

of the SiO_4 unit are linked to Si and the fourth is linked to Al. The shifts observed for the inverted SiO_4 tetrahedra are in the range normally observed for $\text{Q}^*(1\text{Al})$ sites in zeolites (-96 to -107 ppm).⁹ Deconvolution of the ^{29}Si MAS NMR spectrum for I indicates that 40% of the SiO_4 tetrahedra in the layers have reacted. Presumably, the Al centers to which the layers couple retain the octahedral environment of a Keggin-like structure, because there is little change in the ^{27}Al MAS NMR spectrum upon layer cross-linking.

The reaction of SiO_4 units in alumina pillared fluorhectorite but not alumina pillared montmorillonite or Laponite apparently is related to the presence of F in the former clay which stabilizes Si-O bonds and promotes coupling. In montmorillonite and Laponite the layers are unreactive and pillaring presumably involves van der Waals interactions or, more likely, simple dative bond formation between the layer oxygens and coordinatively unsaturated sites on the alumina aggregates.

Cross-linking mechanisms that involve structural rearrangements of the host layers should be of fundamental importance in understanding the thermal stability and catalytic properties of the pillared clay. Future studies will relate changes in structural properties with differences in stability and catalytic activity.

Acknowledgment. The partial support of this research by the National Science Foundation through Grant CHE-8306583 is gratefully acknowledged. We thank Bruker Instruments for use of the AM-400 spectrometer and, especially, Dr. Mark Mattingly for assistance in obtaining spectra. Also, we thank Dr. Eric Oldfield for a preprint of ref 8.

Highly Conductive Metallomacrocyclic Assemblies. Synthesis via Electrocrystallization and Single-Crystal Properties of a Phthalocyanine "Molecular Metal" without Halogen Counterions

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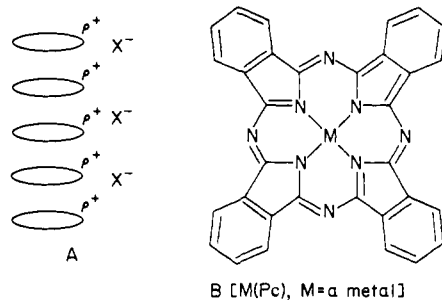
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The structural, electrical, magnetic, and optical properties of many low-dimensional molecular conductors¹ are a sensitive function of the interactions taking place between the band-forming molecular arrays and charge-compensating, off-axis counterions (e.g., A). To varying, largely unquantified degrees, such in-



teractions likely influence crystal structure,^{1,2} band-filling (ρ^+),¹⁻³ Coulombic screening,^{1,3,4} and charge and spin density wave phenomena,^{1,5} as well as the onset of superconductivity.^{1,5} Despite recent advances that have been achieved in modifying the M and Pc components of phthalocyanine (B) molecular conductors,^{2a,6} materials having counterions other than halogens (usually I_3^-)^{2a} are conspicuous in their paucity.⁷ We communicate here the single-crystal synthesis via high-temperature electrocrystallization⁸ and some of the interesting properties of the first non-halogenated phthalocyanine "molecular metal", $\text{Ni}(\text{Pc})(\text{BF}_4)_{0.33}$ (**1**).⁹

Because of severe solubility limitations, fragile, needlelike, golden crystals of **1** were necessarily grown at high temperatures (>100 °C), galvanostatically (0.5 μA , Pt wire anode) from solutions of rigorously purified $\text{Ni}(\text{Pc})$, $\text{Bu}_4\text{N}^+\text{BF}_4^-$, and 1-chloronaphthalene under anaerobic/anhydrous conditions. Larger quantities in powder form (identical spectroscopically, analytically, and diffractometrically) can be prepared from $\text{Ni}(\text{Pc})$ and NO^+BF_4^- in CH_2Cl_2 .⁹ Preliminary work^{10a} indicates that this electrochemical approach is generalizable to a wide range of counterions (e.g., PF_6^- , ClO_4^- , etc.) and phthalocyanines. Although BF_4^- and I_3^- differ substantially in spatial requirements, single-

