Notes

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Antiferromagnetic Copper(II) Halide Adducts of Copper(II) Dithiocarbamates

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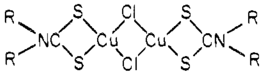
Received May 28, 1976 AIC604005

The reaction of copper(II) dithiocarbamates, Cu(dtc)$_2$, with copper(II) halides, CuX$_2$, in a variety of anhydrous solvents, produces 1:1 adducts Cu(dtc)$_2$·CuX$_2$ whose magnetic moments decrease with decreasing temperatures.[1,2] Cryomagnetic measurements down to liquid nitrogen temperatures suggested, but did not confirm, a binuclear structure [Cu(dtc)X]$_2$: the magnetic susceptibility maximum expected[3-7] for such dimers appeared to occur just within this temperature range but was not well-defined and did not permit unambiguous interpretation of the results. Lower temperature data are compatible with a ligand-bridged binuclear structure but, in the absence of x-ray structural confirmation, were not considered suitable for journal publication.[8] Crystallographic work[9,10] confirms the basic structural unit, **1**. We now report the synthesis, properties, and magnetic evidence for a similar structural unit in a series of such complexes.



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Experimental Section

Preparation of Complexes. Copper (II) dithiocarbamates are usually prepared by mixing the appropriate sodium dithiocarbamate with aqueous copper(II), and the formation of the diethyl complex is used in a colorimetric analysis for copper.[11,12] For some dithiocarbamates, side reactions complicate the situation, presumably due to the formation of halide adducts or copper(I) or copper(II) derivatives, discussed below. A better method was found to be the action of dithiocarbamic acids on fresh copper(II) hydroxide, prepared by mixing concentrated aqueous copper sulfate with dilute sodium hydroxide without heating. A large excess of the blue precipitate was immediately mixed with the appropriate diamine, followed by slow addition of excess carbon disulfide and recrystallization of the product from chloroform or dichloromethane. The complexes were all obtained as black crystals, except bis(*N*,*N*-di-*n*-pentyldithiocarbamato)copper(II) which was a black oil, as is characteristic of *n*-pentyl derivatives, such as tetra-*n*-pentylthiuram disulfide, which is an oil, and the di-*n*-pentyldithiocarbamates of iron(III)[13] and cobalt(III),[14] which have lower melting points than the other *n*-alkyl complexes.

Reaction of potassium dicyclohexyldithiocarbamate with copper(II) chloride produced dicyclohexylammonium chloride quantitatively, while the copper hydroxide method yielded the copper dithiocarbamate.

Copper(II) chloride adducts of copper(II) dithiocarbamates, Cu(dtc)·CuCl$_2$, appear to form when solutions of CuCl$_2$ and any copper(II) dithiocarbamate are mixed but undergo significant decomposition on recrystallization. Thus purification was not possible when the parent dithiocarbamates and the adduct complexes were equally insoluble (as in dimethyl, diethyl, dicyclohexyl, pyrrolidyl, and *N*-methyl-*N*-cyclohexyl). The diallyl- and dicyclohexyldithiocarbamates yielded pale solids which presumably resulted from reduction to copper(I).

Bis(*N*,*N*-di-*n*-butyldithiocarbamato)di-*μ*-chloro-copper(II). The parent dithiocarbamate (6 g), dissolved in a minimum of dichloromethane/methanol (about 1:1), was mixed with excess of anhydrous copper(II) chloride (3.4 g) dissolved in a minimum of methanol, and the mixture was allowed to stand at 0 °C. Small black crystals formed rapidly and these were filtered off and dried over silica gel. Anal. Calcd for $C_{18}H_{36}N_2Cl_2S_4Cu_2$: C, 35.6; H, 6.0; N, 4.6; Cl, 11.7; S, 21.1; Cu, 21.0. Found: C, 35.6; H, 5.8; N, 4.9; Cl, 12.6; S, 21.5; Cu, 21.3.

