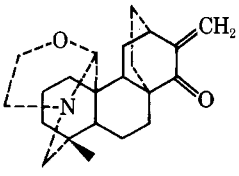
Table II. A Temperature Dependence Study of Atisine[a]

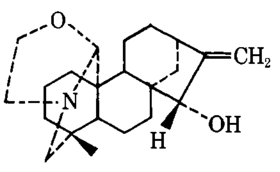
Temp, °C	Atisine **1A**[b] %	Atisine **1B** %	Isoatisine **2** %
25	65	35	—
40	65	35	—
56	55	35	10
70	55	35	10
90	50	30	20
RT[c]	50	30	20
RT[d]	50	30	20

[a] Study was performed in deuterated toluene (d_8) using HMDS[$(CH_3)_3Si]_2O$ as an internal reference. [b] The percentage of compounds in the mixture at a given temperature was determined by monitoring the C-20 peak for **1A** and **1B** and the C-19 peak for **2** in the ^{13}C NMR spectrum. [c] The ^{13}C spectrum was taken at room temperature after the sample had been held at 90 °C for 50 min [d] The spectrum was taken 60 h later at room temperature after temperature had been held at 90 °C for 50 min.

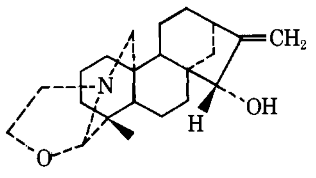
isoatisine (**3**) occurs as low as 56 °C but, that even at 90 °C, the two sets of signals do not coalesce to a single resonance. These results confirm the existence of the C-20 epimers of atisine. The ^{13}C NMR analysis also indicates that epimer **1A** exists in greater amount than **1B**, presumably, because in **1A** the formation of the oxazolidine ring occurs from the least hindered side of the C-20 carbon.



5 atisinone



6 veatchine



7 garryine

The carbon-13 NMR spectra of atisinone (**5**) and veatchine (**6**) also show two sets of signals for ring E and F carbons (Table I), a result which indicate that these compounds also exist as a mixture of C-20 epimers.

It should be noted that early work[15] on the configuration of atisine and related alkaloids assumed, without evidence, a β configuration for the hydrogen at C-20. Because atisine and veatchine are isolated as the ternary iminium salts (e.g., **2**) which on treatment with base generate the respective alkaloids, the question of which of the C-20 epimers of each alkaloid occurs in the plant is unanswered.

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References and Notes

(1) K. Wiesner, R. Armstrong, M. F. Bartlett, and J. A. Edwards, *Chem. Ind.* (*London*), 132 (1954).
(2) S. W. Pelletier and W. A. Jacobs, *J. Am. Chem. Soc.*, **76**, 4496 (1954).
(3) K. Wiesner and J. A. Edwards, *Experientia*, **11**, 255 (1955).
(4) J. W. ApSimon and O. E. Edwards, *Can. J. Chem.*, **40**, 896 (1962), and references cited therein.
(5) H. Vorbrueggen and C. Djerassi, *J. Am. Chem. Soc.*, **84**, 2990 (1962).
(6) S. W. Pelletier and P. C. Parthasarathy, *J. Am. Chem. Soc.*, **87**, 777 (1965), and references cited therein.
(7) W. Nagata, T. Sugasawa, M. Narisuda, T. Wakabayashi, and Y. Hayase, *J. Am. Chem. Soc.*, **85**, 2342 (1963), and **89**, 1483 (1967).
(8) S. Masamune, *J. Am. Chem. Soc.*, **86**, 291 (1964).
(9) W. A. Jacobs and L. C. Craig, *J. Biol. Chem.*, **147**, 567 (1943).
(10) S. W. Pelletier, K. W. Gopinath, and K. Kawazu, *Chem. Ind.* (*London*), 28 (1966); S. W. Pelletier, R. Aneja, and K. W. Gopinath, *Phytochemistry*, 7, 635 (1968).
(11) S. W. Pelletier and T. N. Oeltmann, *Tetrahedron*, **24**, 2019 (1968).
(12) S. K. Pradhan and V. M. Girijavallabhan, *Chem. Commun.*, 644 (1970).
(13) S. W. Pelletier and N. V. Mody, unpublished results.
(14) N. L. Allinger, personal communication.
(15) See W. Klyne and J. Buckingham, "Atlas of Stereochemistry. Absolute Configurations of Organic Molecules", Oxford University Press, New York, N.Y., 1974, p 171, and references therein.