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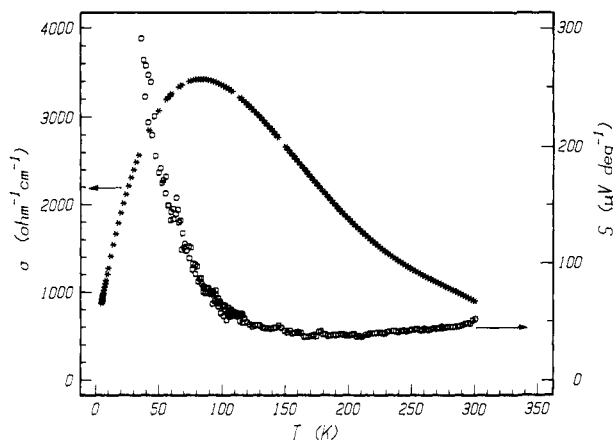


Figure 1. Variable-temperature charge-transport data for typical Ni(Pc)(BF₄)_{0.33} crystals measured in the macrocycle stacking direction. * Four-probe dc electrical conductivity; □ thermopower.

crystal diffraction data (300 K) indicate that Ni(Pc)(BF₄)_{0.33} is structurally (*P4/mcc*, *a* = 13.97 (2) Å, *c* = 6.48 (1) Å)^{10b} rather similar to H₂(Pc)I (2, *P4/mcc*, *a* = 13.979 (6) Å, *c* = 6.502 (3) Å)^{6b} and Ni(Pc)I (3, *P4/mcc*, *a* = 13.936(6), *c* = 6.488(3) Å).^{6g} This implies a crystal structure consisting of Ni(Pc)⁺ ions stacked in columns at 3.240 (5) Å separations and surrounded by BF₄⁻ counterions. Room temperature powder EPR measurements confirm the ligand-centered character of the oxidation (*g* = 2.000) and the unidimensional nature of the electronic structure (line width = 1.1 G).

Despite the structural similarities, the electrical properties of **1** differ significantly from those of H₂(Pc)I^{6b,c} and Ni(Pc)I.^{6e,f} Over 100 crystals were measured by four-probe dc techniques^{6b,11a} using automated instrumentation described elsewhere.^{6f} Appropriate precautions were taken to avoid thermal shock.^{6b} Thermoelectric power measurements were performed by using a conventional type of apparatus.^{11b} As can be seen in Figure 1, typical Ni(Pc)(BF₄)_{0.33} crystals exhibit room temperature conductivity in the macrocycle stacking direction of ca. 1000 Ω⁻¹ cm⁻¹—comparable to or higher than that of any known phthalocyanine conductor. Interestingly, and unlike **2** and **3**, the “metallike” (*dσ/dT* < 0) temperature dependence of **1** is not sharply peaked but rather goes through a broad metal-to-semiconductor transition at relatively high temperature (*T*_{max} ~ 80 K). While *σ*_{max} is comparable to that of very pure H₂(Pc)I crystals (3000–4000 Ω⁻¹ cm⁻¹),^{6b} the conductivity maximum in the latter occurs at ca. 15 K, with a transition to a semiconductor below.^{6b-d} Even at 1.5 K, the conductivity of Ni(Pc)(BF₄)_{0.33} remains in the 300–600 Ω⁻¹ cm⁻¹ range.

At *T* ≥ 150 K, the thermopower of Ni(Pc)(BF₄)_{0.33} crystals (Figure 1) evidences “metallike” (*σ* approximately linear with *T* but less so than for **2** and **3**) hole conduction (*S* > 0), implying transport primarily if not exclusively through the Ni(Pc)^{+0.33} stacks. The magnitude of *S* (300 K) and the extrapolated nonzero intercept at *T* = 0 are typical of many radical cation conductors.^{1,2a,5e,6c,12} Assuming a simple tight-binding band model, thermopower can be related to the bandwidth (*4t* = 4 times the Hückel β integral for ring–ring interaction¹³) via eq 1,¹² where

$$S = \frac{2\pi^2 k_B^2 T \cos(\pi\rho/2)}{3e(4t) \sin^2(\pi\rho/2)} \quad (1)$$

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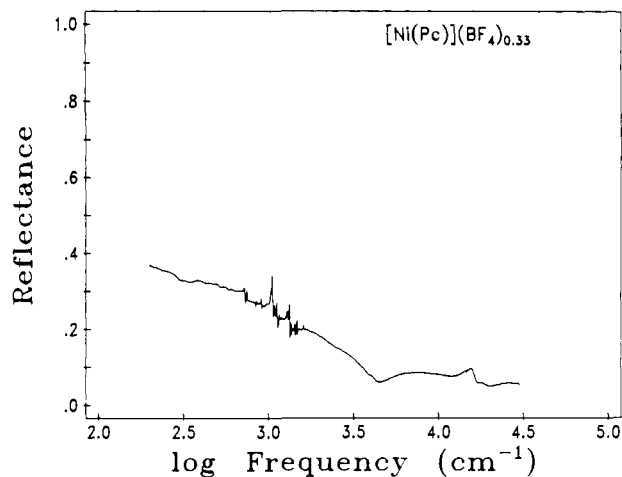


Figure 2. Optical reflectance spectrum of a polycrystalline Ni(Pc)(BF₄)_{0.33} sample.