Bis(*N*,*N*-di-*n*-propyldithiocarbamato)di-*μ*-chloro-copper(II). Fine black crystals resulted from the same procedure as above, but with the addition of 2 mL of triethoxymethane and gentle heating of the reaction mixture prior to cooling. Anal. Calcd for $C_{14}H_{28}N_2Cl_2S_4Cu_2$: C, 30.5; H, 5.1; N, 5.1; Cl, 12.9. Found: C, 30.1; H, 5.0; N, 5.3; Cl, 12.7.

Bis(*N*,*N*-diethyldithiocarbamato)di-*μ*-chloro-copper(II). The same method as above resulted in more than one product. Separation by crystal picking isolated one component which was found to have the binuclear structure already reported elsewhere.[9] Anal. Calcd for $C_{10}H_{20}N_2Cl_2S_4Cu_2$: C, 24.3; H, 4.1. Found: C, 24.4; H, 4.4.

Bis(*N*,*N*-di-*n*-pentyldithiocarbamato)di-*μ*-chloro-copper(II). Various preparations provided the complex with various degrees of purity. The following was typical. The parent dithiocarbamate (16.5 g of the *oil*) in chloroform was mixed with an excess of anhydrous copper(II) chloride (11.5 g) in methanol. A black precipitate formed on standing in an ice bath (yield 10.5 g after filtration and drying). Attempts to purify the product by recrystallization regenerated the parent oil in each case. Anal. Calcd for $C_{22}H_{44}N_2Cl_2S_4Cu_2$: C, 39.9; H, 6.7; N, 4.2, Cl, 10.7. Found: C, 38.9; H, 6.8; N, 4.1; Cl, 10.5.

Bis(*N*,*N*-di-*n*-hexyldithiocarbamato)di-*μ*-chloro-copper(II). The parent dithiocarbamate (7 g), in a minimum of chloroform, was mixed with excess copper(II) chloride in methanol. Small black crystals formed after refrigeration. Anal. Calcd for $C_{26}H_{52}N_2Cl_2S_4Cu_2$: C, 43.4; H, 7.3; N, 3.9; Cu, 17.7. Found: C, 43.7; H, 7.6; N, 4.0; Cu, 17.3.

Bis(*N*,*N*-dibenzyldithiocarbamato)di-*μ*-chloro-copper(II). This preparation was carried out by mixing various proportions of the dithiocarbamate in chloroform/methanol with copper(II) chloride, and the product was identical in all cases. Anal. Calcd for $C_{30}H_{28}N_2Cl_2S_4Cu_2$: C, 48.5; H, 3.8; N, 3.8; Cl, 9.6; S, 17.3; Cu, 17.1. Found: C, 48.4; H, 3.8; N, 3.7; Cl, 9.9; S, 17.2; Cu, 16.9.

Bis(*N*-*n*-propyl-*N*-benzyldithiocarbamato)di-*μ*-chloro-copper(II). Fine black crystals were obtained as above. Anal. Calcd for $C_{22}H_{28}N_2Cl_2S_4Cu_2$: C, 40.9; H, 4.4; Cl, 11.0. Found: C, 40.9; H, 4.3; N, 4.5; Cl, 10.7.

Substitution of copper(II) bromide for copper chloride in the above procedures generally afforded oxidation states other than II, in addition to analogues of the chloro complexes, the following being typical. Cu(S$_2$CNR$_2$)$_2$·CuBr$_2$, R = ethyl, was separated by crystal picking as was the chloro analogue, but no crystals suitable for x-ray structural determination were found. Anal. Calcd for $C_{10}H_{20}N_2Br_2S_4Cu_2$: C, 14.9; H, 2.5; N, 3.5. Found: C, 14.8; H, 2.5; N, 3.5.

Magnetic susceptibilities, χ_M, were determined using Gouy,[14,15] Faraday,[16] Foner,[17] and SQUID[18] magnetometers. Each complex was studied with at least two of the four types of magnetometer. Agreement was good, and there is no field dependence within experimental error. The accuracy is considered to be about 4% for the absolute values and somewhat higher for the relative values at various temperatures, but errors should be considered in the context of paramagnetic impurities, which are descussed below. We are grateful to Professor H. B. Gray for access to the Foner magnetometer and to Mr. A. Schweizer for help with the apparatus. X-ray powder diffraction patterns, obtained on a Philips PW1352 x-ray diffractometer, using Cu Kα radiation in the range $3° < 2\theta < 40°$, indicated the reproducibility of the synthesis and the absence of observable amounts of starting materials. Electronic spectra were obtained by reflectance from samples diluted with magnesium carbonate, using a Unicam SP-200 recording spectrophotometer. Infrared spectra were obtained using a Unicam SP-200, in the range 650–5000 cm^{-1}, on samples dispersed in both hexachlorobutadiene and Nujol mulls. ESR spectra were recorded on a Varian V4502-15 spectrometer. We are grateful to Mr M. Collins for access to this instrument.

