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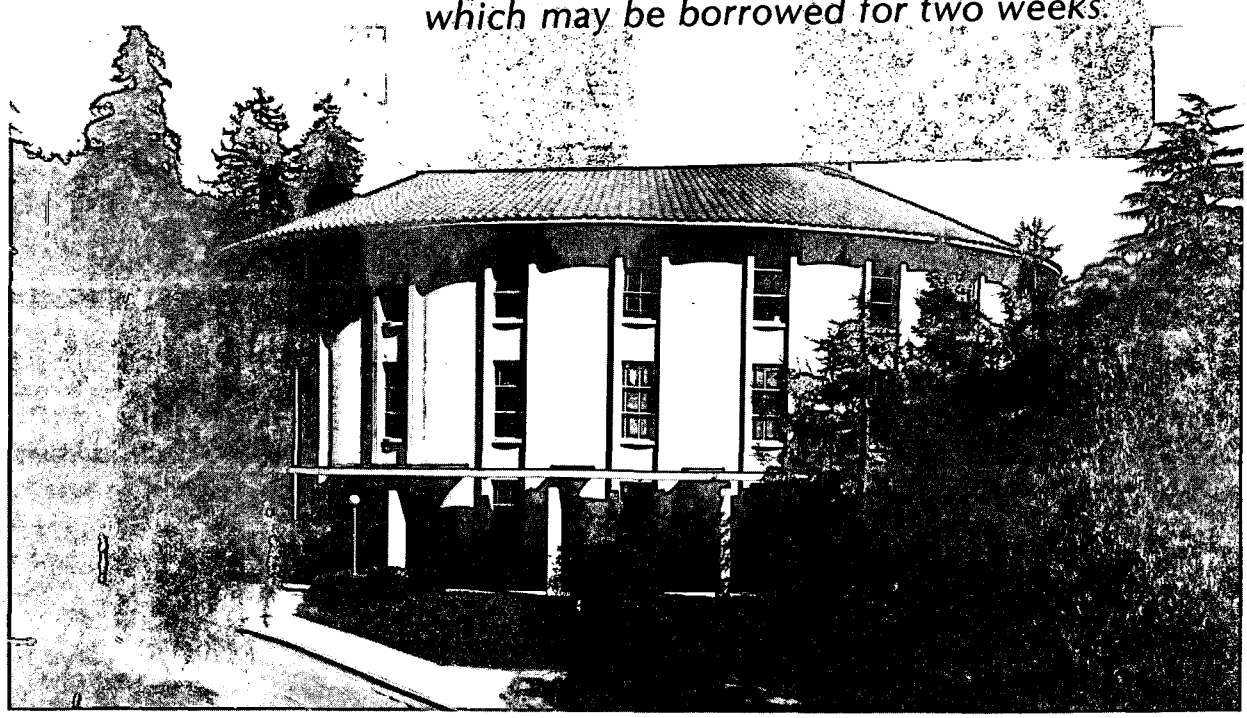

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A TEMPERATURE-DEPENDENT SPIN-STATE CHANGE IN A MANGANESE TETRAPHENYL PORPHYRIN

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Abstract

The complex (5,10,15,20-tetraphenylporphinato)manganese ditrifluoromethanesulfonate, $MnTPP(CF_3SO_3)_2$, 1, was prepared by the oxidation of MnTPP(Cl) in dichloromethane with a mixture of iodine in dichloromethane and silver trifluoromethanesulfonate in toluene at -70°C. Compound 1 is characterized as a Mn(III)TPP -cation radical species at higher temperature but a Mn(IV)TPP species at lower temperatures. These assignments of 1 were based on its absorption spectrum, EPR spectra and magnetic properties. The absorption spectrum of compound 1 in dichloromethane at -25°C shows a split-Soret band with peaks at 390 and 445 nm. The solid-state magnetic measurements of 1 showed non-linear Curie-Weiss behavior in the temperature range studied, 5-280 K. The plot of $\frac{1}{\chi_m^c}$ versus temperature showed curvature with two distinct linear regions in the 50-50 K and 100-200 K range. Magnetic moments of 3.9 and 4.9 μ_B were respectively calculated for 1 from these linear portions. The EPR spectrum of 1 in dichloromethane at 8 K shows two

anisotropic sextets centered at g = 2 and 4.5. The signal intensity diminished with increase in temperature. All these results are consistent with a spin-state change in 1 dependent upon temperature.

