

Metalloporphyrin Photochemistry with Matrix Isolation

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Abstract: The photochemistry of a number of metalloporphyrin oxoanion complexes has been examined by matrix isolation techniques, using both frozen solvent glasses and polymer films. After an extensive search for a noncoordinating, unreactive, glassing solvent, a 3:1 mixture of 2,2-dimethylbutane and *tert*-butylbenzene was found to work well at temperatures below 70 K. Alternatively, the photochemistry of metalloporphyrins was monitored in polymer films by the evaporation on a sapphire window of metalloporphyrin solutions in toluene containing either poly(methyl methacrylate) or poly(α -methylstyrene). The polymer films have the added advantage of a greatly increased temperature range, providing diffusional isolation even at room temperature. The photoreduction of the metal by homolytic α -bond cleavage and loss of the axial ligand appears to be a general mechanism for all metalloporphyrin complexes examined. The formation of metal-oxo species from photolysis of metalloporphyrin oxoanion complexes in solution derives from secondary, thermal reactions.

Introduction

The role of metalloporphyrins in two very separate biological processes, oxoanion reduction (nitrite and sulfite reductases)¹⁻⁴ and hydrocarbon oxidation (cytochrome P450),⁵ has led us to examine the photochemistry of metalloporphyrin complexes⁶ of a number of anions including nitrate and nitrite,⁷ sulfate and bisulfate,⁷ perchlorate,⁸ and chloride.⁹ The photochemistry of porphyrins¹⁰⁻¹⁴ and metalloporphyrins^{6-9,15-21} continues to command substantial interest. In this area, one of the more surprising observations is β -bond cleavage in the solution photochemistry of metalloporphyrin oxoanion complexes;⁶⁻⁸ this results in oxygen atom transfer to form metal-oxo complexes and can occur with either homolytic or heterolytic transfer.

The use of frozen inert gas matrices, frozen solvent glasses, and polymer films has been well-established²² for spectroscopic studies of metalloporphyrins,²³ especially the (relatively) volatile four-coordinate metal(II) complexes.²⁴⁻³² Matrix isolation, however, has only rarely been used for *photochemical* studies of metalloporphyrins. The unexpected formation of Fe(porph)(O) from laser photolysis of the co-condensation products of Fe(porph) and O₂ at 15 K is a notable exception.^{32a} Glasses of 2-methyltetrahydrofuran have been used for the photolyses of Mn(porph)(N₃) and Cr(porph)(N₃) at 77 K, but reactions with this non-innocent matrix were observed.²¹

To explore the mechanism of photochemical oxygen atom transfer, we have examined the photochemistry of several porphyrin complexes by matrix isolation techniques. We find that both frozen solvent glasses and polymer films, if properly chosen, can be used effectively over a wide temperature range for a variety of metalloporphyrin complexes. Our results suggest that the photoreduction of porphyrin metal centers by homolytic metal-ligand α -bond cleavage is a general reaction and oxygen atom transfer and other reactions observed with solution photochemistry actually result from secondary thermal reactions.

Experimental Section

Materials. Solvents used were of reagent grade and distilled from sodium or from sodium-benzophenone prior to use. Low molecular weight (\approx 81 kD) poly(methyl methacrylate) (PMMA) or poly(α -methylstyrene) (PMS) were obtained from Aldrich Chemical Company and used as received. Inorganic salts were purchased from Aldrich and used without further purification. H₂TPP, Mn(TPP)(Cl), [Mn(TPP)]₂O, Fe(TPP)(Cl), and [Fe(TPP)]₂O were prepared by published methods.³³⁻³⁶ The oxoanion complexes have been fully characterized in the

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literature and are synthesized either by metathesis of the chloride complexes with the appropriate silver or sodium salt or by cleavage of $[\text{M}(\text{TPP})_2\text{O}]$ with the appropriate acid. $\text{Mn}(\text{TPP})(\text{ClO}_4)$, $\text{Mn}(\text{TPP})(\text{NO}_3)$, $\text{Mn}(\text{TPP})(\text{NO}_2)$, $[\text{Mn}(\text{TPP})_2\text{SO}_4]$, and $\text{Fe}(\text{TPP})(\text{ClO}_4)$ were prepared by the former method;^{6-8,37} $\text{Mn}(\text{TPP})(\text{OSO}_3\text{H})$ and $\text{Fe}(\text{TPP})(\text{NO}_3)$ were prepared by the latter method.^{7,38}

