matic rate difference, greater than 10^{16}, is primarily a consequence of the large differences in reaction free energies. The electron-transfer step for the thermal reaction is energetically unfavorable by $\Delta G° = 1$–2 kcal/mol;[45] photoexcitation increases reactant energies by 50–100 kcal/mol, which substantially diminishes nuclear activation barriers. Additionally, sufficient excess energy exists to form Co(II) in its $t_{2g}^6 e_g$ excited electronic state, thereby removing potential ligand field spin restrictions on Co(II) reduction, and charge transfer to olefin π^* orbitals in the photoexcited state may act to incrrease orbital overlap of the transferred electron with the acceptor.

Thermal electron transfer does occur in the A_5Ru^{II}-4-vinyl-pyridine–Cu^I ion,[56] but not when π conjugation in the bridging ligand is disrupted by introduction of intervening methylene groups.[17] Unlike the Co^{III}–Cu^I photochemistry, this behavior is conventional in the sense that long-range transfer is identified with the presence of π-delocalized structures. Because the driving forces for thermal reactions with A_5Co^{III} and A_5Ru^{III} oxidants are comparable, the reactivity differences are a clear manifestation of orbital symmetry requirements for electron transfer.[1]

Thermodynamics of Molecular Metal Formation: Metallophthalocyanine and Tetrathiafulvalene Iodides

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Abstract: Solid-state electrochemical cells are employed to investigate the formation reaction of several iodinated materials, DI_x, where D is a metallophthalocyanine (M(Pc), M = H_2, Ni, Co, Cu) or tetrathiafulvalene (TTF). I_2 and $[(CH_3)_4N]I_3$ cells were also studied as controls. The M(Pc)I constitute a set of isostructural and isoionic molecular conductors; in contrast, the $TTFI_x$ ($x = 0.7$, 2, 3) differ in structure, level of oxidation, and the state of the iodine. For none of the DI_x studied does the formation reaction of the parent D and molecular iodine have a free energy more favorable than −5.2 kcal/mol. This is so despite the highly favorable lattice stabilization energies, L, that are calculated from appropriate Born–Haber cycles: L ranges from −103 to −117 kcal/mol in the nonintegrally (partially) oxidized materials while $L = -164 \pm 5$ kcal/mol in the integrally oxidized $TTFI_3$. Individual contributions to L, namely the nonbonded, ionic, and mixed-valence, or carrier-delocalization, contributions, are also discussed. The first two of these are large and contribute in different proportions for the M(Pc)I and $(TTF)I_x$. The third, though small, can be of the same magnitude as or greater than the total free energy of formation.

The preparation and characterization of new highly conductive molecular crystals, the so-called molecular metals, has as yet been accompanied by only a limited understanding of the nature and strength of the interactions that govern the formation of such materials.[1] We report here the thermodynamics of crystal formation for two types of conductive molecular compounds, the iodide complexes of the metallophthalocyanines (M(Pc)I) and of tetrathiafulvalene ($TTFI_x$), and use the results to calculate the lattice energies of these materials.
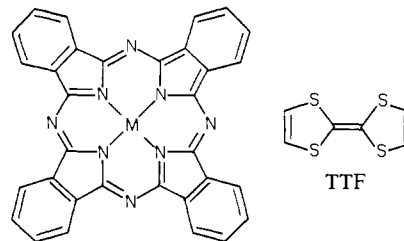
(1) (a) Metzger, R. M. *J. Chem. Phys.* **1977**, *66*, 2525–2533. (b) Torrance, J. B.; Silverman, B. D. *Phys. Rev. B: Solid State* **1977**, *15*, 788–801. (c) Aronson, S.; Mittelman, J. S. *J. Solid State Chem.* **1981**, *36*, 221–224. (d) Metzger, R. M. In "Crystal Cohesion and Confirmational Energies"; Metzger, R. M., Ed.; Springer-Verlag New York: New York, 1981.

M(Pc)   TTF

The reaction of Ni(Pc) with I_2 results in a highly conducting compound, Ni(Pc)I, which consists of metal-over-metal stacks of planar Ni(Pc) macrocycles surrounded by parallel chains of

triiodide ions.[2] The Ni(Pc) building blocks are in a nonintegral oxidation and the stoichiometric formula may be written formally as $[Ni(Pc)]^{0.33+}(I_3^-)_{1/3}$. The individual triiodide chains are ordered, but are disordered with respect to their neighbors. The other metallophthalocyanine iodides studied here, M = "H_2", Co, and Cu, are also good conductors. They have the same stoichiometry, M(Pc)I, contain triiodide chains, and although not yet fully characterized are quite clearly isostructural, as well as isoionic, with Ni(Pc)I.[2a,e,f]

The TTFI$_x$ exhibit a complex set of compositions, each containing oxidized or partially oxidized TTF$^{\rho+}$ ions ($0.65 \leq \rho \leq 1$) and I$_n^-$ counterions (n = 1 or 3).[3] The most iodine-rich phase, with x = 3, consists of dimers of (TTF)$^+$ ions dispersed between pairs of triiodide ions.[4] The composition $x \simeq 2$ is apparently represented by two phases that vary only in the degree of order–disorder.[5] One contains disordered stacks of partially oxidized TTF moieties and disordered chains of I$_3^-$ ions; in the other the TTF stacks are ordered. This intermediate composition is reported to be a quasi-line phase existing over the range $2.0 \leq x \leq 2.3$.[3a,5] The most conductive TTF iodide has the lowest reported iodine content, x = 0.71, and possesses ordered, modulated stacks of TTF$^{0.71+}$ ions but parallel chains of iodide, rather than triiodide, ions.[6] This composition also is reported to encompass a small composition range, $0.70 \leq x \leq 0.72$, with a linear relationship between x and the c dimension of the iodide sublattice. In addition, a disordered phase with x = 0.69 has been reported.[3b]

The most straightforward way to measure the thermodynamics of formation of an iodinated compound, DI$_x$, would be through use of electrochemical cells with DI$_x$ cathode, iodide electrolyte, and I$_2$ anode. However, there are no good low-temperature solid-state halide ionic conductors,[7] and an iodine solution electrolyte cannot be used because the equilibrium I$^-$ + I$_2$ = I$_3^-$ constitutes an electronic short circuit of the cell. We instead obtain the desired information from solid-state electrochemical cells that employ a silver anode, a solid Ag$^+$ electrolyte, and a DI$_x$ cathode, using equations presented in the Appendix. A series of such measurements has recently been employed to establish the phase diagram for the (phenothiazine)I$_x$.[8] Lattice energies of the DI$_x$ are then calculated through use of the appropriate Born–Haber cycles.

