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

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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.

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

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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.

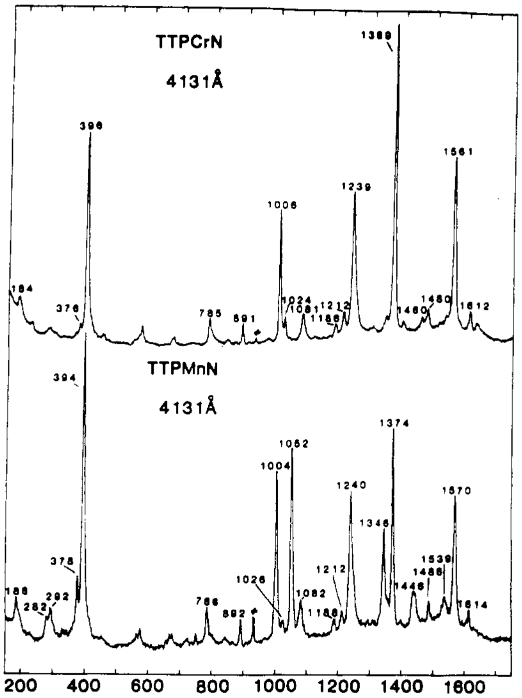

Figure 1. B-state resonance Raman spectra of solid (TTP)CrN and (TTP)MnN in a 1:2 $NaCl/Na_2WO_4$ pellet. Peaks due to Na_2WO_4 are denoted by daggers. See Experimental Section for spectral conditions.

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	$\nu(C_m$–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.

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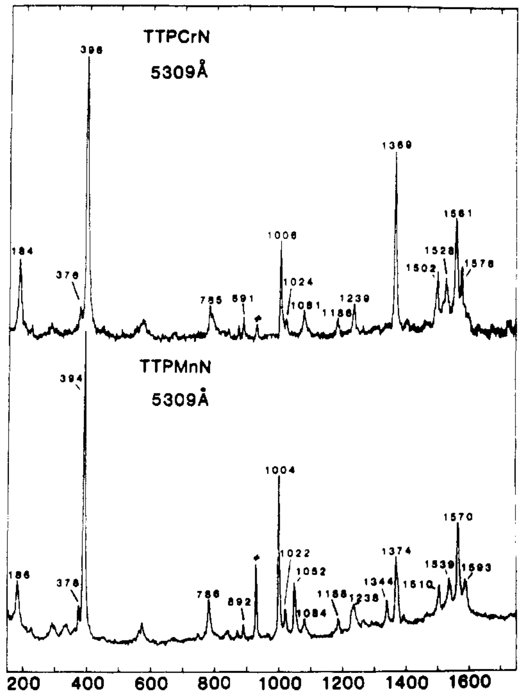

Figure 2. Q-state resonance Raman specta of solid (TTP)CrN and (TTP)MnN in a 1:2 NaCl/Na_2WO_4 pellet. Peaks due to Na_2WO_4 are denoted by daggers. See Experimental Section for spectral conditions.

RR spectra were collected at 2-cm^{-1} intervals at the rate of 1 s/point with a spectral slit width of 4 cm^{-1}. The incident laser power was less than 100 mW. Either the 932-cm^{-1} band of Na_2WO_4 or the 796-cm^{-1} band of CS_2 was used as internal standard.

Results and Discussion

The RR spectra of solid (TTP)CrN and (TTP)MnN in 1:2 NaCl/Na_2WO_4 pellets observed with excitation near the maxima of the Soret (λ_{ex} 4131 Å) and visible (λ_{ex} 5309 Å) bands are shown in Figures 1 and 2. The RR spectra obtained in CS_2 solution are identical with those of the solid except that a few of the bands show slight shifts (~2 cm^{-1}) in frequency. The frequencies of the observed RR bands are listed in Table I and categorized according to D_{4h} symmetry classifications as determined by their depolarization ratios, ρ: A_{1g}, $\rho < 0.75$ (polarized); A_{2g}, $\rho > 0.75$ (anomalously polarized); B_{1g} and B_{2g}, $\rho = 0.75$ (depolarized). The spectrum observed with λ_{ex} 4131 Å exhibits mostly polarized bands, while the RR spectrum obtained with λ_{ex} 5309 Å exhibits mostly depolarized and anomalously polarized bands. There are, however, several polarized bands observed with visible region excitation, notably the modes ca. 1004, 394, and 186 cm^{-1}.

