species, μ-$Et_2NB_2H_5$.[19,22-24] The formation of μ-$Et_2NB_2H_5$ occurred slowly at room temperature and continued to take place with time. The formation of these subsequent products can occur via the proposed reaction pathway (4)-(6). Reactions analogous

$$\mathrm{Me_2As\overline{NEt_2\cdot B}H_3 \rightarrow Me_2AsH + Et_2NBH_2} \tag{4}$$

$$\mathrm{Et_2NBH_2 + BH_3\cdot THF \rightarrow \mu\text{-}Et_2NB_2H_5 + THF} \tag{5}$$

$$\mathrm{Me_2AsH + BH_3\cdot THF \rightarrow Me_2AsH\cdot BH_3 + THF} \tag{6}$$

to (4) have been observed previously during the decomposition of $F_2AsNMe_2\cdot BF_3$[12] and $F_2PNMe_2\cdot BF_3$.[16] In solution, compound I decomposed over a period of 3 days to give a product mixture. The ^{11}B NMR spectrum showed the mixture contained approximately 70% μ-$Et_2NB_2H_5$, 25% $Et_2NH\cdot BH_3$, a small amount of dimeric $(Et_2NBH_2)_2$,[21,23] and As-B-bonded species such as $Me_2AsH\cdot BH_3$ and Me_2AsBH_2[19] (monomeric and/or oligomeric) (Table II). The absence of any $BH_3\cdot THF$ and the presence of $(Et_2NBH_2)_2$ in the final product mixture support the formation of μ-$Et_2NB_2H_5$ via eq 5. The substantial yield of $Et_2NH\cdot BH_3$, obtained from the initial reaction mixture upon standing, could result from side reactions that involve Et_2NBH_2, Et_2NH, and I. Irreversible decomposition of the addition compounds formed by boranes with molecules having group 15[27] donor atoms are known.[17]

When the reaction was carried out with THF as the solvent, cleavage of the As-N bond and the subsequent rearrangements were facile. These reactions occurred at lower temperatures as compared to those in the previously described reaction. Currently we are investigating the reactions of boron halides, mixed halides, and higher boranes with aminoarsines.

Experimental Section

General Data. Standard high-vacuum line techniques and a Vacuum Atmospheres Model HE-43 Dri-Lab equipped with a Model HE-493 Dri-Train were used throughout for the handling of all compounds. (Diethylamino)dimethylarsine (bp 80.5 °C (90 mm)) was synthesized by the reaction of Me_2AsCl with excess Et_2NH[25] and was purified prior to use. Diborane(6) was synthesized by the dropwise addition of a diglyme solution of iodine to $NaBH_4$ in diglyme. Trap-to-trap distillation afforded pure diborane(6) in the -126 °C trap. THF-d_8 and toluene-d_8 were purchased from Wilmad Glass Co. and stored over molecular sieves. ^{11}B, ^{13}C, and ^{1}H NMR spectra were recorded on a Nicolet 300-MHz multinuclear FT NMR spectrometer operating at 96.3, 75.4, and 300.1 MHz, respectively. Chemical shift values for the ^{11}B resonance signals were measured relative to the signal of $BF_3\cdot OEt_2$, high-field shifts being taken as negative. The ^{1}H and ^{13}C NMR chemical shifts were measured with respect to Me_4Si as an internal reference.

Reaction of $BH_3\cdot THF$ with Me_2AsNEt_2. A 2.0-mL portion of THF-d_8 and 2.0 mL of toluene-d_8 were placed in the NMR reaction tube (12 mm × 22.5 cm, Pyrex; equipped with a greaseless vacuum stopcock). The tube was evacuated at -196 °C and 2.2 mmol of B_2H_6 condensed into it. The reaction solution was warmed to 20 °C to form $BH_3\cdot THF$. The solution was then cooled to -196 °C, and 2 mmol of Me_2AsNEt_2 was condensed onto it. The contents of the tube were shaken gently at -90 °C. The tube was sealed and inserted into the precooled (-90 °C) probe of the NMR spectrometer. The NMR spectra of the reaction solution were recorded from -90 to +25 °C). The NMR spectral assignments are tabulated in Tables I and II.

