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Reactions of Dinitriles with Manganese Powder: First Synthesis of Manganese(II) Octaphenylporphyrazine and a Convenient Synthesis of Manganese(II) Phthalocyanine

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Abstract

The one-step preparation of the manganese(II) tetraaza macrocyclic compounds, Mn phthalocyanine and Mn octaphenylporphyrazine from dinitriles and metallic manganese is described. The magnetic and other physical properties of the heretofore unknown Mn octaphenylporphyrazine complex are addressed.

Introduction

Despite the apparent structural similarity of porphyrin and phthalocyanine complexes, the chemical properties of the complexes of these two ligands are often very different. For example, the phthalocyanine ligand is more easily oxidized and more easily reduced than the porphyrin ligand [1]. The phthalocyanine ligand has also been shown to be a much stronger field ligand than a porphyrin and the hole radius is smaller for phthalocyanine complexes by ~0.07 Å [1]. The stronger ligand field of the phthalocyanine ligand causes its complexes to be intermediate or low spin even in many cases where the analogous porphyrin complexes are high spin [1]. An example is manganese(II) phthalocyanine which is believed to have an unusual $S = 3/2$ spin state [2] whereas manganese(II) tetraphenylporphyrin has an $S = 5/2$ ground state [3]. We have been investigating the coordination and reaction chemistry of high-valent manganese tetraphenylporphyrin complexes and we wished to compare this chemistry with that of manganese phthalocyanine and other manganese tetraazaporphyrin complexes. Unfortunately, the study of the solution chemistry of phthalocyanine complexes is severely limited by their low solubility in most solvents [4]. The low solubility of these complexes is probably due to the very efficient stacking of the flat phthalocyanine molecules in the solid phase. Syntheses of more soluble analogues of phthalocyanines are needed.

Linstead and co-workers have described the synthesis of a series of octaphenyltetraazaporphyrin complexes (also called octaphenylporphyrazines) [5] and reported that the complexes were both more soluble in organic solvents and more stable toward oxidation than the corresponding phthalocyanine complexes [5]. In this paper we describe the first synthesis of the complex manganese(II) octaphenylporphyrazine and attempts to make what were hoped would be a soluble manganese(II) octaethylphthalocyanine complex. A new synthesis of manganese(II) phthalocyanine has also been developed. All of these reactions utilize the direct reaction of the appropriate dinitriles with manganese powder as shown in Fig. 1.

Experimental

Physical Measurements

Elemental analyses were performed by the microanalytical laboratory, Department of Chemistry, University of California, Berkeley. Electronic spectra were recorded on a Hewlett-Packard 8450A UV-visible spectrometer. Electron paramagnetic resonance spectra (X-band) were recorded on a Bruker ER200D instrument at temperatures ranging from 85 K to 298 K. Variable temperature magnetic susceptibility measurements in the solid state were recorded on a SQUID apparatus (SHE Corp. VTS 800 susceptometer) which had been calibrated at low temperature by using a Pt standard. Fourier transform ^{1}H NMR spectra were recorded on the UCB-200 instrument at 201.96 MHz.

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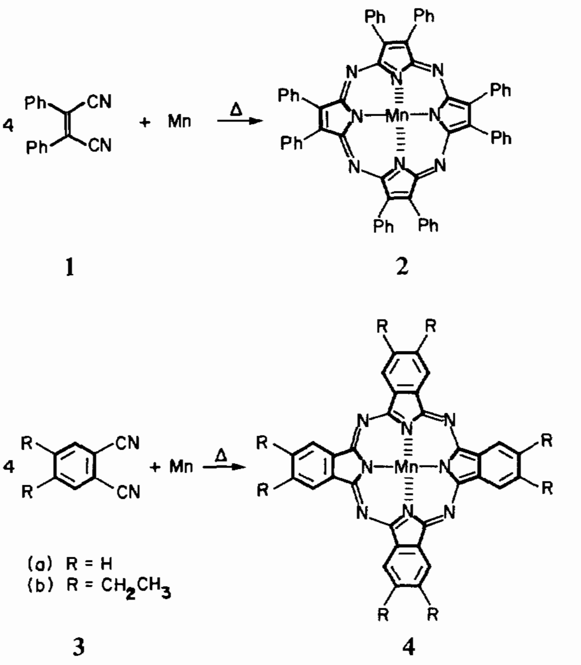

Fig. 1. One step syntheses of Mn tetraazamacrocyclic complexes.

Materials

Manganese powder, 10 micron, was purchased from Alfa. Ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, was reagent grade crystalline material.