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Table I. Magnetic Data for $Cu(S_2CNR_2)_2 \cdot CuCl_2$ ($g = 2.06$, T in K, χ in 10^{-6} cgs emu, μ in μ_B)

R = Benzyl; $J = -49$ cm^{-1}, $p = 0.016$											
T	4.95	6.53	8.55	11.6	14.7	20.1	25.7	31.7	39.3	49.6	62.1
χ	1273	951	829	654	551	623	845	1191	1553	1928	2123
μ	0.22	0.22	0.23	0.24	0.24	0.30	0.40	0.54	0.69	0.86	1.01
T	68.8	80.3	90.0	104.3	108.2	118.4	126.7	140.4	152.6	165.7	177.3
χ	2246	2351	2362	2296	2331	2242	2166	2047	1952	1860	1778
μ	1.10	1.21	1.29	1.37	1.40	1.44	1.46	1.49	1.52	1.54	1.56
T	198.5	212	235	255.5	274						
χ	1643	1561	1466	1307	1286						
μ	1.59	1.60	1.63	1.60	1.64						
R = n-Propyl; $J = -55$ cm^{-1}, $p = 0.021$											
T	5.85	7.82	14.3	20.7	26.2	35.8	50.6	63.7	75.1	90.0	108.6
χ	1738	1051	680	638	647	767	1371	1782	1989	2084	2080
μ	0.28	0.25	0.27	0.31	0.35	0.45	0.73	0.94	1.08	1.21	1.33
T	117.3	135.2	155.2	171.3	188.0	214.5	232.0	258.5	275.0		
χ	2022	1935	1786	1695	1683	1464	1382	1281	1195		
μ	1.36	1.42	1.46	1.50	1.56	1.55	1.57	1.59	1.58		
R = n-Butyl; $J = -65$ cm^{-1}, $p = 0.038$											
T	28.5	35.2	58.5	72.3	78.2	91.8	105.7	122.3	133.5	154.0	182.3
χ	665	682	1220	1569	1638	1825	1819	1835	1802	1750	1553
μ	0.37	0.42	0.74	0.93	0.99	1.14	1.22	1.32	1.37	1.44	1.48
T	211.0	245.2	272.4								
χ	1525	1319	1260								
μ	1.57	1.57	1.63								
R = n-Pentyl; $J = -70$ cm^{-1}, $p = 0.06$											
T	26.8	42.0	59.7	77.4	89.3	102.5	131.3	172.5	220.0	258.3	275.0
χ	1097	982	1151	1538	1647	1725	1731	1600	1395	1273	1234
μ	0.47	0.56	0.72	0.96	1.07	1.17	1.32	1.46	1.53	1.58	1.61
R = n-Hexyl; $J = -68$ cm^{-1}, $p = 0.045$											
T	30.2	49.1	63.2	84.3	92.1	122.7	144.5	173.8	237.0	251.0	274.2
χ	765	895	1253	1662	1675	1741	1720	1563	1278	1286	1221
μ	0.41	0.57	0.78	1.04	1.09	1.28	1.39	1.45	1.52	1.57	1.59
R, R = Benzyl, n-Propyl; $J = -50$ cm^{-1}, $p = 0.02$											
T	12.5	22.7	38.5	46.3	67.1	79.3	87.1	90.0	95.2	98.9	107.2
χ	791	468	1110	1463	2247	2410	2335	2316	2320	2295	2258
μ	0.27	0.27	0.57	0.72	1.08	1.22	1.26	1.27	1.31	1.33	1.37
T	117.3	131.0	153.6	164.3	187.1	223.0	241.1	260.8	273.2		
χ	2215	2132	1951	1831	1673	1543	1433	1389	1310		
μ	1.42	1.47	1.52	1.53	1.55	1.63	1.63	1.67	1.65		

Result and Discussion

Under suitable conditions, copper(II) dithiocarbamates, Cu(dtc), form 1:1 adducts with copper(II) chloride (and apparently with copper(II) bromide in some cases). The adducts are decomposed when shaken with water, and the original Cu(dtc) is regenerated in better than 85% yield, indicating that the dithiocarbamate ligand remains intact in the $Cu(dtc) \cdot CuCl_2$ complexes.