Acknowledgment. We are pleased to acknowledge the support of this research through the University College Committee on Faculty Research Grants at the University of Alabama—Birmingham.

---

(22) Gaines, D. F.; Schaeffer, R. *J. Am. Chem. Soc.* **1964**, *86*, 1505-1507.

(23) Schwartz, L. D.; Keller, P. C. *J. Am. Chem. Soc.* **1972**, *94*, 3015-3018.

(24) Phillips, W. D.; Miller H. C.; Muetterties, E. L. *J. Am. Chem. Soc.* **1959**, *81*, 4496-4500.

(25) Modritzer, K. *Chem. Ber.* **1959**, *92*, 2637-2640.

(26) Young, D. E.; McAchran, G. E.; Shore, S. G. *J. Am. Chem. Soc.* **1966**, *88*, 4390-4396.

(27) The group notation is being changed in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is being eliminated because of wide confusion. Group I becomes groups 1 and 11, group II becomes groups 2 and 12, group III becomes groups 3 and 13, etc.

Contribution from the Department of Chemistry,
North-Eastern Hill University, Shillong 793003, India

Direct Synthesis of Potassium Tris(oxalato)manganate(III) and First Synthesis of Alkali-Metal and Ammonium Trifluoro(oxalato)manganates(III)

Manabendra N. Bhattacharjee, Mihir K. Chaudhuri,*
and Ranendra N. Dutta Purkayastha

Received March 12, 1984

The compound $K_3[Mn(C_2O_4)_3]\cdot 3H_2O$, known for quite some time,[1] has served as a very oft-quoted example whenever the subject of inorganic photochemistry is discussed.[2] The method involving the reaction of $KMnO_4$ with oxalic acid and $K_2C_2O_4$ in the presence of an excess of K_2CO_3 is universally accepted for the synthesis of $K_3[Mn(C_2O_4)_3]\cdot 3H_2O$. This method requires very careful manipulation and uses an excess of K_2CO_3 in order to control the pH. The chances of contamination of the end product, owing to the use of K_2CO_3 in such quantities, cannot be ruled out. It is possible to synthesize $K_3[Mn(C_2O_4)_3]\cdot 3H_2O$ in a more nearly quantitative way directly from MnO(OH) without making use of any buffer. It will also be shown that $[Mn(C_2O_4)_3]^{3-}$ can exist in solutions in the presence of countercations like Na^+, Rb^+, Cs^+ or NH_4^+. Attempts to stabilize manganese(III)-oxalate systems have now led to the first synthesis of alkali-metal and ammonium trifluoro(oxalato)manganates(III), $A_2[MnF_3(C_2O_4)]$ (A = Na, K or NH_4), providing a very good opportunity to demonstrate the enhanced stability of (oxalato)manganates(III) and to obtain a set of internally consistent data concerning the effect on the magnetic properties of trivalent manganese on going from $K_3[Mn(C_2O_4)_3]$ to $A_2[MnF_5]$ via $A_2[MnF_3(C_2O_4)]$.

Experimental Section

The chemicals used were all reagent grade products. The compound MnO(OH) was prepared by the oxidation of $Mn(OH)_2$ with hydrogen peroxide.[3]

Infrared spectra were recorded on a Perkin-Elmer Model 683 spectrophotometer. Electronic spectra were recorded on a Beckman Model UV-26 spectrophotometer. The Gouy method was used to measure the magnetic susceptibility of the complexes using $Hg[Co(NCS)_4]$ as the standard.

