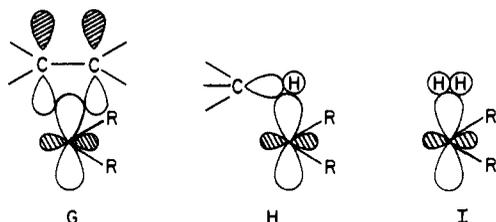


in d^0 Cp_2MX_2 systems should be qualitatively applicable to C-H and H-H activation, with C-H and H-H a_1 and b_2 σ and σ^* orbitals replacing ethylene a_1 and b_2 π and π^* orbitals. Initial coordination to the a_1 LUMO^{61,62} (G, H, and I) places the substrates in the appropriate spatial orientation for concerted M-C or M-H bond formation, M-R bond scission, and H-R bond formation.⁶³ More quantitative theoretical results on the hy-



(61) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729-1742.

(62) (a) Cauletti, C.; Clark, J. P.; Green, J. C.; Jackson, S. E.; Fragalà, I.; Ciliberto, E.; Coleman, A. W. *J. Electron Spectrosc. Rel. Phenom.* **1980**, *18*, 61-73. (b) Petersen, J. L.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6422-6433. (c) Petersen, J. L.; Lichtenberger, D. L.; Fenske, R. F.; Dahl, L. F. *J. Am. Chem. Soc.* **1975**, *97*, 6433-6441. (d) Condorelli, G.; Fragalà, I.; Centineo, A.; Tondello, E. *J. Organomet. Chem.* **1975**, *87*, 311-315. (e) Prout, K.; Cameron, T. S.; Forder, R. A.; Critchley, S. R.; Denton, B.; Rees, G. V. *Acta Crystallogr., Sect. B* **1974**, *30*, 2290-2304 and references therein.

drogenolysis process from Brintzinger (Zr)⁶⁴ and from Rabaã, Saillard, and Hoffmann (lanthanides)⁶⁵ support this view. Although the role of 4f and 5f orbitals in such processes cannot yet be quantitatively assessed, a highly electrophilic metal center which would bind and positively polarize the substrate for nucleophilic attack by a proximate, negatively polarized ligand would appear to offer a major advantage in facilitating eq 26, 27, and 32. Optimizing the rates and selectivities of such processes will be the goal of future investigations.

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Registry No. 1, 83692-52-8; 2, 94138-25-7; 3, 99477-03-9; 4, 99458-65-8; 7, 99477-04-0; 8, 99477-05-1; 9, 99477-06-2; 10, 99477-07-3; 11, 99494-81-2; 12, 99477-08-4; 13, 99477-09-5; TMS, 75-76-3; $Cp'_2Th(Cl)[CH_2C(CH_3)_3]$, 74587-39-6; Cp'_2ThCl_2 , 67506-88-1; CH_4 , 74-82-8; $Sn(CH_3)_4$, 594-27-4; $LiCH_2P(CH_3)_2$, 64065-06-1; $P(CH_3)_3$, 594-09-2; LiC_3H_5 , 3052-45-7; H_2 , 1333-74-0; C, 7440-44-0; cyclopropyllithium, 3002-94-6; cyclopropane, 75-19-4; ethane, 74-84-0; propylene, 115-07-1; ethylene, 74-85-1.

Supplementary Material Available: ¹NMR of spectra of $Cp'_2Th(CHCH_2CH_2)_2$ (3) (Figure S-1) and $Cp'_2Th[CH_2C(CH_3)_3][CH_2Sn(CH_3)_3]$ (7) (Figure S-2) (2 pages). Ordering information given on any current masthead page.

(63) An alternative picture could be drawn by using an unoccupied a_1 MO quantized between the two M-R bonds.

(64) Brintzinger, H. H. *J. Organomet. Chem.* **1979**, *171*, 337-344.

(65) Rabaã, H.; Saillard, J.-Y.; Hoffmann, R., submitted for publication.

Electrically Conductive Metallomacrocyclic Assemblies. High-Resolution Solid-State NMR Spectroscopy as a Probe of Local Architecture and Electronic Structure in Phthalocyanine Molecular and Macromolecular "Metals"

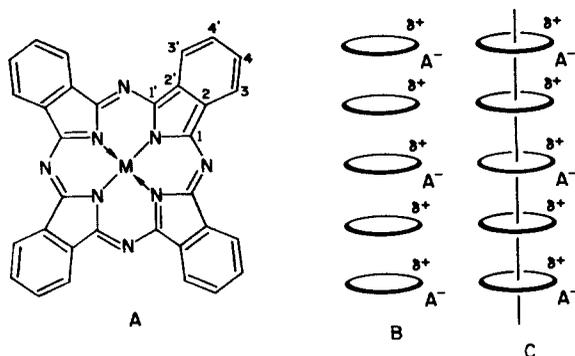
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Contribution from the Department of Chemistry and the Materials Research Center,
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Abstract: This contribution reports a high-resolution solid-state ¹³C CPMAS study of the low-dimensional phthalocyanine (Pc) conductors Ni(Pc)I, H₂(Pc)I, {[Si(Pc)O]I_{1.1}}_n, {[Si(Pc)O]X_y}_n (X = BF₄, PF₆, SbF₆, y ~ 0.35), {[Ge(Pc)]I_{1.1}}_n, and Ni(Pc)X_z (X = BF₄, PF₆, SbF₆, z ~ 0.33), as well as of the precursors Ni(Pc), H₂(Pc), [Si(Pc)O]_n, and [Ge(Pc)O]_n. For the partially oxidized materials, large, locally resolved ¹³C-conduction electron Knight shifts with dispersions as large as 400 ppm and multiplicities in accord with crystallographic site symmetries are observed. By using Ni(Pc)I selectively labeled with ¹³C at the 1,1' skeletal positions and with ²H at the 4,4' hydrogen atom positions, along with dipole dephasing techniques, it is possible to completely and unambiguously assign the CPMAS spectrum. From this information is obtained a map of the conduction electron hyperfine interaction about the carbon framework of the macrocycle. In Ni(Pc)I, the ratios of the 1,1' to the 2,2' ¹³C spin-lattice relaxation times conform approximately to the Korringa relationship at room temperature. For the partially oxidized phthalocyanine series as a whole, a linear relationship is observed between the individual 1,1' and 2,2' ¹³C Knight shifts and the corresponding Pauli-like magnetic susceptibilities.

As precursors for electrically conductive low-dimensional solids,¹ robust and chemically flexible phthalocyanines (A, M(Pc)) have

proven to be extremely versatile.² The simple molecular compounds can be converted, using halogens^{3,4} or a limited range of



other oxidants,⁵ into "molecular metals" having high structural, electrical, and optical anisotropy (B).²⁻⁶ A more refined approach to enforcing macrocycle stacking relationships in such materials has been to chemically link the phthalocyanine subunits together in regular cofacial arrays (C).^{2,3,7} Such a strategy has allowed for greater manipulation of interplanar spacing, band-filling, and band structure-counterion interactions than has been possible for the molecular analogues.^{5,7,8} Furthermore, studies of monomeric and dimeric polymer fragments by small molecule spectroscopic and theoretical methods have afforded important complementary information on cofacial π - π interactions.⁹

Taken together, the above investigations have provided a broad picture of the physical relationships connecting a wide range of microscopic and macroscopic observables. Nevertheless, at the atomic level, there is still a paucity of information on architecture and electronic structure. To this end and because conductive phthalocyanine assemblies can serve (by virtue of the growing

chemical/physicochemical data base) as a testing ground for new physical techniques, we have carried out a study of a series of these compounds by high-resolution solid-state ¹³C CPMAS NMR spectroscopy.^{10,11} Although this technique has considerable potential for studying low-dimensional conductors,¹² the research to date has largely involved qualitative structural investigations of a limited number of polymers (principally polyacetylene).¹³⁻¹⁵ In the present contribution, we report that CPMAS NMR is a straightforwardly applied and powerful structural/dynamic probe for metallomacrocyclic molecular and polymeric conductors. In addition, we report the observation of locally resolved ¹³C nuclear-conduction electron Knight shifts¹⁶ with dispersions as large as 400 ppm. By using site-selective ¹³C and ²H isotopic labeling as well as dipole dephasing experiments, it is possible to unambiguously map out the local fields about the carbon framework of the phthalocyanine skeleton. Furthermore, by examining a series of related compounds, it is possible to demonstrate a direct, linear relationship between the observed shifts and the "Pauli-like" static magnetic susceptibilities^{2,3,6,7} of these materials (as expected for a classical metal¹⁶) as well as to assess carbenium ion contributions to the observed chemical shifts. In addition, we report here new synthetic methods for labeling phthalocyanines with ¹³C at the 1,1' carbon positions^{2b} and with ²H at the 4,4' hydrogen positions.^{2b}

Experimental Section

Materials. Quinoline (Eastman) and *N,N*-dimethylformamide (DMF, Mallinckrodt) were dried by storage over activated Davison 4 Å molecular sieves. *tert*-Butyl alcohol-*d* (Aldrich, 98+%) was dried over sodium and distilled in vacuo. *o*-Dibromobenzene (Aldrich) and K¹³CN (Merck Isotopes, 90% enriched in ¹³C) were used as received. The phthalocyanines H₂(Pc),⁶ H₂(Pc)I,⁶ Ni(Pc)I,^{7a} [Si(Pc)O]_m,^{7b} {[Si(Pc)O]I_{1,1}]_m,^{7a} {[Si(Pc)O](BF₄)_{0.33}]_m,⁵ {[Si(Pc)O](PF₆)_{0.33}]_m,⁵ {[Si(Pc)O](SbF₆)_{0.36}]_m,⁵ [Ge(Pc)O]_m,^{7b} {[Ge(Pc)O]I_{1,1}]_m,^{7a} Ni(Pc)(PF₆)_{0.33},⁵ Ni(Pc)(BF₄)_{0.33},⁵ and Ni(Pc)(SbF₆)_{0.33}⁵ were prepared and purified by literature procedures.