Attempted Synthesis of 2,3,9,10,16,17,23,24-Octaethylphthalocyanatomanganese(II), 4b

A mixture of 1.85 g (10 mmol) of 1,2-dicyano-4,5-diethylbenzene [6], 0.20 g (3.6 mmol) of 10-micron manganese powder (Alfa), 5 mg of iodine, 5 mg of ammonium molybdate, and a boiling chip were heated to 220 °C under nitrogen. The dinitrile melted but little color was forming, so the mixture was slowly heated to 340 °C over a 40 min. period. By this time the reaction mixture had resolidified. The mixture was let cool to yield 1.86 g of a glassy black solid. This solid was slowly heated to 480 °C *in vacuo* (<5 microns Hg) to give only 6.7 mg of sublimed product. The visible spectrum of this product dissolved in N,N-dimethylacetamide under air is given in Fig. 2 and is distinct from the spectra exhibited by unmetallated phthalocyanine complexes[†]. The visible spectrum is similar to that observed when $Mn^{II}Pc$ is oxygenated in N,N-dimethylacetamide. The oxygenated complex formed in that reaction has been suggested to be the superoxide complex $Mn^{III}PcO_2$ [8].

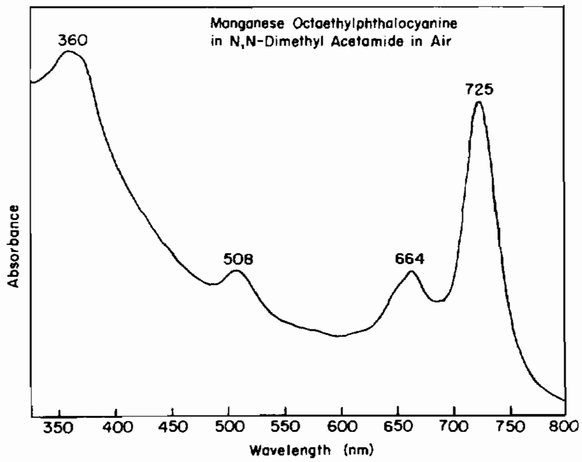

Fig. 2. Ultraviolet-visible spectrum of $Mn(Et_8Pc)$, 4b, in N,N-dimethylacetamide after exposure to air.

Synthesis of Octaphenylporphyrazinemanganese(II), 2

Diphenylmaleinitrile, 1, was synthesized by literature methods [5]. A large test tube containing 2.3 g (0.01 mol) of diphenylmaleinitrile, 0.25 g (4.6 mmol) of 10-micron manganese powder (Alfa), 10 mg of iodine and 10 mg of ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$) was heated to 320 °C under nitrogen. When the diphenylmaleinitrile began subliming up the walls of the tube, 0.25 mL of toluene was added. The refluxing of the toluene recycled the diphenylmaleinitrile into the reaction mixture. The reaction mixture formed a solid green mass after 1 h and was heated an additional 24 h. The product was then heated to 420 °C *in vacuo* to remove the unreacted dinitrile. Sublimation *in vacuo* from 420 to 480 °C yielded 280 mg of the crude product. Resublimation *in vacuo* at temperatures less than 480 °C yielded 140 mg (5.7%) of the pure product as black crystals. No attempt has been made to optimize the yield. *Anal.* Calcd for $C_{64}H_{40}N_8Mn$: C, 78.76; H, 4.13; N, 11.48; Mn, 5.63. Found: C, 78.78; H, 4.13; N, 11.44; Mn, 5.48. Mass spectrum: m/e (relative abundance) = 975 (M^+, 100%), 488 (M^{2+}, 13%). All other peaks between 489 and 974 were <0.3% intensity indicating that the phenyl groups are not lost in the gas phase. No peaks corresponding to unmetallated octaphenylporphyrazine were observed.

The crystalline product is insoluble in chloroform and exhibits low solubilities in common solvents. Variable-temperature magnetic susceptibility measurements from 5 to 300 K were performed on a sample of 3 that had been bottled for two years. The susceptibility of a 91 mg sample was determined at field values of 5 and 40 kG. Some of the low temperature data determined at 40 kG were discarded due to levitation of the sample holder. A

[†] For representative spectra see ref. 7 (spectrum of Bu_8PcH_2) or ref. 6 (Et_8PcH_2).