Syntheses. Potassium Tris(oxalato)manganate(III) Trihydrate, $K_3[Mn(C_2O_4)_3]\cdot 3H_2O$. To a water suspension (20 cm^3) of 0.89 g (10.1 mmol) of MnO(OH) was added a concentrated solution of 2.82 g (15.3 mmol) of $K_2C_2O_4$. The mixture was cooled in an ice bath for ca. 15 min, followed by addition of a concentrated solution of 1.93 g (15.3 mmol) of oxalic acid. The solution was stirred for ca. 50 min in an ice bath. The solution, which became cherry red, was filtered quickly, and an excess of precooled (~0 °C) ethanol (about 1/1 v/v) was added with stirring to obtain the cherry red $K_3[Mn(C_2O_4)_3]\cdot 3H_2O$. The microcrystalline compound was isolated by quick filtration, washed twice with precooled ethanol, and finally dried in vacuo in the absence of light. The yield of $K_3[Mn(C_2O_4)_3]\cdot 3H_2O$ was 3.1 g (62.5%).

Alkali-Metal and Ammonium Trifluoro(oxalato)manganates(III), $A_2[MnF_3(C_2O_4)]$ (A = Na, K, NH_4). Representative Procedure. Freshly prepared MnO(OH) was dissolved in 40% HF with maintenance of the molar ratio of MnO(OH) to HF at 1/4-5 (2.5 cm^3, 40% HF/1 g of MnOOH), and the solution was warmed at ca. 100 °C for ca. 5 min, followed by filtration. The filtrate was cooled to room temperature, and a concentrated solution of $A_2C_2O_4$ (A = Na, K, NH_4) was slowly added with stirring, with the molar ratio of MnO(OH) to $A_2C_2O_4$ being maintained at 1/1. The solution was stirred for a further period of ca. 10 min at room temperature (ca. 20 °C). Addition of an excess of ethanol, in an amount not exceeding half of the original volume of the solution, precipitated pink alkali-metal or ammonium trifluoro(oxalato)managanage(III), $A_2[MnF_3(C_2O_4)]$. The compound was separated by filtration, washed thrice with ethanol, and finally dried in vacuo. Starting from 1.0 g of MnO(OH) in each case, the yields of $Na_2[MnF_3(C_2O_4)]\cdot 5H_2O$, $K_2[MnF_3(C_2O_4)]\cdot H_2O$, and $(NH_4)_2[MnF_3(C_2O_4)]$ were 3.4 g (89%), 3.2 g (94%), and 2.4 g (90%), respectively. Anal. Calcd for

---

(1) Cartledge, G. H.; Erricks, W. P. *J. Am. Chem. Soc.* **1936**, *58*, 2061, 2063, 2065.

(2) Harriman, A. *Coord. Chem. Rev.* **1979**, *28*, 156.

(3) Brauer, G., Ed. "Handbook of Preparative Inorganic Chemistry"; Academic Press: New York, 1965; Vol. 2, p 1457.