ρ is the degree of partial oxidation.¹² Linear regression analysis of the *S*, *T* data in the high temperature, quasi-linear region (>200 K) yields *4t* = 1.3 (1) eV. Below ca. 100 K, the thermopower data reveal that Ni(Pc)(BF₄)_{0.33} undergoes a gradual transition to a semiconductor (cf., TTT₂I₃^{12b,c}).

The specular reflectance of Ni(Pc)(BF₄)_{0.33} samples exhibits a typical “molecular metal”^{11,5e} plasma edge in the infrared (Figure 2). Analysis of the line shape^{6b,f} using a Drude model for the dielectric function¹⁴ and procedures described elsewhere^{6b,f,15} yields the following parameters for the plasma frequency, the electronic relaxation time, and the high frequency dielectric constant: *ω*_p = 6020 (30) cm⁻¹, *τ* = 2.49 (5) × 10⁻¹⁵ s, *ε*_{core} = 2.46 (3). These values are similar to those for **2**^{6b} and **3**.^{6f} Furthermore, *ω*_p can be related to the tight-binding bandwidth via eq 2, where *c* is the

$$4t = \frac{\rho(\hbar\omega_p)^2}{4N_c e^2 c^2 \sin(\pi\rho/2)} \quad (2)$$

interplanar spacing and *N*_c is the carrier density per unit volume.^{6f} The optically derived bandwidth of Ni(Pc)(BF₄)_{0.33} is found to be 1.2 (1) eV, in excellent agreement with the thermopower result as well as with *4t*_{optical} = 1.3 (1) eV for **2**^{6b} and 1.0 (1) eV for **3**.^{6f} The weak paramagnetic susceptibility of **1**, measured with a SQUID susceptometer, is also reminiscent of the triiodides: *χ*_s = 1.30 (4) × 10⁻⁴ emu mol⁻¹ and, with the exception of slight “Curie tailing” (attributable to defects, impurities, disorder^{6b,e,17}) at low temperatures, is virtually temperature-independent. In comparison, *χ*_s(**2**) = 2.21 (5) × 10⁻⁴ emu mol⁻¹^{6b} and *χ*_s(**3**) = 1.90 (10) × 10⁻⁴ emu mol⁻¹,^{6f} with similar temperature dependencies. For **1**, we calculate a tight-binding “magnetic” bandwidth^{6b,f} of 0.64 (3) eV, the credibility of which likely reflects electron–electron (*U*)^{16,18} and/or electron–phonon¹⁹ interactions.

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These results indicate that phthalocyanine "molecular metal" chemistry is considerably broader than that involving only halogen counterions. In the case of highly conductive $\text{Ni}(\text{Pc})(\text{BF}_4)_{0.33}$, similarities to halogenated analogues in crystal and band structure are accompanied by significant differences in transport/metal-to-semiconductor transition characteristics. Further phthalocyanine counterion effects are under investigation.

Acknowledgment. This research was supported by the NSF through the Northwestern Materials Research Center (Grant DMR82-16972, T.J.M. and C.R.K.) and by the Office of Naval Research (T.J.M.). We thank Prof. S. H. Carr for helpful comments.

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Organometallic Clusters Containing Oxygen Atoms: Preparation, Structure, and Properties of $(\eta\text{-C}_5\text{H}_5)_{11}\text{V}_{13}\text{O}_{18}(\text{N}(\text{CH}_3)_3)_2$ and $(\eta\text{-C}_5\text{H}_5)_{14}\text{V}_{16}\text{O}_{24}$, Dimeric Derivatives of $(\eta\text{-C}_5\text{H}_5)_6\text{V}_6\text{O}_8$