Instrumentation. Matrix-isolated UV-visible spectra were recorded on an IBM double monochromator spectrophotometer (Model 9430); other routine spectra were taken with a Hewlett-Packard 8452A diode array spectrophotometer. For low-temperature matrix-isolation studies, a Janis Research Co. closed cycle refrigeration system (Model C5W21-OL-5), cooled by a Leybold-Heraeus Cryogenerator (RW-3), was used. Temperature control was maintained by a Scientific Instruments digital temperature controller (Model 9600). The controller uses a silicon diode sensor with a ± 0.5 K accuracy in the 1.5–35 K range.

Photochemical Reactions. All photochemical reaction solutions were prepared in a Vacuum Atmospheres inert atmosphere box (<2 ppm O_2). In a typical experiment with a solvent glass, a saturated solution of the metalloporphyrin complex in a 3:1 (v/v) mixture of 2,2-dimethylbutane and *tert*-butylbenzene was placed under inert atmosphere in a sample holder consisting of a 0.125 in. thick silicone rubber spacer between two sapphire windows. In experiments utilizing polymer films, a 0.25 mM metalloporphyrin solution in toluene containing approximately 20 mg of polymer per mL was allowed to evaporate slowly on a sapphire window. The slower the rate of solvent evaporation, the more uniform were the films. The dried film was then sandwiched between a second window in the sample holder and mounted. In both methods, the holder was assembled inside an inert atmosphere box, removed, and attached to the Janis Research refrigeration system.

Irradiation was generally carried out with a 300-W xenon arc lamp focused onto the matrix. Wavelengths were selected by the use of various band-pass filters. For experiments where a single wavelength of light was desired, a 450-W medium-pressure Hg arc lamp (Ace glass No. 679A36) was used. Chemical filters were used³⁹ to isolate specific mercury lines: e.g., a dual chemical filter of I_2 in CCl_4 and 2,3-diphenylindenone in hexane for the 366-nm line.

Photoaction Studies. The determination of which bands in the absorbance spectrum of a given molecule are responsible for the photo-reactivity was accomplished by the use of commercially available narrow-pass and long-pass filters. The Soret (B) band (420–480 nm) and the α and β (Q) bands (>500 nm) could each be isolated by selection of the appropriate narrow-band-pass filter. In the case of manganese porphyrins, to the blue of the Soret band are the N, L, M and porphyrin to metal charge transfer bands. These overlap (and mix) so extensively that they were examined as a whole; a 290–420-nm band-pass filter suffices to isolate these bands. UV-vis spectra of both starting complexes and final products were compared to authentic samples.

Quantum Yield Determinations. Quantum yields for these reactions were measured with use of the Hg-arc lamp described above at 366 nm. The chemical actinometer used,⁴⁰ sold by Aberchromics, Ltd.^{40d} under the trade name of Aberchrome 540, is a member of the class of compounds known as fulgides. This actinometer has the advantage of being very quick, of requiring only photometric measurements, and of being reversible and therefore reusable.

Results and Discussion

We have found that both frozen solvent glasses and polymer films, when properly chosen, are well-suited for photochemical investigations of metalloporphyrin complexes. Compared to inert gas matrices often used for spectroscopic studies, solvent glass and polymer matrices avoid the limitation of low volatility of most metalloporphyrin complexes and simplify the experimental apparatus. To pursue such studies, however, it was essential to find

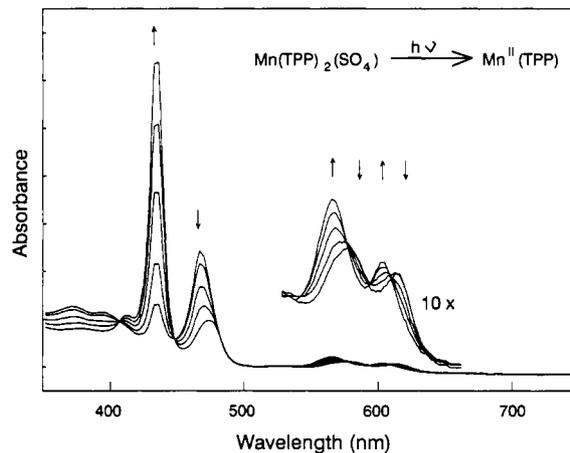
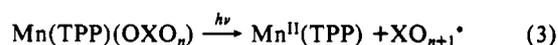
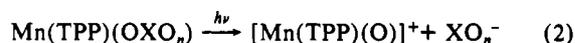
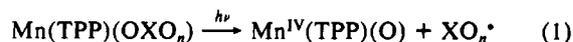