0020-1669/85/1324-0447$01.50/0

$Na_2[MnF_3(C_2O_4)]\cdot5H_2O$: Na, 13.69; Mn, 16.37; C_2O_4, 26.19; F, 16.96. Found: Na, 13.9; Mn, 16.7; C_2O_4, 26.5; F, 17.2. Estimated oxidation state of Mn: 3.0. μ_{eff}: 4.3 μ_B. IR: 1670 s (ν_{as}(O–C–O)), 1365 w and 1320 m (ν_s(O–C–O)), 778 m and 755 w (δ(O–C–O)), 425 s (ν(Mn–O)), 495 m (ν(Mn–F)), 3455 m (ν(O–H)), 1640 s cm^{-1} (δ(H–O–H)). Anal. Calcd for $K_2[MnF_3(C_2O_4)]\cdot H_2O$: K, 26.35; Mn, 18.58; C_2O_4, 29.73; F, 19.26. Found: K, 26.1; Mn, 18.8; C_2O_4, 29.7; F, 19.4. Estimated oxidation state of Mn; 3.1. μ_{eff}: 4.3 μ_B. IR: 1672 s (ν_{as}(O–C–O)), 1365 w and 1320 m (ν_s(O–C–O)), 778 m and 750 w (δ(O–C–O)), 425 s (ν(Mn–O)), 490 m (ν(Mn–F)), 3460 m (ν(O–H)), 1640 s cm^{-1} (δ(H–O–H)). Electronic spectra: 19 800 ($^5B_{1g} \rightarrow {}^5B_{2g}$), 22 700 cm^{-1} ($^5B_{1g} \rightarrow {}^5E_g$). Anal. Calcd for $(NH_4)_2[MnF_3(C_2O_4)]$: N, 11.86; Mn 23.31; C_2O_4, 37.29; F, 24.15. Found: N, 11.4; Mn, 23.2; C_2O_4, 37.6; F, 24.4. Estimated oxidation state of Mn: 3.1. μ_{eff}: 4.2 μ_B. IR: 1670 s (ν_{as}(O–C–O)), 1360 w and 1315 m (ν_s(O–C–O)), 780 m and 750 s (δ(O–C–O)), 425 s (ν(Mn–O)), 490 m (ν(Mn–F)), 3160 m, 3040 s, and 1400 s cm^{-1} (ν_3, ν_1, and ν_2 modes of NH_4^+). Electronic spectra: 19 500 ($^5B_{1g} \rightarrow {}^5B_{2g}$), 22 500 cm^{-1} ($^5B_{1g} \rightarrow {}^5E_g$).

Elemental Analyses. Manganese was estimated volumetrically by complexometric titration with EDTA[4] using Erio T as the indicator. Oxalate was estimated by redox titration with a standard potassium permanganate solution.[5] Fluoride was precipitated, after destroying oxalate, as lead chloride fluoride, PbClF, and chloride was estimated by Volhard's method, from which the fluoride content was calculated.[6] Sodium, potassium, and nitrogen were determined by the methods described in a previous paper.[7]

Chemical Determination of the Oxidation State of Manganese. The oxidation state of manganese was determined iodometrically by treating a freshly prepared ice-cold potassium iodide solution, acidified with dilute sulfuric acid, with the compound followed by titration of the liberated iodine with a standard sodium thiosulfate solution. The iodine titration was done under an ice-cold condition.

Results and Discussion

In order to overcome the difficulties involved in the synthesis[1] of the classic, oft-quoted, $K_3[Mn(C_2O_4)_3]\cdot3H_2O$, a direct method has now been improvised. The new method involves two steps. First, the reaction of MnO(OH) with 1/1.5/1.5 stoichiometric amounts of $H_2C_2O_4$ and $K_2C_2O_4$ leading to the synthesis of $K_3[Mn(C_2O_4)_3]$ in solution.

$$MnO(OH) + 1.5H_2C_2O_4 + 1.5K_2C_2O_4 \rightarrow K_3[Mn(C_2O_4)_3] + 2H_2O$$

Second, isolation of $K_3[Mn(C_2O_4)_3]$ in the solid state by the addition of ethanol, which facilitated precipitation. The strategy for the present synthesis was that MnO(OH) would react with oxalic acid to generate Mn^{3+}, which would be trapped immediately by the $C_2O_4^{2-}$ ions, arising out of $H_2C_2O_4$ and $K_2C_2O_4$, affording the complex $[Mn(C_2O_4)_3]^{3-}$ in the presence of K^+. The method is rapid, giving $K_3[Mn(C_2O_4)_3]\cdot3H_2O$ in a higher yield than the earlier method.[1] The room-temperature magnetic moment was found to be 4.92 μ_B in conformity with that reported in the literature.[1] The IR spectrum is unambiguous and shows the characteristics of chelated oxalato groups. The electronic spectrum of a solution of $K_3[Mn(C_2O_4)_3]$ showed the maximum absorption, a characteristic[1] of the $[Mn(C_2O_4)_3]^{3-}$ ion, at 19 050 cm^{-1}, while the reflectance spectrum showed a broad band at 9200, a shoulder at 19 050, and a peak at 20 500 cm^{-1} assigned[8] to the transitions $^5B_{1g} \rightarrow {}^5A_{1g}$, $^5B_{1g} \rightarrow {}^5B_{2g}$, and $^5B_{1g} \rightarrow {}^5E_g$, respectively, lending support to the identity of the compound.