Introduction

The characterization of oxidized metalloporphyrins is of much current interest because they serve as model systems for many redox reactions of metalloporphyrin-containing enzymes. It is well established that oxidation of a metalloporphyrin can be metal-centered or ligand-centered, the latter producing a π-cation radical. Our interest in this subject, particularly in the characterization of high-valent manganese porphyrins, derives from our work on potential multiple-electron redox catalysts for an artificial photosynthesis assembly.[1] A prerequisite for a multiple-electron redox catalyst is the accessibility of a variety of oxidation states. Manganese porphyrins have been fully characterized with manganese in the +2, +3[2] and +4[3,4] oxidation state, and several reports have cited evidence for Mn(V)[5] porphyrins as intermediates in redox processes. In addition, several groups have described manganese π-cation radical porphyrins[6,7] where oxidation has occurred on the macrocycle.

The axial ligands on the metal are of prime importance in determining the electronic configuration of oxidized metalloporphyrin Recently we described a case in which a Mn(III) tetraphenyl porphyrin π-cation radical, $Mn(III)TPP^{+\cdot}$, is converted to a Mn(IV)TPP species by addition of a strong -donating ligand, CH_3O^-.[8] In the present paper we describe the preparation and properties of a compound $MnTPP(CF_3SO_3)_2$ that we believe undergoes a temperature-dependent spin-state change from

a manganese(III) π-cation radical at higher temperature to a anganese(IV) porphyrin at reduced temperatures.

Experimental Section

The chemicals used were all reagent grade. Dichloromethane and toluene were purified by distillation and stored over activated molecular sieves. Preparation of Mn(III)TPPCl is discussed elsewhere.[8]

Synthesis of $MnTPP(CF_3SO_3)_2$: To a solution of Mn(III)TPPCl (0.5 mM) in dichloromethane (50 ml) at -70°C were added solutions of iodine (2.0 mM) in dichloromethane (15 ml) and silver trifluoro- methanesulfonate (1.0 mM) in toluene (10 ml). After stirring for 15 minutes the precipitate of silver iodide and silver chloride was filtered off quickly. The filtrate was then added to an excess of hexane kept at -70°C. The resulting precipitate was collected by filtration and air dried. Anal. Calculated for $MnTPP(CF_3SO_3)_2$; Mn, 5.69; C, 57.20; N, 5.80; H, 2.90; S, 6.63. Found: Mn, 5.41; C, 54.30; N, 5.31; H, 2.97; S, 6.28. (The experiment values are low compared to calculated but the experimental N/Mn mole ratio is 4.0 and the experimental S/Mn mole ratio is 2.0. Contamination by a small amount of moisture would account for the discrepancies.) The compound was free from Ag and I (0.5%).

Visible absorption spectra were recorded on a Hewlett-Packard 845A spectrometer. Variable-temperature magnetic susceptibility measurements in the solid state were carried out on a SQUID apparatus (SHE Corp., VPS 800 Susceptometer). The experimental details are discussed elsewhere.[8] The X-band EPR spectra were recorded on a Varian Model E-109 spectrometer equipped with a low-temperature Dewar (Air Products, Ltd.).

Results and Discussion

The compound $MnTPP(CF_3SO_3)_2$, 1, is produced by a one-electron oxidation from the starting Mn(III)TPPCl material. The oxidation could conceivably take place at the metal, producing a $Mn(IV)TPP^{+2}$ ion, or at the porphyrin ring, producing a Mn(III) π-cation radical species. In fact, the electronic spectrum and solid-state magnetic susceptibility data, both near room temperature, support designation of 1 as a Mn(III) π-cation radical. However, the magnetic moment of 1 shows a significant temperature dependence and this, coupled with the featuraes of the low temperature (< 80 K) EPR spectrum, strongly suggests that a temperature-dependent spin-state change takes place. At the lower temperatures the ground state electronic configuration of 1 becomes that of a manganese(IV) tetraphenylporphyrin.