Figure 1. Photolytic conversion of $[\text{Mn}(\text{TPP})_2(\text{SO}_4)]$ to $\text{Mn}^{\text{II}}(\text{TPP})$ under matrix-isolation conditions in a poly(α -methylstyrene) film at 298 K. Very similar spectra were also observed at 10 K. Arrows indicate the change in absorbance during irradiation.

a matrix that (1) formed good glasses on freezing, (2) was non-coordinating, (3) lacked easily oxidizable sites (e.g., benzylic, tertiary, or β -heteroatom hydrogens), and (4) still was able to dissolve metalloporphyrin complexes. In spite of the many glasses that have been used for a variety of spectroscopic studies, we are unaware of any prior solvent glasses that met all of these criteria. After an extensive search, our best choice is a 3:1 mixture of 2,2-dimethylbutane and *tert*-butylbenzene, which forms excellent glasses with little cracking at temperatures below 70 K.

Alternatively, metalloporphyrin complexes could be easily dispersed in nonreactive polymer films on a sapphire window by evaporation of metalloporphyrin solutions in toluene containing either poly(methyl methacrylate) or poly(α -methylstyrene), both of which meet our four criteria. The polymer films have the added advantage of a greatly increased temperature range, providing diffusional isolation even at room temperature.^{22c} In the preparation of such films, solvents of high volatility work best since less solvent remains trapped in the films after drying. In addition, polymer films can be cooled and warmed repeatedly with no loss of sample integrity over a range of 12–298 K.

In our earlier work with manganese porphyrin oxoanion complexes, two distinct types of reactivity were observed in solution: oxygen atom transfer from the oxoanion to the metal and photoreduction of the metal. In the first class, both nitrate and nitrite complexes underwent β -bond cleavage to form $\text{Mn}^{\text{IV}}(\text{TPP})(\text{O})$ (eq 1, $\text{TPP} = 5,10,15,20$ -tetraphenylporphyrinate(2-)). In the case of perchlorate and periodate complexes, the formation of $[\text{Mn}(\text{TPP})(\text{O})]^+$ was inferred from the nature of the observed hydrocarbon oxidations⁸ (eq 2). On the other hand, sulfate and bisulfate complexes underwent homolytic α -bond cleavage⁷ to form $\text{Mn}^{\text{II}}(\text{TPP})$, as shown in eq 3. The possibility that all oxoanion complexes may actually undergo initial α -bond cleavage as in eq 3, followed in some cases by a rapid thermal reaction to form metal-oxo species (eqs 4 and 5), was also recognized. Solution photochemical studies could not differentiate between these two mechanisms.



Matrix-isolation techniques can prevent, in principle, the thermal reactions shown in eqs 4 and 5, and thus distinguish between initial α - and β -bond cleavage as the primary photo-reaction. A wide range of Mn^{III} complexes directly produce

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Table I. Photochemical Products and Quantum Yields in Solution and Frozen Matrix

complex	solution		matrix isolated ^a	
	product	10 ⁴ φ	product	10 ⁴ φ
Mn(TPP)(NO ₃)	Mn ^{IV} (TPP)(O) ^b	1.6	Mn ^{II} (TPP)	5.3
Mn(TPP)(NO ₂)	Mn ^{IV} (TPP)(O) ^b	3.2	Mn ^{II} (TPP)	12.0
[Mn(TPP)] ₂ (SO ₄)	Mn ^{II} (TPP) ^c	7.1	Mn ^{II} (TPP)	5.1
Mn(TPP)(OSO ₃ H)	Mn ^{II} (TPP) ^c	9.8	Mn ^{II} (TPP)	
Mn(TPP)(ClO ₄)	Mn ^{III} (TPP)(Cl) ^{d,e}	0.27	Mn ^{III} (TPP)(Cl)	0.11
Mn(TPP)(Cl)	Mn ^{II} (TPP) ^f	0.02	Mn ^{II} (TPP)	0.01
Fe(TPP)(NO ₃)	Fe ^{II} (TPP) ^{b,g}	1.3	photostable	0.00
Fe(TPP)(Cl)	Fe ^{II} (TPP) ^h	5.1	Fe ^{II} (TPP)	0.34
Fe(TPP)(ClO ₄)	photostable ^d	0.00	photostable	0.00