Since the structure of the TTFI$_x$ compounds, the level of oxidation (ionicity) of the TTF, and the state of the iodine (I$^-$ or I$_3^-$) all vary with the stoichiometry, a study of this set of organic conductors allows us to examine the energetics of such variations. On the other hand, the M(Pc)I (M = H$_2$, Cu, Co, Ni) constitute a set of macrocyclic conductors that are isostructural and isoionic, and this allows us to observe the influence of purely electronic changes in the parent complex. To the best of our knowledge, no such comparative thermodynamic study has been reported. We note that analogous measurements, involving voltammetry and potentiometry at electrolyte–electrode interfaces, have been re-

ported,[9] but the results cannot be readily interpreted in the manner presented here. The measured potentials reflect a reaction that involves one or more solution species, and their interpretation through use of a gas-phase Born–Haber cycle would require an estimate of the solvation energy of the solution species; these are rarely known and are difficult to estimate accurately.

Experimental Section

Metallophthalocyanines were purchased from Eastman Co. and purified by sublimation. The macrocycles and iodine were diffused together in an H-tube to form the metallophthalocyanine iodides of stoichiometry M(Pc)I, as confirmed by elemental analysis.[2b,e] TTF was purchased from Aldrich Co. and used as received. The various phases of the TTFI$_x$ were prepared by mixing stoichiometric quantities of TTF and I$_2$ in benzene. It is difficult to obtain elemental analyses of these materials that are sufficiently accurate to define a position within the small stoichiometric ranges of the quasi-line phases. The lowest phase iodide was therefore characterized by X-ray powder diffraction following ref 3b and was found to be TTFI$_{0.71}$. Different batches of materials with different x, all falling within the range $2.0 \leq x \leq 2.3$, were indeed prepared, as expected from ref 3. We show in the Appendix that for our purposes it is adequate to refer to these materials by a single composition and use x = 2. The electrolyte [(CH$_3$)$_4$N]$_2$Ag$_{13}$I$_{15}$ was prepared by mixing stoichiometric quantities of (CH$_3$)$_4$NI and AgI with a small amount of water and grinding this mixture in a mortar and pestle.[10] The resulting mixture was dried under vacuum and annealed at 125 °C for several days.

Cells were prepared by layering ~3 mg of cathode material, ~50 mg of electrolyte, and ~10 mg of anode material in a reinforced Fiberglas bushing ($^5/_{16}$ in. i.d.) and pressing under a pressure of about 2000 kg/cm^2. Typically, the pressed cells were approximately 1 mm thick, with the anode and cathode layers each being less than 10% of the total thickness. No observation suggested that the cell voltages are particularly sensitive to such details of preparation. However, cells were stored in a desiccator because high humidity was found to cause erratic cell voltages.

The complex electrolyte [(CH$_3$)$_4$N]$_2$Ag$_{13}$I$_{15}$ is a good Ag$^+$ ionic conductor at near-ambient temperatures but is able to react with I$_2$[11] and thus offers a potential complication in the thermodynamic interpretation of cell potentials. AgI is inert with respect to I$_2$ or I$_3^-$ but has a much lower Ag$^+$ mobility.[10] Since only open circuit voltages and the implied thermodynamics are being considered here, use of the two electrolytes provides a useful test of the validity of the measurements. Both electrolytes have very high ionic transference numbers (in excess of 0.999[10,11]) so that complications due to electronic conduction should be negligible.

Voltage measurements were made with a locally built high-impedance (~10^{12} Ω) electrometer. This ensures that an insignificant amount of current passes through the cell during a measurement so that mass-transfer polarization problems are minimized. Contact to the cells was made with a spring-loaded holder. For measurement of the temperature dependences of the voltages, the cells were wrapped with heating tape, thermally insulated, and then slowly warmed, ~7°/h. This procedure

Table I. Ag|Electrolyte|Cathode Cells[a]

| | $E°$, V | | |
cathode[b]	[(CH$_3$)$_4$N]$_2$Ag$_{13}$I$_{15}$ electrolyte]	AgI electrolyte	$(\partial E°/\partial T)_P$, V/K
I$_2$	0.678	0.687	1.5×10^{-4}
(CH$_3$)$_4$NI$_3$	0.660	0.662	
H$_2$(Pc)I	0.571	0.573	5.0×10^{-4}
Ni(Pc)I	0.592	0.596	5.0×10^{-4}
Co(Pc)I	0.571	0.562	3.1×10^{-4}
Cu(Pc)I	0.630	0.625	4.0×10^{-4}
TTFI$_{0.71}$[c]	0.572	0.569	4.6×10^{-4}
TTFI$_2$	0.621	0.625	5.8×10^{-4}
TTFI$_3$	0.632	0.630	4.8×10^{-4}

[a] T = 25 °C. Uncertainties: $E°$, ±0.002 V; $(\partial E°/\partial T)_P$, ±0.5 × 10^{-4} V/K. [b] As described in the text cathodes were prepared by mixing the listed DI$_x$ phase with the phase having the next lowest I composition. Voltages are independent of the ratio, except as noted. [c] Voltage not composition independent. Reported values are for cells without added TTF.

