9. Metallic Conductivity in Metal Tetraaza[14]Annulene Iodides: The Crystal Structures of Dihydrodibenzo-[*b, i*]-1,4,8,11-tetraazacyclotetradecinenickel and -palladium Iodides

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Summary

Single crystals of dihydrodibenzo[*b, i*]-1,4,8,11-tetraazacyclotetradecinenickel iodide show metallic conductivity between room temperature and approx. 110 K. The crystals are orthorhombic, space group I_{bam} with four formula units per cell of the following dimensions: $a = 20.245$, $b = 13.416$, $c = 6.418$ Å. The analogous palladium complex is isomorphous, the cell constants being $a = 20.452$, $b = 13.430$ and $c = 6.499$ Å. A number of other partially oxidized metal tetraaza[14]annulenes also show electrical conductivity.

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1. Introduction. - Iodine doping of conjugated metallomacrocycles has proved to be a valuable method for the preparation of low-dimensional electrically conductive compounds [1]. Among the macrocycles employed were transition metal phthalocyanines [2] and porphyrins [3] and, more recently, tetraaza[14]annulenes [4]. Although high electrical conductivities were reported in many instances, the only system showing metallic behaviour of the conductivity below room temperature was phthalocyaninenickel iodide (abbreviated Ni(pc)I). In this paper, we wish to present the first measurements showing metallic behaviour of a compound in the class of the iodine-doped tetraaza[14]annulenes, namely dihydrodibenzo[*b, i*]-1,4,8,11-tetraazacyclotetradecinenickel iodide (abbreviated Ni(bdtaa)I_2).

2. Experimental. - The syntheses of the tetraaza[14]annulenes were performed according to literature procedures [5]. For Ni(dpdbtaa) and Ni(dtdbtaa) (s. *Scheme*) the procedure was modified by using arylmalondialdehydes [6] instead of 4-aryl-1,2-dithiolium salts [7], and in the preparation of the new H_2(hmdbtaa), *o*-phenylenediamine was substituted by 4,5-dimethyl-*o*-phenylenediamine (cf. [8]).

Efficient purification of the macrocycles was achieved by up to five gradient sublimations *in vacuo* at 10^{-2} to 10^{-3} Torr. Single crystals of Ni(dbtaa)I_2 and Pd(dbtaa)I_2 were grown by a co-sublimation technique at *ca.* 10 Torr argon pressure. The black needle-like crystals with typical dimensions of 5×0.05

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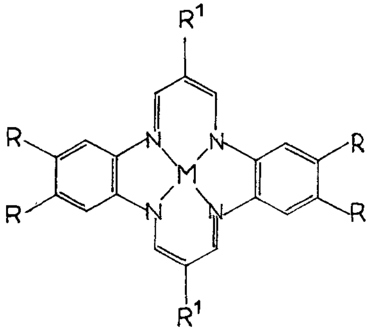
Scheme



R = H;	R^1 = H;	M = H_2, Ni, Pd	[M(dbtaa)]
R = H;	$R^1 = CH_3$;	M = H_2, Ni	[M(dmbdtaa)]
R = H;	R^1 = phenyl;	M = Ni	[Ni(dpdbtaa)]
R = H;	R^1 = p-tolyl;	M = Ni	[Ni(dtdbtaa)]
$R = CH_3$;	$R^1 = CH_3$;	M = H_2, Ni	[M(hmdbtaa)]

×0.04 mm^3 were grown within *ca.* 14 days on a quartz substrate kept at *ca.* 15°. More details on the co-sublimation technique are given elsewhere [9]. Single crystals of $H_2(hmdbtaa)I_{2.45}$, $Ni(dtdbtaa)I_{2.6}$ and $Ni(hmdbtaa)I_x$ were grown by slow diffusion of chloroform solutions in H-tubes. All crystals are extremely fragile. Doped powders were prepared whenever possible by dissolving the macrocycles and adding an excess of iodine, whereupon immediate precipitation of dark brown or black iodinated powders occurred. Doping was achieved equally well by exposure to iodine vapour in a desiccator evacuated to 20 Torr and kept at room temperature.