The visible absorption spectrum of $MnTPP(CF_3SO_3)_2$, 1, in dichloromethane at -25°C is shown in Fig. 1. Also shown in the figure are the absorption spectra of $MnTPP(Cl)(SbCl_6)$ [8] which has been identified as a Mn(III) π-cation radical species and of $MnTPP(OCH_3)_2$ which has been well characterized as a Mn(IV)TPP compound. [9] There are important similarities in the spectra of 1 and the species characterized as a $Mn(III)TPP^{+\cdot}$ species while a bona-fide Mn(IV) porphyrin shows marked differences. Compound 1 is unstable even at -25°C and reverts quickly to Mn(III)TPP at room temperature. The shoulder at 476 nm in the spectrum of 1 in Fig. 1 is probably due to decomposition.

The magnetic susceptibility of 1 was measured in the solid state at temperatures of 5 to 280 K. These measurements were done at field strengths ranging from 5,000 to 40,000 Gauss. A plot of the reciprocal of the molar susceptibility, after appropriate correction for the

diamagnetism of all constituent atoms, against temperature is shown in Fig. 2. The shapes of the plots are independent of field strength. The Curie-Weiss plot for 1 showed appreciable curvature with a linear region in the 5-50 K temperature range and another linear region above 100 K. The top portion of Fig. 2 shows the low temperature region with all data points included. In contrast the Curie-Weiss plot for $MnTPP(Cl)(SbCl_6)$ is remarkably linear and is shown as an insert in Fig. 2. Magnetic moments for 1 were calculated from the linear portions of the plots and were 3.9 Bohr Magnetons at low temperature and 4.9 for the high temperature region.

Expected magnetic moments for different electronic configurations are shown in Table 1. Mn(IV) is a d^3 ion and would have a spin-only moment of 3.87 $_{B.}$(A). Three different spin states must be considered if 1 is a Mn(III), S = 2, π-cation radical species, S = ½. These are: (B) the ferromagnetically-coupled state with a resultant spin of 5/2 and an expected moment of 5.91 μ_B; (C) the anti-ferromagnetically coupled state with resultant S = 3/2 and a magnetic moment of 3.87 μ_B; (D) the independent spin state composed of S = 2 and S = ½ with a theoretical moment $(\mu_1^2 + \mu_2^2)^{\frac{1}{2}} = 5.19\ \mu_B$. The observed value of 4.9 μ_B at temperatures above 100 K effectively rules out the Mn(IV) configuration (A) and the anti-ferromagnetically coupled $Mn(III)TPP^{+\cdot}$ configuration (C). The value is close to that for a $Mn(III)TPP^{+\cdot}$ with independent spins (D), and this is consistent with the visible spectrum of 1 which supports a π-cation radical species.

However, the value of 3.9 μ_B at low temperature does not agree with moments expected for configurations (B) or (D) and is close to the

expected moments either for a Mn(IV) porphyrin or an anti-ferromagnetically coupled Mn(III) π-cation radical species.

The temperature-dependent EPR spectra of 1 provide a means of distinguishing between the Mn(IV) and Mn(III) π-cation radical anti-ferromagnetically coupled states. The X-band EPR spectrum of 1 in CH_2Cl_2 at 8 K is given as the upper spectrum in Fig. 3. A pronounced sextet with a central g value of 4.5 is observed. The spectrum is anisotropic, having another sextet pattern in the g = 2 region. The hyperfine splitting arises from the I = 5/2, ^{55}Mn nucleus, and the hyperfine splitting constants are 64 G in the g = 4.5 region and 60 G in the g = 2 region. This spectrum is entirely consistent with interpretation as a Mn(IV)TPP configuration with Mn in the high spin 3/2 state and in an environment lower than octahedral symmetry. Very similar spectra have been reported for well characterized Mn(IV)TPP [9,10] species with methoxide, azide, or cyanate as anionic ligands. In contrast Mn(III) porphyrins are in general EPR silent. This has been attributed to very fast relaxation times with broadened signals. Goff [7] has reported that the Mn(III) π-cation radical with Cl^- and ClO_4^- as ligands gave a broadened g = 2 signal at 70 K. The Mn(III)TPP(Cl)($SbCl_6$) compound [8] showed no EPR spectrum from room temperature to 8 K.