Magnetic Properties. The magnetic properties of each of the $Cu(dtc) \cdot CuCl_2$ complexes are quite similar, suggesting a similar structure. In each case, χ_M passes through a maximum near liquid nitrogen temperature, so that measurements below this temperature are necessary to establish the existence of the maximum. The data (Figure 1) conform well to the curve calculated from eq 1 for a "spin-only" dimer from the

$$\chi_M = \frac{Ng^2\beta^2}{3kT}(1 + {}^1/_3 e^{-2J/kT})^{-1}(1 - p) + N\alpha + \frac{g^2 p}{10.7T}$$
$$\mu_{\text{eff}} = [8.0(\chi_M - N\alpha)T]^{1/2} \tag{1}$$

Hamiltonian $\mathcal{H} = -2J\mathbf{S}_1 \cdot \mathbf{S}_2$. (The symbols in eq 1 have their usual meanings.) Equation 1 has been corrected for temperature-independent paramagnetism ($N\alpha$) assumed to be constant for copper at 6×10^{-5} cgs emu and for a proportion p of paramagnetic impurity, estimated from the low-temperature limit of μ_{eff}, to which the dimeric units make zero contribution. In each case, the paramagnetic impurity makes negligible contribution at room temperature and very little even at the susceptibility maximum, but the results demonstrate the utility of the low-temperature measurements for the detection of small amounts of paramagnetic impurities.

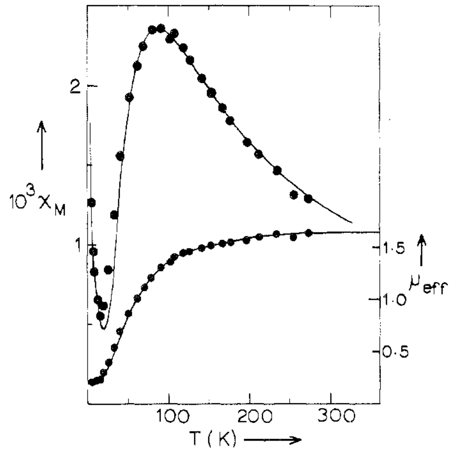

Figure 1. Temperature dependence of the magnetic properties of the dibenzyl complex $Cu(dtc)CuCl_2$. The curves are calculated from eq 1.

The similarity of the magnetic properties implies a similar structure for the $Cu(dtc) \cdot CuCl_2$ complexes. The nitrogen substituent therefore has little effect on the molecular structure, as expected from the Cu_2Cl_2 bridging unit, **1**. The crystal structure data on the diethyl complex indicate weak out-of-plane ligand bridges between the dimeric molecules to form a weakly linked tetrameric structure which may or may

Table II. Electronic Spectra (cm^{-1}) of $Cu(S_2CNR_2)_2$, A, and the $CuCl_2$ Adducts, B

R	A	B
Methyl	21 700 15 200	
Ethyl	21 800 (21 900[c]) 14 700	22 200 15 600
Di-*n*-propyl	21 900 15 300	22 400 15 500
n-Butyl	22 300 (22 750[a]) 15 800 (16 000[a])	22 500 15 700
n-Pentyl		22 600 (17 800[b]) 15 700
n-Hexyl	22 300 15 800	22 400 16 100
Benzyl	22 300 16 200	22 000 (17 700[b]) 15 600
Benzyl, propyl	22 100 16 000	22 300 15 700

[a] In CCl_4. [b] Weak shoulder. [c] Reference 29.