^a Samples irradiated with a 300-W Xe arc lamp using narrow pass filters. UV-vis spectra were compared to authentic samples. Results were the same in solvent glass at 10 K, in polymer matrix at 10 K, and in polymer matrix at 298 K. Quantum yields were determined with use of the 366-nm line of a low-pressure Hg arc; results were the same to within experimental error ($\pm 10\%$) at both 30 and 298 K. Matrix-isolated Mn(TPP)(OH) and [Fe(TPP)]₂O were also photoreduced; quantum yields were not determined but were qualitatively similar to the other complexes. ^b Reference 7a. ^c Reference 7b. ^d Reference 8. ^e The initial formation of [M(TPP)(O)]⁺ was inferred from oxidation of hydrocarbons. Due to its high reactivity, this species was not directly observed. ^f Reference 17. ^g Reference 9.

Mn^{II}(TPP) upon irradiation under matrix-isolation conditions. This is shown representatively in Figure 1 and quantified in Table I. The direct photoreduction occurs for the nitrate, nitrite, hydrosulfate, μ -sulfate, chloro, and hydroxo complexes. Results were the same in solvent glass at 10 K, in polymer matrix at 10 K, and in polymer matrix at 298 K, thus ensuring that matrix effects were not influencing the observed photochemistry. Using narrow-pass filters, we have established that the Q bands (>500 nm) are not photochemically active, either in solution⁶⁻⁹ or in matrix isolation. These transitions are strictly porphyrin π to π^* in nature.²³ In manganese complexes, the B (Soret) band is strongly mixed with porphyrin ligand-to-metal charge-transfer transitions, giving rise to the multiple bands in the blue and near-UV. These d-type hyper²³ spectral features are responsible for the photoreductions that we observe in matrix photolysis.

In contrast to the solution photochemistry of both Mn(TPP)(NO₃) and Mn(TPP)(NO₂) complexes, no formation of Mn^{IV}(TPP)(O) was detected in matrices. The quantum yield (ϕ) for Mn^{II}(TPP) formation in the matrix is only slightly larger than those measured for Mn^{IV}(TPP)(O) formation in solution, and the ratio of $\phi(\text{Mn(TPP)(NO}_3)/\phi(\text{Mn(TPP)(NO}_2))$ is the same in both solution and matrix. Taken together, these data demonstrate that the *initial* photoreaction is reduction of the manganese. For the nitrate and nitrite complexes, in solution photolysis, this photoreduction is followed by rapid thermal reactions that give the observed Mn^{IV}(TPP)(O).

It has been previously recognized that some iron porphyrin complexes can be photoreduced. The photoreduction of solutions of Fe^{III}(porph)(X) where X is a halide or hydroxide has been well-established.^{9,41} By examining the energy of the absorbance bands as a function of axial ligation, we have previously assigned a near-UV absorption that is responsible for this photoreduction as a halide-to-metal charge transfer. On irradiation under matrix-isolation conditions (Figure 2), Fe^{II}(TPP)(Cl) was cleanly produced with a quantum yield similar to that in solution. [Fe^{III}(TPP)]₂O is also photoreduced in both solution⁴² and matrix.