(2) (a) Hoffman, B. M.; Martinsen, J.; Pace, L. J.; Ibers, J. A. In "Extended Linear Chain Complexes"; Miller, J. S., Ed.; Plenum Press: New York, in press. (b) Peterson, J. L.; Schramm, C. S.; Stojakovic, D. R.; Hoffman, B. M.; Marks, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 286–288. (c) Schramm, C. S.; Stojakovic, D. R.; Hoffman, B. M.; Marks, T. J. *Science (Washington, D.C.)* **1978**, *200*, 47–48. (d) Schramm, C. S.; Scaringe, R. P.; Stojakovic, D. R.; Hoffman, B. M.; Ibers, J. A.; Marks, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 6702–6713. (e) Schramm, C. S. Ph.D. Thesis, Northwestern University, 1979. (f) Martinsen, J.; Euler, W. B.; Palmer, S.; Hoffman, B. M.; unpublished. (g) Ibers, J. A.; Pace, L. J.; Martinsen, J.; Hoffman, B. M. *Struct. Bonding (Berlin)* **1982**, *50*, 1–55. (h) Martinsen, J.; Greene, R. L.; Palmer, S. M.; Hoffman, B. M. *J. Am. Chem. Soc.*, submitted for publication.

(3) (a) Somoano, R. B.; Gupta, A.; Hadek, V.; Datta, T.; Jones, M.; Deck, R.; Hermann, A. M. *J. Chem. Phys.* **1975**, *63*, 4970–4976. (b) Scott, B. A.; La Placa, S. J.; Torrance, J. B.; Silverman, B. D.; Welber, B. *J. Am. Chem. Soc.* **1977**, *99*, 6631–6639.

(4) Teitelbaum, R. C.; Marks, T. J.; Johnson, C. K. *J. Am. Chem. Soc.* **1980**, *102*, 2986–2989.

(5) Johnson, G. K.; Watson, C. R.; Marmack, R. *J. Am. Cryst. Assoc. Meeting Abstr.* **1975**, *3*, 19.

(6) Johnson, C. K.; Watson, C. R. *J. Chem. Phys.* **1976**, *64*, 2271–2286.

(7) Mrgudich, J. N.; Louzos, D. V. In "The Primary Battery"; Heise, G. W., Cahoon, N. C., Eds.; Wiley: New York, 1971; Vol. 1, pp 373–432.

(8) Matsumoto, T.; Matsunaga, Y. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 648–653.

(9) (a) Jaeger, C. D.; Bard, A. J. *J. Am. Chem. Soc.* **1979**, *101*, 1690–1699. (b) Wallace, W. L.; Jaeger, C. D.; Bard, A. J. *Ibid.* **1979**, *101*, 4840–4843. (c) Jaeger, C. D.; Bard, A. J. *Ibid.* **1980**, *102*, 5435–5442.

(10) McKechnie, J. S.; Turner, L. D. S.; Vincent, C. A.; Lazzari, M.; Scrosati, B. *J. Chem. Educ.* **1978**, *55*, 418–422.

(11) Owens, B. B. *J. Electrochem. Soc.* **1970**, *117*, 1536–1539.

gave a convenient, accurate (±0.2 K), and reproducible method of temperature control. A copper–constantan thermocouple was placed in local proximity of the cell, and the cell voltage and thermocouple voltage were simultaneously measured, digitized by an Interactive Structures, Inc., AI13 A/D, and recorded by an Apple II Plus computer. Voltages were found to vary linearly with temperature over the range $20 \, °C \leq T \leq 40$ °C, and the slopes, $(\partial E°/\partial T)_p$, were obtained by a linear least-squares procedure. The reported room temperature voltages and slopes are the average of values obtained from between 5 and 15 independently prepared cells, with the typical number being ca. 7.

Results

Cells were prepared with two different electrolytes in order to validate a thermodynamic interpretation of the measured voltages. Table I gives the room temperature potentials, $E°$, and the temperature responses, $(\partial E°/\partial T)_p$, of cells constructed with I_2, $(CH_3)_4NI_3$, $TTFI_x$, and $M(Pc)I$ cathodes and each of the two electrolytes. With the exception of the I_2 cathode, there is no significant difference between the potentials of a cell with the AgI electrolyte cells and its partner with the complex electrolyte. Therefore, in none of these cases does adventitious reaction of the complex electrolyte occur, and the measured voltages may be viewed as thermodynamically well-defined quantities.

The I_2 cathode does give slightly different voltages with the two electrolytes. This is expected, however, for Owens has shown that the complex electrolytes have rich phase diagrams,[11] exhibiting multiple iodine stoichiometries. Thus, the difference between the potentials of $Ag|AgI|I_2$ cells and $Ag|[(CH_3)_4N]_2Ag_{13}I_{15}|I_2$ cells reflect the reaction of I_2 with the electrolyte to form a new phase at the cathode–electrolyte boundary. However, the voltage and slope of the thermodynamically well-defined $Ag|AgI|I_2$ cell are completely consistent with literature values.[12]

$((CH_3)_4N)I_3$. Cells of the form $Ag|electrolyte|(CH_3)_4NI_3$ were examined as a model study, and the results (Table I) demonstrate an effect of lattice stabilization energies in determining a cell voltage. Although the reduction potentials of I_2 and I_3^- differ by less than a millivolt in aqueous solution,[13] the voltage of this I_3^- cell is significantly lower than the I_2 cell. From the procedure outlined in the Appendix, the difference between the voltages of the $Ag||(CH_3)_4NI_3$ cell ($E_{I_3}°$) and the $Ag||I_2$ cell (E_{AgI}) gives the difference between the free energy of formation of the tetramethylammonium iodide and triiodide; from eq A7, $\Delta G°$-$((CH_3)_4NI_3) - \Delta G°((CH_3)_4NI)) = -52$ mV $= -1.2$ kcal/mol.