Table III. Position of the "Thioureide Band" (cm^{-1}) in $Cu(S_2CNR_2)_2$, A, and Adducts with $CuCl_2$, B, and $CuBr_2$, C[a]

R	A	B	C
Ethyl	1504 s	1518 s	1519 m
n-Propyl	1505 s	1515 s	
n-Butyl	1505 s	1515 s	
n-Pentyl	1505 s	1515 s	
n-Hexyl	1500 s	1520 s	
Benzyl	1495 m 1485 s	 1505 s	

C–S Region for R = Benzyl

A 1030 m, 990 s, 935 m, 905 vw, 885 w, 845 w, 825 w, 750 m, 735 w, 695 s

B 1030 m, 1005 w, 990 m, 975 m, 935 m, 900 w, 880 w, 850 w, 830 w, 750 m, 720 w, 690 s

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

not persist in the other complexes. However, conformity of the magnetism with eq 1 implies that interdimer interactions are unimportant compared with the intradimer interactions. This is in keeping with the general observation[7,19,20] that such out-of-plane intermolecular links oppose strong magnetic interactions, as do long intermolecular distances. Such links in the relatively weakly dimeric $[Cu(S_2CNEt_2)_2]_2$[21] have been said to lead to ferromagnetic interactions,[22] though our measurements and those of Carlin et al.[23] on this compound and our data on a variety of the parent copper dithiocarbamates have failed to reveal such interactions.[20] In any case, interdimer ferromagnetic or weak antiferromagnetic interactions may be predicted to be relatively unimportant compared to the intradimer interactions and to appear at worst as a small source of errors in the estimated exchange constants *J*.

The estimated exchange constants *J* are in the range of *J* values found in halogen-bridged copper(II) complexes.[7,24] Average *g* values of 2.061, 2.058, 2.058, 2.058, 2.060, 2.055, and 2.05 were obtained[25] from ESR spectra for $Cu(S_2CNR_2)_2 \cdot CuCl_2$ where R = ethyl, *n*-propyl, *n*-butyl, *n*-pentyl, *n*-hexyl, benzyl, and *n*-propyl, benzyl, respectively. The known (temperature-independent) spectra of the parent dithiocarbamates could also be detected in the ESR signals, but the intensities were deemed too low to identify the parent complexes as the main type of paramagnetic impurities observed in the magnetic susceptibility measurements on the dimers. The *g* values are slightly lower than normal but are in agreement with ESR data obtained by Martin et al.[9] and are compatible with a roughly planar copper(II) environment; $g = 2.06$ was assumed in fitting the data in Table I to eq 1, *J* and *p* being the variable parameters. The magnetic properties are determined by the combined effect of several factors that effect the *J* values, such as the copper environment, the copper–ligand–copper bridging angles, and the extent of interdimer bridging, as well as the paramagnetic impurities. Thus a more detailed attribution of the variation of *J* should not be made. From the shapes of the magnetic susceptibility curves and from the observation that different preparations of the same complexes produce large variations in *p* but small changes in *J*, it seems reasonable to assume that the impurities represented behave as simple paramagnets. However, the accuracy of this assumption is not readily tested further, since the nature of the impurities is unknown.

For each compound, the experimental data can be approximated more closely by a tetramer model[7] using $\mathcal{H} = -2\sum J_{ij}\mathbf{S}_i\cdot\mathbf{S}_j$, as would be expected from the increased number of parameters in the model (*J*, *J′*, *J″*, *p*, and optionally *g*). However the improvement is small compared to experimental error, generally requires *g* values of 2.0 or less, and gives *J* values close to those obtained from eq 1. For example, for the dibenzyl complex, this model gives 11 cm^{-1} for the two equivalent interdimer interactions *J′*, −21 cm^{-1} for the unique short (diagonal) interdimer interaction *J″* (with zero being assumed for the long unique interaction), and −52 cm^{-1} for *J*. The fit is not unique as the intermolecular parameters are correlated but *J* remains essentially the same. This compares with $J = -49$ cm^{-1} from eq 1. Thus the two parameter model gives a good estimate of the intramolecular interaction, and a detailed evaluation of the intermolecular interactions is unwarranted by the data and the theoretical fit.