Synthesis of ¹³C-Labeled Nickel Phthalocyanine Iodide, Ni*(Pc)I. In the following synthetic procedures leading to Ni*(Pc)I, which is enriched in ¹³C at the isoindoline (C1,1') carbon atoms, an asterisk (*) denotes compounds which are enriched to approximately 5 times the natural abundance level of ¹³C at the indicated position.

Cu*CN. The following preparation is a modification of literature procedures.^{17a,b} Solutions of CuSO₄·5H₂O (63.76 g, 0.255 mol) in water

(1) Pecile, C.; Zerbi, G.; Bozio, R.; Girlando, A., Ed. "Proceedings of the International Conference on the Physics and Chemistry of Low-Dimensional Synthetic Metals (ICSM 84)", Abano Terme, Italy, June 17-22, 1984. *Mol. Cryst. Liq. Cryst.* **1985**, *117-121*. (b) Miller, J. S., Ed. "Extended Linear Chain Compounds"; Plenum Press: New York, 1982; Vol. 1-3. (c) Epstein, A. J.; Conwell, E. M., Eds. "Proceedings of the International Conference on Low-Dimensional Conductors"; Boulder, Colorado, August 9-14, 1981. *Mol. Cryst. Liq. Cryst.* **1981-1982**, *77, 79, 81, 83, 85, 86*, Parts A-F. (d) Alcaicer, L., Ed. "The Physics and Chemistry of Low-Dimensional Solids"; D. Reidel: Dordrecht, 1980. (e) Devreese, J. T.; Evrard, R. P.; van Doren, V. E., Eds. "Highly Conducting One-Dimensional Solids"; Plenum Press: New York, 1979.

(2) (a) Marks, T. J. *Science* **1985**, *227*, 881-889. (b) For the sake of simplicity, we will employ the M(Pc) atom numbering scheme shown in A rather than the more rigorous but cumbersome *Chemical Abstracts* scheme.

(3) Marks, T. J.; Kalina, D. W., ref 1b, Vol. 1, pp 197-331.

(4) Martinsen, J.; Palmer, S. M.; Tanaka, J.; Greene, R. C.; Hoffman, B. M. *Phys. Rev. B* **1984**, *30*, 6269-6276 and references therein.

(5) (a) Inabe, T.; Lyding, J. W.; Moguel, M. K.; Kannewurf, C. R.; Marks, T. J. *Mol. Cryst. Liq. Cryst.* **1983**, *93*, 355-367. (b) Inabe, T.; Lyding, J. W.; Moguel, M. K.; Marks, T. J. *J. Phys., Colloq. (Paris)* **1983**, *C3*, 625-631. (c) Inabe, T.; Nakamura, S.; Liang, W.-B.; Marks, T. J.; Burton, R. L.; Kannewurf, C. R.; Imaeda, K.-I. *J. Am. Chem. Soc.* **1985**, *107*, 7224-7226. (d) Inabe, T.; Gaudiello, J. G.; Moguel, M. K.; McCarthy, W. J.; Lyding, J. W.; Kannewurf, C. R.; Marks, T. J., submitted for publication.

(6) (a) Inabe, T.; Marks, T. J.; Burton, R. L.; Lyding, J. W.; McCarthy, W. J.; Kannewurf, C. R.; Reisner, G. M.; Herbstein, F. H. *Solid State Commun.* **1985**, *54*, 501-503 and references therein. (b) Inabe, T.; Marks, T. J.; Lyding, J. W.; Imaeda, K.-I.; McCarty, W. J.; Kannewurf, C. R., submitted for publication.

(7) (a) Diel, B. N.; Inabe, T.; Lyding, J. W.; Schoch, K. F., Jr.; Kannewurf, C. R.; Marks, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 1551-1567. (b) Dirk, C. W.; Inabe, T.; Schoch, K. F., Jr.; Marks, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 1539-1550. (c) Dirk, C. W.; Inabe, T.; Lyding, J. W.; Schoch, K. F., Jr.; Kannewurf, C. R.; Marks, T. J. *J. Polym. Sci., Polym. Symp.* **1983**, *70*, 1-29. (d) Dirk, C. W.; Mintz, E. A.; Schoch, K. F., Jr.; Marks, T. J. *J. Macromol. Sci.-Chem.* **1981**, *A16*, 275-298. (e) Schoch, K. F., Jr.; Kundalkar, B. R.; Marks, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 7071-7073.

(8) (a) Marks, T. J.; Dirk, C. W.; Schoch, K. F., Jr.; Lyding, J. W. In "Molecular Electronic Devices"; Carter, F. L., Ed.; Marcel Dekker, Inc.: New York, 1982; pp 195-210. (b) Inabe, T.; Lyding, J. W.; Gaudiello, J. G.; McCarthy, W. J.; Moguel, M. K.; Kannewurf, C. R.; Marks, T. J., submitted for publication.

(9) (a) Pietro, W. J.; Marks, T. J.; Ratner, M. A. *J. Am. Chem. Soc.* **1985**, *107*, 5387-5391. (b) Pietro, W. M.; Ellis, D. E.; Marks, T. J.; Ratner, M. A. *Mol. Cryst. Liq. Cryst.* **1984**, *105*, 273-278. (c) Ciliberto, E.; Doris, K. A.; Pietro, W. J.; Reisner, G. M.; Ellis, D. E.; Fragalá, I.; Herbstein, F. H.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* **1984**, *106*, 7748-7761. (d) Ciliberto, E.; Doris, K. A.; Fragalá, I.; Marks, T. J., submitted for publication.

(10) (a) Fyfe, C. A. "Solid State NMR for Chemists"; CRC Press: Guelph, 1983. (b) Maciel, G. E. *Science* **1984**, *226*, 282-288. (c) Yannoni, C. S. *Acc. Chem. Res.* **1982**, *15*, 201-208. (d) Gerstein, B. C. *Anal. Chem.* **1983**, *55*, 781A-790A. (e) Gerstein, B. C. *Anal. Chem.* **1983**, *55*, 889A-907A.

(11) (a) Presented in part at the "International Conference on the Physics and Chemistry of Low-Dimensional Synthetic Metals (ICSM 84)", Abano Terme, Italy, June 17-22, 1984. (b) Preliminary communication: Toscano, P. J.; Marks, T. J., ref 1a, *118*, 337-344.

(12) (a) While this paper was in preparation, a preliminary communication appeared by Mehring and Spengler^{12b} describing the CPMAS spectrum of (fluoranthenylyl)₂SbF₆.^{12b} Locally resolved Knight shifts were also observed; however, it was not possible to unambiguously assign all of the resonances. (b) Mehring, M.; Spengler, J. *Phys. Rev. Lett.* **1984**, *53*, 2441-2444.

(13) For leading references on polyacetylene CPMAS studies, see: (a) Audenaert, P.; Bernier, P., ref 1a, *117*, 83-95. (a) Audenaert, P.; Bernier, P., ref 1a, *11m*, 83-95. (b) Sederholm, L.; Mathis, C.; Francois, B.; Friedt, J. M. *Synth. Met.* **1985**, *10*, 251-272. (c) Terao, T.; Maeda, S.; Yamabe, T.; Akagi, K.; Shirakawa, H. *Solid State Commun.* **1984**, *49*, 829-832. (d) Peo, M.; Förster, H.; Menke, K.; Hocker, J.; Gardner, J. A.; Roth, S.; Dransfeld, K. *Solid State Commun.* **1981**, *38*, 467-468 and references therein. (e) Clarke, T. C.; Scott, J. C. *Solid State Commun.* **1982**, *41*, 389-391. (f) Maricq, M. M.; Waugh, J. S.; MacDiarmid, A. G.; Sturakawa, H.; Heeger, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 7729-7731.