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We described previously $\text{Cp}_5\text{V}_5\text{O}_6$ and $\text{Cp}_4\text{Cr}_4\text{O}_4$ ¹ ($\text{Cp} = \eta^5\text{-C}_5\text{H}_5$) which with $\text{Cp}_6\text{Ti}_6\text{O}_8$ described by Caulton et al.² form a series of $(\text{CpM})_m(\mu_3\text{-O})_n$ clusters. In a theoretical study we suggested that in each cluster there were 12 orbitals occupied by 2 ($\text{Cp}_6\text{Ti}_6\text{O}_8$), 8 ($\text{Cp}_5\text{V}_6\text{O}_6$), or 12 ($\text{Cp}_4\text{Cr}_4\text{O}_4$) electrons, and a variety of more or less distorted octahedral $(\text{CpM})_6\text{O}_8$, trigonal bipyramidal $(\text{CpM})_5\text{O}_6$, and tetrahedral $(\text{CpM})_4\text{O}_4$ clusters should be obtainable.³ We report here the preparation of $\text{Cp}_6\text{V}_6\text{O}_8$ and two remarkable derivatives of it, $[(\text{Cp}_5\text{V}_6(\mu_3\text{-O})_8)_2(\mu\text{-O})_2\text{Cp}(\text{N}(\text{CH}_3)_3)_2]$ (I) and $[(\text{Cp}_5\text{V}_6(\mu_3\text{-O})_8)_2(\text{CpV})_4(\mu_2\text{-O})_8]$ (II).

When Cp_2V was oxidized by $(\text{CH}_3)_3\text{NO}$ in toluene a black solid and a black-brown solution were obtained. The solid was not crystalline but mass spectrometry (all m/e peaks corresponding to $\text{Cp}_m\text{V}_6\text{O}_8^+$ with $m = 6 \rightarrow 0$), microanalysis (found, C, 42.5; H, 3.9%; calcd for $\text{C}_{30}\text{H}_{30}\text{V}_6\text{O}_8$, C, 43.7; H, 3.7%) and ¹H NMR (singlet at -171.4 ppm) established it as paramagnetic $\text{Cp}_6\text{V}_6\text{O}_8$.

The solution deposited large crystals on storage at 5 °C. These were shown to be I by X-ray crystallography (Figure 1).⁴ The cluster is derived from $\text{Cp}_6\text{V}_6\text{O}_8$ by removal of one Cp and linking of two $\text{Cp}_5\text{V}_6\text{O}_8$ fragments via the oxygen of $(\text{CpV}(\text{N}(\text{CH}_3)_3)_2(\mu\text{-O})_2)$. The $\text{Cp}_5\text{V}_6\text{O}_8$ units contain regular octahedra of vanadium with an average V-V distance of 2.906 (4, 29) Å.⁵ The oxygen atoms lie over the triangular faces with an average V-O distance of 1.940 (10, 55) Å. The V-V distances are similar to the Ti-Ti in $\text{Cp}_6\text{Ti}_6\text{O}_8$, 2.891 Å (1, 14).² The V-O distance to the linking oxygen is 1.679 (15) Å.

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(5) The first figure is the average standard deviation, the second the maximum deviation from the average.

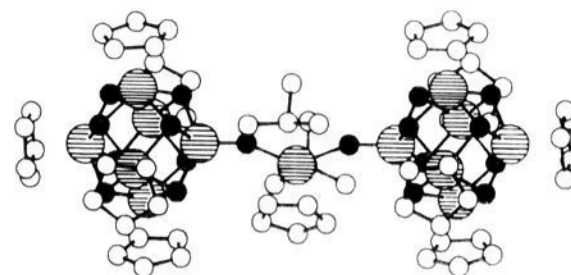


Figure 1. Structure of $(\eta\text{-C}_5\text{H}_5)_{11}\text{V}_{13}\text{O}_{18}(\text{N}(\text{CH}_3)_3)_2$.

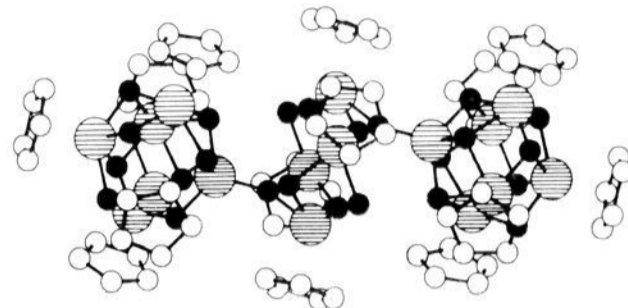


Figure 2. Structure of $(\eta\text{-C}_5\text{H}_5)_{14}\text{V}_{16}\text{O}_{24}$.