Reactions of MnO(OH) with $A_2C_2O_4$ (A = Na, Rb, Cs, NH_4) and $H_2C_2O_4$ gave a cherry red solution, stable at ca. 0 °C in the dark, showing the electronic spectral absorption at 19 050 cm^{-1}, and allowing us to infer the formation and existence of the $[Mn(C_2O_4)_3]^{3-}$ ion. However, attempts to isolate the corresponding compounds in the solid state resulted in the formation of white decomposition products.

To control photochemical decomposition, it was expected that the stability of the manganese(III)–oxalato system can be enhanced by the presence of F^- ions, since fluoromanganates(III) are stable. It was observed, in line with the contention, that addition of 40% HF to the aforementioned reactions greatly increased the stability of the solutions as evidenced by their unaltered color at ca. 20 °C in light. Accordingly, the reaction of MnO(OH) with 40% HF and $A_2C_2O_4$ (A = Na, K, NH_4) in the ratio of $Mn/F^-/C_2O_4^{2-}$ at 1/4–5/1 at any temperature between 0 and 20 °C gave a pink solution from which the deep pink microcrystalline $A_2[MnF_3(C_2O_4)]$ was isolated by the addition of ethanol that facilitated precipitation. It is believed that MnF_3 is first formed in the solution, which then reacts with $C_2O_4^{2-}$ to generate the complex $[MnF_3(C_2O_4)]^{2-}$ ion, and weak acidity is conducive to the process while the application of heat annihilates the complex ion.

The compounds $A_2[MnF_3(C_2O_4)]$ are comparatively more stable than $K_3[Mn(C_2O_4)_3]\cdot3H_2O$ and can be stored in sealed polyethylene bags. The chemical determination of oxidation states of manganese in such compounds is emphasized because many Mn^{3+} compounds show abnormal magnetic moments,[9-11] leading to confusion regarding the actual oxidation state of the metal. The chemically estimated oxidation state was found to fall between 3.0 and 3.1, suggesting that manganese occurs in its +3 state. The room-temperature magnetic moments of the compounds, lying between 4.2 and 4.3 μ_B, suggest the possibility of a polymeric structure of $[MnF_3(C_2O_4)]^{2-}$ in the solid state, through –Mn–F–Mn– linkage or involving both F^- and $C_2O_4^{2-}$ as the bridging groups, allowing a weak antiferromagnetic interaction between the contiguous Mn^{3+} ions to be operative. Similar observations were recently made in the case of $A_2[MnF_3(SO_4)]$.[11] It is therefore apparent that antiferromagnetic interaction in manganese(III) complexes sets in with the partial replacement of $C_2O_4^{2-}$ by F^- ligands and becomes fully operative on complete removal of the $C_2O_4^{2-}$ ligands by F^- as evidenced by the lowering of magnetic moments on going from $[Mn(C_2O_4)_3]^{3-}$[1] through $[MnF_3(C_2O_4)]^{2-}$ (present work) to $[MnF_5]^{2-}$.[9,10]