(14) Polypyrrole CPMAS Studies: Street, G. C.; Clarke, T. C.; Krounbi, M.; Kanazawa, K.; Lee, V.; Pfluger, P.; Scott, J. C.; Weiser, G. *Mol. Cryst. Liq. Cryst.* **1982**, *83*, 253-264.

(15) Polythietylene CPMAS studies: Hotta, S.; Hosaka, T.; Shimotsuma, W. J. *J. Chem. Phys.* **1984**, *80*, 954-956.

(16) (a) Carrington, A.; McLachlan, A. D. "Introduction to Magnetic Resonance"; Harper and Row: New York, 1967; pp 221-225. (b) Slichter, C. P. "Principles of Magnetic Resonance", 2nd ed.; Springer-Verlag: Berlin, 1978; pp 106-121. (c) Abragam, A. "The Principles of Nuclear Magnetism"; Oxford University Press: London, 1970; pp 199-206.

(17) (a) Barber, H. J. *J. Chem. Soc.* **1943**, 79. (b) Meinert, M. C.; Nunez, H. A.; Byerum, R. U. *J. Labelled Compd.* **1978**, *14*, 893-896. (c) Cuellar, E. A.; Marks, T. J. *Inorg. Chem.* **1981**, *20*, 3766-3770. (d) "Handbook of Chemistry and Physics", 60th ed.; CRC Press, Inc.: Boca Raton, FL, 1980; p C-436.

(200 mL) and NaHSO₃ (17.68 g, 0.170 mol) in water (50 mL) were heated to 60 °C. Concentrated H₂SO₄ (5 mL) was added to the aqueous cupric sulfate solution, followed by portions of the sodium bisulfite solution over a period of 1 min. A warm (60 °C) solution of K^{*}CN (prepared from 10.9 g of natural abundance KCN and 0.5 g of K¹³CN which was 90% enriched in ¹³C, ~0.175 mol) in water (40 mL) was carefully added, producing an off-white precipitate. The suspension was stirred for 15–20 min at 60 °C. The product was then collected by suction filtration and washed with hot water until the washings were colorless. The Cu^{*}CN was then washed with a little acetone and dried in an oven (100 °C) overnight to give 14.0 g of fine, off-white powder.

1,2-C₆H₄(^{*}CN)₂.^{17c} An apparatus consisting of a 250 mL, two-necked, round-bottomed flask which was fitted with a condenser (topped with a gas inlet adapter) and a ground glass stopper was evacuated and back-filled with Ar three times and then flamed under high vacuum. Under Ar flush, the stopper was removed and the flask was charged with Cu^{*}CN (5.0 g, 55.8 mmol), nitrogen-saturated DMF (46 mL), and 1,2-C₆H₄Br₂ (5.32 g, 2.7 mL, 22.5 mmol) in that order, to give a pale yellow-green solution. The flask was next immersed in an oil bath, and the temperature was raised to 155–160 °C and held constant for 5 h. During this time, the solution color became dark blue-green. The heating was then removed and the reaction mixture allowed to cool to room temperature. A flocculent light blue-green solid formed. Workup proceeded by opening the reaction mixture to air and diluting it with 10% FeCl₃·6H₂O in water (46 mL). The aqueous suspension was then extracted with benzene (1 × 200 mL, 2 × 100 mL). The combined benzene extracts were washed with saturated aqueous NaCl (2 × 300 mL) and dried over anhydrous Na₂SO₄. The benzene solution was then decolorized with Norit A (Matheson, Coleman, and Bell) and filtered by gravity. A slight green tinge persisted, so the Norit treatment was repeated to give a colorless solution, which was next evaporated to dryness. The residue was dissolved in CHCl₃ (10 mL) and heptane was added to induce crystallization. The yield of colorless product was 1.17 g, mp 139–141 °C (lit.^{17d} mp 141 °C). The ¹H NMR spectrum (90 MHz, CDCl₃) of this product was identical with that of an authentic, unenriched sample of phthalonitrile.

Ni(^{*}Pc).¹⁸ Under ambient conditions, a 25-mL one-necked, round-bottomed flask was charged with NiCl₂·6H₂O (0.40 g, 1.7 mmol), 1,2-C₆H₄(^{*}CN)₂ (0.86 g, 6.7 mmol), and quinoline (5 mL). It was then fitted with a stir bar and condenser. The flask was next immersed in an oil bath and with stirring the bath temperature was brought to 195–200 °C in an hour and held at that temperature for 2.5 h. The resulting dark suspension was then cooled, diluted with methanol, and filtered, and the solid product was washed successively with methanol, water, acetone, heptane, and acetone again. The crude product was air-dried overnight and then sublimed at 400 °C (10⁻³ torr) to give 0.25 g of small purple crystals. The infrared spectrum (Nujol mull) and X-ray powder diffraction pattern (Rigaku Geigerflex recording diffractometer, Cu K α radiation) of this product were identical with those of an authentic, sublimed sample of Ni(Pc).

Ni(^{*}Pc)I. The literature procedure for Ni(Pc)I^{7a,19} was employed with Ni(^{*}Pc) as the starting material. The X-ray powder diffraction pattern (Rigaku Geigerflex, Cu K α) of this product was identical with that of an authentic Ni(Pc)I sample.^{7a}

Synthesis of Nickel Phthalocyanine Iodide Perdeuterated at the 4,4'-Positions, Ni(Pc-d₈)I. **1,2-Dimethylbenzene-4,5-d₂.** This compound was prepared from the corresponding dibromodimethylbenzene²⁰ by lithium metal reduction²¹ in THF/*tert*-butyl alcohol-*d*. Under an Ar atmosphere, a three-necked, round-bottomed flask equipped with a gas inlet adapter, a vacuum line adapter, a magnetic stirring bar, and a glass stopper was charged with hexane-washed Li sand (1.50 g, 217 mmol, slightly less than 3 equiv/halogen). Under Ar flush, the stopper was removed and dry THF (100 mL) was added by syringe. The suspension was then frozen at 77 K and evacuated; next, *tert*-butyl alcohol-*d* (13.6 mL, 143 mmol, slightly less than 2 equiv/halogen) was trap-to-trap distilled in vacuo onto the frozen solid. The mixture was warmed slightly, and while still frozen, the stopper was removed under Ar flush and 1,2-dimethyl-4,5-dibromobenzene (10.0 g, 37.9 mmol) was added. Under Ar flush, the high vacuum line adapter was removed and replaced with a condenser topped with a gas inlet. The mixture was allowed to warm to room temperature and stirred for 48 h under Ar. After this period of time, the stopper was replaced with a filtration frit, and the reaction mixture was suction

filtered through Celite. The filtrate was then exposed to air and washed with water (2 × 100 mL). The organic fraction was dried over anhydrous Na₂SO₄ and fractionally distilled to give 1,2-dimethylbenzene-4,5-d₂. ¹H NMR (C₆D₆, 90 MHz) δ 7.02 (br s, 2 H), 2.00 (s, 6 H). The mass spectrum (15 eV) showed a parent ion at *m/e* 108 and indicated that the material was \geq 98% d₂.

Phthalic Acid-4,5-d₂. A mixture of KMnO₄²² (9.43 g, 59.7 mmol) and 1,2-dimethylbenzene-4,5-d₂ (1.33 g, 12.3 mmol) in 70% pyridine/H₂O (20 mL) was refluxed under air for 2 h and then cooled to room temperature. The reaction mixture was next filtered through Celite and the brown, precipitated MnO₂ washed with methanol (3 × 15 mL). The aqueous methanolic filtrate was acidified to pH 2 with concentrated HCl and the methanol evaporated. Water (20 mL) was next added, and the aqueous solution was extracted with diethyl ether (5 × 50 mL). The combined ether fractions were dried over anhydrous Na₂SO₄ and concentrated to give a white solid product, which was collected and washed with heptane. Yield 1.09 g (53%); ¹H NMR (Me₂SO-*d*₆, 90 MHz) δ 7.69 (s).

Ni(Pc-d₈). A mixture of phthalic acid-4,5-d₂ (0.950 g, 5.65 mmol), urea (1.30 g, 21.6 mmol), NiCl₂·6H₂O (0.360 g, 1.51 mmol), and ammonium molybdate (0.01 g) in 1,2,4-trichlorobenzene (5 mL) was heated under air with stirring in a round-bottomed flask fitted with a magnetic stir bar and condenser at 200 °C for 4.5 h. From time to time, sublimed white material was scraped down into the dark-colored, stirring reaction mixture from the inside of the condenser with a glass rod. After 4.5 h, the reaction mixture was allowed to cool, diluted with 25 mL of methanol, and filtered. The crude product was washed with three 25-mL portions of methanol, water, methanol, acetone, heptane, and acetone and then air dried. Yield 0.54 g. Pure product in the form of small purple crystals was obtained by sublimation at 400 °C (10⁻³ torr). The purity of this product was verified by X-ray powder diffraction as described for Ni(^{*}Pc) above.

