New Class of Electrically Conductive Metallomacrocycles: Iodine-doped Dihydrodibenzo[*b*,*i*][1,4,8,11]tetra-azacyclotetradecine Complexes

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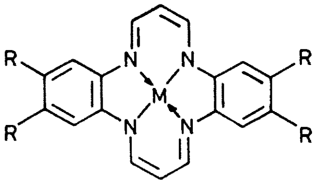
Summary. Iodine doping of metallodihydrodibenzo[*b*,*i*]-[1,4,8,11]tetra-azacyclotetradecine complexes produces a new class of electrically conductive, mixed-valent metallomacrocycles.

IODINE doping of conjugated macrocycles with an MN_4 core (M = metal) is a viable method for the preparation of low-dimensional, mixed-valent compounds.[1] Moreover, the degree of incomplete charge-transfer in such solids can be readily assessed from the stoicheiometry and spectroscopic identification of the form of iodine present.[1,2] In the case of 22π-electron phthalocyanines [M(pc)][3] and related porphyrins,[4] molecular-stacking axis conductivities are relatively high [$\sigma(300\ K) = 1$—$650\ (\Omega\ cm)^{-1}$, depending on M and the macrocycle substituents] and frequently exhibit a region of 'metal-like' ($d\sigma/dT < 0$) temperature dependence. To understand the role of the metallomacrocycle molecular and electronic structure in stabilizing the mixed-valent, highly conductive state, we need to establish whether facile charge-transport is restricted to 22π-electron systems or whether it occurs in other materials. Although different in molecular structure and symmetry, dihydrodibenzo[*b*,*i*][1,4,8,11]tetra-azacyclotetradecine (taa) complexes exhibit distinct electronic similarities to phthalocyanines (MO topologies,[5] ionization potentials,[5] reduction potentials,[6] and optical spectra[5]). We report here that the iodine oxidation of taa derivatives yields a large, new class of highly conductive metallocrocycles[7] in which properties can be manipulated by substituent variation and in which a 'metal-like' conductivity is observed.



(**1**) R = H, M = Co, Ni, Cu, Pd, H_2 [M(taa)]
(**2**) R = Me, M = Ni, Pd, H_2 [M(tmtaa)]

Solution iodination of purified M(taa) and M(tmtaa) compounds[8] yields darkly coloured powders, the stoicheiometries of which (Table) can be systematically varied with reaction conditions. Diffusion-growth techniques have yielded needle-like single crystals of $[Ni(taa)]I_{1.80}$ (A) and $[Ni(tmtaa)]I_{2.44}$ (B). Resonance Raman spectra (ν_0 5145 Å) of all the $[M(taa)]I_x$ and $[M(tmtaa)]I_y$ compounds with $x,y \leqslant \sim 3$ exhibit the characteristic I_3^- scattering pattern[1,2] (ν 108 cm^{-1}), while for $x,y \geqslant \sim 3$, I_5^- (ν 165 cm^{-1})[1,2] is the predominant polyiodide. For (A) and (B) the charge distributions can thus be represented as $[Ni(taa)]^{0.6+}(I_3^-)_{0.6}$ and $[Ni(tmtaa)]^{0.8+}(I_3^-)_{0.8}$. Preliminary single-crystal diffraction studies[9] on (A) and (B) are consistent with the now common structural pattern[1] of segregated, partially oxidized metallomacrocyclic donor stacks and parallel chains of acceptor counterions. With respect to the nature of the oxidation, the variety of M derivatives which can be oxidized (including M = H_2) and the supporting e.s.r. data[6] indicate that the oxidation involves MOs which are predominantly ligand-centred, producing a π-radical cation-hole, as found for iodinated phthalocyanines[3] and porphyrins.[4] With respect to substituent effects, it is noteworthy that the incorporation of electron-releasing methyl groups (R = Me) is accompanied, in (B), by a higher degree of partial oxidation while, for R = Cl, the metallomacrocycle cannot be oxidized with iodine.