$M(Pc)I$. Cells of the form $Ag|electrolyte|M(Pc)I,M(Pc)$ were prepared with cathodes in which the amount of unoxidized parent compound varied from 0 to 20%. More extensive potential vs. composition studies were deemed unnecessary since the phase diagram for $x \leq 1$ is well established (see below). Each $M(Pc)I$ was found to be characterized by a cell voltage that is independent of cathode composition (Table I). This is completely consistent with the established phase diagram of the $Ni(Pc)I_x$, which consists of line phases at $x = 0$ and $x = 1$ (and $x \sim 3$),[2a–e] and with the conclusion that the other $M(Pc)I_x$ considered also exhibit only phases with these stoichiometries.[2f] Thus, the voltages, free energies, and entropies of the cells with $M(Pc)I,M(Pc)$ cathodes, $M =$ "H_2", Co, Ni, and Cu, are all to be interpreted in terms of the cell reaction

$$M(Pc)I + Ag \rightarrow M(Pc) + AgI \qquad (1)$$
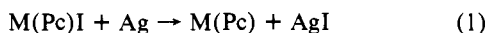
The temperature dependence of the cell voltage for each $M(Pc)I$ was linear from room temperature to about 40 °C (Figure 1), and the slopes of the E vs. T curves obtained by least-squares analysis are tabulated in Table I. The room temperature voltages give the standard free energy of formation of the $M(Pc)I$ (eq 1) through use of eq A3, and the standard entropies are obtained analogously from the temperature response. In addition, these two quantities have been used to calculate the standard enthalpy of formation. All three results are listed in Table II.
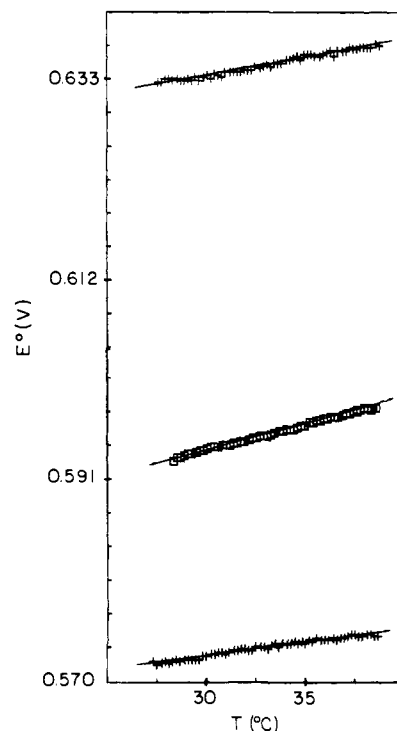
(12) Topol, L. E. *Inorg. Chem.* **1968**, *7*, 451–454.

(13) Desideri, P. G.; Lepri, L.; Meimler, D. In "Encyclopedia of Electrochemistry of the Elements"; Bard, A. J., Ed.; Marcel Dekker: New York, 1973; Vol. 1, pp 91–153.

Figure 1. Typical temperature responses of the voltage for cells with cathodes made from $TTFI_3$ (upper), $Ni(Pc)I$ (middle), and $Co(Pc)I$ (lower). The solid lines are obtained from linear least-squares fits.

Table II. Standard Free Energy and Entropy of the Iodination Reactions[a] (Eq A6)

$$((x_k - x_j)/2)I_2 + DI_{x_j} \rightarrow DI_{x_k}$$

D	x_j	x_k	$\Delta G°$, kcal/mol	$\Delta S°$, cal/K	$\Delta H°$, kcal/mol
$H_2(Pc)$	0	1.0	-2.6	-8.1	-5.0
$Ni(Pc)$	0	1.0	-2.1	-8.1	-4.5
$Co(Pc)$	0	1.0	-2.9	-3.7	-4.0
$Cu(Pc)$	0	1.0	-1.4	-5.8	-3.1
TTF	0	0.71	-1.9^b	-5.0^b	-3.4^b
	0.7	2	-2.0	-12.9	-5.8
	2	3	-1.3	-7.6	-3.6

[a] $T = 25$ °C. Uncertainties: $\Delta G°$, ±0.1 kcal/mol; $\Delta S°$, ±0.3 cal/K; $\Delta H°$, ±0.2 kcal/mol. [b] These values are approximations and not thermodynamically rigorous; they depend on the assumption discussed in the text.

The voltages and slopes of the several $Ag||M(Pc)I$ cells are similar but not identical, with $M =$ Cu cells having a noticeably higher voltage. For $Ni(Pc)I$, the partial oxidation to achieve the $(M(Pc))^{1/3+}$ formal valency is ligand based,[2] and the similar behavior of $Ni(Pc)I$ cells and the other $M(Pc)I$ cells suggests that the same is true in each case. This observation is of particular significance in regard to $Co(Pc)I$, since in solution the Co(II) → Co(III) oxidation is more favorable than the macrocycle oxidation by ~330 mV.[14]

Interestingly, all the cells showed the tabulated voltage promptly upon construction, except for those prepared without added $M(Pc)$, which showed a slow rise (hours–days) to that value. This we interpret to indicate that the cells with added $M(Pc)$ are in equilibrium and exhibit the thermodynamic voltage characteristic of reaction 1 but that the thermodynamic voltage of the other cells is not achieved until small quantities of $M(Pc)$ are generated at the electrolyte–cathode interface.

$TTFI_x$. Three series of cells of the form $Ag||TTFI_{x_k},TTFI_{x_j}$ were prepared with cathodes containing various proportions of material representing adjacent phases: $x_k = 0.71$, $x_j = 0$; $x_k = 2$, $x_j = 0.71$; $x_k = 3$, $x_j = 2$. Cells with $TTFI_{0.71}$,TTF cathodes

(14) Wolberg, A.; Manassen, J. *J. Am. Chem. Soc.* **1970**, *92*, 2982–2991.