Ni(Pc-d₈)I. The literature procedure for Ni(Pc)I^{7a,18} was employed with Ni(Pc-d₈) as starting material. The purity of this product was verified by X-ray powder diffraction as described for Ni(^{*}Pc)I above.

High-Resolution Solid-State ¹³C NMR Experiments. ¹³C CPMAS NMR spectra were measured at a carbon frequency of 15.0 MHz on a JEOL FX-60QS spectrometer with Chemagnetics solid-state accessories. High-power ¹H decoupling and magic angle spinning were employed. Bullet rotors made of Kel-F were used at a spinning speed of 2.2–2.6 kHz. The magic angle was set for each spectrum by observing the ⁷⁹Br resonance of a small amount of dry KBr which was partitioned from the sample in the rotor by a thin Teflon disk. All solid-state ¹³C NMR spectra were externally referenced to liquid Me₄Si based on substitution of hexamethylbenzene (HMB) as secondary reference and assigning 132.3 ppm to the shift of the aromatic carbon atoms of HMB relative to liquid Me₄Si. The proton 90° pulse width was 5 μ s. For ¹³C, the routinely employed contact time for cross polarization was 2 ms for diamagnetic complexes and 20 ms for the paramagnetic (partially oxidized) complexes. The former contact time was found to give optimal sensitivity (especially for C1,1' and C2,2'), with no improvement observed at longer contact times. The 20-ms time was found to be optimal for observing the C1,1' and C2,2' resonances in the oxidized materials (the intensities of C3,3' and C4,4' resonances were not appreciably affected by this longer polarization time). The repetition time was 4 s for all spectra. In general, 1000–5000 scans were required to obtain satisfactory spectra of the undoped complexes, while 10000–20000 scans were required for doped complexes. Interrupted decoupling experiments for Ni(^{*}Pc)I and Ni(Pc-d₈)I were performed by inserting a 40- μ s delay during which the decoupler was turned off before data acquisition. In such an experiment, the intensities of resonances due to carbon atoms bearing protons are greatly attenuated or disappear due to ¹³C–¹H dipolar dephasing while intensities for nonprotonated carbons are not appreciably affected. A high-field ¹³C CPMAS NMR spectrum of Ni(Pc)I (4800 accumulations, 20 ms contact time, 10 s repetition time) was recorded by the Colorado State University Regional NMR Center on a Nicolet NT-150 spectrometer (37.735 MHz, ¹³C). ¹³C spin-lattice relaxation (T₁) times were measured by the method of Torchia²³ locally adapted to JEOL FX-60QS software. Low-power ¹H decoupling was not applied during the wait time (τ).

Results

Background. The crystal structures of the partially oxidized phthalocyanine conductors {[M(Pc)O]I_{1,1}]_n (M = Si, Ge),^{7a} Ni(Pc)I,^{2a} H₂(Pc)I,^{6a} Ni(Pc)X_{0.33} (X = BF₄, PF₆, SbF₆),^{5a-c} and {[Si(Pc)O]X_y]_n (X = BF₄, PF₆, SbF₆, $y \approx 0.35$)^{5d} are all rather similar, P4/mcc, and differ only slightly in interplanar spacings

(18) Ebert, A. A., Jr.; Gottlieb, H. B. *J. Am. Chem. Soc.* **1952**, *74*, 2806–2810.

(19) Schramm, C. J.; Scaringe, R. P.; Stojakovic, D. R.; Hoffman, B. M.; Ibers, J. A.; Marks, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 6702–6713.

(20) Klingsberg, E. *Synthesis* **1972**, 29–30.

(21) (a) Bruck, P. *Tetrahedron Lett.* **1962**, 449–452. (b) Bruck, P.; Thompson, D.; Winstein, S. *Chem. Ind.* **1960**, 405.

(22) Hopff, H.; Gallegra, P. *Helv. Chim. Acta* **1968**, *51*, 253–260.

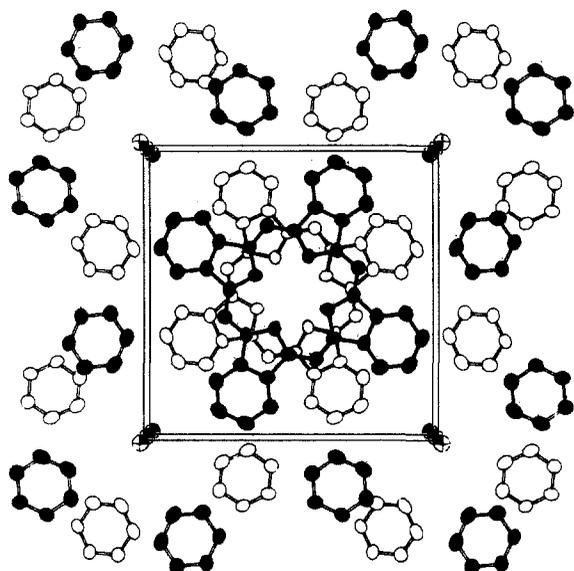


Figure 1. Solid-state structure of $H_2(Pc)I$ viewed parallel to the macrocycle stacking direction. From ref 6a.

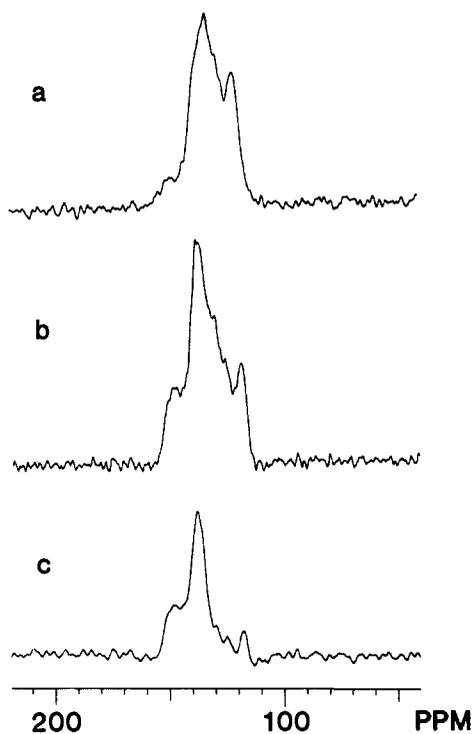


Figure 2. ^{13}C CPMAS NMR spectra (15.0 MHz) of (a) $Ni(Pc)$ (1600 scans), (b) $Ni(*Pc)$ (12000 scans), (c) difference spectrum, $b - a$. In each spectrum, the repetition time was 4.0 s and the contact time was 2 ms.

($c/2$) and interchain dimensions (a). A representative crystal structure is shown in Figure 1. One important consequence of this packing arrangement is that individual $M(Pc)$ units have only C_{4h} site symmetry. That is, nearest-neighbor ring-ring staggering angles are ca. 40° so that isoindoline units lack mirror symmetry perpendicular to the $M(Pc)$ plane. Thus, sites 1 and 1', 2 and 2', 3 and 3', 4 and 4' are chemically and magnetically non-equivalent. Furthermore, these nonequivalences would not be averaged by simple $\pi/4$ rotations of any individual $M(Pc)$ unit. Another ubiquitous feature of the materials under discussion is the weakly paramagnetic, essentially temperature independent static magnetic susceptibility which is observed.^{2,3,6,7} This behavior is reminiscent of the Pauli susceptibility of classical metals.^{7a,24}

(23) Torchia, D. A. *J. Magn. Reson.* **1978**, *30*, 613–616.

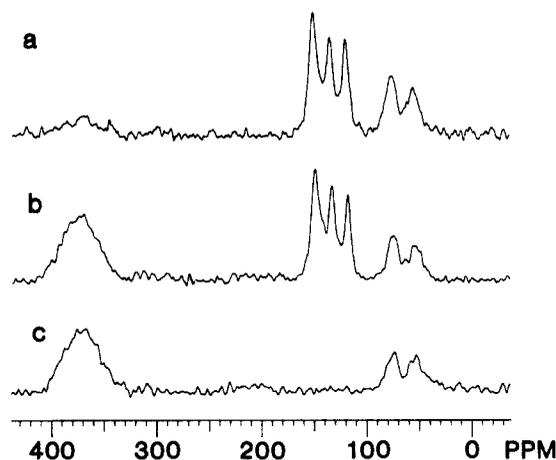


Figure 3. ^{13}C CPMAS NMR spectra (15.0 MHz) of (a) $Ni(Pc)I$ (18000 scans), (b) $Ni(*Pc)I$ (18000 scans), (c) $Ni(*Pc)I$ with a $40 \mu s$ dipolar dephasing delay (12000 scans). In each spectrum, the repetition time was 4.0 s and the contact time was 20 ms.