The photostability of Fe(TPP)(ClO₄) and Fe(TPP)(NO₃) is in direct contrast to that of the other metalloporphyrins examined. It is worth noting that iron complexes of the type Fe(TPP)(OXO_n) show "normal" rather than the "d-type hyper" spectra of the analogous manganese porphyrin complexes. This indicates that the Fe(TPP)(OXO_n) complexes lack the porphyrin ligand-to-metal charge-transfer transitions responsible for the photoreduction observed in the manganese porphyrins. In addition, they do not

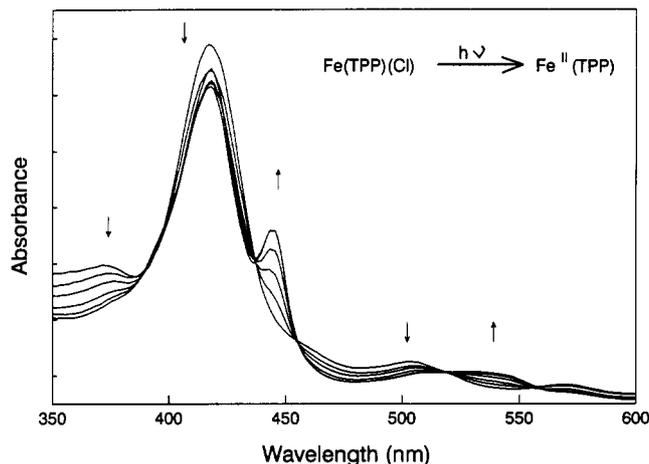


Figure 2. Photolytic conversion of Fe(TPP)(Cl) to Fe^{II}(TPP) under matrix isolation conditions in a poly(α -methylstyrene) film at 10 K. Very similar spectra were also observed at 298 K. Arrows indicate the change in absorbance during irradiation.

show the near-UV band associated with halide-to-metal charge-transfer transition. The absence of accessible charge-transfer transitions is consistent with the lack of photochemical reactivity.

Thus, the photoreduction of the metal center appears to be a general mechanism. There are no other photochemical processes observed in these systems. The porphyrins do not decompose and they do not fluoresce. The low quantum yields for photoreduction reflect very high efficiency of nonradiative decay processes for metalloporphyrins. This is to be expected since this photochemistry arises only from high-lying (rather than the lowest energy) excited states. The subsequent thermal chemistry is probably determined by several factors, including the relative stabilities of the leaving groups and the remnant porphyrin species, as well as relative solvation energies of products.

The one apparent exception to this photoreduction route is Mn(TPP)(ClO₄). Both in solution and in matrices, the direct formation of Mn(TPP)(Cl) is observed. In solution photolysis,⁸ this can be explained by the extreme reactivity⁴³ of [Mn(TPP)(O)]⁺: after all four oxygen equivalents are incorporated into substrate, the remaining chloride forms Mn(TPP)(Cl). Under matrix-isolation conditions, however, the secondary thermal reactions should not have occurred, especially at 10 K. We suggest that here too the initial photoreaction is α -bond cleavage and photoreduction to form Mn^{II}(TPP) and ClO₄⁻. ClO_x species, however, are known⁴⁴ to undergo efficient photochemical reactions, resulting finally in Cl^{*} that even in the matrix could give the observed Mn(TPP)(Cl). Given the relatively low quantum yields of metalloporphyrin photoreduction, the secondary photoreactions of ClO_x predominate the observed products.

Conclusions

We have shown that both solvent glasses and polymer films are viable alternatives for matrix-isolation studies of nonvolatile metalloporphyrin complexes. The photoreduction of the metal by homolytic α -bond cleavage and loss of the axial ligand appears to be a general mechanism for all metalloporphyrin complexes examined. This is consistent with the nature of the excited states involved. Irradiation of the lowest energy π to π^* transitions does not produce photochemical reactions in these complexes. Metalloporphyrin photochemistry is unusual in this way: the observed photoreactions do *not* come from the lowest available excited state.

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Instead, metalloporphyrin photochemistry arises from higher excited states that involve charge-transfer transitions, either from the axial ligand to the metal or from the porphyrin itself to the metal. The formation of metal-oxo species from photolysis of various metalloporphyrin oxoanion complexes in solutions derives from secondary, thermal reactions.

