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Synthesis and Characterization of New Iron–Dithiolene Complexes

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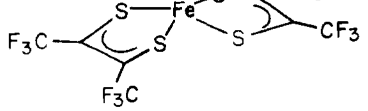
In the past decade several iron–carbonyl–dithiolene complexes have been characterized.[1] The reaction of iron pentacarbonyl with bis(perfluoromethyl)dithietene has been shown to form $\{Fe[S_2C_2(CF_3)_2]_2\}_2$,[2] **1**, and $[Fe(CO)_3]_nS_2C_2(CF_3)_2$, n = 1,[3] 2.[4] The reaction of **1** with Lewis bases has yielded pentacoordinate complexes of the $Fe[S_2C_2(CF_3)_2]_2$(base) type.[5] Herein is reported the parent member of the series: $Fe[S_2C_2(CF_3)_2]_2CO$, **2**. Compound **2** is prepared in quantitative yield by the evaporation of a filtered dichloromethane solution of **1** with a stream of carbon monoxide.[6a] The resulting deep blue complex exhibits a ν_{CO} absorption of 2059 cm^{-1} (KBr and CH_2Cl_2). This complex is thermally unstable with respect to loss of CO (equilibrium 1).[6b] Anal. Calcd:[9]

$$OCFe[S_2C_2(CF_3)_2]_2 = CO + {}^1/_2\{Fe[S_2C_2(CF_3)_2]_2\}_2 \qquad (1)$$

C, 20.16; H, 0.0; S, 23.92. Found: C, 19.70; H, 0.16; S, 23.87. Differential scanning calorimetry measurements reveal a broad endothermic peak at ~97.5° of 21 kcal/mol indicating CO loss over a broad temperature range, Figure 1. Reduction of **2** with hydrazine in dichloromethane yields an unstable red solution which does not exhibit a ν_{CO} absorbance in the 1750–2300-cm^{-1} region in dichloromethane indicating carbonyl extrusion. Attempts to isolate this red reduction product as the tetrabutylammonium salt lead to the isolation of $(Bu_4N)_2\{Fe[S_2C_2(CF_3)_2]_2\}_2$[2] suggesting instability of this red material. In dichloromethane **2** exhibits absorptions (log ϵ) at ~16,725 cm^{-1} (sh) (3.97), 21,420 cm^{-1} (3.38), 24,040 cm^{-1} (3.52), 30,490 cm^{-1} (3.56), 37,880 cm^{-1} (4.36). The absorptions are similar to that reported for $Fe[S_2C_2(CF_3)_2]_2L$ (L = $P(OPh)_3$, $AsPh_3$)[5] indicating the same electronic structure. By analogy to the X-ray structure of $Ph_3AsFe[S_2C_2(CF_3)_2]_2$,[7] **2** is proposed to have a square-pyramidal structure with an apical carbonyl group.



2

The reaction of **2** with monodentate phosphines results in the displacement of CO and the formation of $Fe[S_2C_2(CF_3)_2]_2PR_3$.[5] Polarographic measurements were thwarted by the decomposition of **2** in dichloromethane solutions of the supporting electrolyte. These results indicate the instability of **2** toward nucleophilic attack. Although crystals and solutions of **2** decompose in short periods of time at room temperatures (eq 1), **2** does not undergo photodecomposition with a high-pressure Hg lamp for 4 hr at −77°. Thus **2** is photoinert while being thermally unstable.

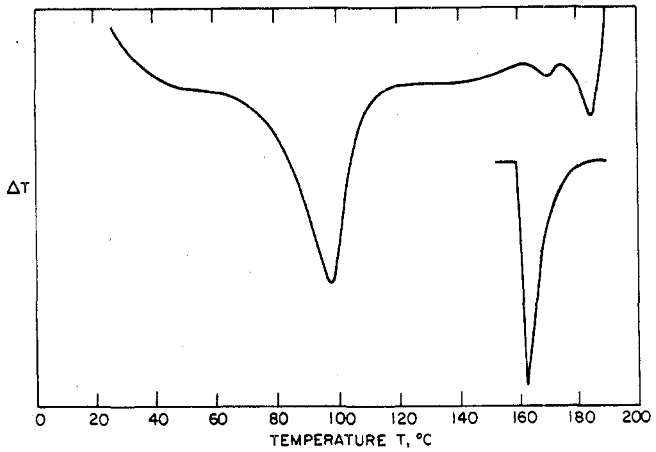


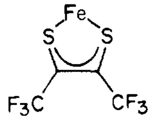
Figure 1. Differential scanning thermograms for 19.4 mmol of $Fe(CO)[S_2C_2(CF_3)_2]_2$ (top) and 0.217 mmol of In^0 calibrant (bottom).