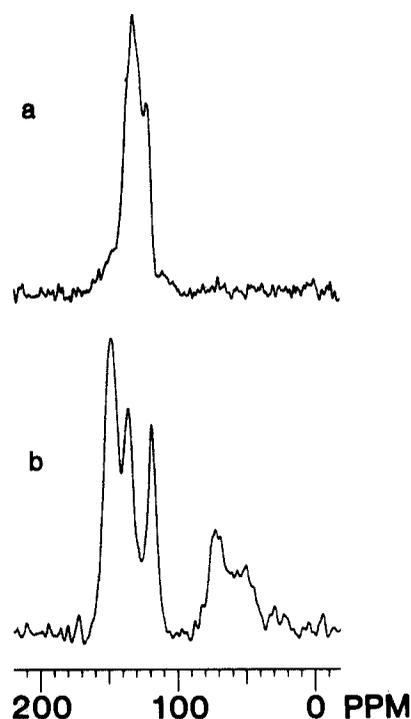


Figure 4. ^{13}C CPMAS NMR spectra (15.0 MHz) of (a) $H_2(Pc)$ (2200 scans) and (b) $H_2(Pc)I$ (14000 scans). The repetition time for each spectrum was 4.0 s and the contact time was 2.0 ms for a and 20.0 ms for b.

Although it scales approximately as the inverse of the tight-binding bandwidth,^{7a} it is likely enhanced by Coulomb correlations^{5a,7a,9c,25} and is relatively insensitive to metal–semiconductor transitions and related phenomena.^{5c,6}

General Spectroscopic Observations. Solid-state CPMAS ^{13}C NMR spectra (15 MHz) of $Ni(Pc)$ and $Ni(Pc)I$ are shown in Figures 2a and 3a, respectively. Spectra of $H_2(Pc)$ and $H_2(Pc)I$ are shown in Figure 4, while spectra of the pairs $[M(Pc)O]_n$, $\{[M(Pc)O]I_{1,1}\}_n$ ($M = Si, Ge$) are presented in Figure 5. Chemical shift data for these and related materials are compiled in Table I. In all cases, the spectra of the *undoped* molecular and poly-

(24) Kittel, C. "Introduction to Solid State Physics", 5th ed.; Wiley: New York, 1976; Chapter 14.

(25) (a) Shiba, H. *Phys. Rev. B* **1972**, *6*, 930–938. (b) Torrance, J. B.; Tomkiewicz, Y.; Silverman, B. D. *Phys. Rev. B* **1977**, *15*, 4738–4749. (c) Mazumdar, S.; Bloch, A. N. *Phys. Rev. Lett.* **1983**, *50*, 207–211. (d) Mortensen, K.; Conwell, E. M.; Fabre, J. M. *Phys. Rev. B* **1983**, *28*, 5856–5862. (e) Coulon, C.; Dalhaes, P.; Flandrois, S.; Lagnier, R.; Bonjour, E.; Fabre, J. M. *J. Phys. (Paris)* **1982**, *43*, 1059–1066.

Scheme I

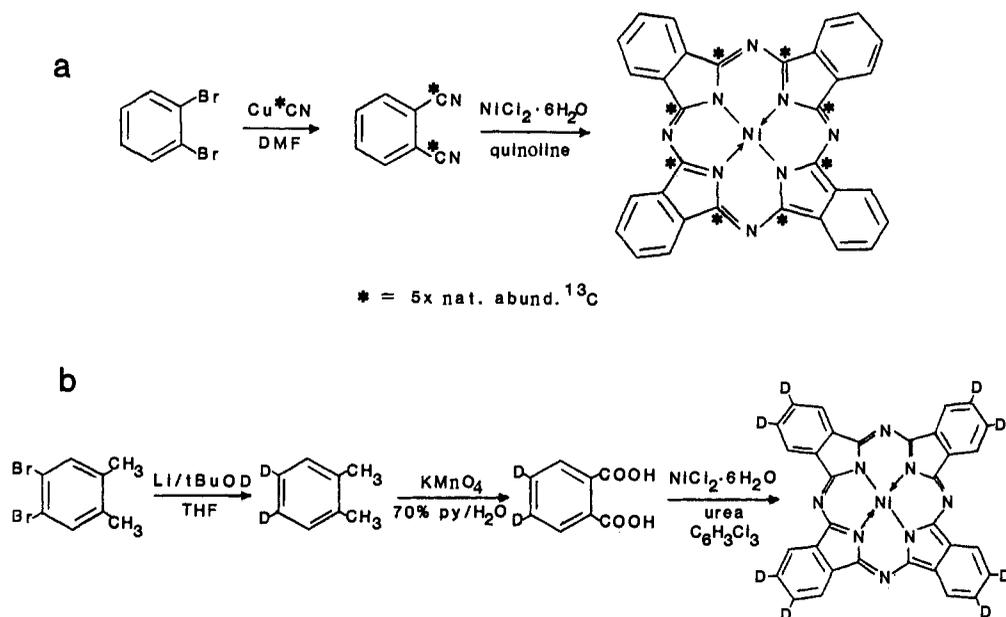


Table I. Solid-State CPMAS ^{13}C NMR Data for Phthalocyanine Materials

compounds	chemical shifts ^a (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 (C4), 134.1 (C3), 150.0 (C3', C4'), 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')
{[Si(Pc)O](BF ₄) _{0.32}] _n	58.0 (C2, C2'), 118.5, 134.5, 145.0
{[Si(Pc)O](PF ₆) _{0.32}] _n	49.1 (C2, C2'), 117.2, 131.5, 141.6, 151.3
{[Si(Pc)O](SbF ₆) _{0.36}] _n	(46.0, 72.0) (C2, C2'), 120.1 (sh), 127.4, 138.3
[Ge(Pc)O] _n	126.8, 134.9, 152.3
{[Ge(Pc)O]I _{1,1} } _n	~35 (C2, C2'), 132.3, 148.6
Ni(Pc)(PF ₆) _{0.33}	(77.5, 94.1 (br)) (C2, C2'), 126.6, 132.8 (sh), 137.4, 140.6 (sh), ~280 (C1, C1')
Ni(Pc)(BF ₄) _{0.33}	(78.3, 91.3) (C2, C2'), 122.4, 132.8, 142.4, ~310 (C1, C1')
Ni(Pc)(SbF ₆) _{0.33}	(92.3, 100.1 (br)) (C2, C2'), 127.4, 136.5, ~275 (C1, C1')

^a In ppm from Me₄Si. ^b ^{13}C -enriched sample.

meric compounds are typical of polycyclic aromatic solids²⁶ and related metallomacrocyclics.²⁷ Magnetic nonequivalences arising from crystallographic site symmetries lower than D_{4h} are not readily discerned. Characteristic of all *partially oxidized* phthalocyanine CPMAS spectra is the presence of a broad resonance (sometimes resolved into a doublet) displaced to high field of the aromatic region and a broader feature (sometimes barely observable) displaced an even greater amount to low field. In addition, features in the aromatic region display a larger chemical shift dispersion than in the undoped precursors. Importantly, the CPMAS spectra of the doped phthalocyanines in general exhibit resonances in excess of the four expected for a D_{4h} M(Pc) molecule. That none of the observed ^{13}C spectral multiplicities are the result of residual ^{14}N - ^{13}C dipolar coupling not removed by the MAS (in the case where ^{14}N quadrupolar and Zeeman in-

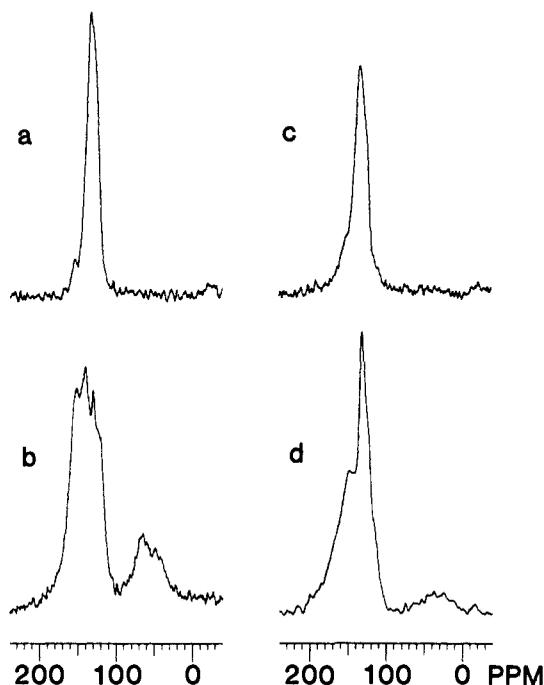


Figure 5. ^{13}C CPMAS NMR spectra (15.0 MHz) of (a) [Si(Pc)O]_n (1800 scans), (b) {[Si(Pc)O]I_{1,1}]_n (18 000 scans), (c) [Ge(Pc)O]_n (10 000 scans), and (d) {[Ge(Pc)O]I_{1,1}]_n (30 000 scans). In each spectrum, the repetition time was 4.0 s. For a and c, the contact time was 2.0 ms, and for b and d it was 20.0 ms.

teraction energies are comparable)²⁸ is confirmed by studies of Ni(Pc)I at 37.735 MHz. As can be seen in Figure 6, no collapse^{28,29} in multiplicities is observed, but rather increased chemical shift dispersion is evident (and the low-field δ 375 resonance now exhibits a spinning sideband progression).

