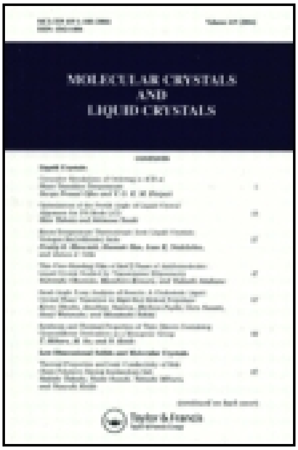

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Electrically Conductive Polymers Composed of Cofacially Joined Metallomacrocycles. Studies of Architecture and Electronic Structure in Phthalocyanine Materials by High Resolution Solid State NMR

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ELECTRICALLY CONDUCTIVE POLYMERS COMPOSED OF COFACIALLY JOINED METALLOMACROCYCLES. STUDIES OF ARCHITECTURE AND ELECTRONIC STRUCTURE IN PHTHALOCYANINE MATERIALS BY HIGH RESOLUTION SOLID STATE NMR

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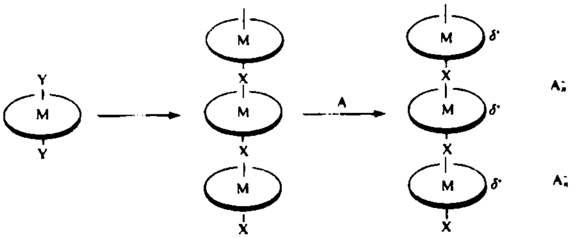
Abstract This contribution describes the use of high resolution ^{13}C NMR spectroscopy with cross polarization, ^{1}H dipolar decoupling, and magic angle spinning to study solid state architecture and electronic structure in molecular and macromolecular phthalocyanine conductors. Isotopic labelling, dipolar dephasing, and variable field techniques are employed to make spectral assignments. The important contribution of conduction electron Knight shifts to the observed resonance positions is emphasized.

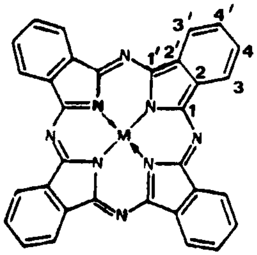
INTRODUCTION

A successful approach to controlling stacking interactions in low-dimensional conductors and, simultaneously, to generate robust new classes of electrically conductive polymers, is the cofacial assembly strategy[1-3] (Eq. (1)). Here, metallomacrocyclic subunits



(1)

such as phthalocyanines (A)[1-5] are assembled into structurally



= M(Pc)

A

constrained molecular arrays and then "doped" with electron acceptors (shown) or donors. Such systems have not only provided a wealth of new information on the molecular "metallic" state,[1-5,6,7] but represent a testing ground for new synthetic and physicochemical techniques. In the latter vein, we communicate here that high resolution solid state NMR techniques[8,9] represent a powerful microstructural and electronic probe of metallomacrocyclic solids.

EXPERIMENTAL

The compounds $\{[M(Pc)O]I_{1.1}\}_n$, M=Si, Ge, Ni(Pc)I, and $H_2(Pc)I$ were prepared by the literature procedures.[1,2,5] Ni(Pc) ^{13}C-enriched to 5% at C1,C1' was prepared using o-$C_6H_4(^{13}CN)_2$. In the case of the molecular materials, the starting phthalocyanines were fractionally sublimed twice under high vacuum (10^{-5} torr). Purity was assessed by elemental analysis and X-ray powder diffraction. ^{13}C CPMAS NMR spectra were measured at 15.0 MHz on a JEOL FX-60QS spectrometer using optimized[10] (spectra in reference 2 were not optimized) cross polarization, high power ^1H decoupling, and magic angle spinning techniques. Several high field measurements (37.735 MHz) were made at the Colorado State Regional NMR Center. Except for greater chemical shift dispersion, spectral features were essentially the same as at 15.0 MHz.

RESULTS AND DISCUSSION

The crystal structures of the $\{[M(Pc)O]I_{1.1}\}_n$, $H_2(Pc)I$, and Ni(Pc)I materials are rather similar (tetragonal--P4/mcc), differing principally in the Pc-Pc interplanar spacings.[2,5] One consequence of this packing motif is that the M(Pc) moieties have only C_{4h} site symmetry, i.e., the nearest neighbor ring-ring staggering angles are ca. 39° and the isoindoline subunits lack mirror symmetry perpendicular to the Pc plane (position $1 \neq 1'$, $2 \neq 2'$, $3 \neq 3'$, $4 \neq 4'$). Moreover, these nonequivalences are not averaged by simple C_4 rotations of any single Pc unit. In the discussion which follows, we make use of this information as well as isotopic labelling, dipolar dephasing (to identify C-H groups), variable field strengths, and the spectra of the undoped analogues, to make spectroscopic assignments.

