft qualitative ideas would lead to the wrong conclusion, whereas the observed trend is in accord with semiempirical thermodynamic data.

It is interesting to observe that the $[PH(t\text{-Bu})_3]_2[Fe_2(\mu\text{-}OEt)_2Cl_6]$ compound corresponds to the minimum formula $[PH(t\text{-Bu})_3][Fe(OEt)Cl_3]$, which can be envisioned to be derived by the replacement of one chloride ion with an ethoxide ion in the corresponding $FeCl_4^-$ salt. However, although the $FeCl_4^-$ complex ion is stable as a mononuclear species, the ethoxide-containing species exists as a bis(ethoxo)-bridged dimer. To explain this difference, we observe that oxygen-based ligands are smaller than the chloride ion, and the expansion of the coordination sphere from 4 to 5 may become possible when the steric bulk around the iron center is relieved by the formal replacement of one Cl^- with one EtO^- group. To illustrate this point better, we observe that although the most stable Fe(III)–chloride complex is the 4-coordinate $FeCl_4^-$ (a claim of the 5-coordinate $FeCl_5^{2-}$ is controversial),[30] the most stable Fe(III)–fluoride complexes are the 5-coordinate FeF_5^{2-} and the 6-coordinate FeF_6^{3-}.[31] Since both the chloride and fluoride complexes have a high-spin configuration, the different geometry cannot be the result of a different ligand field stabilization energy.

Another interesting point is the relationship between the reaction described in eq 3 and the synthesis of homoleptic iron(III) alkoxides, described by Bradley et al. (eq 4).[32] The latter involves

$$FeCl_3 + 3ROH + 3NH_3 \rightarrow Fe(OR)_3 + 3NH_4Cl \qquad (4)$$

the interaction of anhydrous $FeCl_3$ with the appropriate alcohol in the presence of excess ammonia. The base traps the alcohol proton and provides the driving force for the reaction. Reaction 3 can be viewed as the first step of Bradley's synthesis. The base in this case is the phosphine ligand coordinated to the iron center, and the 1:1 $FeCl_3$:phosphine stoichiometry in the starting material limits the reaction to the inclusion of only one ethoxide ligand per iron.

Concerning the difference of outcome between the reactions of the two different phosphine complexes with ethanol (reactions 2 and 3), we cannot draw conclusions without the knowledge of the identity of the other products of eq 2. It would be tempting to propose that the first intermediate of both reactions is $[PHR_3][FeCl_3(OEt)]$, which subsequently forms the stable dinuclear product for R = *t*-Bu. In the case of R = Cy, exchange of the ligands might occur to afford the $FeCl_4^-$ and $[FeCl_2(OEt)_2]^-$ ions. If this is the case, the reason for the difference in outcome might simply be related to the different lattice energy for the $[Fe_2(\mu\text{-}OEt)_2Cl_6]^{2-}$ salt and the $FeCl_4^-$ salts with the different phosphonium cations. Thus, under this assumption, the unidentified product of eq 2 should be $[PHCy_3][FeCl_2(OEt)_2]$ or perhaps a corresponding oligonuclear species.

Concerning the antiferromagnetic coupling of the Fe(III) centers in the $[Fe_2(\mu\text{-}OEt)_2Cl_6]^{2-}$ dianion, the value of -24.6 cm^{-1} for the coupling constant J is more negative than those reported for analogous bis(alkoxide)-bridged dimers (in the range -7 to -17 cm^{-1}),[18-20,33] although dimers with different structures can have larger values [e.g. ca. -95 cm^{-1} for dimers based on the Fe_2O^{4+} unit[34] and -121 cm^{-1} for the hemerythrin model compound,[35] $Fe_2O(O_2CCH_3)_2(HBpz_3)_2$]. How the exchange coupling constants for dinuclear Fe(III) compounds containing the Fe_2O_2 bridging system are influenced by variations in the geometrical and chemical features of the bridging and nonbridging ligands is not well understood.[19]

Conclusions

We have reported the synthesis and characterization of tetrahedral 1:1 adducts of $FeCl_3$ with monodentate phosphines. Only by using bulky substituents on the phosphine ligands were we able to isolate these products, which are still thermally sensitive and slowly decompose at room temperature in the solid state. The reaction of these derivatives with ethanol affords phosphonium salts and casts doubts on an earlier report on the formation of $FeCl_3(PCy_3)$ from $FeCl_3$ and PCy_3 in ethanol.

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Supplementary Material Available: A description of the experimental crystallography for $FeCl_3[P(t\text{-}Bu)_3]$ and tables of complete crystal data, bond distances and angles, anisotropic displacement parameters, and hydrogen atom coordinates for $[PH(t\text{-}Bu)_3]_2[Fe_2(\mu\text{-}OEt)_2Cl_6]$ (8 pages); a listing of calculated and observed structure factors for $[PH(t\text{-}Bu)_3]_2[Fe_2(\mu\text{-}OEt)_2Cl_6]$ (18 pages). Ordering information is given on any current masthead page.