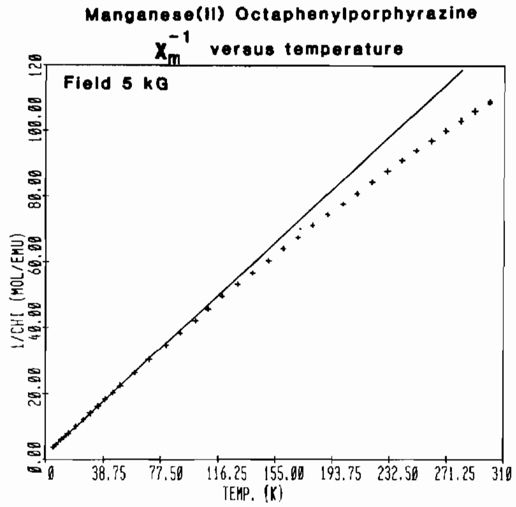

Fig. 3. Curie plot of 2 from 5 to 300 K.

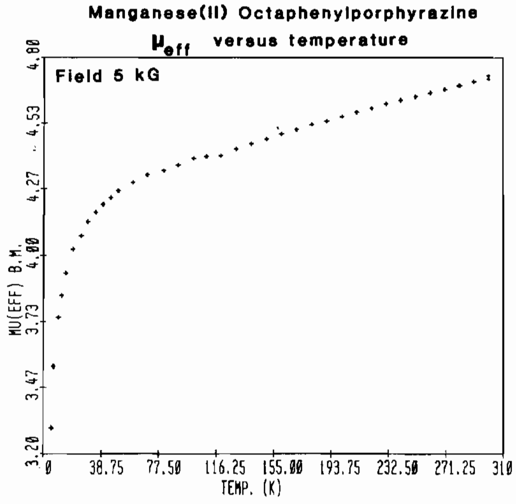

Fig. 4. Magnetic moment, μ_{eff}, of 2 as a function of temperature from 5 to 300 K.

diamagnetic correction of -930×10^{-6} cgsu/mol was estimated by summing the literature susceptibility values for one tetraphenylporphyrin [9], four benzenes [10] and a Mn(IV) ion [11]. No attempt to correct for any temperature-independent paramagnetism was made. Plots of $1/\chi_M$ and μ_{eff} *vs.* temperature for the 5 kG data are given in Figs. 3 and 4[††]. At least-squares analysis of $1/\chi_M$ *vs.* T for the 11 lowest temperature measurements (5 to 45 K) showed excellent Curie-Weiss behavior with an intercept of $\theta = -3.85 \pm 0.08$ K. Negative deviations from Curie-Weiss behavior are evident at the higher temperatures. The calculation of μ_{eff} for the 11 lowest temperature data according to the equation $\mu_\theta = 2.828[\chi_M(T - \theta)]^{1/2}$ gave $\mu_\theta = 4.40 \pm 0.01$ μ_B for all 11 data points. Complex 2 exhibits no EPR signals either in the solid state or in *m*-dichlorobenzene glasses at temperatures from 85 to 298 K.

Synthesis of Manganese Phthalocyanine, 4a

A large test tube was loaded with 15 g (0.117 mol) of phthalonitrile, 3.1 g (0.056 mol) of 10-micron manganese powder (Alfa), 30 mg of iodine, 50 mg of ammonium molybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, and a boiling chip. The tube was stoppered with a septum, flushed with nitrogen, and immersed in a 300 °C salt bath. The phthalonitrile rapidly melted and began refluxing for approximately two minutes, after which the reaction mixture solidified into a dark solid. The reaction mixture was left at 300 °C for 6 h. After cooling, the small amount of white organic solid that had sublimed was scraped from the upper walls of the tube. The remaining black powder was then sublimed in a tube furnace *in vacuo* over a 2-day period and at temperatures up to 480 °C to give 4.4 g of crude MnPc. (Caution: the unsublimed material remaining is pyrophoric and may burn with intense heat when exposed to air). The crude product was resublimed *in vacuo* at $\leq$460 °C to yield 3.45 g (21%) of pure MnPc. *Anal.* Calc for $C_{32}H_{16}N_8Mn$: C, 67.73; H, 2.84; N, 19.75; Mn, 9.68. Found: C, 67.90; H, 2.86; N, 19.75; Mn, 9.54.

Results and Discussion

The usual syntheses of manganese(II) phthalocyanine, MnPc, use the reaction of a manganese(II) salt with phthalonitrile in an appropriate reducing solvent, *e.g.* in 1,2-propanediol [12]. The reducing solvent is necessary since a net two-electron reduction of the four dinitriles is needed to form the phthalocyanine macrocycle. We thought that the stoichiometric reaction of manganese powder with four dinitriles might lead to a simpler, solvent-free, synthesis for manganese tetraazaporphyrins (Fig. 1). This reaction works well for the synthesis of the complexes MnPc and manganese(II) octaphenylporphyrazine, 2, but is not a convenient method for the synthesis of manganese(II) octaethylphthalocyanine 4b (Fig. 1).