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A New Class of Highly Conductive Molecular Solids: the Partially Oxidized Phthalocyanines

Sir:

Crystals composed of molecular ions and exhibiting strongly anisotropic metallic behavior are currently of great experimental and theoretical interest.[1] These materials invariably consist of stacks of strongly interacting, planar inorganic (e.g., $Pt(CN)_4^{-m}$) or organic ($TCNQ^{-n}$) ions; weak interactions between the stacks lead to the anisotropic transport properties. It appears that high conductivity requires a nonintegral formal oxidation state for the ions within a stack,[1] a result which may be understood in terms of the low "conduction electron density" in a molecular crystal.[2] Since these materials are not common, a broadly applicable synthetic procedure would have considerable significance. In most instances, the plausible approach of a substoichiometric oxidation of planar organic molecules or transition ion complexes of integral oxidation state does not consistently produce the desired mixed valencies. However, we anticipated that iodine[3,4] would be an especially advantageous oxidant,[3] because of the high stability of I_3^- in nonpolar environments,[5] and because of the ability of I_3^- to accommodate itself to channels in one-dimensional lattices.[3,4] Thus, oxidation of a divalent metal complex according to eq 1 would yield a trivalent metal ion if I^- were produced, but a nonintegral oxidation state if all metal sites in the material were crystallographically similar and if only I_3^- were formed, e.g., $(LM)(I_3^-)_{1/3}$ where M has a formal oxidation state of 2.33. Furthermore, the products of such oxidations are particularly amenable to characterization by spectroscopic means. We confirm here the utility of this synthetic approach, and report that, when applied to the phthalocyanines, it results in an extensive new class of highly conducting molecular solids.

$$(L)M^{II} + {}^{1}\!/_{2}I_2 \rightarrow (LM)(I) \qquad (1)$$

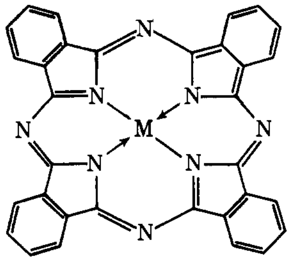
The oxidation[6] of purified Fe, Co, Ni, Cu, Zn, Pt, and metal-free phthalocyanines, by iodine vapor or solutions (e.g., chlorobenzene), results in darkly colored solids with a range of stoichiometries[6,7a] (eq 2), the exact composition obtained depending on the conditions. The reaction is reversible, and iodine can be completely removed by warming the solids in vacuo.[7b] That these materials exhibit truly mixed valency is supported by several lines of evidence. First, resonance Raman spectroscopy shows that the iodine is present as I_3^- in all samples with $x < 3$. The Raman spectra taken with spinning samples and 6471, 5145, or 4880 Å excitation clearly reveal the resonance-enhanced totally symmetric $I-I-I^-$ stretch (ν 105-108 cm^{-1})[3b,8] and expected overtone progression[3b,8] of I_3^- (Figure 1). Calculated anharmonicity constants and

Table I. Conductivity Parameters[a]

		Room temp conductivity Ω^{-1}(cm^{-1})	E_a (eV)
$(CuPc)I_x$	$x = 1.71$	4.2	0.021
$(PtPc)I_x$	$x = 0.93$	2.4	0.016
$(PcH_2)I_x$	$x = 2.20$	2.3	0.040
$(NiPc)I_x$	$x = 0.56$	0.7	0.024
	1.0	0.7	0.036
	1.74	0.8	0.021
$(CoPc)I_x$	$x = 0.60$	0.1	0.065
	1.0	0.06	0.082
$FePcI_x$	$x = 1.93$	4×10^{-3}	0.127
	2.74	2×10^{-3}	0.070
	3.85	1×10^{-4}	0.254
$(Qn)(TCNQ)_2$[b]		4.0	0.03
$(Qn)(TCNQ)_2$ (single crystal)[c]		100	~0
NiPc[d]		1×10^{-11}	1.6
CoPc[d]		2×10^{-10}	1.6
FePc[d]		2×10^{-10}	