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J. Am. Chem. Soc., Vol. 104, No. 22, 1982 5969
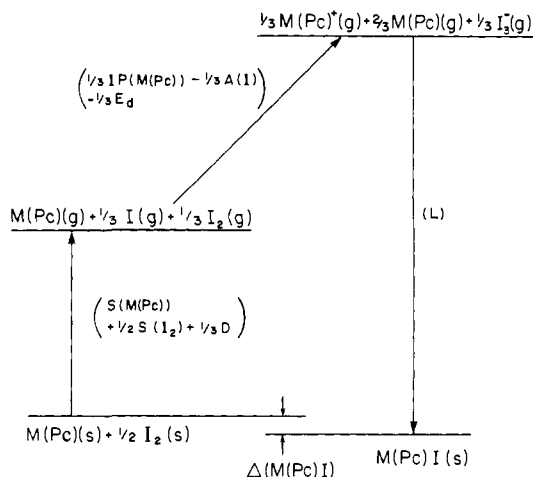
Figure 2. Born–Haber cycle for the reaction $M(Pc)I(s) + \frac{1}{2}I_2(s) \rightarrow M(Pc)I(s)$. The quantities in the cycle are defined in Table III. Vertical distances are approximately to scale when the cycle is defined for enthalpy.

were prepared with from 0% to as much as 20% by weight of neutral TTF. Cells with $TTFI_2$, $TTFI_{0.71}$ cathodes were prepared with the ratio of phases ranging from 1/3 to 3/1. Cells with $TTFI_3$, $TTFI_2$ cathodes contained up to 75% of the lower iodine phase. In addition, cells were prepared with cathodes containing the pure $TTFI_x$ phases, as isolated.

In each of the three series of cells with cathodes containing mixtures of phases, the voltages observed were obtained promptly and were independent of electrolyte; this we interpret as indicating equilibrium conditions obtain. Within the two series $TTFI_3$, $TTFI_2$ and $TTFI_2$, $TTFI_{0.71}$ the voltages are invariant with respect to cathode composition, a result consistent with the reported absence of intervening $TTFI_x$ phases and with the thermodynamic validity of the voltages and their temperature variations. Cell voltages and their temperature responses (Figure 1) are listed in Table I. The standard free energy change for reaction 2, denoted

$$TTFI_2 + 0.5I_2 \rightarrow TTFI_3 \qquad (2)$$

ΔG° (3←2), was calculated according to eq A5 and A6, and the entropy change was calculated analogously from the temperature response of the voltage. These quantities are presented in Table II, along with the derived enthalpies. The free energy change ΔG (2←0.71) and the other thermodynamic changes that accompany reaction 3 are likewise given in Table II.

$$TTFI_{0.71} + 0.65I_2 \rightarrow TTFI_2 \qquad (3)$$
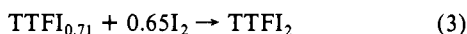
The voltage of cells made with $TTFI_{0.71}$, TTF cathodes is not independent of composition and decreases with increasing amounts of TTF. This can be interpreted in one of two ways. If TTF and the iodinated material are mutually soluble, then the cell voltage would vary in this fashion. The other possibility is that there exists another phase (or several) between TTF and $TTFI_{0.71}$. In this case the two components are not simply connected chemically so that the measured voltage is not a simple thermodynamic quantity. Scott et al. have reported a disordered phase at $x = 0.69$.[3b] If this phase also mainly contains I^- counterions, as they believe, we would not expect it to be sufficiently different from the $x = 0.71$ material to cause the effects observed, and these results would thus indicate the occurrence of as yet unobserved, iodine-poor phase(s). If the $x = 0.69$ disordered phase has a polyiodide as counterion, it could well be (one of) the phase(s) contributing to the composition-dependent voltage.

Thermodynamic Analysis. M(Pc)I. The measured free energy and entropy of formation of the M(Pc)I, M = H_2, Ni, Co, Cu, have been used to calculate the corresponding enthalpies, and all three quantities are listed in Table II. They can be analyzed further by employing the Born–Haber cycle of Figure 2, where the resultant for the formation of M(Pc)I is written as $\Delta(M(Pc)I)$ because the cycle is, of course, appropriate for any thermodynamic

Table III. Reference Thermodynamic Data

compd	sublimation enthalpy, kcal/mol	ionization potential, kcal/mol
TTF	22.0^a	158.4^b
$H_2(Pc)$	51.1^c	170.2^d
Ni(Pc)	56.6^c	172.2^d
Co(Pc)	60.0^c	172.5^d
Cu(Pc)	59.5^c	170.4^d
I_2	14.9^e	
dissociation energy of $I_2(g)$ $\frac{1}{2}I_2(g) \rightarrow I(g)$	$D = 18.1$ kcal/mol^e	
electron affinity of $I(g)$ $I(g) + e^- \rightarrow I^-(g)$	$A = 72.1$ kcal/mol^e	
dissociation energy of $I_3^-(g)$ $I_3^-(g) \rightarrow I_2(g) + I^-(g)$	$E_d = -2.1$ kcal/mol^f	

^{a} Sandman, D. J.; Epstein, A. J.; Chickos, J. S.; Ketchum, J.; Fu, J. S.; Scheraga, H. A. *J. Chem. Phys.* 1979, *70*, 305-313. ^{b} Gleiter, R.; Schmidt, E.; Cowan, D. O.; Ferraris, J. P. *J. Electron Spectrosc. Rel Phenom..* 1973, *2*, 207-210. ^{c} MacKay, A. G. *Aust. J. Chem.* 1973, *26*, 2425-2433. ^{d} Eley, E. E.; Hazeldine, D. J.; Palmer, T. F. *J. Chem. Soc., Faraday Trans. 2* 1973, *69*, 1808-1814. ^{e} Sharpe, A. G. In "Halogen Chemistry"; Gutmann, V., Ed.; Academic Press: London, 1967; Vol. I, pp 1-40. ^{f} Weibenga, E. H.; Kracht, D. *Inorg. Chem.* 1969, *8*, 738-746.

