

common to two corner-sharing  $\text{ZnCl}_4$  tetrahedra — there are no shared edges or faces. Each chloride ion thus has two zinc, six intratetrahedral chloride, and six intertetrahedral chloride ion nearest neighbors. Cl(1) ions join tetrahedra lying at adjacent levels along the  $c$  axis, while Cl(2) ions join tetrahedra lying at a given level. Zigzag chains of corner-sharing tetrahedra, internally related by  $a$  glide planes, extend parallel to the  $a$  direction at a given level. They do not share any corners with parallel chains at that level, but, utilizing  $2_1$  screw axes, share corners with tetrahedra at the levels above and below.

Registry No.  $\text{ZnCl}_2$ , 7646-85-7.

**Supplementary Material Available:** A listing of observed and calculated  $F^2$  values (4 pages). Ordering information is given on any current masthead page.

### References and Notes

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- (2) Metals and Ceramics Division.
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### The Characterization of Molecular $\text{V}_4\text{O}_{10}$ , an Analogue of $\text{P}_4\text{O}_{10}$

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Mass spectrometric studies<sup>1,2</sup> of the vapor species above heated vanadium pentoxide (1000–1200 K) have identified the prominent ions  $\text{V}_4\text{O}_{10}^+$  and  $\text{V}_4\text{O}_8^+$ , and although solid  $\text{V}_2\text{O}_5$  does not vaporize congruently, it has been suggested<sup>2</sup> that the most abundant ion peak  $\text{V}_4\text{O}_{10}^+$  arises from a molecular species  $\text{V}_4\text{O}_{10}$  isostructural with  $\text{P}_4\text{O}_{10}$ . We have carried out matrix isolation studies on this system in an attempt to characterize this interesting molecule more completely.

In a series of exploratory studies, samples of commercially available  $\text{V}_2\text{O}_5$  (BDH) were first degassed in vacuo at  $\sim 750^\circ\text{C}$  in either silica or alumina sample holders. The temperature was then raised to  $800\text{--}850^\circ\text{C}$  and the vapor codeposited with an excess of nitrogen onto a CsI window cooled to  $\sim 10\text{ K}$ . Details of the apparatus have been described elsewhere.<sup>3</sup> The resulting IR spectrum showed two prominent bands at 1029.9 and  $828.4\text{ cm}^{-1}$  which always maintained the same intensity

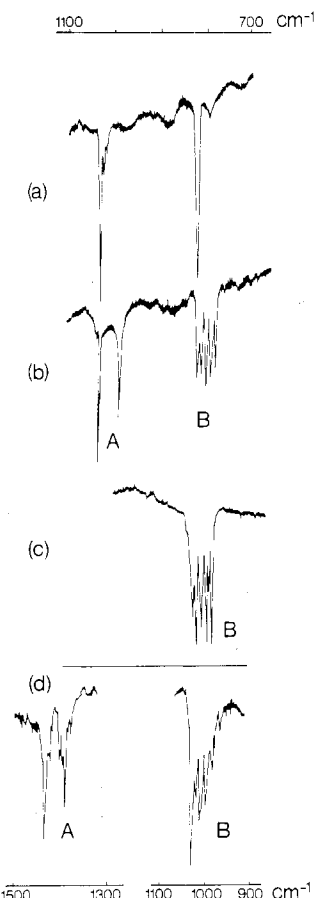


Figure 1. Matrix isolation IR absorption spectra of (a)  $\text{V}_4\text{O}_{10}$ , (b)  $^{18}\text{O}$ -enriched  $\text{V}_4\text{O}_{10}$ , (c)  $^{18}\text{O}$ -enriched  $\text{As}_4\text{O}_6$ , and (d)  $^{18}\text{O}$ -enriched  $\text{P}_4\text{O}_{10}$ .

ratio, and extended deposition yielded an additional weak feature at  $\sim 626\text{ cm}^{-1}$ . During deposition, a film of yellow solid was observed to condense on the cooler (off-axis) walls of the effusion chamber, and the vanadium pentoxide sample slowly turned black. The same two prominent bands were also observed from samples of substoichiometric vanadium pentoxide prepared by heating elemental vanadium in an excess of pure oxygen gas, and a typical spectrum is shown in Figure 1, part a.