[a] All measurements employed compressed pellets except as noted. [b] Reference 14a. [c] Reference 14b. [d] Taken from F. Gutmann and L. E. Lyons, "Organic Semiconductors", Wiley, New York, N.Y., 1967, p 718.

$$\mathrm{MPc} + x/2\mathrm{I}_2 \rightleftarrows (\mathrm{MPc})(\mathrm{I})_x$$
$$\mathrm{M} = \mathrm{Fe, Co, Ni, Cu, Zn, Pt, H_2}$$



= MPc (2)

bandwidths are also in agreement with I_3^-. For $x \leq 3$ no I_2 ($\nu \approx 210$–180 cm^{-1})[8a] is evident even though corollary studies[9a] with $(phenacetin)_2H^+I_3^-\cdot I_2$,[9b] $(Cs^+)_2(I_3^-)_2\cdot I_2$,[9c] and $(C_2H_5)_4N^+I_3^-\cdot 2I_2$[9d] indicate it would be readily detectable. Iodine-129 Mössbauer studies on $NiPcI_x$ further indicate that for $x < 3$ iodine is present only as I_3^-: negligible amounts of I_2 and I^- (≤ 10 and 5%, respectively) are present,[10] and isomer shift and quadrupole splitting paramters are in good agreement with literature values for I_3^-.[11] For $x > 3$, both techniques reveal the presence of I_2.

Furthermore, x-ray powder patterns of the oxidized phthalocyanine complexes can be indexed in the tetragonal crystal system and lattice parameters are very similar to those of $(dpg)_2NiI$[3a,c] (tetragonal, a = 19.887 (4), c = 6.542 (2) Å). The latter structure exhibits a common motif for such materials,[3,12] and consists of regular stacks of equivalent $(dpg)_2Ni$ units and polyiodide chains extending parallel to the stacking direction. In view of the similar dimensions of $(dpg)_2Ni$ and PcM moieties a similarity in lattice structures is not surprising. Oscillation photographs of the rather poor quality $NiPcI_{1.0}$ needle-like crystals so far obtained give a c axis dimension of 6.45 Å and indicate that c is parallel to the needle axis. These spectral and structural results together support the contention that iodine oxidation of PcM units can produce materials with nonintegral oxidation states.

Electrical conductivity measurements were performed on pressed pellets using a locally designed four-probe apparatus.[13] Representative plots of ln σ vs. $1/T$ are presented in Figure 2, which also presents the published powder and single-crystal data for $(quinolinium)(TCNQ)_2$,[14] one of the earliest known highly conducting TCNQ salts. The powder data could be fit to eq 3 where E_a is the activation energy for conductivity.

$$\sigma = \sigma_\infty e^{-E_a/kT} \qquad (3)$$

Values of E_a derived from a least-squares fit are given in Table I, along with ambient temperature conductivity values and data for the unoxidized phthalocyanines. For all values of x the