Table IV. Lattice Enthalpy of DI_x

material	lattice enthalpy,^{a} kcal/mol	sublimation enthalpy of D,^{b} kcal/mol
$H_2(Pc)I$	-103	51.1
Ni(Pc)I	-109	56.6
Cu(Pc)I	-110	59.5
Co(Pc)I	-112	60.0
$TTFI_{0.71}$	-109^c	
$TTFI_2$	-117^c	22.0
$TTFI_3$	-164^c	

^{a} Uncertainty, ±5 kcal/mol. ^{b} Sources listed in Table III. ^{c} Differences between values for the $TTFI_x$ are rigorously valid, but the values themselves are dependent on assumptions described in the text.

variable. The available reference thermodynamic quantities defined by these equations, for example the sublimation enthalpies, ionization potentials, and electron affinities, are listed in Table III along with their sources. Ionization potentials (IP) and electron affinities (A) are satisfactorily viewed as changes in internal energy that closely correspond to enthalpies. The sublimation free energy of I_2 is also available, but only sublimation enthalpies are available for TTF and the M(Pc). If necessary, such enthalpies could be related to free energies by statistical mechanical entropy calculations.

The quantity L in Figure 2 represents the lattice stabilization of an M(Pc)I and is a chief goal of this study. It is useful to partition L further,[1d] into a mixed-valence contribution, E_{mv}, and the normal lattice energy of a molecular crystal, LE, arising from ionic (Madelung), LM, and nonbonded (van der Waals, etc.), LN, terms: $L = (E_{mv} + LE)$, $LE = LM + LN$. The term LE is like the IP and A in being an energy that corresponds closely to an enthalpy. Therefore, we have used the appropriate quantities in Tables II and III to calculate the lattice enthalpies of formation from the enthalpy Born–Haber cycle, Figure 2. The results for the M(Pc)I complexes are tabulated along with the sublimation enthalpy of the unoxidized macrocycle (Table IV). Although precise calculations of Madelung energies, etc.,[1d] are necessary for further detailed analysis, some useful insights can be obtained without them. The negative of the sublimation enthalpy measures the stabilization of the unoxidized solid by nonbonded interactions between the M(Pc). The strength of these interactions will not be appreciably diminished by partial oxidation, and their contribution is likely to be similar in the stacked structure of the iodinated materials; different M(Pc) polymorphs do not appear

to differ appreciably in energy,[15] and the L(M(Pc)I) do change in parallel with $S(M(Pc))$ (Table IV). Along with similar considerations regarding iodine, this suggests that forces not associated with oxidation stabilize the M(Pc)I lattice by an amount LN $\sim$ $-(S(M(Pc)) + \frac{1}{2}S(I_2)) \sim -65$ kcal/mol, which is more than half of L.

The mixed-valence term may be viewed as the electronic (or vibronic, if electron–phonon coupling is considered) energy of the conduction electrons. Both Ni(Pc)I and H$_2$(Pc)I are well described as "molecular metals", each with a high room temperature conductivity having a metal-like temperature dependence and with a low, nearly temperature-independent paramagnetic susceptibility.[2] In these cases one can approximate E_{mv} by considering the mixed-valence M(Pc) stack in terms of a one-dimensional tight-binding band with single-particle energies $\epsilon(k) = 2t \cos(kc)$ and Fermi wavevector, k_f, and Fermi energy, ϵ_f, determined by the degree of partial oxidation ($\rho = \frac{1}{3}$): $k_f = \pm((2 - \rho)\pi)/2c$. In this approximation E_{mv} is essentially the difference in energy between a filled and partially filled band:

$$
\begin{aligned}
E_{mv} &= -2 \int_{-2|t|}^{2|t|} \epsilon \, (1 - f(\epsilon - \epsilon_f))N(\epsilon) \, d\epsilon \\
&\simeq -2 \int_{\epsilon_f}^{2|t|} \epsilon N(\epsilon) \, d\epsilon \\
&\simeq -2|t| \qquad\qquad\qquad\qquad (4)
\end{aligned}
$$

where $N(\epsilon)$ is the one-dimensional density of states[2a] and the Fermi function has been approximated by its low-temperature value: $f(x) = 0, x > 0; f(x) = 1, x < 0$. The measured static susceptibilities of H$_2$(Pc)I and Ni(Pc)I each give $t \simeq 0.1$ eV, and thus E_{mv} might be as large as -5 kcal/mol, roughly twice the net free energy of formation (Table II). The mixed-valence term clearly does not make a large fractional contribution to the crystal energy, even for a good molecular metal, but because it can be bigger than the net free energy of formation of the solids (Table I), it can nevertheless play a significant or even decisive role in stabilizing the mixed-valence solid.

TTFI$_x$. The measurements reported in Table I determine the free energy differences $\Delta G^\circ(3 \leftarrow 2)$ and $\Delta G^\circ(2 \leftarrow 0.71)$ and the other thermodynamic quantities that accompany reactions 2 and 3 (Table II). Because the voltage for cells with TTFI$_{0.71}$,TTF cathodes is composition dependent, the free energy of formation for the $x = 0.71$ phase is not rigorously determined, and the same is therefore true for the free energies for individual higher phases (see Appendix). However, if we make the reasonable assumption that the voltage of the TTFI$_{0.71}$ cells without added TTF (Table I) approximates the energetics for $x = 0.71$ (eq A1), then the thermodynamics for this phase are given by the entries in Table II. Furthermore, the thermodynamics for the formation of the more highly iodinated phase can be obtained by adding the values for the individual steps (e.g., $\Delta G^\circ(\text{TTFI}_3) \simeq (-1.9) + (-2.0) + (-1.3) = -5.2$ kcal/mol). The formation reactions, TTF + $(x/2)$I$_2$ $\rightarrow$ TTFI$_x$, can be described by a Born–Haber cycle analogous to Figure 2. For the phases $x = 2$ and $x = 3$, the only changes to Figure 2 are the coefficients determined by the amount of charge transfer. Also, for $x = 0.71$ the iodine is in the form of iodide rather than triiodide, and the term E_d does not contribute. The reference data of Table III were used to estimate the lattice enthalpies (L) for the individual compounds, and these are given in Table IV.