CPMAS ^{13}C spectra (15.0 MHz) of $[M(Pc)O]_n/\{[M(Pc)O]I_{1.1}\}_n$ pairs are shown in Figure 1, Ni(Pc) in Figure 2A, and Ni(Pc)I in Figure 3A. Spectra of $H_2(Pc)$ and $H_2(Pc)I$ are closely analogous. Data are compiled in Table I. While the spectra of the undoped metallomacrocycles are typical of polycyclic aromatics; the doped phthalocyanines invariably feature a broad resonance (frequently resolved into a doublet) at significantly higher fields, and an additional broad resonance displaced to very low fields. Enriching Ni(Pc) to 5% in ^{13}C at the 1(1′) skeletal position (Figures 2B,3B) reveals that the low field resonance is due to C1,C1′. The breadth may reflect, among other factors, the crystallographic nonequivalence of C1,C1′. Dipolar dephasing experiments (Figure 3C) show that the three Ni(Pc)I resonances in the 119-150 ppm range are associated with C-H groups (C3,C3′,C4, C4′). The relative intensities and spatial proximity to the Pc core suggests that the 119 and 134 ppm resonances are assignable to crystallographically nonequivalent C3 and C3′ sites. The remaining high field quaternary carbon doublet can then be assigned to C2 and C2′.

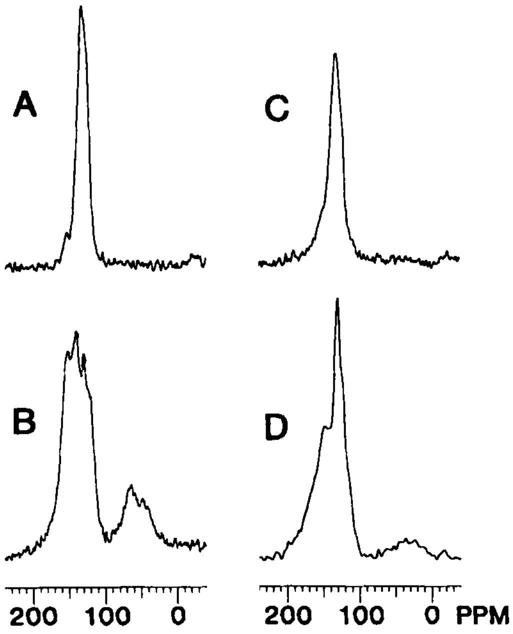


FIGURE 1 ^{13}C CPMAS spectra (15.0 MHz) of:
(A) $[Si(Pc)O]_n$,
(B) $\{[Si(Pc)O]I_{1.1}\}_n$
(C) $[Ge(Pc)O]_n$
(D) $\{[Ge(Pc)O]I_{1.1}\}_n$

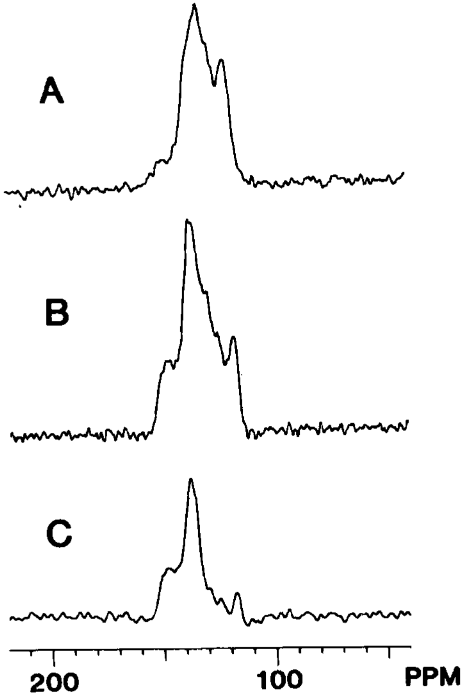


FIGURE 2 ^{13}C CPMAS spectra (15.0 MHz) of: (A) Ni(Pc), (B) Ni(Pc), 5% ^{13}C at C1,C1′, (C) Difference spectrum (B)-(A).