Virtually all the bands of the two tetratolylporphyrins observed with Soret and visible region excitation have analogues in the RR spectra of tetraphenylporphyrin complexes.[14-18] We have assigned these bands of (TTP)CrN and (TTP)MnN by comparison and listed the approximate normal-mode compositions in Table I. Most of the prominent high-frequency (>1000 cm^{-1}) RR bands are due to in-plane porphyrin skeletal modes.[14,15] On the other hand, the very low-frequency bands (200–400 cm^{-1}) are due to out-of-plane deformations of the porphyrin skeleton.[16] RR bands are also observed that are not due to in-plane or out-of-plane porphyrin modes. For example, a resonance-enhanced internal vibration of the tolyl group is observed near 1612 cm^{-1} in the spectrum of both complexes.[16] More striking, however, are the two strong polarized modes observed at 1052 and 1346 cm^{-1} in the B-state excitation spectrum of (TTP)MnN. The analogous bands are completely absent in the spectrum of (TTP)CrN. Neither of these bands can be assigned as a totally symmetric fundamental porphyrin skeletal mode, since all such modes are already assigned. The 1052-cm^{-1} band corresponds to $\nu(Mn{\equiv}N)$ (1049 cm^{-1} in the IR spectrum[12]), while the 1346-cm^{-1} mode is probably a combination band of $\nu(Mn{\equiv}N)$ and one of the out-of-plane porphyrin skeletal deformations near 290 cm^{-1} (Figure 1). It should be noted that $\nu(Cr{\equiv}N)$ (1017 cm^{-1} in the IR spectrum[10,11]) is not resonance enhanced in the RR spectrum with excitation at *any* wavelength between 360 and 650 nm.

Although the most prominent difference between the RR spectra of (TTP)MnN and (TTP)CrN is the strong resonance enhancement of the metal–nitride stretch of the former complex and its complete absence in the latter, there are other differences in the RR spectra of the two nitrides. In particular, the high-frequency porphyrin skeletal modes involving $\nu(C_\alpha C_m)$ and $\nu(C_\beta C_\beta)$ (bands 2, 14, 17, and 18, Table I) are substantially lower in frequency (10–15 cm^{-1}) for the Cr complex. We attribute these lower frequencies to the weakening of the ring bonds due to the severe distortion of the macrocycle in the saddle-shaped system.[11] In contrast, the frequencies observed for (TTP)MnN are similar to those observed for metallotetraphenylporphyrin systems with fairly regular core structures.[16-18] The more regular core structure allows for increased C_α–C_m and C_β–C_β bond order. (It should be noted that the crystal structure of the tetra-*p*-tolyl–Mn complex has not been reported; however, the tetra-*p*-methoxyphenyl–Mn system does indeed exhibit a very regular core structure.[13a])

The strong resonance enhancement of $\nu(Mn{\equiv}N)$ can be explained by the more regular structure of the porphyrin core in the Mn complex. This structure allows for increased metal–nitride π bonding and better coupling to the electronic system of the porphyrin macrocycle. The higher bond order of the Mn≡N system compared to Cr≡N is reflected in the frequency of the two metal–nitride stretching modes (1049 cm^{-1} (Mn) and 1017 cm^{-1} (Cr)). Simple mass effects alone would result in a *lower* frequency for $\nu(Mn{\equiv}N)$ compared to $\nu(Cr{\equiv}N)$. Increased metal → porphyrin electron donation is indicated by the more "hypso" character of the electronic absorption spectrum[19,20] of the Mn compared to the Cr complex.[10-12] It should be noted that a second possible explanation for the strong resonance enhancement of $\nu(Mn{\equiv}N)$ is that a charge-transfer excited state lies in the region of the porphyrin B and Q states and is contributing to the scattering tensor. In order to explore this possibility, we obtained detailed excitation profiles of the RR bands of both (TTP)MnN and (TTP)CrN (not shown). It was found that the enhancement for the analogous porphyrin modes of the two complexes followed the same pattern and also that the enhancement of $\nu(Mn{\equiv}N)$ followed the same pattern as the porphyrin modes. All of the RR bands appear to gain intensity through excitation of the porphyrin B and Q states, and there is no evidence for a charge-transfer transition localized in the Mn≡N bridge in the region 360–650 nm.

Finally, it is interesting that there is such a dramatic difference in the structure and electronic properties of the porphyrin– and metal–nitride systems in the d^1 Cr and d^2 Mn complexes. The d electrons for (TTP)CrN and (TTP)MnN are in a d_{xy} orbital,[10-12] which is nonbonding for a planar or domed metalloporphyrin–nitride system. Apparently the additional charge density in the d_{xy} orbital of the Mn complex is extremely important for maintaining a regular structure in the porphyrin macrocycle. This, in turn, allows for increased bond order and substantial shortening of the Mn≡N bond (1.515 Å[13a]) compared to the Cr≡N bond (1.565 Å[11]).

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Registry No. (TTP)CrN, 84174-28-7; (TTP)MnN, 84206-81-5.

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