Although the above results are highly informative, additional data are required for rigorous spectral assignments. This has been achieved for Ni(Pc)I by synthesizing derivatives which are specifically labeled at the phthalocyanine 1,1' and 4,4' skeletal positions.

(26) (a) Reference 10a, Chapter 7. (b) Janson, T. F.; Katz, J. J. In "The Porphyrins"; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. IV, pp 1-59. (c) Johnson, L. F.; Jankowski, W. S. "Carbon-13 NMR Spectra"; Wiley-Interscience: New York, 1972.

(27) (a) Dirk, C. W.; Marks, T. J. *Inorg. Chem.* **1984**, *23*, 4325-4332. (b) Okazaki, M.; McDowell, C. A. *J. Am. Chem. Soc.* **1984**, *106*, 3185-3190.

(28) (a) Naito, A.; Ganapathy, S.; McDowell, C. A. *J. Magn. Reson.* **1982**, *48*, 367-381. (b) Naito, A.; Ganapathy, S.; McDowell, C. A. *J. Chem. Phys.* **1981**, *74*, 5393-5397. (c) Hexam, J. G.; Frey, M. H.; Opella, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 224-226.

(29) Toscano, P. J.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 653-659.

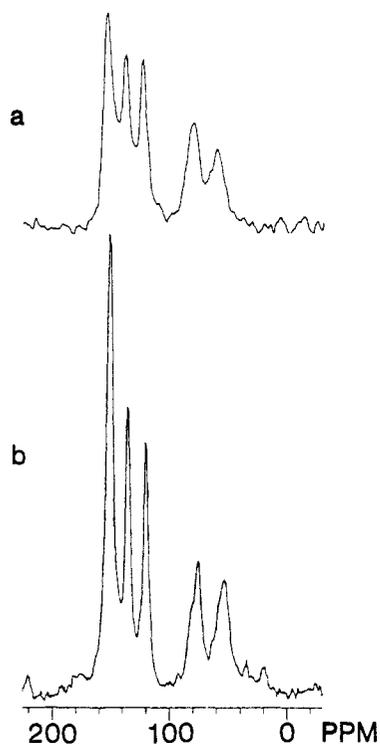


Figure 6. ^{13}C CPMAS spectra of Ni(Pc)I at (a) 15.0 MHz (18 000 4-s repetitions with 20-ms contact time) and (b) 37.735 MHz (4600 10-s repetitions with 20-ms contact time).

Synthesis of Isotopically Labeled Ni(Pc)I Derivatives. Ni(Pc)I enriched to ca. 5 times the ^{13}C natural abundance at positions C1 and C1' (Ni(*Pc)I) was prepared as shown at the top of Scheme I. First, *o*-dibromobenzene was reacted with ^{13}C -labeled cuprous cyanide in a Rosenmund-von Braun reaction to yield labeled phthalonitrile; the latter, in the presence of NiCl₂, was converted to Ni(*Pc) by using standard procedures. Ni(*Pc) was subsequently doped with I₂ to give Ni(*Pc)I.

The synthesis of Ni(Pc-*d*₈)I in which the C4, C4' positions are perdeuterated is shown at the bottom of Scheme I. First, 1,2-dimethyl-4,5-dibromobenzene was reduced with Li/*tert*-butyl alcohol-*d* to give 1,2-dimethylbenzene-4,5-*d*₂. The latter compound was then oxidized with KMnO₄ to yield phthalic-4,5-*d*₂ acid, which in the presence of NiCl₂, urea, and a catalytic amount of ammonium molybdate was converted to Ni(Pc-*d*₈). This complex was then doped with I₂ to give Ni(Pc-*d*₈)I.

Assignment of the CPMAS NMR Spectrum of Solid Ni(Pc)I. The CPMAS spectrum of Ni(*Pc) is shown in Figure 2b. Subtraction of this spectrum from that of Ni(Pc) in Figure 2a yields a difference spectrum, containing primarily the contributions of the labeled 1,1' carbon atoms (Figure 2c). The multiplicity of resonances likely reflects the low site symmetry in the monoclinic Ni(Pc) crystal structure³⁰ and possibly ^{14}N - ^{13}C quadrupolar effects.²⁸

Turning now to the CPMAS spectra of Ni(Pc)I and Ni(*Pc)I (spectra a and b, Figure 3), it can be seen that the low-field resonance at $\delta \sim 375$ can be assigned to carbon atoms 1 and 1'. The breadth of this signal may reflect the crystallographic non-equivalence of these sites (cf., Figure 1) as well as the short T_1 of ca. 20 ms (vide infra), which would imply a short T_2 as well. Dipolar dephasing experiments³¹ (Figure 3c) indicate that the three resonances in the δ 119–150 region are assignable to the ^{13}C -H groups of carbon atoms 3,3' and 4,4'. The remaining pair of high-field signals at $\delta \sim 50$ –80 can then be assigned to crystallographically nonequivalent, nonprotonated positions C2 and C2'.

(30) Robertson, J. M.; Woodward, I. *J. Chem. Soc.* **1937**, 219–230.

(31) (a) Alemany, L. B.; Grant, D. M.; Alger, T. D.; Pugmire, R. J. *J. Am. Chem. Soc.* **1983**, *105*, 6697–6704. (b) Opella, S. J.; Frey, M. H.; Cross, T. A. *J. Am. Chem. Soc.* **1979**, *101*, 5854–5856.

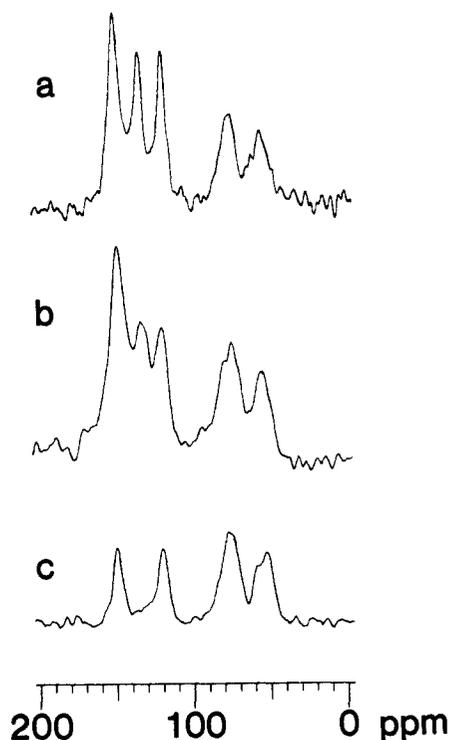


Figure 7. High-field region of ^{13}C CPMAS NMR spectra (15.0 MHz) of (a) Ni(Pc)I (18 000 scans), (b) Ni(Pc-*d*₈)I (16 000 scans), and (c) Ni(Pc-*d*₈)I with a 40- μs dipolar dephasing delay (17 000 scans). In each spectrum the repetition time was 4.0 s and the contact time was 20 ms.

The assignment of the "triplet" due to ^{13}C -H functionalities was pursued via the 4,4' deuterated derivative Ni(Pc-*d*₈)I. The CPMAS spectra of Ni(Pc)I and Ni(Pc-*d*₈)I are compared in spectra a and b of Figure 7. While some broadening of 3,3',4,4' ^{13}C signals is observed in Ni(Pc-*d*₈)I, ^2H - ^{13}C interactions are expected to be small because of the low ^2H ($I = 1$) quadrupole moment.³² However, under dipolar dephasing conditions, resonances associated with C-H groups should be suppressed, while those associated with ^{13}C -D groups should not be appreciably affected.³³ The results of this experiment are shown in Figure 7c. It is evident that the resonances at δ 118.8 and 150.0 can be assigned to carbon atoms 4 and 4'. Therefore, the resonances of C3 and C3' are located at δ 134.1 and 150.0, with an accidental degeneracy of one 4,4' and one 3,3' resonance occurring at δ 150.0.