The electronic spectra of $A_2[MnF_3(C_2O_4)]$ (A = K, NH_4) recorded in solution containing a small amount of 40% HF, required to check hydrolysis, show bands at ca. 19 600 and ca. 22 600 cm^{-1}, assigned to the transitions[8] $^5B_{1g} \rightarrow {}^5B_{2g}$ and $^5B_{1g} \rightarrow {}^5E_g$, respectively. This suggests an appreciable splitting of the ^5E_g ground state of Mn^{3+} in $[MnF_3(C_2O_4)]^{2-}$ as a consequence of Jahn–Teller effects. The infrared spectra of the compounds are similar and show characteristic absorptions for the coordinated $C_2O_4^{2-}$ and F^- groups. The band observed between 490 and 495 cm^{-1} has been assigned to the ν_{Mn-F} mode of coordinated fluoride. The absorptions due to the $C_2O_4^{2-}$ group imply the presence of a bridging oxalato group. Particularly significant is the absence of any band at 1680–1750 cm^{-1}, which is regarded as typical for a chelated oxalato ligand. Thus, the following assignments, which are also in agreement with those of Curtis,[12-14] were made in the present case: ν_{as}(O-C-O) at ~1670 s, ν_s(O–C–O) at ~1360 w and ~1320 m, δ(O-C-O) at ~780 m, and ~750 w cm^{-1}. The two additional bands at ca. 3455 m and ca. 1640 cm^{-1} in each of the sodium and potassium salts resemble in their shapes and positions those of the uncoordinated water in $K_2[MnF_5]\cdot H_2O$[10,15] and have been assigned to ν(O–H) and δ(H–O–H) modes. Further, it was emphasized in the literature[14] that the ν(O–H) band at 3455 cm^{-1} is rather typical of lattice water. These and the absence of any water in the $(NH_4)_2[MnF_3(C_2O_4)]$ compound lead us to infer that the water is not coordinated to the Mn^{3+} center. The three extra bands at 3160 m, 3040 s, and 1400 s cm^{-1} in the case of $(NH_4)_2[MnF_3(C_2O_4)]$ have been assigned to the ν_3, ν_1, and ν_2 modes of NH_4^+. It is presumed, on the basis of the present results, that the structure of and Jahn–Teller effect in the

---

(4) Vogel, A. I. "A Text Book of Quantitative Inorganic Analysis"; Longmans, Green and Co.: New York, 1962; p 434.

(5) Vogel, A. I. Reference 4, p 280.

(6) Vogel, A. I. Reference 4, p 269.

(7) Chaudhuri, M. K.; Ghosh, S. K. *Inorg. Chem.* **1982**, *21*, 4020.

(8) Davis, T. S.; Fackler, J. P.; Weeks, M. J. *Inorg. Chem.* **1968**, *7*, 1994.

(9) Emori, S.; Inoue, M.; Kishita, M.; Kubo, M. *Inorg. Chem.* **1969**, *8*, 1385.

(10) Bhattacharjee, M. N.; Chaudhuri, M. K.; Dasgupta, H. S.; Khathing, D. T. *J. Chem. Soc., Dalton Trans.* **1981**, 2587.

(11) Bhattacharjee, M. N.; Chaudhuri, M. K. *Polyhedron* **1984**, *3*, 599.

(12) Curtis, N. F. *J. Chem. Soc.* **1963**, 4109.

(13) Curtis, N. F. *J. Chem. Soc.* **1964**, 2644.

(14) Curtis, N. F. *J. Chem. Soc. A* **1968**, 1584.

(15) Edwards, A. J. *J. Chem. Soc. A* **1971**, 2653.

complex $[MnF_3(C_2O_4)]^{2-}$ are essentially analogous to those of the $[MnF_3(SO_4)]^{2-}$ complex.[16]

Acknowledgment. The authors are grateful to the Department of Atomic Energy for financial support (Grant No. 37/16/82-G) and to the University for awarding a UGC senior fellowship to M.N.B.

Registry No. $K_3[Mn(C_2O_4)_3]$, 14874-30-7; $Na_2[MnF_3(C_2O_4)]$, 94138-06-4; $K_2[MnF_3(C_2O_4)]$, 94138-07-5; $(NH_4)_2[MnF_3(C_2O_4)]$, 94138-08-6.

---

(16) Edwards, A. J. *J. Chem. Soc. A* **1971**, 3074.