A consistent diminution of signal intensity of a given sample was observed as the temperature was raised from 8 K to 100 K. The loss of signal intensity was not due to decomposition of the sample since return to lower temperature gave all of the original absorption. One possible explanation for the disappearance of signal with increasing temperature is an increasing rate of relaxation, which leads to broadening of the signal. However, our observations of the non-linear Curie-Weiss

behavior of the solid and changes in magnetic moment with temperature support an interpretation of a spin-state change at temperature above 100 K. The electronic spectrum, solid-state magnetic moment and absence of an EPR signal for 1 all support its characterization as a Mn(III) π-cation radical at temperatures above 100 K, while at temperatures between 8 and 50 K the solid-state magnetic moment and EPR spectrum indicate a Mn(IV)TPP species. The ground state of $MnTPP(CF_3SO_3)_2$ appears to be a Mn(IV) oxidation level. But there is a low-lying Mn(III) π-cation radical state that becomes the predominant form at higher temperatures. Thus 1 mimics the behavior of nickel tetraphenylporphyrin where the room temperature species is $Ni(II)TPP^{+\cdot}$ while at 77K it is characterized as $[Ni(III)TPP]^{+}$.[11]

Summary

A survey of recent papers of oxidized Mn tetraphenylporphyrins demonstrates the importance of the axial ligands on the Mn in determining the electronic properties of the compound. Species with one coordinating anion such as Cl^- and a poorly coordinating anion such as ClO_4^- or $SbCl_6^-$ [7,8] are characterized as Mn(III) π-cation radicals over all temperature ranges but they can be converted to Mn(IV) porphyrins by addition of such ligands as CH_3O^- or N_3^-. The present paper describes $MnTPP(CF_3SO_3)_2$, a species with two poorly coordinating anions, which has a Mn(IV) ground state and a low-lying Mn(III) π-cation radical configuration that are in equilibrium. There is another report in the literature of a $MnTPPCl_2$ compound that also exhibits a temperature-dependent spin-state change.[12] However, in this compound with two coordinating anions the ground state appears to be a Mn(III)

π-cation radical and the predominant species at room temperature is a Mn(IV)TPP species.

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Table 1

Calculated Magnetic Moments for Manganese Porphyrin Configurations

	Configuration	μ_{eff} (calcd) μ_B
(A)	$Mn^{IV}TPP$	3.87
(B)	$Mn^{III}TPP^{+\cdot}$ (ferromagnetic coupling)	5.91
(C)	$Mn^{III}TPP^{+\cdot}$ (antigerromagnetic coupling)	3.87
(D)	$Mn^{III}TPP^{+\cdot}$ (independent spins)	5.19

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Figure Captions

Figure One. Electronic Spectra of Several Manganese Tetraphenylporphyrin Species $Mn(IV)TPP(OCH_3)_2$ — ; $Mn^{III}TPP(Cl)(SbCl_6)$ (Mn^{III} -cation radical)– – – ; $MnTPP(CF_3SO_3)_2$ ....

Figure Two. Solid State Magnetic Data for $MnTPP(CF_3SO_3)_2$. The molar susceptibility has been corrected for diagmagnetic contribution of the constituent atoms. Field strength is 5,000 Gauss; Weiss constant is -1.19 K. The upper part shows all the low temperature data. Insert shows data for $MnTPP(Cl)(SbCl_6)\cdot 4\ C_2H_2Cl_4$ from ref. 8.