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Crystal Structure and Magnetic Properties of Potassium Bis(dithiooxalato)nitrosylferrate(2−), a Compound with a Sulfur-Bridged Iron Dimer

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A dimer of potassium bis(dithiooxalato)nitrosylferrate(2−) monohydrate formula units, $\{K_2Fe(C_2O_2S_2)_2NO\cdot H_2O\}_2$, crystallizes in the monoclinic space group $C2/c$ with unit cell dimensions of a = 18.416 (6) Å, b = 15.800 (6) Å, c = 9.834 (4) Å, and β = 111.26 (3)° with Z = 4. The coordination around the iron atom is distorted tetragonal pyramidal with an average basal Fe–S distance of 2.27 Å. The sixth coordination position of iron is filled by a sulfur atom from an adjacent complex ion with an Fe–S distance of 3.823 Å. The Fe–N–O fragment has an angle of 161.8 (3)°, and the N–O distance is 1.148 (3) Å. The loosely bound dimer exhibits surprisingly strong intramolecular antiferromagnetic interactions. The magnetic susceptibility data may be fit with a dimer model by using the exchange Hamiltonian $H_{ex} = -2JS_1\cdot S_2$ with $S_1 = S_2 = {}^1/_2$ and an exchange-coupling constant of −23.8 cm^{-1}. This is a large exchange-coupling constant in view of the long Fe–S superexchange pathway.

Introduction

Studies have shown that sulfur atoms as bridging ligands are very effective in transmitting superexchange interactions over long distances between paramagnetic metal ions in clusters and low-dimensional systems.[1] To more fully understand the chemical and structural features that govern these superexchange interactions, we have undertaken a systematic study of the structural and magnetic properties of sulfur-bridged transition-metal clusters, chains, and sheets. Here, we report the crystal structure and magnetic properties of the dimer $K_4[Fe_2(C_2O_2S_2)_4(NO)_2]\cdot 2H_2O$,[2] a compound that has been found to have an unsymmetrical Fe_2S_2 antiferromagnetically exchange-coupled unit with two short iron–sulfur distances and two rather long iron–sulfur distances.

Experimental Section

Synthesis. Commercially available ferric chloride, potassium nitrite, and potassium dithiooxalate were used without further purification. A crystalline sample of the compound was prepared by a modification of the procedure described by Coucouvanis and co-workers.[2] All experimental manipulations were carried out under a nitrogen atmosphere, and deoxygenated distilled water was used. $K_2C_2O_2S_2$ (0.047 mol) was dissolved in 20 mL of H_2O, and 20 mL of an aqueous solution of $FeCl_3$ $6H_2O$ (0.015 mol) was added. The solution turned violet, and an aqueous solution of KNO_2 (20 mL, 0.015 mol) was added dropwise to this violet solution. The resulting solution was maintained at 70 °C with stirring for 2 h, and the hot solution was then filtered. The green precipitate was discarded, and the green solution was cooled slowly to room temperature and then placed in a refrigerator for several days. Black crystals were obtained upon filtration, and these were recrystallized from aqueous solution. Elemental analysis and the X-ray single-crystal determination, described below, confirmed the identity of the material.

Crystallographic Data Collection. X-ray diffraction data were collected by using a Nicolet R3m/μ diffractometer that was equipped with a graphite monochromator and molybdenum radiation (wavelength 0.7107 Å). Cell dimensions were obtained by least-squares fitting from 25 high-angle reflections. Systematic absences indicated that the crystal belonged to the monoclinic space group Cc or $C2/c$. The latter was confirmed as the correct space group by the successful refinement of the structure. Two check reflections collected after every 90 reflections revealed no unexpected variation in intensity. Of the 3238 unique reflections recorded in the range 3° < 2θ < 55°, 2880 reflections having $I > 3\sigma(I)$ were used in the structure determination. Data were corrected for Lorentz and polarization effects but not for absorption owing to a moderately low absorption coefficient (23.4 cm^{-1}). An isotropic sec-

Table I. Crystallographic Data for $K_4[Fe_2(C_2O_2S_2)_4(NO)_2]\cdot 2H_2O$

fw 844.66	space group $C2/c$
a = 18.416 (6) Å	$T \simeq$ 20 °C
b = 15.800 (6) Å	λ = 0.7107 Å
c = 9.834 (4) Å	ρ_{obsd} = 2.08 g cm^{-3}
β = 111.26 (3)°	ρ_{calcd} = 2.10 g cm^{-3}
V = 2667 (2) Å^3	R = 0.035
Z = 4	R_w = 0.05

Table II. Atomic Coordinates (×10^4) and Isotropic Thermal Parameters (Å^2 × 10^3)

	x	y	z	U^a
K(1)	0	4656 (1)	2500	38 (1)
K(2)	5000	4229 (1)	2500	66 (1)
K(3)	4296 (1)	1880 (1)	252 (1)	46 (1)
Fe	8044 (1)	1262 (1)	1547 (1)	33 (1)
S(1)	7175 (1)	1734 (1)	2540 (1)	36 (1)
S(2)	7205 (1)	190 (1)	484 (1)	49 (1)
S(3)	8512 (1)	1050 (1)	−250 (1)	52 (1)
S(4)	8460 (1)	2619 (1)	1709 (1)	38 (1)
N	8784 (1)	829 (1)	2945 (3)	46 (1)
C(1)	6425 (1)	1013 (1)	2068 (2)	31 (1)
C(2)	6454 (1)	253 (2)	1115 (3)	34 (1)
C(3)	9119 (1)	1882 (2)	−159 (3)	37 (1)
C(4)	9105 (1)	2646 (2)	813 (2)	32 (1)
O(1)	5852 (1)	1081 (1)	2442 (2)	42 (1)
O(2)	5925 (1)	−262 (1)	810 (2)	48 (1)
O(3)	9549 (1)	1924 (1)	−861 (2)	46 (1)
O(4)	9533 (1)	3249 (1)	851 (2)	39 (1)
O(5)	9396 (1)	615 (2)	3680 (3)	76 (1)
O(6)	8609 (2)	1612 (2)	5948 (3)	67 (1)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

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