The two prominent bands at 1029.9 and  $828.4\text{ cm}^{-1}$  suggest the presence of both terminal ( $\text{V}=\text{O}$ ) and bridge ( $\text{V}-\text{O}-\text{V}$ ) units in the trapped species.<sup>4</sup> These bands are close in frequency to two of the most prominent IR absorptions ( $1022$  and  $840\text{ cm}^{-1}$ ) in solid vanadium pentoxide<sup>5</sup> which contains both bridging and terminal oxygens. We also note that  $\nu_{\text{V}=\text{O}}$  in the molecular species  $\text{VOCl}_3$  occurs<sup>6</sup> at  $1035\text{ cm}^{-1}$ . These results, taken in conjunction with the mass spectral data and the apparent volatilization and condensation of a vanadium(V) species (yellow sublimate), indicate that molecular  $\text{V}_4\text{O}_{10}$  has been isolated in the matrix. In an attempt to confirm this,  $^{18}\text{O}$ -enrichment studies were carried out using oxide samples prepared from vanadium metal and  $^{16}/^{18}\text{O}_2$  gas.

Figure 1, part b, shows typical spectra obtained from an oxide sample enriched to the extent of  $\sim 50\%$   $^{18}\text{O}$ . The high-frequency feature at 1029.9 now appears essentially as a prominent doublet at 1029.9 and  $988.7\text{ cm}^{-1}$  (group A), while the  $828.4\text{-cm}^{-1}$  band becomes an approximately equally spaced quintet at 828.4, 818.7, 809.8, 800.1, and  $790.3\text{ cm}^{-1}$  (group B). For comparison, Figure 1, part c, shows the matrix IR spectrum<sup>7</sup> of  $\sim 50\%$  enriched  $\text{As}_4\text{O}_6$  in the region of the highest  $T_2$  cage mode ( $\nu_{\text{As}-\text{O}-\text{As}}$ ) and Figure 1, part d, shows the matrix IR spectrum of 40%  $^{18}\text{O}$  enriched  $\text{P}_4\text{O}_{10}$  in the

corresponding P=O and P-O-P spectral regions. It is evident that there is an almost exact parallel regarding the number of prominent bands and their relative spacings. The difference in relative intensities is due to the different extents of  $^{18}\text{O}$  enrichment.

A detailed interpretation of all these isotope patterns will be presented elsewhere,<sup>8</sup> but it has already been shown that pattern B in particular is distinctive<sup>9</sup> of the highest  $T_2$  vibration in  $\text{M}_4\text{O}_6$  cage units. We believe that the similarity in isotope patterns strongly supports our identification of matrix-isolated  $\text{V}_4\text{O}_{10}$  ( $T_d$  symmetry), and these results therefore confirm the basic conclusions of the mass spectrometric studies.

Registry No.  $\text{V}_4\text{O}_{10}$ , 12503-98-9.

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## A Tetracyanoethylene Complex of (*meso*-Tetraphenylporphinato)manganese(II)

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Recently we have been investigating the chemical and spectroscopic properties<sup>1,2</sup> of porphyrinatomanganese-dioxygen complexes formed from the reaction of molecular oxygen with high-spin  $d^5$  porphyrinatomanganese(II) complexes in toluene at  $-78^\circ\text{C}$ . The resulting dioxygen complexes have the form  $\text{Mn}(\text{por})(\text{O}_2)$  (por = porphyrin), and on the basis of EPR evidence<sup>2</sup> have been described in terms of a  $\text{Mn}^{\text{IV}}(\text{O}_2^{2-})$  formalism. Although the structures of these manganese-dioxygen complexes have not yet been determined, on the basis of analogy with other metal-dioxygen systems containing a coordinated peroxide ( $\text{O}_2^{2-}$ ) moiety as well as on the basis of recent chemical evidence,<sup>1</sup> it has been postulated that the dioxygen is bound to the manganese in a  $\pi$ -bonded symmetrical, Griffith-type conformation.

During our investigation of the reactivity of porphyrinatomanganese(II) complexes we have observed that in nonpolar aromatic hydrocarbon solvents, complexes of the type  $\text{Mn}^{\text{II}}(\text{TPP})(\text{L})^3$  react with TCNE to form an adduct which is reversible upon the addition of a strongly coordinating neutral ligand such as pyridine. Since TCNE has been shown to be capable of reacting with low-valent organometallic complexes to form adducts in which the TCNE is bound to the metal center in a  $\pi$ -bonded olefin structure,<sup>4</sup> similar to the structure proposed for the bonding of  $\text{O}_2$  in the manganese-dioxygen complexes, we have characterized the complex formed between (tetraphenylporphinato)manganese(II) complexes and TCNE.

## Experimental Section

Tetracyanoethylene was obtained from Aldrich Chemical Co. and was used without further purification. Toluene was reagent grade and was distilled from sodium-benzophenone ketyl immediately prior to use. All procedures were carried out under a  $\text{N}_2$  atmosphere using

standard Schlenk-type glassware and techniques.

The resonance Raman spectra were obtained by excitation with a Coherent Radiation Model CR-3  $\text{Ar}^+$  laser. The spectra were collected with a 0.75-m Spex Model 1400-II double monochromator equipped with a cooled RCA C31034A photomultiplier tube with standard low-level threshold photocounting electronics. The samples were spun rapidly in evacuated 5 mm o.d. Pyrex tubes to avoid laser-induced thermal decomposition.