Figure Three. X-band EPR Spectra for $MnTPP(CF_3SO_3)_2$ in CH_2Cl_2 as a function of Temperature. Instrument settings were kept constant.

Fig. 1

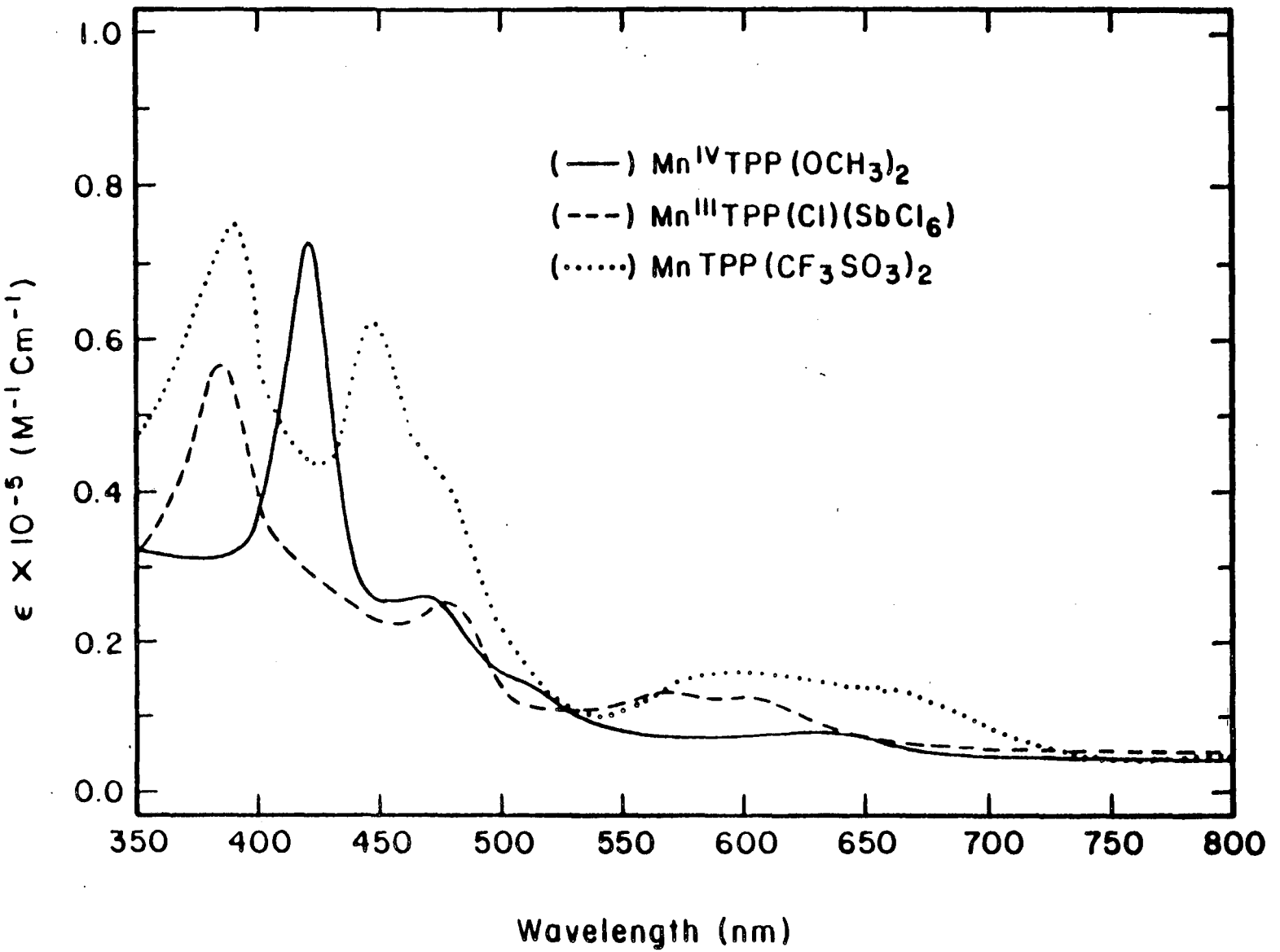

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Fig. 2

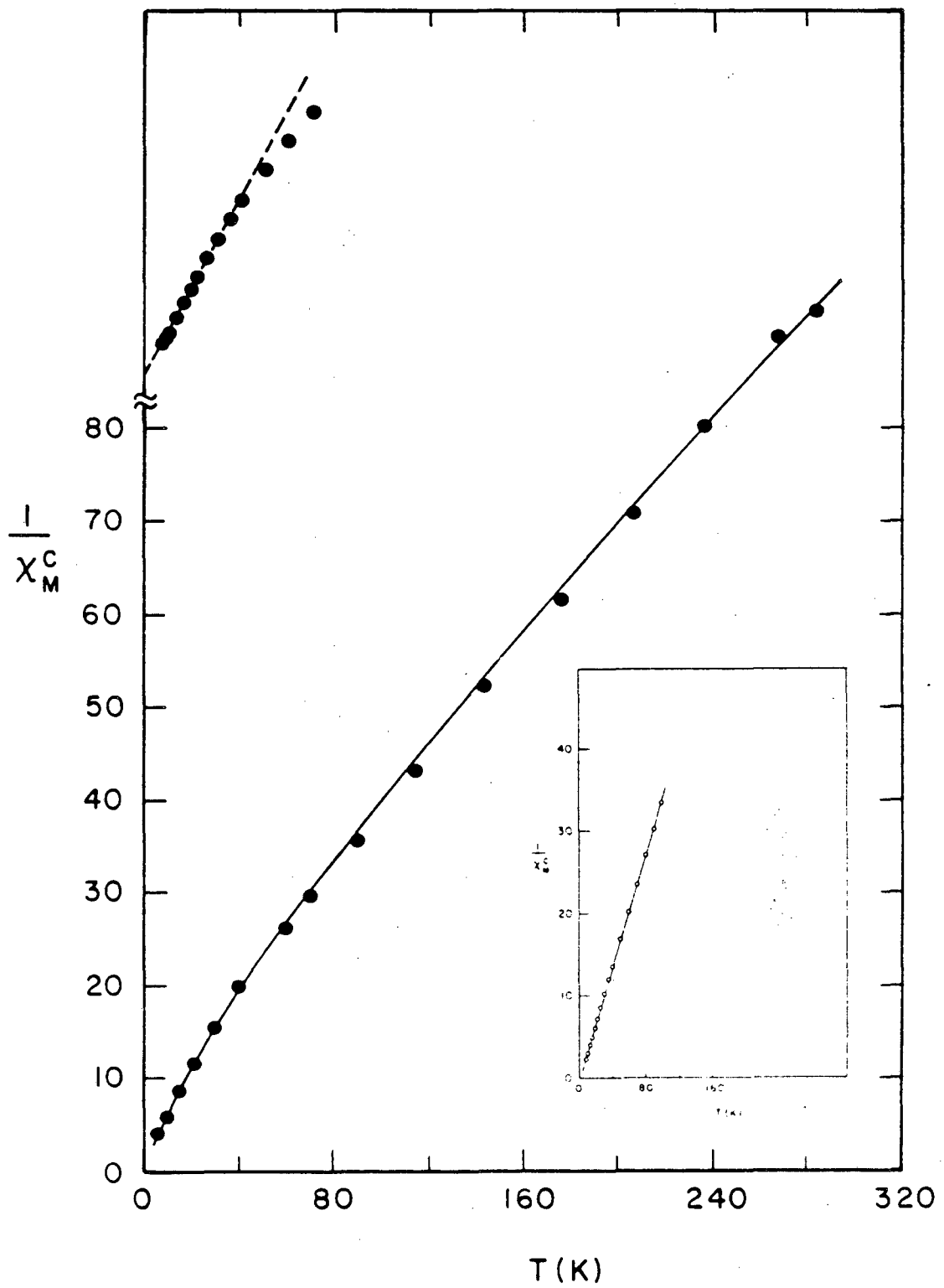