Although η^5-$C_5H_5Fe[S_2C_2(CF_3)_2]$, **3**, has been characterized mass spectrally from the reaction product resulting from the reaction of cyclopentadienyl-μ-dicarbonyl-iron(I) dimer and bis(perfluoromethyl)dithietene[4] and reportedly exhibits a melting point of 150°,[1] no synthesis has yet been reported. Complex **3** has now been prepared by a rational synthesis from a reaction of cyclopentadienyl-μ_3-carbonyl-iron(I) tetramer[8] and bis(perfluoromethyl)dithietene (eq 2) in refluxing toluene

$$S_2C_2(CF_3)_2 + [Fe(\mu_3\text{-}CO)(\eta^5\text{-}C_5H_5)]_4 \rightarrow (F_3C)_2C_2S_2Fe(\eta^5\text{-}C_5H_5) \qquad (2)$$

for 12 hr. Recrystallization was effected from dichloromethene–n-hexane. The observed analysis is consistent with the formation. Anal. Calcd:[9] C, 31.14; H, 1.45; S, 18.47. Found: C, 30.95; H, 1.26; S, 19.06. A mass spectral parent ion was observed to be centered at m/e 347 (calcd 347 (^{56}Fe)). The solution molecular weight is 340 in N,N-dimethylformamide. A melting point of >300° was observed which is in sharp contrast with the previously cited melting point.[1] The infrared spectrum of **3** reveals characteristic cyclopentadienyl and dithiolene absorbances and indicates that bridging and terminal carbonyl groups are absent. These data suggest that **3** is monomeric and thus should possess one unpaired electron per metal site.

The structure of **3** is proposed to be similar to the diamagnetic complexes $(\eta^5\text{-}C_5H_5)Co(S_2C_2R_2)$ (R = CN,[10] CF_3[11,12]), $(\eta^5\text{-}C_5H_5)Ni[S_2C_2(CF_3)_2]$,[13] and $(\eta^5\text{-}C_5H_5)M[S_2C_2(CF_3)_2]$ (M = Rh, Ir).



3

Polarographic investigations show a single one-electron reduction wave at −0.44 V (vs. SCE electrode). Thus the reduced form of **3** was not readily isolated under ambient conditions.[1]

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Registry No. $\{Fe[S_2C_2(CF_3)_2]_2\}_2$, 19570-24-2; $[Fe(\mu_3\text{-}CO)(\eta^5\text{-}C_5H_5)]_4$, 12203-87-1; $S_2C_2(CF_3)_2$, 55162-21-5; $Fe[S_2C_2(CF_3)_2]_2CO$, 55162-25-9; $\eta^5\text{-}C_5H_5Fe[S_2C_2(CF_3)_2]$, 12261-16-4.

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Resonance Raman Spectra of Metal Complexes of Substituted Dithiophosphinic Acids[1a]

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Resonance Raman scattering may occur if the exciting radiation falls within an electronic absorption band of the scattering molecule.[2] The intensity of the Raman lines arising from vibrations coupled to the electronic transition may be increased by several orders of magnitude compared with their intensity in normal Raman spectra thus enabling Raman spectroscopic investigations to be carried out at very low concentrations of the chromophoric scattering moiety. In this communication we report the resonance Raman scattering observed from three metal complexes of dithiophosphinic acid derivatives $Ni[S_2P(OEt)_2]_2$, $Ni[S_2PPh_2]_2$, and $Cr[S_2PPh_2]_3$. The physical properties of these compounds have been studied earlier but their Raman spectra were not obtained as these compounds show strong self-absorption.[3,4]

Many papers have appeared recently dealing with the resonance Raman spectra of biological systems containing MS_n chromophores (see ref 5 and references cited therein). The spectral information obtained about the complexes described in this paper (having well-defined geometries) may be of interest in the resonance Raman studies of such biological systems.