The ESR of I showed an asymmetrical eight-line spectrum typical of vanadium in a low-symmetry environment. The ¹H NMR showed a broad, weak, symmetrical resonance at -79.4, a multiplet at -7.15, and a singlet at -2.29 ppm. The latter resonances had an intensity ratio of 2.6:1. We assign the resonance at -79.4 ppm to an $\eta^5\text{-C}_5\text{H}_5$ group attached to paramagnetic vanadium, the resonance at -7.15 ppm to $\eta^5\text{-C}_5\text{H}_5$ attached to diamagnetic vanadium, and that at -2.29 ppm to the $\text{N}(\text{CH}_3)_3$. This interpretation means that the $\text{Cp}_5\text{V}_6\text{O}_8$ units are diamagnetic and the vanadium(III) in the bridge has two unpaired electrons.

The diamagnetism and regularity of the $\text{Cp}_5\text{V}_6\text{O}_8$ may be rationalized by arguments developed for $\text{Cp}_6\text{M}_6\text{O}_8$.³ The $\text{Cp}_5(\mu\text{-O})\text{V}_6\text{O}_8$ units are derivatives of $\text{Cp}_6\text{V}_6\text{O}_8$ in which an OR group replaces one Cp. This leaves the number of cluster electrons at eight but increases the cluster orbitals by two. If the unique vanadium lies on z the four orbitals it contributes to the cluster are the same two as in $\text{Cp}_6\text{V}_6\text{O}_8$, $d_{x^2-y^2}$ and d_{z^2} , plus d_{xz} and d_{yz} . Of these, $d_{x^2-y^2}$ is nonbonding and the other three are antibonding counterparts of V-O bonds. In addition d_{xz} is the antibonding counterpart of the π -bond between the bridging oxygen and vanadium. Therefore $d_{x^2-y^2}$ remains localized on the unique vanadium and is occupied by two electrons; d_{z^2} and d_{yz} contribute to the cluster and d_{xz} is of high energy. Only six electrons occupy the 12 cluster orbitals. The configuration is $a_{1g}^2e_g^4$; therefore $\text{Cp}_5\text{V}_6\text{O}_8$ is diamagnetic and undistorted.

When Cp_2V was oxidized by $(\text{CH}_3)_3\text{NO}$ in tetrahydrofuran a black, diamagnetic, crystalline solid of formula $\text{Cp}_{14}\text{V}_{16}\text{O}_{24}$ was obtained. It too is derived from $\text{Cp}_6\text{V}_6\text{O}_8$: two $\text{Cp}_5\text{V}_6\text{O}_8$ are linked by $(\text{CpV})_4(\mu_2\text{-O})_8$ (Figure 2).⁶ The latter is a rectangle of vanadium with pairs of oxygen along the edges; the connections to $\text{Cp}_5\text{V}_6\text{O}_8$ are diagonally opposed oxygens (V-O 1.701 (13) Å). The V-V distances in the $\text{Cp}_5\text{V}_6\text{O}_8$ units average 2.900 (5, 21) and the V-O distances 1.942 (14, 67) Å, very similar to I. In the $(\text{CpV})_4(\mu_2\text{-O})_8$ bridge the V-V distances are 2.989 (6) and 3.296 (6) Å and the V-O distance to the doubly bridging oxygens 2.020 (14, 29) Å but to the two triply bridging ones 2.179 (14, 26).

These clusters are extreme cases of those obtained by binding organometallic fragments to polyoxometalate ions;⁷⁻⁹ $\{[(\text{C}_7\text{H}_8)\text{-Rh}]_5(\text{cis-Nb}_2\text{W}_4\text{O}_{19})_2\}^{3-7}$ is a spectacular example. Both I and II are true molecular clusters, being highly soluble in toluene.

(6) Crystallographic data: $\text{C}_{77}\text{H}_{78}\text{O}_{24}\text{V}_{16}$ ($(\eta\text{-C}_5\text{H}_5)_{14}\text{V}_{16}\text{O}_{24} \cdot 4\text{C}_6\text{H}_5\text{CH}_3$), $M_r = 2202.5$, $P\bar{1}$, $a = 11.582$ (2) Å, $b = 13.099$ (2) Å, $c = 13.969$ (4) Å, $\alpha = 94.10$ (2)°, $\beta = 90.03$ (2)°, $\gamma = 104.72$ (2)°, $Z = 1$; $D_c = 1.78$ g cm⁻³; $R = 0.070$, $R_w = 0.076$ for 1657 observed ($I > 3\sigma(I)$) reflections with $2\theta < 45^\circ$. Anisotropic V and O; C_5H_5 groups as rigid bodies (287 variables).

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