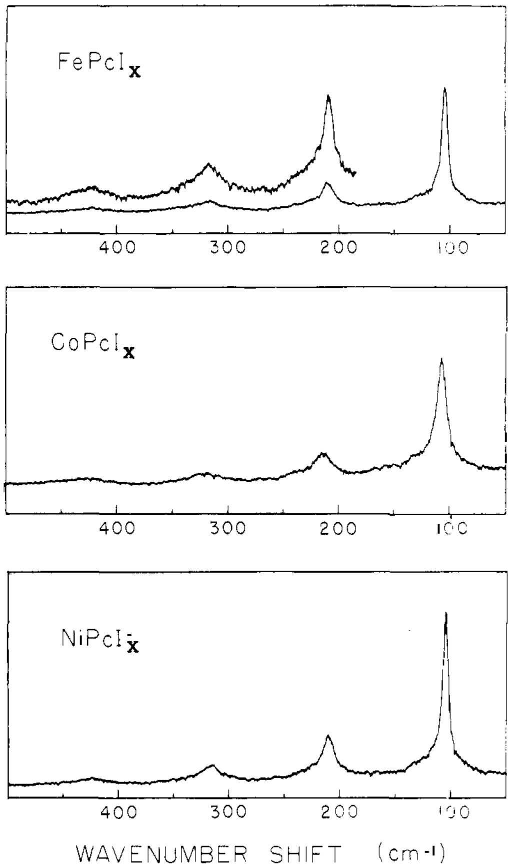


Figure 1. Resonance Raman spectra of partially oxidized phthalocyanines with Ar$^+$ 5145 Å excitation. Stoichiometries are: Fe, x = 1.9; Co, x = 1.0; Ni, x = 1.0.

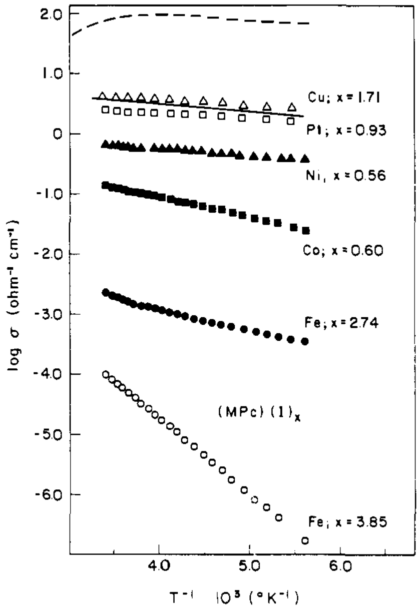


Figure 2. Log of the powder conductivity for $(MPc)(I)_x$ plotted vs. inverse temperature. M and x are indicated in figure. Also included are the powder (—), ref 14a, and single-crystal (- - -), ref 14b, conductivity data for $(quinolinium)(TCNQ)_2$.

conductivities are dramatically increased by iodine oxidation, but in particular for $x < 3$, the increases are roughly nine to ten order of magnitude! In these cases the activation energies are nearly zero—roughly 50-fold less than the parent complex. As shown in Figure 1 and Table I, the pressed pellet conductivites of $(CuPc)(I)_{1.71}$ and $(PtPc)(I)_{0.93}$ are comparable to those of $(Qn)(TCNQ)_2$, with even lower activation energies for conduction. These conductivity results, along with the structural and magnetic[15] data, lead us to suggest that the partial iodine oxidation of phthalocyanines indeed produces "molecular metals": We anticipate that single-crystal conductivities will be much higher than the pressed pellet values as is true for $Qn(TCNQ)_2$ (Figure 2) and will be highly anisotropic and that near or above room temperature the activation energies will be vanishingly small in the stacking direction.

In this context it is interesting to note that near room temperature the single-crystal conductivity of Krogmann's salt $K_2Pt(CN)_4Br_{0.30}\cdot 3H_2O$[1,16] is roughly comparable to that of single-crystal $Qn(TCNQ)_2$, and larger than the powder conductivity of either the latter material or of the oxidized phthalocyanines. Nevertheless, below $T \sim 90$ K, we find that for example, the powder conductivities of $(CuPc)(I)_{1.71}$ and $(PtPc)(I)_{0.93}$ exceed the single-crystal values for Krogmann's salt when conduction is parallel to the chain axis.

In these preliminary powder measurements on $(MPc)(I)_x$ materials with a limited number of compositions, no dramatic dependence of the conductivity on composition has been observed for M = Ni, Co, Cu, or Zn and for $0.5 \lesssim x \lesssim 3.0$. As can be seen in Table I and Figure 2, the situation is not the same for M = Fe. At this time it is not possible to rigorously differentiate between situations where x is continuously variable between 0 and 3, or within portions of that range (by virtue of filling the channels in the lattice with variable amounts of I_3^-), and those where mixtures containing discrete values or ranges of x are present.[17] Nevertheless, our preparation of a range of highly conducting compositions appears to contrast with the single, isolated stoichiometries of the Krogmann salts.