With these experiments, the ^{13}C CPMAS NMR spectrum of Ni(Pc)I is completely assigned. Structurally, it can be seen that, with the exception of the very broad C1, C1' signal, a doubling of all skeletal carbon-13 signals is observed, in accord with the descent of the crystallographic site symmetry from D_{4h} . In addition, there is no evidence for a motional process which would impart time-averaged D_{4h} symmetry to the structure. Electronically, it is evident that partial oxidation results in very large upfield and downfield displacements of the Ni(Pc)^{0.33+} skeletal ^{13}C resonances. This result is not in accord with a simple closed-shell carbocation origin of the shifts, since a downfield shift of ca. 160 ppm is expected per one π electron decrease per carbon atom.³⁴

Ni(Pc)I Relaxation Time Measurements. Spin-lattice relaxation time measurements were performed for individual carbon atom sites in solid Ni(*Pc)I by using an inversion-recovery

(32) (a) $Q = 2.77e \times 10^{-27} \text{ cm}^2$ (Drago, R. S. "Physical Methods in Chemistry"; W. B. Saunders: Philadelphia, 1977). (b) Deuterium nuclear quadrupole coupling constants in organic molecules are typically in the 100–200 kHz range (Lucken, E. A. C. "Nuclear Quadrupole Coupling Constants"; Academic Press: New York, 1969; pp 111–117).

(33) (a) Barker, P.; Burlinson, N. E.; Dunell, B. A.; Ripmeester, J. A. *J. Magn. Reson.* **1984**, *60*, 486–489. (b) Hall, L. D.; Lim, T. K. *Carbohydr. Res.* **1983**, *124*, C1–C4.

(34) (a) Blann, W. G.; Fyfe, C. A.; Lyeria, J. R.; Yannoni, C. S. *J. Am. Chem. Soc.* **1981**, *103*, 4030–4033. (b) Spiesecke, K.; Schneider, W. G. *Tetrahedron Lett.* **1961**, 468–472. (c) Olah, G. A.; Matescu, G. D. *J. Am. Chem. Soc.* **1970**, *92*, 1430–1432.

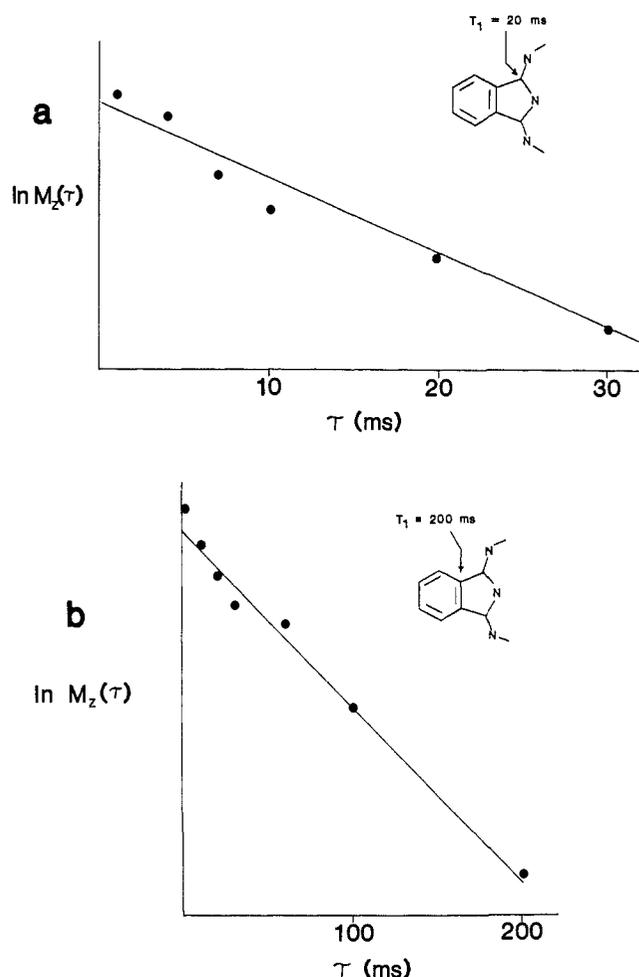


Figure 8. Least-squares plots of $\ln M_z(\tau)$ (natural logarithm of the magnetization in arbitrary units) vs. τ (wait time in ms) for Ni(*Pc)I: (a) C1,C1' positions (averaged); (b) C2,C2' positions (averaged).

technique²³ (see Experimental Section for details). Least-squares magnetization plots are shown in Figure 8. Derived T_1 values are 20 ± 9 ms for C1,C1', 200 ± 30 ms for C2,C2', and ca. 1–2 s for C3,C3' and C4,C4'.

Other Phthalocyanine Systems. As already noted, the CPMAS spectral patterns of the other partially oxidized phthalocyanine conductors compiled in Table I are rather similar to those of Ni(Pc)I. In view of this, similar degrees of partial oxidation, and the similar crystal structures, it is reasonable to advance analogous CPMAS spectral assignments for all of the phthalocyanine conductors under discussion. These assignments have been entered in Table I.

Discussion

From the foregoing account, it is apparent that neither the signs nor the magnitudes of the ^{13}C CPMAS shift patterns observed in the present phthalocyanine conductors are explicable purely on the basis of oxidation-induced positive charge/chemical shift effects. Rather, the displacements of the resonances from the field positions in the undoped materials can be explained as Knight shifts, arising from the interaction between conduction electrons and the ^{13}C nuclei. For a classical (isotropic degenerate electron gas) metal, where the electron spin-lattice relaxation is rapid, the Knight shift of nucleus i (K_i) can be related to the Pauli susceptibility (χ_p) and the isotropic part of the electron-nuclear hyperfine coupling constant (a_i) by eq 1. Here N is Avogadro's

$$K_i = \frac{\Delta H_i}{H} = -\frac{a_i \chi_p}{Ng\beta g_N \beta_N} \quad (1)$$

number, and the remaining terms have their usual meaning. For a randomly oriented nonspinning powder sample, the isotropic part of ΔH_i can in principle be obtained from the first moment of the

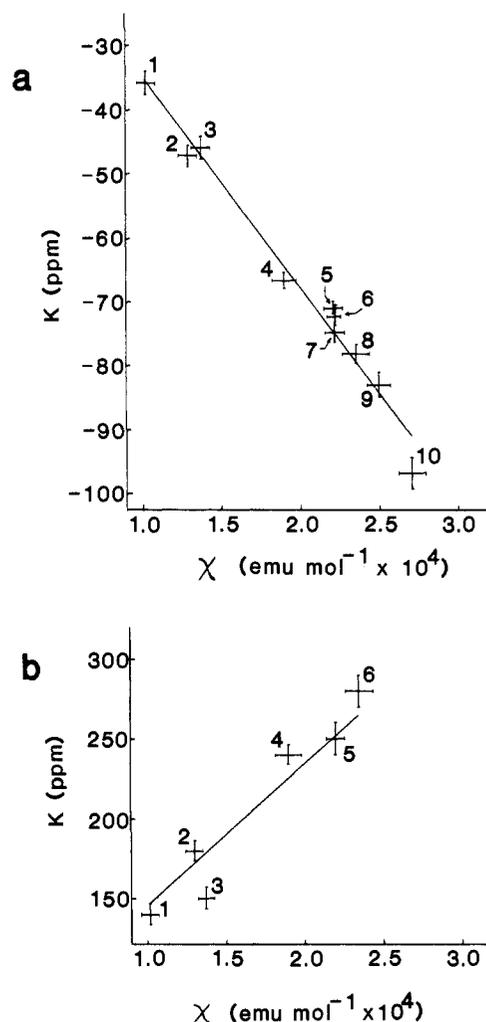


Figure 9. Least-squares plots of K (Knight shift in ppm) vs. χ (Pauli-like magnetic susceptibility). (a) For C2,C2' positions (averaged). Data points correspond to the following: (1) Ni(Pc)(SbF₆)_{0.33}, (2) Ni(Pc)(BF₄)_{0.33}, (3) Ni(Pc)(PF₆)_{0.33}, (4) Ni(Pc)I, (5) H₂(Pc)I, (6) {[Si(Pc)O](BF₄)_{0.32}]_n, (7) {[Si(Pc)O](SbF₆)_{0.36}]_n, (8) {[Si(Pc)O]I_{1.1}]_n, (9) {[Si(Pc)O](PF₆)_{0.32}]_n, (10) {[Ge(Pc)O]I_{1.1}]_n. (b) For C1,C1' positions. Points are the following: (1–5) same complexes as in a above, (6) {[Si(Pc)O]I_{1.1}]_n.

NMR line shape.³⁵ In practice, however, such experiments are only successful when a relatively small number of nonoverlapping nuclear resonances are involved (high levels of isotopic enrichment have been necessary for ^{13}C studies).³⁵ This is not the case under MAS conditions, and both the anisotropic part of the Knight shift as well as the conventional chemical shift anisotropy are expected to be, in large part, removed.³⁶ That such a regime obtains in the present case is supported by the observation that spinning sidebands are only observed for the resonance(s) experiencing the greatest shift(s) (C1,C1') and only at 37.735 MHz.