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Spin Frustration: A Hexanuclear Ferric Complex with a $S = 5$ Ground State

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Abstract: The preparation and characterization of a hexanuclear Fe^{III} complex possessing an unusual $S = 5$ ground state are described. Reaction of 1,1-bis(*N*-methylimidazol-2-yl)-1-hydroxyethane (**1**) with $[\text{Fe}_3\text{O}(\text{OAc})_6\text{L}_3]\text{X}$ (**2**), where L = pyridine or H_2O and X = ClO_4^- or NO_3^- , in CH_3CN followed by recrystallization in CH_2Cl_2 affords crystals of $[\text{Fe}_6\text{O}_2(\text{OH})_2(\text{OAc})_{10}(\text{C}_{10}\text{H}_{13}\text{N}_4\text{O}_2)_2] \cdot x\text{CH}_2\text{Cl}_2$ (**3**· $x\text{CH}_2\text{Cl}_2$). Complex **3**· $8\text{CH}_2\text{Cl}_2$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 12.167$ (2) Å, $b = 12.921$ (4) Å, $c = 15.394$ (4) Å, $\alpha = 114.41$ (2)°, $\beta = 97.641$ (15)°, $\gamma = 102.17$ (2)°, $V = 2087.4$ (8) Å³, and $Z = 1$ at -100 °C. The structure was refined with 4179 observed reflections ($F > 6.0\sigma$) to give $R = 0.0465$ and $R_w = 0.0591$. The molecule resides at a center of inversion, making only three of the iron ions unique. Two of the iron ions have O_6 coordination spheres, while the third has an O_5N environment due to binding by one of the imidazole nitrogen atoms; the second imidazole ring of complex **1** remains uncoordinated. Complex **3** consists of two μ_2 -oxo Fe^{III}_3 triangular complexes bridged together at two vertices by two μ_2 -OH and four μ_2 - O_2CCH_3 ions. ^{57}Fe Mössbauer data can be fit to two quadrupole-split doublets in a 2:1 area ratio with $\delta = 0.383$ (3) and 0.406 (6) mm/s and $\Delta E_Q = 0.729$ (5) and 1.056 (11) mm/s, respectively, at 300 K. The parameters are consistent with high-spin Fe^{III} . Magnetic susceptibility data at 10.00 kG in the temperature range 6–350 K reveal an increase in effective moment with decreasing temperature from 9.21 μ_B at 346.1 K to a maximum of 10.90 μ_B at 20.00 K. Variable-field magnetization data measured to 1.57 K at 40.00 kG saturate at a reduced magnetization $M/N\mu_B$ of 9.2. Fitting of the magnetization data by full-matrix diagonalization and including axial zero-field interactions establish the ground state as having $S = 5$ with $g = 1.94$ and $D = 0.22$ cm⁻¹. The origin of this ground state is described in terms of spin frustration within the hexanuclear core, and the results are compared to those found for a similar hexanuclear complex for which a $S = 0$ ground state was found.

Introduction

Polynuclear oxo- or hydroxo-bridged transition-metal centers have been found in a variety of iron¹ and manganese² metalloproteins. Hemerythrin,³ methane monooxygenase,⁴ and ribonucleotide reductase⁵ have diiron active sites with μ -oxo and μ -carboxylato bridges. In the course of making model complexes for these oxo-diiron protein sites, several interesting polynuclear ferric complexes with Fe_4 , Fe_6 , Fe_8 , Fe_{10} , and Fe_{11} compositions

have been reported.⁶ The largest nuclearity discrete oxo-hydroxo ferric complex is heteronuclear: $[\text{Fe}_{16}\text{MO}_{10}(\text{OH})_{10}(\text{O}_2\text{CPh})_{20}]$ ($M = \text{Mn}^{\text{II}}, \text{Co}^{\text{II}}$).⁷ The pursuit of model complexes for the active sites of catalases and the water oxidation center of photosystem II has also yielded polynuclear manganese complexes with compositions of $\text{Mn}^{\text{II}}_2\text{Mn}^{\text{III}}_2$, $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}_3$, Mn^{III}_4 , $\text{Mn}^{\text{II}}_4\text{Mn}^{\text{III}}_2$, Mn^{III}_8 , $\text{Mn}^{\text{II}}\text{Mn}^{\text{III}}_8$, $\text{Mn}^{\text{III}}_4\text{Mn}^{\text{IV}}_6$, $\text{Mn}^{\text{II}}_{12}$, and $\text{Mn}^{\text{III}}_8\text{Mn}^{\text{IV}}_4$.⁸ The most

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