Furthermore, theoretical considerations based on the Hubbard model in one-dimension do suggest that for a substantial range of hole concentrations, σ should vary only modestly.[18] Whatever the nature of the charge transport process (hopping, etc.), the high conductivity which we observe for oxidized PcH_2 shows that the conductive path in these new materials does not depend exclusively on metal-metal overlap, and that π-π and perhaps d-π overlap is important; indeed the "hole" produced by partial oxidation may either be metal- or ligand-centered, and this may vary with M.[6,19] Further experiments to test these ideas are in progress.

The results of this study demonstrate that iodine oxidation is a viable synthetic route to highly conducting mixed valence materials, and that partially oxidized phthalocyanines represent a broad new class of "molecular metals". They also constitute the first highly conducting system involving a number of first-row transition metals.

Note Added in Proof. High quality single crystals of $MPcI_x$ have now been obtained. The x-ray crystal structure of NiPcI is currently being refined, in collaboration with R. Scaringe and J. A. Ibers, and these results confirm our structure discussion. In addition, preliminary measurements show that c-axis conductivities are indeed considerably higher than powder values.

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References and Notes

(1) (a) J. S. Miller and A. J. Epstein, *Prog. Inorg. Chem.*, **20,** 1 (1976); (b) H. J. Keller, Ed., "Low-Dimensional Cooperative Phenomena", Plenum Press, New York, N.Y., 1975; (c) L. V. Interrante, Ed., "Extended Interactions between Metal Ions in Transition Metal Complexes", Vol. 5, American Chemical Society Symposium Series, Washington, D.C., 1974; (d) H. R. Zeller, *Adv. Solid State Phys.*, **13,** 31 (1973); (e) E. B. Yagubskii and K. L. Khidekel, *Russ. Chem. Rev.*, **41,** 1011 (1972); (f) T. W. Thomas and A. E. Underhill, *Chem. Soc. Rev.*, 1, 99 (1972).

(2) See N. Mott, "Metal-Insulator Transitions", Barnes and Noble Books, New York, N.Y., 1974.

(3) (a) A. Gleizes, T. J. Marks, and J. A. Ibers, *J. Am. Chem. Soc.*, **97,** 3545 (1975); (b) T. J. Marks, D. F. Webster, S. L. Ruby, and S. Schultz, *J. Chem. Soc., Chem. Commun.*, 444 (1976); (c) M. A. Cowie, A. Gleizes, G. W. Grynkewich, D. F. Webster, S. L. Ruby, B. Zabransky, T. J. Marks, and J. A. Ibers, manuscript in preparation (dpg = diphenylglyoximato); (d) C. S. Schramm and B. M. Hoffman, manuscript in preparation.

(4) (a) H. J. Keller and K. Seibold, *J. Am. Chem. Soc.*, **93,** 1309 (1971); (b) H. Endres, H. J. Keller, M. Megnamise-Belombe', W. Moroni, and D. Nöthe, *Inorg. Nucl. Chem. Lett.*, **10,** 467 (1974); (c) H. Endres, H. J. Keller, and R. Lehmann, *ibid.*, **11,** 769 (1975).

(5) A. I, Popov, *MTP Int. Rev. Sci., Inorg. Chem., Series One*, **3,** Chapter 2 (1972).

(6) (a) For previous phthalocyanine work with chlorine- and bromine-containing oxidants, see J. F. Myers, G. W. R. Canham, and A. B. P. Lever, *Inorg. Chem.*, **14,** 461 (1975); (b) $FePcI_2$ and CoPcI have been noted in a review article: R. Taube, *Pure Appl. Chem.*, **38,** 427 (1974).

(7) (a) All compounds were analyzed for C, H, N, and I. The reported percentage iodine was identical within experimental error to that determined by weight loss upon heating. The reported C:H:N ratios were those expected for phthalocyanines. (b) An analogous observation was made in the case of $(dpg)_2NiI$: A. S. Foust and R. H. Soderberg, *J. Am. Chem. Soc.*, **89,** 5507 (1967).