The estimated lattice stabilization energies, L, for the mixed-valence $x = 2$ and $x = 0.71$ TTFI$_x$ stoichiometries are similar to those of the M(Pc)I, but that for $x = 3$ is much larger (Table III). Following the discussion given above, for a compound DI$_x$ the forces not associated with charge transfer (nonbonded interactions) should contribute to L roughly the amount LN $\sim$ $-(S(D) + (x/2)S(I_2))$. Since $S(\text{TTF}) < \frac{2}{5}S(\text{M(Pc)})$ (Table III), this term is much smaller for the TTFI$_x$. Susceptibility measurements indicate that E_{mv} for TTFI$_{0.71}$ is ~ -3 kcal/mol[16] (eq

4), small but again comparable to the free energy of formation. The L for the TTFI$_x$ is thus dominated by the ionic term, LM. Torrance and Silverman[1b] considered the ionic Madelung energy plus the band energy for TTFBr$_{0.76}$ and obtained a value of -104 kcal/mol. This is comparable to, but larger than, the value of roughly -80 kcal/mol we would estimate for TTFI$_{0.71}$. The level of agreement is encouraging, considering the slightly different stoichiometries, the slightly larger unit cell for the iodide, the increased polarizability of iodide vs. bromide, and the crudeness of the two estimates.

The lattice energy of the integrally oxidized, nonconducting, TTFI$_3$ is more favorable by ~ 50 kcal/mol (Table IV). The difference is thermodynamically rigorous and independent of the assumption regarding the energetics for $x = 0.71$. The discussion of nonbonded contributions indicates that this difference is primarily of electrostatic origin. TTFI$_3$ exhibits a structure of alternating $[(\text{TTF})_2]^{2+}$ and I$_3^-$ ions rather than the extended segregated chains observed in the lower I phases. The absence of TTF stacks and the accompanying 50 kcal more favorable stabilization energy presumably results in large part because of the enhanced Madelung stabilization by the higher charge densities of the fully oxidized $x = 3$ compound but may also reflect the absence of a mixed-valence term to help stabilize a stacked structure.

Conclusions

All the materials in this study have very small net free energies of formation, with lattice energies just slightly overbalancing the gas-phase ion creation energies. This indicates that a subtle balance of several large contributions controls the formation of these molecular metals and that no one contribution can be identified as the critical driving force for the formation reaction. Nonbonded forces are more important and ionic less for the M(Pc)I than for the mixed-valence TTF iodides, both features being understandable in terms of the larger size of the conjugated M(Pc) aromatic system. The mixed-valence state is necessary for the observed high electrical conductivity,[2a] and these results show that interactions associated with this state indeed can contribute in an energetically significant way to the formation of the highly conducting molecular solid.

Appendix. Determination of Thermodynamic Parameters

Consider the compound DI$_{x_1}$, corresponding to the phase with minimum value of x. A cell of the form $(\text{Ag}|\text{AgI}|\text{DI}_{x_1},\text{D})$ will give a voltage, E_1°, corresponding to the reaction

$$x_1\text{Ag} + \text{DI}_{x_1} \rightarrow x_1\text{AgI} + \text{D} \qquad (A1)$$
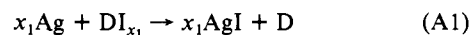
with standard free energy, $\Delta G^\circ(1) = -x_1FE_1^\circ$; the standard entropy is obtained from the temperature dependence of E_1°, $\Delta S^\circ(1) = x_1F(\partial E_1^\circ/\partial T)_p$. The free energy for the reaction forming DI$_{x_1}$ from its components

$$(x_1/2)\text{I}_2 + \text{D} \rightarrow \text{DI}_{x_1} \qquad (A2)$$
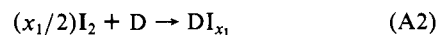
is simply obtained from E_1° and the potential for the Ag|AgI|I$_2$ cell, E_{AgI}°

$$\Delta G(\text{DI}_{x_1}) = -x_1F(E_{\text{AgI}}^\circ - E_1^\circ) \qquad (A3)$$

and the entropy is obtained similarly, from the difference in temperature derivatives. These equations are appropriate for analyzing the voltages of cells with M(Pc)I as cathode material,

(15) Lever, A. B. P. In "Advances in Inorganic Chemistry and Radiochemistry"; Emeleus, H. J.; Sharpe, A. G., Eds.; Academic Press: New York, 1965; Vol. 7, pp 28–114.

(16) Wudl, F.; Schafer, D. E.; Walsh, W. M., Jr.; Rupp, L. W.; DiSalvo, F. J.; Waszczak, J. V.; Kaplan, M. L.; Thomas, G. A. *J. Chem. Phys.* **1977**, *66*, 377–385.

since this composition represents the iodinated phase with smallest value of x (ref 2 and see below), and similarly for the $TTFI_x$ phase of lowest iodine content.