Electronic and Infrared Spectra. Some shifts are observed in the ligand field region in going from the parent dithiocarbamates to the copper chloride adducts (Table II), but these are very small and may be attributed to the changes in ligand environment (from S_4 to S_2Cl_2) as much as in copper stereochemistry.[6,26] More significantly, no new bands appear in the binuclear spectra, suggesting that only one kind of copper environment exists in each case, as expected from the bridging arrangement **1**. The similarity of the spectra indicates relative independence of the nitrogen substituents, as before. This conclusion is strongly supported by similarity of the parallel changes in the relevant vibrational absorptions in the available infrared region (Table III). In dithiocarbamates, the formation of metal–sulfur bonds leads to an increase in the C–N(thioureide) stretching frequency.[27] A further increase in this frequency is consistently observed in the formation of $Cu(S_2CNR_2)_2 \cdot CuCl_2$ from $Cu(S_2CNR_2)_2$, presumably due to the bonding changes between the CuS_4 and CuS_2Cl_2 metal environments, as well as the weak interdimer Cu–S bonds. Smaller shifts in the C–S stretching region[28] (the *N,N*-bibenzyl complex is typical) are presumably due to perturbations of the C–S vibrations by the formation of the $CuCl_2$ adducts.

Registry No. $Cu(S_2CN(ethyl)_2)_2 \cdot CuCl_2$, 58320-50-6; $Cu(S_2CN(n\text{-propyl})_2)_2 \cdot CuCl_2$, 59778-91-5; $Cu(S_2CN(n\text{-butyl})_2)_2 \cdot CuCl_2$, 59778-92-6; $Cu(S_2CN(n\text{-pentyl})_2)_2 \cdot CuCl_2$, 59778-93-7; $Cu(S_2CN(n\text{-hexyl})_2)_2 \cdot CuCl_2$, 59778-94-8; $Cu(S_2CN(benzyl)_2)_2 \cdot CuCl_2$, 51321-39-2; $Cu(S_2CN(benzyl)(propyl))_2 \cdot CuCl_2$, 59778-95-9; $Cu(S_2CN(ethyl)_2)_2 \cdot CuBr_2$, 62637-59-6; $Cu(S_2CN(methyl)_2)_2$, 137-29-1; $Cu(S_2CN(ethyl)_2)_2$, 13681-87-3; $Cu(S_2CN(n\text{-propyl})_2)_2$, 14354-08-6; $Cu(S_2CN(n\text{-butyl})_2)_2$, 13927-71-4; $Cu(S_2CN(n\text{-pentyl})_2)_2$, 36190-66-6; $Cu(S_2CN(n\text{-hexyl})_2)_2$, 62637-60-9; $Cu(S_2CN(benzyl)_2)_2$, 34409-33-1; $Cu(S_2CN(benzyl)(propyl))_2$, 62637-61-0; $CuCl_2$, 7447-39-4.

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A Reinvestigation of the Reaction of Dioxygen with (Phthalocyaninetetrasulfonate)iron(II)[1a]

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Received August 30, 1976 AIC60638T

Recent investigations of oxygen complexation by transition metals have generated considerable interest.[2] Iron–dioxygen complexes are of particular interest as biological models. Recent investigations have suggested that iron–dioxygen adducts are stabilized by, first, providing a hydrophobic environment for the iron and, second, inhibiting dimerization, which appears to offer a pathway for irreversible oxidation. One apparent curious exception to these generalizations is provided by the report of Fallab[3] that (tetrasulfophthalocyanine)iron(II), referred to below as Fe$^{\mathrm{II}}$PTS, reversibly complexes dioxygen in aqueous solution, presumably forming a μ-peroxo complex. At about the same time, Weber and Busch[4] described the formation and reactions of some metal phthalocyanines which indicated that irreversible oxidation of Fe$^{\mathrm{II}}$PTS to Fe$^{\mathrm{III}}$PTS occurs in aqueous solution.

In the present note, we have reexamined the reaction of Fe$^{\mathrm{II}}$PTS with dioxygen in an attempt to resolve these conflicting conclusions.