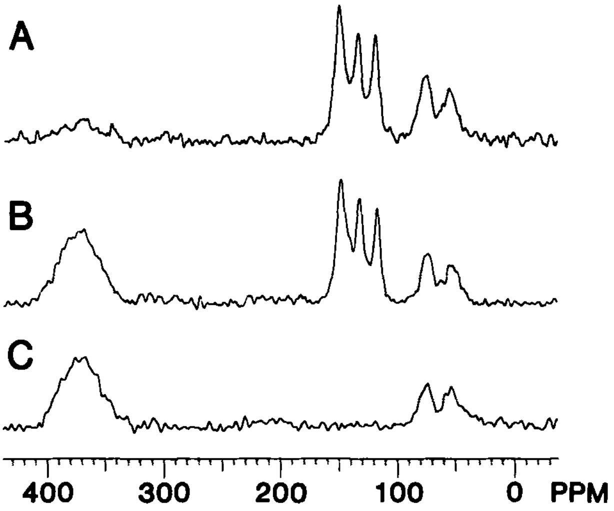


FIGURE 3 ^{13}C CPMAS spectra (15.0 MHz) of: (A) Ni(Pc)I, (B) Ni(Pc)I, 5% ^{13}C at C1,C1′ (C) Sample of (B) with 40 μs delay (during which the decoupler is turned off) before data acquisition.

Of the phenomena which can explain the very large isotropic displacements of the Pc ^{13}C resonances upon doping, chemical shift effects reflecting the carbocationic character of the Pc$^{\delta+}$ π system appear inadequate to account for the large magnitudes (cf., polyacetylene[9]), the large shift variation with essentially constant degree of partial oxidation, and the displacements to high field. More plausible are Knight shifts,[11,12] which classically can be expressed as in Eq. (2), where a_c is the isotropic hyperfine

$$K = \frac{\Delta H}{H} = \frac{a_c\ \chi}{N g \beta g_N \beta_N} \qquad (2)$$

TABLE I Solid State ^{13}C NMR Data for Phthalocyanine Materials[a]

Compound	Chemical Shift (Assignment)
Ni(Pc)	120.6, 132.0, 148.4
Ni(Pc)[b]	138.0 + 148.4 (C1,C1′)
Ni(Pc)I	54.4 + 75.9 (C2,C2′), 118.8, 134.1, 150.0, 375(C1,C1′)
H_2(Pc)	121.1, 131.3 148.7
H_2(Pc)I	50.0 + 72.3(C2,C2′), 118.0, 135.4, 147.4, ~380(C1,C1′)
$[Si(Pc)O]_n$	126.1, 133.6, 154.1
$\{[Si(Pc)O]I_{1.1}\}_n$	43.2 + 64.2(C2,C2′), 120.1, 129.2, 139.3, 151.0, ~410(C1,C1′)
$[Ge(Pc)O]_n$	126.8, 134.9, 152.3
$\{[Ge(Pc)O]I_{1.1}\}_n$	~35(C2,C2′), 132.3, 148.6

[a] In ppm vs. TMS.

[b] ^{13}C-enriched sample.

coupling constant, χ is the Pauli susceptibility, and the other terms have their usual meaning. Importantly, this equation predicts a linear relationship between K and χ. As can be seen in Figure 4 for the Pc C2,C2′ resonances and our published magnetic data,[2,5] eq.(1) is approximately obeyed. Moreover, the observed distribution of both positive and negative spin densities is not surprising for a polycyclic π radical cation.[13,14]

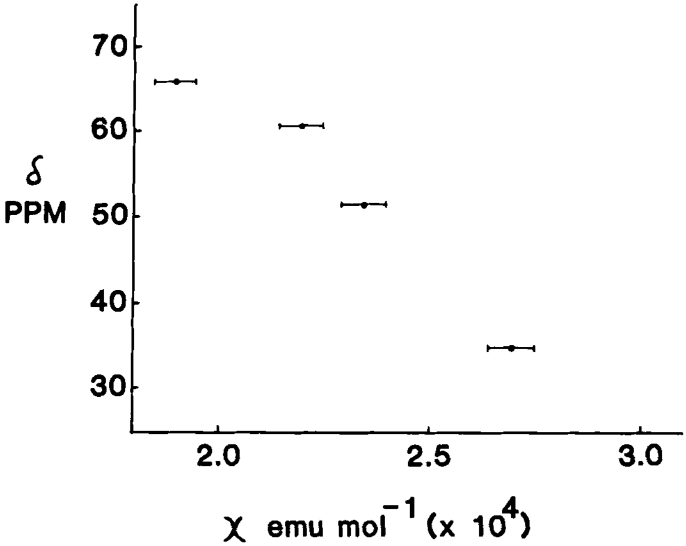


FIGURE 4 Plot of the average C2,C2′ chemical shift in various iodinated phthalocyanines versus the Pauli susceptibility reported in references 1 and 5.

ACKNOWLEDGMENTS

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