Several lines of evidence support the contention that the present very large spectral displacements are largely Knight shift in origin. First, eq 1 predicts a linear relationship between the observed K_i (defined here as the shift from the resonance position in the unoxidized phthalocyanine) and χ_p . In principle, χ_p could be varied by studying a closely related series of compounds with differing χ_p ^{37a} or, less readily, by changing the temperature of

(35) (a) Takahashi, T.; Jérôme, D.; Masin, F.; Fabre, J. M.; Giral, L. *J. Phys. C* **1984**, *17*, 3777–3792. (b) Devreux, F.; Jeandey, Cl.; Nechtschein, M.; Fabre, J. M.; Giral, L. *J. Phys.* **1979**, *40*, 671–677. (c) Rybaczewski, E. F.; Smith, L. S.; Heeger, A. J.; Silbernagel, B. G. *Phys. Rev. B* **1976**, *14*, 2746–2756.

(36) (a) Andrew, E. R.; Hinshaw, W. S.; Tiffen, R. S. *J. Magn. Reson.* **1974**, *15*, 191–195 and references therein. (b) Reference 10a, Chapter 4. (c) Mehring, M. "Principles of High Resolution NMR in Solids", 2nd ed.; Springer-Verlag: Berlin, 1983; Chapter 2.

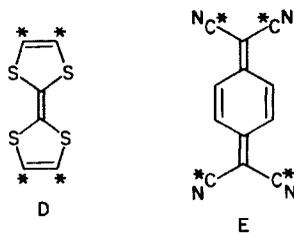
Table II. Knight Shifts and Derived Hyperfine Coupling Constants for Conductive Phthalocyanine Materials^a

compounds	<i>K</i> - (C1,C1') ^b	<i>a</i> - (C1,C1') ^c	<i>K</i> - (C2,C2') ^b	<i>a</i> - (C2,C2') ^c
Ni(Pc)I ^d	240	-15.0	-67	4.2
H ₂ (Pc)I	250	-13.5	-71	3.8
{[Si(Pc)O]I _{1,1} } _n	280	-16.5	-78	4.0
{[Si(Pc)O](BF ₄) _{0,32} } _n	<i>e</i>	<i>e</i>	-74	4.0
{[Si(Pc)O]- (SbF ₆) _{0,36}] _n	<i>e</i>	<i>e</i>	-72	3.9
{[Si(Pc)O](PF ₆) _{0,32}] _n	<i>e</i>	<i>e</i>	-83	4.0
{[Ge(Pc)O]I _{1,1}] _n	<i>e</i>	<i>e</i>	-97	4.3
Ni(Pc)(PF ₆) _{0,33}	150	-17.4	-46	4.4
Ni(Pc)(BF ₄) _{0,33}	180	-13.6	-47	4.1
Ni(Pc)(SbF ₆) _{0,33}	140	-13.9	-36	4.2

^aCalculated from eq 1. The chemical shift in the diamagnetic compound is assumed to be approximately 132 ppm. ^bIn ppm. ^cIn MHz. ^d*K*(C3,C3') and *K*(C4,C4') are no greater than 15 ppm which implies that *a*(C3,C3') and *a*(C4,C4') are less than 1.0 MHz. ^eNot observed.

a single material over a very wide range.^{37b} In Figure 9a is shown a plot of *K_i* values for the averaged C2,C2' signal position in a large series of partially oxidized phthalocyanines vs. the corresponding room-temperature paramagnetic susceptibilities (measured with a highly accurate SQUID susceptometer⁵⁻¹⁰). The linear relationship is visually evident, and the correlation coefficient of a line fit by least-squares techniques is found to be 0.985. That the shifts are almost purely Knight shift in origin is confirmed by the calculated, near-zero, intercept of *K* = -2 ± 3 ppm at *χ_p* = 0. Similar results are obtained for the C1,C1' resonances (Figure 9b); however, the greater breadth of these signals and the correspondingly larger uncertainties in *K_i* parameters renders the comparison less accurate. *K_i* values for all partially oxidized phthalocyanine compounds are compiled in Table II.

A further verification that the observed ¹³C spectral patterns observed arise from the conduction electron spin density distribution (the conduction band should be composed, in a tight-binding picture, primarily of M(Pc) ligand-centered π HOMO's⁹) is the presence of both upfield and downfield shifts. Such sign alternation patterns are commonly observed in the unpaired spin density distributions of open-shell, conjugated organic and metal-organic molecules.³⁸ In the present case, individual *a_i* values can be calculated for different M(Pc) skeletal positions in the various compounds; these data are set out in Table II and provide a direct map of the conduction electron spin density distribution. These results can be favorably compared with those from broad line studies of TTF-TCNQ prepared with the ¹³C enriched components shown below (D,^{35a} E^{35c}). Here, *a_c*(TTF) ≈ +3.6 MHz and

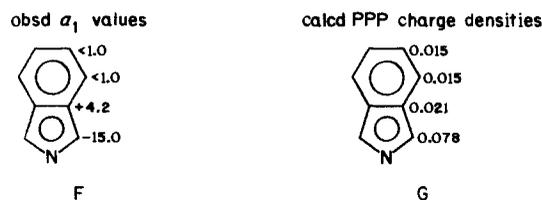


a_c(TCNQ) ≈ -11.5 MHz. Hyperfine constants of magnitudes similar to the phthalocyanine systems as well as sign alternation have also been reported in a recent CPMAS study of (fluoranthenyl)₂SbF₆.^{12b} Although electron correlation effects^{38,39} abrogate

(37) (a) This approach makes the reasonable assumption that *a_i* values for the same skeletal position will vary negligibly in a closely related series of compounds. (b) Such experiments are in progress.

(38) (a) Reference 16a, pp 221-225. (b) Jesson, J. P. In "NMR of Paramagnetic Molecules"; La Mar, G. N., Horrocks, W. DeW., Jr., Holm, R. H., Eds.; Academic Press: New York, 1973, Chapter 1. (c) La Mar, G. N., ref 38b, Chapter 3.

a simple 1:1 relationship between charge and spin densities, it is interesting to compare the present *a_i* parameters (F, averaged Ni(Pc)I) with HOMO charge densities (orbital coefficients squared) calculated for an M(Pc) molecule via the Pariser-Parr-Pople SCF LCAO CI π electron formalism (G).^{40a,b} It can be seen that C1,C1' is not only the location of greatest calculated charge density but it is also of greatest experimental positive spin density. More sophisticated calculations are now underway.^{40c}



For a classical metal, the Knight shift can be related to the nuclear spin-lattice relaxation time (*T₁*) via the Korringa approximation (eq 2).⁴¹ Here *T* is the temperature and *S* is a scaling

$$T_1 K^2 = \frac{h}{4\pi kT} \frac{\gamma_e^2}{\gamma_N^2} S \quad (2)$$

factor.^{35a} For classical metals, *S* = 1, while for highly anisotropic systems, *S* is usually much less than unity. Equation 2 predicts a relationship between *K* and *T₁* values for individual sites which can be tested with the experimental data for Ni(Pc)I. From the observed ratio *T₁*(C2,C2')/*T₁*(C1,C1'), the ratio *K*²(C1,C1')/*K*²(C2,C2') is predicted to be 10.0. The observed value of 12.8 is in acceptable agreement. With use of the experimental *T₁* and *K* data, it is also possible to calculate *S* values for the C(1,1') and C(2,2') sites. These are found to be 0.083 for 1,1' and 0.065 for 2,2' at 300 K, in favorable agreement with results for (fluoranthenyl)₂SbF₆,^{12b} TTF-TCNQ,^{35a} and the markedly unidimensional nature of partially oxidized phthalocyanines evident in the anisotropy of charge transport,⁶ optical reflectivity,⁶ and EPR line widths.^{4,8b}

Conclusions

This work demonstrates that high-resolution solid-state CPMAS NMR techniques are a powerful tool for investigating local crystal and electronic structure in low-dimensional phthalocyanine-based molecular metals and conductive polymers. When used with isotopic labeling and dipole dephasing methodology, it is possible to completely and unambiguously map out isotropic conduction electron hyperfine interactions, as expressed by locally resolved Knight shifts, about the carbon atom framework of a molecular metal such as Ni(Pc)I. Further efforts are under way to explore both the range of materials amenable to this technique as well as the types of information that can be obtained.

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Registry No. Ni(Pc), 14055028; Ni(*Pc), 99476-50-3; Ni(Pc)I, 84624839; H₂(Pc), 574-93-6; [Si(Pc)O]_n, 39114-20-0; [Ge(Pc)O]_n, 55948-70-4; Ni(*Pc)I, 99476-51-4; Ni(Pc-d₈), 99494-60-7; Ni(Pc-d₈)I, 99494-61-8.

(39) Reference 16a, pp 86-94.

(40) (a) Marks, T. J.; Stojakovic, D. R. *J. Am. Chem. Soc.* **1978**, *100*, 1696-1705. (b) Stojakovic, D. R. Ph.D. Thesis, Northwestern University, August, 1977. (c) Hung, S.; Ellis, D. E.; Marks, T. J., Research in progress.

(41) Reference 16b, pp 144-150.