*meso*-Tetraphenylporphine was synthesized by the method of Adler et al.<sup>5</sup> The complex  $\text{Mn}^{\text{II}}(\text{TPP})(\text{py})$  was prepared by the literature method.<sup>1</sup> In a typical preparation of  $\text{Mn}(\text{TPP})(\text{TCNE})$  a toluene solution of TCNE (150 mg in 20 mL of toluene) was added via a gastight syringe to a toluene solution of  $\text{Mn}^{\text{II}}(\text{TPP})(\text{py})$  (300 mg in 30 mL of toluene). The solution was stirred briefly at room temperature and was allowed to stand for 0.5 h. The purple crystalline product was collected by filtration and washed twice with 10-mL portions of toluene. The solid was dried overnight in vacuo to yield 270 mg (84%) of product. Anal.<sup>6</sup> Calcd for  $\text{C}_{50}\text{H}_{28}\text{N}_8\text{Mn}$ : C, 75.47; H, 3.55; N, 14.08; Mn, 6.90. Found: C, 75.82; H, 3.90; N, 13.55; Mn, 6.58.

## Results

Mixing toluene solutions of  $\text{Mn}^{\text{II}}(\text{TPP})(\text{py})$  and TCNE in an inert atmosphere at room temperature results in the precipitation of a solid complex having the empirical formula  $\text{Mn}(\text{TPP})(\text{TCNE})$ . The solid, which is moderately air stable, is insoluble in aromatic hydrocarbons but dissolves readily in deoxygenated weakly coordinating polar solvents, such as methanol, to give solutions having optical spectra characteristic of (tetraphenylporphinato)manganese(III) complexes. The optical spectrum of  $\text{Mn}(\text{TPP})(\text{TCNE})$  exhibits absorption maxima between 650 and 350 nm identical with those obtained from a methanol solution of  $\text{Mn}^{\text{III}}(\text{TPP})(\text{Cl})$ . Dissolving solid  $\text{Mn}(\text{TPP})(\text{TCNE})$  in deoxygenated pyridine results in an optical spectrum showing a mixture of both manganese(II) and manganese(III) tetraphenylporphinato species.<sup>8</sup>

When spectroscopic amounts of  $\text{Mn}^{\text{II}}(\text{TPP})(\text{py})$  are dissolved in toluene (concentration  $\sim 10^{-5}$  M) a characteristic (tetraphenylporphinato)manganese(II) type spectrum is observed.<sup>9</sup> Adding a toluene solution of TCNE to the metalloporphyrin solution results in the disappearance of the  $\text{Mn}(\text{TPP})(\text{py})$  spectrum. The addition of pyridine to the  $\text{Mn}(\text{TPP})(\text{TCNE})$  solution results in the regeneration of the  $\text{Mn}^{\text{II}}(\text{TPP})(\text{py})$  spectrum in about 85% yield with the rest of the material being present as a manganese(III) porphyrin species.<sup>10</sup>

The optical spectrum of solid  $\text{Mn}(\text{TPP})(\text{TCNE})$  in Nujol was obtained, Figure 1. This spectrum is not characteristic of either a manganese(II) or manganese(III) tetraphenylporphinato complex. This spectrum is identical with that obtained when an excess of a toluene solution of TCNE is added to a toluene solution containing spectral amounts of  $\text{Mn}^{\text{II}}(\text{TPP})(\text{TCNE})$  with the exception that a broad band is observed at 405 nm which is attributable to the presence of a TCNE-toluene charge-transfer band arising from the presence of excess TCNE.

The X-band EPR spectrum of a frozen toluene solution of  $\text{Mn}^{\text{II}}(\text{TPP})(\text{py})$  shows a spectrum characteristic of high-spin  $d^5$  systems having a large zero-field splitting.<sup>11</sup> The addition of TCNE as either a solid or in toluene solution to an EPR tube containing a toluene solution of  $\text{Mn}^{\text{II}}(\text{TPP})(\text{py})$  and rapidly cooling the mixture to 78 K result in the disappearance of the  $\text{Mn}^{\text{II}}(\text{TPP})(\text{py})$  spectrum and the replacement by a featureless spectrum between 0 and 7000 G. When tetrafluoroethylene was added to an EPR tube containing a toluene solution of  $\text{Mn}^{\text{II}}(\text{TPP})(\text{py})$ , no adduct formation was observed, as indicated by no change in the EPR spectrum.<sup>12</sup>

Both resonance Raman (Figure 2) and infrared spectra were taken of the solid  $\text{Mn}(\text{TPP})(\text{TCNE})$  complex and indicate extensive transfer of electron density from the manganese center to the coordinated TCNE moiety (see Discussion).