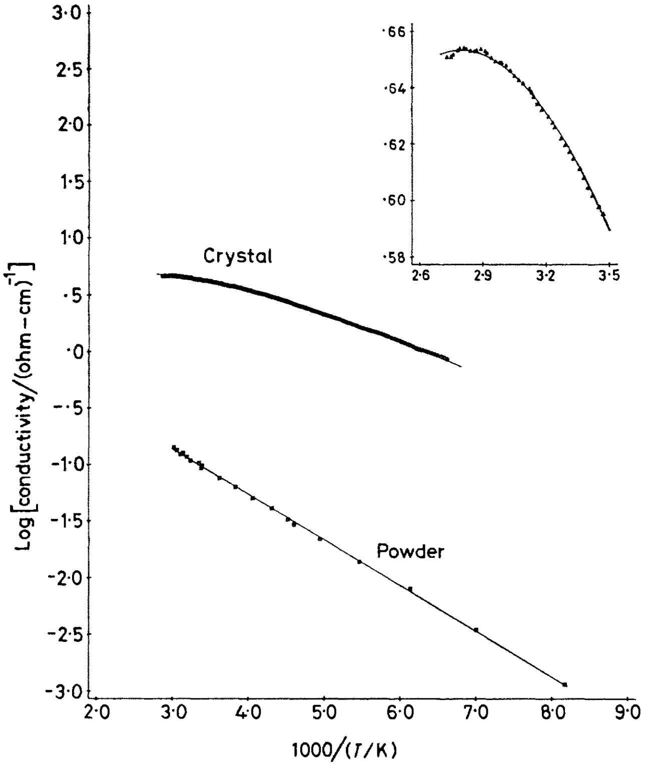


FIGURE. Variable-temperature electrical-conductivity data for a single crystal of $[Ni(tmtaa)]I_{2\cdot44}$ (B) and a powder sample of $[Ni(tmtaa)]I_{2\cdot9}$. The single crystal data fit equation (1) with α 2·51 and Δ 0·090 eV; an exponential fit of the powder data is made with Δ 0·079 eV. The inset shows the single crystal data in the high temperature region.

Four-probe van der Pauw data on pressed pellets reveal large increases in electrical conductivity upon M(taa) and M(tmtaa) iodination (Table). The $[M(taa)]I_x$ powder values are generally greater than those for $[M(tmtaa)]I_y$ and are comparable to the 'molecular metal' $[Ni(pc)]I_{1\cdot0}$.[3] With the exception of M = H_2, conductivities are relatively insensitive to x, y, and M. The temperature dependence of powder conductivities is thermally activated (Table, Figure). Four-probe single crystal data for samples of (B) (Figure) exhibit a region approaching 'metal-like' behaviour, which, above 130 K, is given approximately by equation (1),[10] which assumes a semiconductor with a

TABLE. Electrical conductivity data for $[M(taa)]I_x$ and $[M(tmtaa)]I_y$ compounds.

Compound	σ (300 K) (Ω cm^{-1}) Powder	Single crystal	Δ/eV[a]
Ni(taa)[b]	$1\cdot8 \times 10^{-15}$		2·25
$[Ni(taa)]I_{0\cdot8}$	$2\cdot1 \times 10^{-1}$		0·093
$[Ni(taa)]I_{1\cdot0}$	$4\cdot5 \times 10^{-1}$		0·051
$[Ni(taa)]I_{1\cdot80}$ (A)		1–50	
$[Ni(taa)]I_{2\cdot6}$	$8\cdot1 \times 10^{-2}$		
$[Ni(taa)]I_{7\cdot0}$	$2\cdot3 \times 10^{-1}$		
Ni(tmtaa)[b]	$4\cdot0 \times 10^{-14}$		1·36
$[Ni(tmtaa)]I_{1\cdot7}$	$1\cdot4 \times 10^{-2}$		
$[Ni(tmtaa)]I_{2\cdot44}$ (B)		1–20	
$[Ni(tmtaa)]I_{2\cdot9}$	$3\cdot8 \times 10^{-2}$		0·079
Co(taa)[b]	$7\cdot9 \times 10^{-13}$		1·33
$[Co(taa)]I_{1\cdot9}$	$1\cdot1 \times 10^{-2}$		
Cu(taa)[b]	$1\cdot8 \times 10^{-10}$		0·89
$[Cu(taa)]I_{1\cdot8}$	$1\cdot1 \times 10^{-3}$		
$[Pd(taa)]I_{0\cdot8}$	$1\cdot3 \times 10^{-1}$		0·080
$[Pd(tmtaa)]I_{0\cdot4}$	$9\cdot3 \times 10^{-4}$		0·154
$[H_2(taa)]I_{1\cdot4}$	$2\cdot4 \times 10^{-5}$		
$[H_2(tmtaa)]I_{1\cdot6}$	$3\cdot8 \times 10^{-6}$		
$[Ni(pc)]I_{1\cdot0}$[c]	$7\cdot0 \times 10^{-1}$	300–650	0·036

[a] From a least-squares fit to $\sigma = \sigma_0 e^{-\Delta/kT}$ of the powder data.
[b] R. Müller and D. Wöhrle, *Makromol. Chem.*, 1975, **176**, 2775.
[c] Ref. **3**.

$$\sigma = AT^{-\alpha}e^{-\Delta/kT} \qquad (1)$$

thermally activated carrier-concentration and a temperature-dependent mobility. Alternatively, a polaron model[11] may apply. Not unexpectedly,[1–4] preliminary static-susceptibility measurements on (A) reveal weak, relatively temperature-independent paramagnetism. Crystals of (A) are exceedingly fragile and σ(300 K) (Table) is probably a minimum value since the powder data are comparable to those of $[Ni(pc)]I_{1\cdot0}$. Single crystals of this latter compound exhibit σ(300 K) 300—650 (Ω cm)$^{-1}$.[3]

Added in proof. After submission of this manuscript, other workers reported corroborative room temperature measurements on powders of $Ni(taa)I_{1\cdot57}$ and $Ni(taa)Br_{2\cdot43}$.[12]

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