Experimental Section

Phthalocyaninetetrasulfonate (PTS) was prepared in low yield by the method of Fallab,[5] with purity characterized by visible spectroscopy (ϵ_{630} 9.3 $\times$ 10^4). Fe$^{\mathrm{II}}$PTS was then prepared by reacting ferrous ammonium sulfate with PTS under strictly anaerobic conditions to give a dark green solution ($\lambda_{\max}$ 670 nm). On exposure to air or on running the synthesis in the presence of air (after the method of Fallab), a blue solution ($\lambda_{\max}$ 634 nm) with a small shoulder at 670 nm is obtained. The product was also prepared by the template synthesis of Weber and Busch.[4] Ferrous ammonium sulfate was slowly added to a refluxing nitrobenzene solution of 4-sulfophthalic acid, urea, and ammonia sulfate. (Slow addition of iron(II) is necessary for maximum yield.) The dark mass so obtained was washed with methanol–water. A number of purification techniques were attempted, the most successful being size separation on a gel permeation (Saphadex G10) column, which eliminates contaminating inorganic salts and results in elution of several distinct fractions. The isolated fractions were characterized by absorption spectroscopy and magnetic susceptibility. Absorbance spectra were obtained on a Cary 14 spectrophotometer using matched quartz cells. Magnetic susceptibility measurements on solid samples were obtained on a Gouy balance and were confirmed in solution by the Evans method, on a Varian A-60A NMR instrument.

Results and Discussion

The complexes prepared herein were made in two ways, with somewhat differing results. Free PTS, prepared in low yield by the method of Fallab[5] and found to be spectrally pure, was reacted with ferrous ammonium sulfate in the presence of air to give a product with a major band at 634 nm with a shoulder at ca. 670 nm. When preparation was by a template condensation however (using ferrous ammonium sulfate as the metal template), a dark green solid resulted with a major peak at 670 nm and a small shoulder at 634 nm. As this was felt to be a possible mixture of products, a number of purification techniques were attempted with the crude material, with little success (using the 632-nm band as a measure of purity).

Finally, size separation on a gel permeation column (Sephadex G10) resulted in the elution of several distinct fractions. The first, dark green, component showed minimal absorption at ca. 630 nm, with a strong peak at 670 nm. This green component was insensitive to oxygen under a pressure of 1 atm at 25 °C. The second major band was dark blue with strong absorption at 632 nm and minimal absorption at 670 nm. The third band showed no 670-nm absorption but was affected by some residual salt contamination. The yellow-green column tailings, which contained most of the inorganic salts and low molecular weight contaminants, were discarded.

The second band could be refractionated into a major blue component and a small green band, with the resulting blue component having a spectrum essentially identical to that obtained by Weber and Busch.[4] A magnetic moment, determined by the Evans method (NMR shift), was ca. 1.90 μ_{B}, in good agreement with 1.80 μ_{B} expected for low-spin ferric iron.

Template condensation with ferric sulfate, fractioned in the same manner, also gave a mixture of 670- and 630-nm bands. On separation, the blue component showed a spectrum identical on the Cary 14 with the blue band obtained from the ferrous preparation. This blue complex thus represents a simple low-spin ferric chelate with no complexed dioxygen.

The product of the Fallab preparation after similar fractionation also gave a blue band that on crystallization gave the same magnetic moment (1.92 μ_{B}) as the Busch preparation, with an identical spectrum.

A referee has pointed out that the solution composition of Fe$^{\mathrm{II}}$PTS is pH sensitive. This sensitivity as we observed is consistent with μ-oxodimerization (i.e., slight shift in $\lambda_{\max}$ 630 nm to give a component which travels more rapidly on Sephadex G10). We have observed no case where changing the pH leads to a net change in uptake of oxygen, as measured by an oxygen-sensitive electrode.

As a secondary characterization, complexes prepared by all three methods (ferric condensation, ferrous condensation, and free ligand reaction) were reacted with imidazole. All three complexes gave identical results, forming a complex with $\lambda_{\max}$ 628 and 664 nm, ϵ_{664} 5.6 $\times$ 10^5, in excellent agreement with the results of Weber and Busch.[4] Reaction of the complexes with dithionite resulted in an immediate loss of the 634-nm band and an increase in absorbance at 670 nm. On subsequent exposure to oxygen, the 634-nm band was recovered, but