Experimental Section

Pure crystalline samples of $Ni[S_2PPh_2]_2$, $Ni[S_2P(OEt)_2]_2$, and $Cr[S_2PPh_2]_3$ were kindly supplied by Dr. R. G. Cavell of the University of Alberta, Edmonton, Alberta, Canada.[3,4] Raman spectra of the dilute ($\sim 5 \times 10^{-3}$ *M*) solutions in CS_2 and CH_2Cl_2 were recorded using a rotating cell to avoid local heating.[6] In addition, spectra of $Ni[S_2PPh_2]_2$ and $Cr[S_2PPh_2]_3$ were recorded as solids dispersed in KBr pellets and again the rotating-cell technique was used.[7,8] All spectra were recorded at a resolution of ~ 5 cm^{-1} and the other details of the spectroscopic method used here have been described earlier.[9]

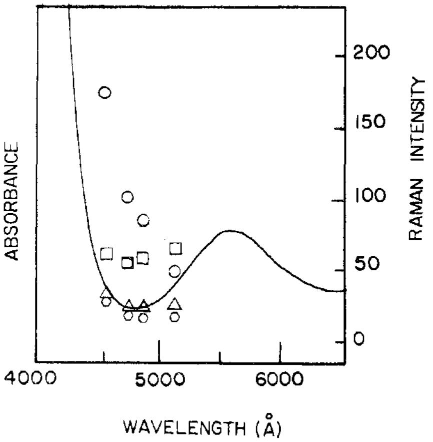

Figure 1. Absorption spectrum of ~0.005 *M* $Cr[S_2PPh_2]_3$ in CS_2 solution. Relative Raman intensities of the above solution as a function of the exciting wavelength for the bands at 282 (○), 999 (□), 1029 (⬡), and 1101 cm^{-1} (△).

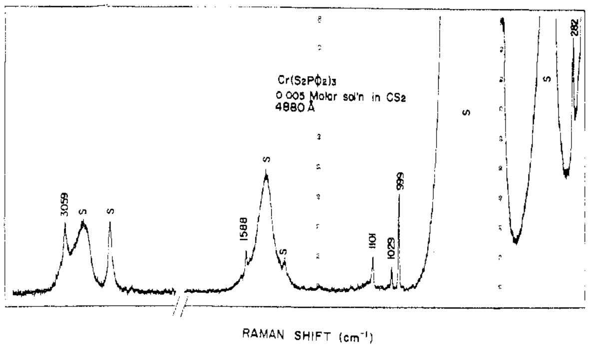

Figure 2. Resonance Raman spectrum of $Cr[S_2PPh_2]_3$ in CS_2 solution; spectral slit width ~5 cm^{-1}; laser power ~1 W. S denotes solvent (CS_2) bands.

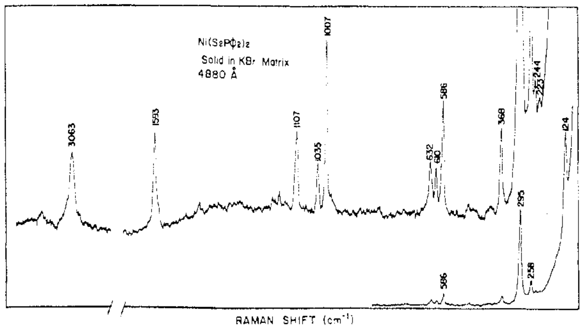

Figure 3. Resonance Raman spectrum of solid $Ni[S_2PPh_2]_2$ dispersed in KBr matrix; spectral slit width ~5 cm^{-1}; laser power at the sample ~400 mW.

Results and Discussion

The absorption spectrum of ~0.005 *M* $Cr[S_2PPh_2]_3$ in CS_2 solution is shown in Figure 1 for the 4000–6500-Å region. The CS_2 solution spectra of the three complexes agreed closely with those reported earlier in CH_2Cl_2 solutions, indicating thereby that the complexes are monomeric and stable in CS_2.[3,4] The Raman spectra of $Cr[S_2PPh_2]_3$ in CS_2 solution and of $Ni[S_2PPh_2]_2$ as solid dispersed in KBr matrix are shown in Figures 2 and 3, respectively. The frequencies of the observed features in the Raman spectra of $Ni[S_2PPh_2]_2$ and $Cr[S_2PPh_2]_3$, both as solids and as solutions in CS_2 and CH_2Cl_2 are given in Table I. The frequency accuracy is ±2 cm^{-1}. Table I also contains the depolarization ratios of the observed features in the solution spectra as obtained with 4880-Å excitations. Three additional lines of Ar$^+$ laser, 4579, 4765, and 5145 Å, were also used to record the Raman spectra. The