Contribution from the Department of Chemistry,
Riverside, California 92521

Resonance Raman Spectra of Chromium(V) and Manganese(V) Porphyrin Nitrides

Cecelia Campochiaro, Joseph A. Hofmann, Jr.,[1a]
and David F. Bocian*[1b]

Received May 18, 1984

The characterization of high-valent metallopophyrins is of much current interest because these species have been identified as intermediates in a number of oxygenation reactions involving heme proteins[2–4] and synthetic catalysts.[5–9] Most attention has focused on the high-valent metalloporphyrin oxides; recently however, nitrido analogues of several of the oxo species have been isolated and structurally characterized.[10–13] These include nitridochromium(V)[10,11] and nitridomanganese(V)[12,13] porphyrin systems. The former complex is a paramagnetic d^1 species with a highly distorted porphyrin core while the latter is a diamagnetic d^2 system containing a very regular core structure.

Resonance Raman (RR) spectroscopy has been used extensively to investigate the structural features of metalloporphyrin complexes.[14,15] The vibrational frequencies and resonance-enhanced Raman intensities are sensitive to small perturbations in the electronic structure of the porphyrin macrocycle. In view of the information that can be obtained from RR studies, we examined in detail the RR spectra of two pentavalent metalloporphyrin nitrides, (TTP)CrN and (TTP)MnN (TTP = tetra-*p*-tolylporphyrin). This study yields a better characterization of the two high-valent metalloporphyrin complexes.

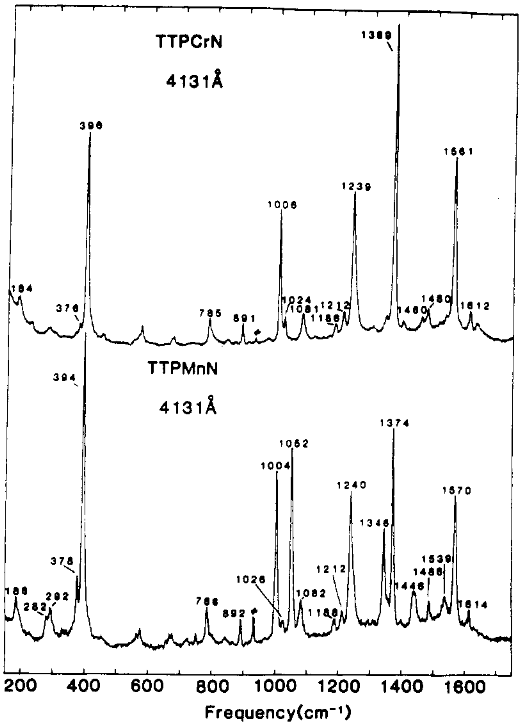

Figure 1. B-state resonance Raman spectra of solid (TTP)CrN and (TTP)MnN in a 1:2 $NaCl/Na_2WO_4$ pellet. Peaks due to Na_2WO_4 are denoted by daggers. See Experimental Section for spectral conditions.

Table I. Comparison of the Principal RR Bands (cm^{-1}) of (TTP)CrN and (TTP)MnN

sym	band	(TTP)CrN	(TTP)MnN	assignt[a]
A_{1g}	1	1612	1614	tolyl
	2	1561	1570	$\nu(C_\beta C_\beta) + \delta(C_\beta H)$
	3	1369	1374	$\nu(C_\alpha N) + \delta(C_\beta H)$
	4		1346	combin (ν(MnN) + out-of-plane deformn)
	5	1239	1240	$\nu(C_m\text{-tolyl})$
	6	1081	1082	$\delta(C_\beta H)$
	7		1052	ν(MnN)
	8	1006	1004	$\nu(C_\alpha C_m)$
	9	396	394	porphyrin deformn
	10	376	378	out-of-plane deformn
	11		282	
	12		292	
	13	184	186	
A_{2g}	14	1528	1539	$\nu(C_\alpha C_m)$
	15		1344	$\nu(C_\alpha C_\beta) + \delta(C_\beta H)$
	16	1212	1212	
B_{1g} and B_{2g}	17	1578	1593	$\nu(C_\alpha C_m)$
	18	1502	1510	$\nu(C_\beta C_\beta)$
	19	1024	1026	$\delta(C_\beta H)$

[a] The subscripts in the assignment labels identify the α- and β-pyrrole and the methine-bridging carbon atoms in the porphyrin macrocycle.