(8) (a) W. Kiefer, *Appl. Spectrosc.*, **28,** 115 (1974); (b) W. Kiefer and H. J. Bernstein, *Chem. Phys. Lett.*, **16,** 5 (1972); (c) K. Kaya, N. Mikami, Y. Udagawa, and M. Ito, *ibid.*, **16,** 151 (1972).

(9) (a) T. J. Marks, D. R. Stojakovic, and D. F. Webster, manuscript in preparation; (b) F. H. Herbstein and M. Kapon, *Nature (London), Phys. Sci.*, **239,** 153 (1972); (c) E. E. Havinga, K. H. Boswijk, and E. H. Wiebenga, *Acta Crystallogr.*, 7, 487 (1954); (d) E. E. Havinga and E. H. Wiebenga, *ibid.*, **11,** 733 (1958).

(10) (a) Unpublished observations with S. L. Ruby and S. Schultz at Argonne National Laboratory. (b) E.g., for $NiPc^{129}I_{2.16}$, IS = 1.34 and 0.27 mm/s vs. ZnTe; $e^2qQ = -1667$ and -862 MHz (^{129}I).(c) Other $MPcI_x$ are similarly being studied.

(11) (a) G. M. Bancroft and R. H. Platt, *Adv. Inorg. Chem. Radiochem.*, **15,** 187 (1972); (b) M. J. Potasek, P. G. Debrunner, W. H. Morrison, Jr., and D. N. Hendrickson, *J. Chem. Phys.*, **60,** 2203 (1974); (c) S. Bukshpan, C. Goldstein, R. Sonnino, L. May, and M. Pasternak, *ibid.*, **62,** 2606 (1975).

(12) (a) H. Endres, H. J. Keller, W. Moroni, and J. Weiss, *Acta Crystallogr., Sect. B*, **31,** 2357 (1975); (b) C. K. Johnson and C. R. Watson, Jr., *J. Chem. Phys.*, **64,** 2271 (1976); (c) S. J. LaPlaca, P. W. R. Corfield, R. Thomas, and B. A. Scott, *Solid State Commun.*, **17,** 635 (1975); (d) K. Huml, *Acta Crystallogr.*, **22,** 29 (1967); (e) K. Simon, J. A. Ibers, and T. J. Marks, unpublished results.

(13) (a) D. Cahen, J. R. Hahn, and J. R. Anderson, *Rev. Sci. Instrum.*, **44,** 1567 (1973); (b) L. J. Van der Pauw, *Philips Res. Rep.*, **13,** 1 (1958); *Philips Tech. Rev.*, **20,** 320 (1958); (c) C. S. Schramm, J. R. Anderson, and B. M. Hoffman, to be submitted.

(14) (a) W. J. Siemons, P. E. Bierstedt, and R. G. Kepler, *J. Chem. Phys.*, **39,** 3523 (1963); TCNQ = 7,7,8,8-tetracyanoquinodimethane; Qn = quinolinium; (b) V. Walatka, Jr., and J. H. Perlstein, *Mol. Crystl. Liq. Cryst.*, **15,** 269 (1971).

(15) Magnetic susceptibility measurements by the Faraday method on $(NiPc)(I)_x$ for several values of $x < 3$, reveal relatively weak, temperature independent paramagnetism between 100 and 298 K, providing a further parallel between the oxidized phthalocyanines and the previously known highly conducting molecular solids.[1]

(16) H. R. Zeller and A. Beck, *J. Chem. Phys. Solids*, **35,** 77 (1974); σ (298 K) $\approx$ 300 ohm^{-} cm^{-1}; σ (90 K) $\approx$ 0.8 ohm^{-1} cm^{-1}.

(17) For $(PcFe)(I)_x$ ^{57}Fe Mössbauer spectroscopy can be used to explore the state of the iron atom, and such measurements, in progress in collaboration with Dr. K. Kim and Professor L. Schwartz, show that with this metal a mixture of phases does occur sometimes.

(18) Professor M. Ratner, private communication.

(19) Both powder and single crystal EPR measurements on $(NiPc)(I)_x$ are in fact consistent with a ligand-centered oxidation ($g \sim 2.0$).

(20) Fellow of the Alfred P. Sloan Foundation; Camille and Henry Dreyfus Foundation Teacher–Scholar.

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