We are also interested in the energetics of the formation of more highly iodinated $TTFI_x$ phases, according to the generalized reaction
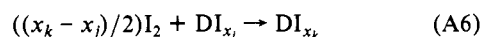
$$D + (x_i/2)I_2 \rightarrow DI_{x_i} \qquad (A4)$$
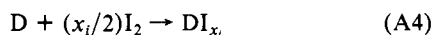
where $i > 1$. If a cathode is prepared from a mixture of two adjacent line phases DI_{x_j} and DI_{x_k}, $x_k > x_j$, then the cell with silver anode will give a voltage $\delta E°(k,j)$ corresponding to

$$(x_k - x_j)Ag + DI_{x_k} \rightarrow (x_k - x_j)AgI + DI_{x_j} \qquad (A5)$$
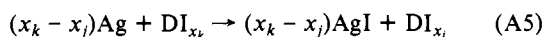
$$E = \delta E°(k,j)$$

and the free energy for the reaction

$$((x_k - x_j)/2)I_2 + DI_{x_j} \rightarrow DI_{x_k} \qquad (A6)$$

$$E = E_{AgI}° - \delta E°(k,j)$$

is simply the difference in formation free energies of DI_{x_j} and DI_{x_k}:

$$\Delta G(DI_{x_k}) - \Delta G(DI_{x_j}) = (x_j - x_k)F(E_{AgI}° - \delta E°(k,j)) \qquad (A7)$$

Thus, the free energy of formation for any phase of interest can be calculated if the free energies are known for the reaction of

eq A2 and for all transformations between adjacent line phases with lower I content, according to eq A6.

The $TTFI_x$ phase with $x = 2.0$–2.3 is not fully treated in the above analysis because it is not a true line phase and because of the observation of two structural modifications within this phase.[5] Then, to be rigorous, we should treat each point within the phase range independently. Also, the composition-independent voltage of cells with this as the lower iodine phase means that the last entry in Table II should have $x_j = 2.3$. However, the composition range for this quasi-line phase is very narrow, the two reported structures are quite similar, and most important, our experiments indicate that there is a negligible free energy change across the composition range: cells prepared from independent batches of "$TTFI_2$" having slightly different stoichiometries showed no discernible differences. Therefore, we treat this phase as a single composition, taking $x = 2$. This treatment is supported by the binding energy calculations done by Torrance and Silverman[1b] for $TTFBr_x$, $x = 0.71$–0.76. They found less than 0.25% change in the binding energy over the observed phase range. Both $TTFBr_x$, $x = 0.71$–0.76, and $TTFI_x$, $x = 2.0$–2.3 (or $x = 0.70$–0.72), have segregated stacks and about the same ionicity so that, qualitatively at least, we would expect the binding energy to behave similarly in both materials.

Crystal Structure of Tetrapropylammonium Fluoride Containing Precursor to Fluoride Silicalite

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Abstract: A precursor to fluoride silicalite was crystallized from a hydrothermal system containing silica, tetrapropylammonium ion (TPA⁺), and fluoride (F⁻). Single-crystal X-ray diffraction data for a twinned crystal ($180 \times 50 \times 50$ μm) of the precursor were refined in space group *Pnma* ($a = 20.044$ (2), $b = 19.918$ (4), and $c = 13.395$ (2) Å). The a axis of one twin component is parallel with the b axis of the other. Combined X-ray intensities (hkl and khl) were separated in a least-squares refinement. The silica framework has the same topology as that of silicalite and ZSM-5 zeolite. A weak negative correlation between the secant of angle (Si–O–Si) and Si–O is consistent with molecular-orbital models. The TPAF has similar geometry to tetrapropylammonium bromide and lies at the intersection of the 10-ring channels of the framework in a position consistent with a template mechanism of crystallization. The end carbon atoms of propyl groups lie 2.7 and 3.1 Å away from the end carbon atoms of adjacent propyl groups, and there is insufficient room for replacement of propyl by *n*-butyl. Oblique optical extinction and slight anomalies in high-angle X-ray diffractions indicate monoclinic symmetry, but the sharpness of X-ray powder diffractions limits angular deviations to less than 0.1° from orthogonal geometry. Slight collapse of the framework and positional disorder of the TPAF may be responsible.

Fluoride silicalite is a new microporous silica polymorph,[2] similar in some properties to silicalite,[3] and the hydrophobic and organophilic nature of these materials may prove commercially important for the removal of organic compounds from wastewater. The framework linkage of silicalite[3] is topologically the same as that of synthetic high-silica zeolite ZSM-5,[4,5] a shape-selective catalyst[5–8] capable of converting methanol into water and hydrocarbons, useful in internal-combustion engines.

The precursor of fluoride silicalite[2] crystallizes from a hydrothermal system containing silica, tetrapropylammonium (TPA⁺), and fluoride (F⁻) ions, and the ideal chemical composition is $TPAF \cdot Si_{24}O_{48}$. Because of the suggestion[3,9–11] that quaternary

ammonium cations can act as templates around which tetrahedral frameworks assemble during crystallization, the crystal structure

(1) Present address: Department of Earth Sciences, Cambridge University, Cambridge, England CB2 3EQ.
(2) Flanigen, E. M.; Patton, R. L. U.S. Patent NM4073865, 1978.
(3) Flanigen, E. M.; Bennett, J. M.; Grose, R. W.; Cohen, J. P.; Patton, R. L.; Kirchner, R. L.; Smith, J. V. *Nature (London)* **1978**, *271*, 512–516.
(4) Argauer, R. J.; Landolt, G. R. U.S. Patent NM3702886, 1972.
(5) Kokotailo, G. T.; Lawton, S. L.; Olson, D. H.; Meier, W. M. *Nature (London)* **1978**, *272*, 437–438.
(6) Kokotailo, G. T.; Meier, W. M. *Spec. Publ.–Chem. Soc.* **1980**, *33*, 133–139.
(7) Meisel, S. L.; McCullough, J. P.; Lechthaler, C. H.; Weisz, P. B. *CHEMTECH* **1976**, *6*, 86–89.
(8) Naccache, C.; Benn Taarit, Y. In "Proceedings of the Fifth International Conference on Zeolites"; Rees, L. V. C., Ed.; Heyden: London, 1980.

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‡ Union Carbide.