Experimental Section

The (TTP)CrN and (TTP)MnN complexes were the generous gift of Professor J. W. Buchler. All solvents were spectral grade and were used without further purification.

The RR spectra were recorded with the optics in a 90° scattering configuration on an apparatus described previously.[16] Excitation wavelengths were provided by the discrete lasing outputs of an Ar ion and Kr ion laser and a tunable dye laser using the tuning ranges of Rhodamine 590, Rhodamine 560, Coumarin 515, and Stilbenzene 420. RR spectra were obtained for both solid samples (in 1:2 $NaCl/Na_2WO_4$ pellets) and CS_2 solutions. Sample concentrations in the pellets were 2 mg of porphyrin/250 mg of salt. Solution concentrations were 0.2 mg/mL for B-state excitation and 1.0 mg/mL for Q-state excitation. All solution samples were deoxygenated and sealed in glass capillary tubes.

---

(1) (a) Present address: Wyeth Laboratories, Biomedical Data Systems Division, Philadelphia, PA. (b) Alfred P. Sloan Fellow, 1982–1984.

(2) Reid, T. V.; Murthy, M. R. N.; Sicignu, A.; Tanaka, N.; Musich, W. D. L.; Rossman, M. G. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 4767.

(3) Hewson, W. D.; Hager, L. P. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. 7, pp 295–332.

(4) Griffin, B. W.; Peterson, J. A.; Eastbrook, R. W. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. 4, pp 197–256.

(5) (a) Groves, J. T.; Kruper, W. J.; Nemo, T. E.; Myers, R. S. *J. Mol. Catal.* **1980**, *7*, 169. (b) Chang, C. K.; Kuo, M.-S. *J. Am. Chem. Soc.* **1979**, *101*, 3413.

(6) Groves, J. T.; Kruper, W. J., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 7613.

(7) Hill, C. L.; Schardt, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 6374.

(8) (a) Groves, J. T.; Kruper, W. J., Jr.; Haushalter, R. C. *J. Am. Chem. Soc.* **1980**, *102*, 6375. (b) Willner, I.; Otvos, J. W.; Calvin, M. *J. Chem. Soc., Chem. Commun.* **1980**, 964.

(9) Buchler, J. W.; Lay, K.-L.; Castle, L.; Ullrich, V. *Inorg. Chem.* **1982**, *21*, 842.

(10) Buchler, J. W.; Dreher, C.; Lay, K.-L.; Raap, A.; Gersonde, K. *Inorg. Chem.* **1983**, *22*, 879.

(11) Groves, J. T.; Takahashi, T.; Butler, W. N. *Inorg. Chem.* **1983**, *22*, 884.

(12) Buchler, J. W.; Dreher, C.; Lay, K.-L. *Z. Naturforsch., B: Anorg. Chem. Org. Chem.* **1982**, *378*, 1155.

(13) (a) Hill, C. L.; Hollander, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 7318. (b) Groves, J. T.; Takahashi, T. *J. Am. Chem. Soc.* **1983**, *105*, 2073.

(14) Spiro, T. G. In "Iron Porphyrins"; Lever, A. B. P., Gray, H. B., Eds.; Addison-Wesley: Reading, MA, 1982; Part II, pp 89–152.

(15) Felton, R. H.; Tu, N.-T. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. 3, pp 347–388.

(16) Schick, G. A.; Bocian, D. F. *J. Am. Chem. Soc.* **1983**, *105*, 1830.

0020-1669/85/1324-0449$01.50/0 © 1985 American Chemical Society