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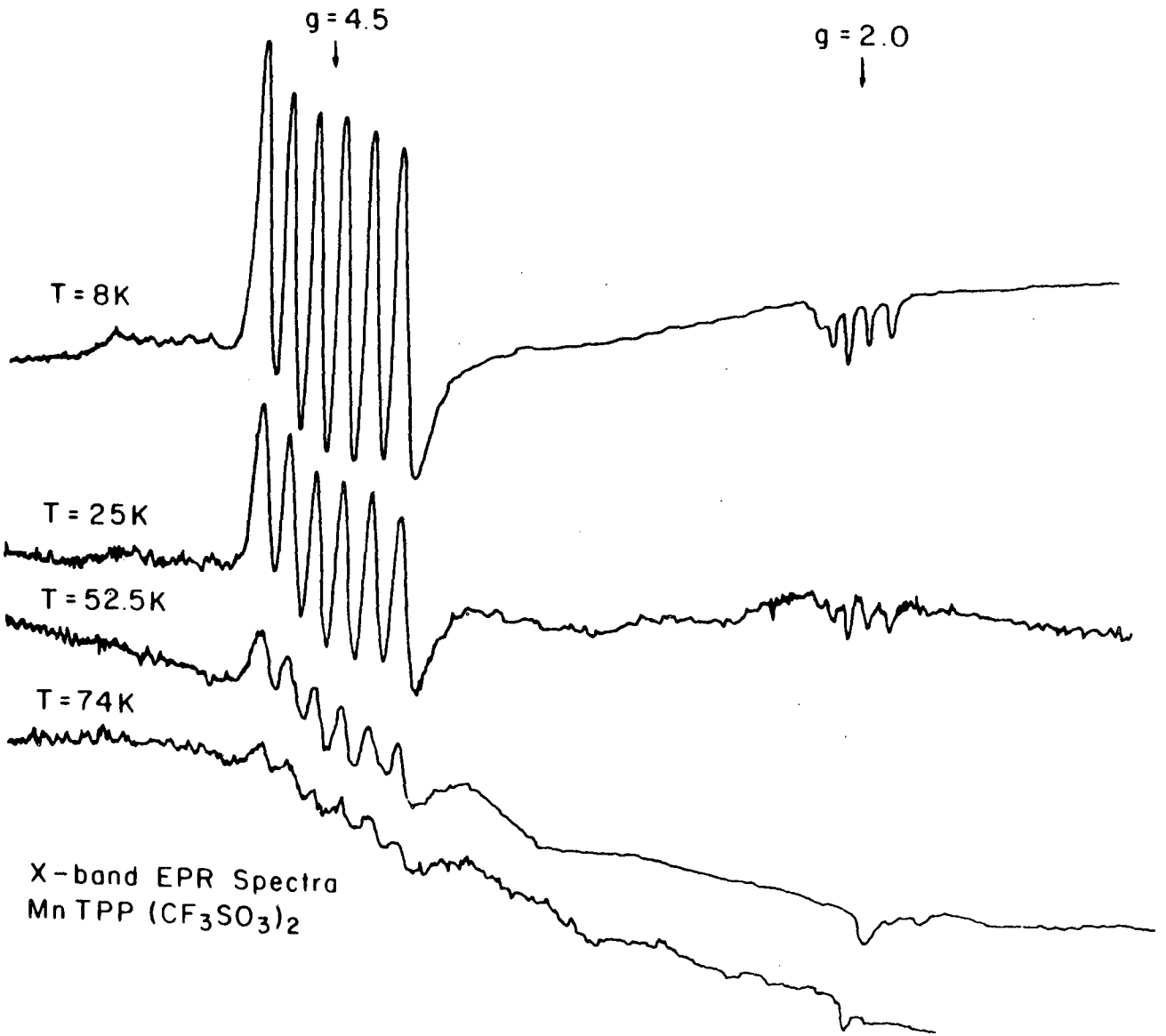
Fig. 3



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