The reaction of phthalonitrile with manganese powder does provide a simple, solvent-free, method for making reasonable yields (21% after two sublimations) of analytically pure MnPc. There are no literature preparations that give comparable yields of an analytically pure product. The analogous reaction of diphenylmaleinitrile with manganese powder provided the first synthesis of manganese(II) octaphenylporphyrazine. The yield of the analytically

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[††] A comprehensive tabulation of the variable temperature magnetic data for 2 is available as supplementary material.

pure product was low (5.7% yield after two sublimations), but no attempt has been made to optimize the yields. Sublimation of the product at 480 °C and the simplicity of its mass spectrum attest to the stability of this molecule.

The heating of the diethylphthalonitrile with manganese powder at temperatures greater than 300 °C did cause complete reaction of the dinitrile since products were formed that were solids well above the melting point of the dinitrile. Strong heating of these solids *in vacuo* yielded only very small amounts of sublimable material. The visible spectra of the sublimed material showed that the metallated macrocycle had indeed formed. It is not known if the low yield was due to the low volatility of the octaethylphthalocyanine product or the lack of its formation. It would be useful to metallate the independently synthesized octaethylphthalocyanine ligand to determine the solubility and volatility properties of the authentic manganese complex. However, the recently reported very low solubilities of even octabutylphthalocyanine complexes [7] and the very low solubilities found for octaethylphthalocyanine [6] suggest that octaalkylphthalocyanine complexes are species with very limited solubilities.

Manganese(II) octaphenylporphyrazine, 2, was conveniently isolated in a pure form from the reaction of diphenylmaleinitrile with manganese powder, but it was also insufficiently soluble in organic solvents to study its ^1H or ^{13}C NMR properties. The magnetic and EPR properties of 2 in the solid state were determined.

Ideally, a magnetically dilute monomeric manganese(II) complex would exhibit one of the three spin states $S = 5/2, 3/2$, or $1/2$. These should give rise to effective magnetic moments of 1.73, 3.87, or 5.92 μ_B, assuming that all orbital angular momentum is quenched. The room temperature magnetic moment of 2, $\mu_{eff} \sim 4.7$ μ_B, does not correspond to any of these values. Although the room temperature magnetic moment is near the value of 4.9 expected for a high-spin Mn(III) ion that might be formed by air-oxidation of 2, the steady decrease in the magnetic moment with temperature to 3.3 μ_B by 5 K is too large for a high-spin Mn(III) ion. For example, magnetic susceptibility measurements of high-spin Mn(III) porphyrin [13] and phthalocyanine [14] complexes have been reported and all exhibit room temperature magnetic moments of ~4.9 μ_B which do not decrease rapidly with temperature.

The magnetic behavior of the $Mn^{II}Pc$ complex related to 2 is complicated by intermolecular interactions. $Mn^{II}Pc$ is believed to have the unusual intermediate spin state $S = 3/2$ [2], and the complex magnetic behavior has been modeled by including ferromagnetic exchange interactions between adjacent MnPc molecules [15] and antiferromagnetic exchange between adjacent MnPc stacks [16]. It was proposed that the interaction of the paramagnetic centers in $Mn^{II}Pc$ is propagated through the very close (3.15 Å) Mn–N intermolecular contacts and/or via the π–π interactions of the closely packed MnPc molecules (the interplanar spacing is ~3.4 Å) [17]. Although the crystal structure of manganese(II) octaphenylporphyrazine, 2, is not known, the eight phenyl groups arranged perpendicularly to the porphyrazine plane might not allow as close an interplanar approach of two molecules of 2 as two molecules of $Mn^{II}Pc$. Nevertheless, the rapid decrease of the magnetic moment of 2 with temperature may indicate the presence of intermolecular antiferromagnetic coupling in the solid state. However, it has recently been reported that solid samples of the manganese(II) complex of tetrasulphonated phthalocyanine have a temperature-dependent magnetic moment that decreases from 5.9 μ_B at 299 K to 3.55 μ_B at 4.42 K. The authors of that report have suggested that the magnetic behavior is consistent only with a spin equilibrium between high, low, and intermediate spin states of a d^5 ion [18].

In conclusion, the magnetic properties of 2 are complex. They may be complicated by intermolecular antiferromagnetic coupling and/or temperature-dependent spin equilibria where the lower multiplicity spin states become increasingly populated at lower temperatures.

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