Electrical conductivities of powders were determined by a two-probe DC. technique on micropellets of 1 mm diameter produced in a glass capillary. Single-crystal conductivity of $Ni(dbtaa)I_2$ was determined by a conventional four-probe DC. technique using gold wires as supporting electrodes and Pt-paste as contacts. The temperature behaviour of the conductivity was measured by cooling the crystals at a rate of 0.3°/min with liquid nitrogen. Conductivities of all the other single crystals were measured by a two-probe DC.-technique and their temperature dependance was determined qualitatively only.

X-ray study of Ni(dbtaa)I_2: *Weissenberg* and precession photographs revealed that the crystals are orthorhombic, space group I_{bam}. Cell constants *(Tab. 1)* were obtained by usual procedures using a *Philips* PW1100 diffractometer and Mo*Kα* radiation. The observed density of 2.27 g/cm^3 may be compared to that of 2.28 g/cm^3 calculated for four formula units in the cell. *Weissenberg* photographs displayed the presence of some diffuse scattering in addition to normal *Bragg* scattering. Diffuse scattering was confined to planes perpendicular to the c*-axis. The few weak diffuse lines may be interpreted as an indication of I_3^--units. In fact, resonance-*Raman* spectra confirmed the presence of I_3^- in the crystals.

Solution and refinement of the structure: From the volume of the unit cell followed that four macrocycles must be present per cell. The space group of the structure and the symmetry of the nickel-macrocycle (C_{2h}) led to the choice of nickel in the origin of the coordinate system. Iodine positions were determined by a 3-dimensional *Patterson* synthesis. All non-hydrogen atoms could be located by

Table 1. *Crystal data and refinement of Ni(dbtaa)I_2 and Pd(dbtaa)I_2*

Compound	$Ni(C_{18}H_{14}N_4)I_2$	$Pd(C_{18}H_{14}N_4)I_2$
Molecular weight	598.8	646.5
Cell: *a*, Å	20.245	20.452
b, Å	13.416	13.430
c, Å	6.418	6.499
V, Å^3	1743.2	1785.1
Z	4	4
Density, g/cm^3 calc.	2.28	2.41
found	2.27	2.35
Space group	I_{bam}	I_{bam}
Radiation	MoK_α	MoK_α
Unique data with $I \geq 2\sigma(I)$	600	483
Final R-factor	0.092	0.088
Final numbers of variables	42	42

structure factor calculations and *Fourier* synthesis. Refinements were made using 600 unique reflections with $I > 2\sigma(I)$. Full matrix least squares refinements with anisotropic temperature factors for nickel and iodine converged at $R = 0.092$. Owing to some disorder in the iodine lattice, the structure could not yet be refined to a better value of R.

Structure determination of Pd(dbtaa)I_2. Weissenberg and precession photographs showed the structure to be isomorphous with that of Ni(dbtaa)I_2, with only slightly different cell constants *(Tab. 1)*. The data were collected as above. Starting from the positional parameters of the nickel structure, refinements were made using 483 reflections with $I > 2\sigma(I)$. Full matrix least squares refinements with anisotropic temperature factors converged at $R = 0.088$.

Again, some disorder in the iodine lattice prevented a better refinement.

3. Results and discussion. - Iodine doping of dihydrodibenzo[*b,i*]-1,4,8,11-tetraaza[14]annulenes leads to a variety of electrically conducting solids which are stable at room temperature and ambient pressure. At higher temperatures and under vacuum the iodine may be completely removed from the compounds.

The electrical conductivity is determined by a number of factors such as substituents, central atom (M) and stoichiometry. In the case of our tetraaza[14]-annulenes, these factors can be varied and controlled relatively easily.

The substituents have a considerable influence on the conductivity. Strongly electron-withdrawing groups such as chlorine, bromine or cyano groups render the macrocyclic system difficult to oxidize and hence no conductivity was observed in such systems upon iodine doping. Electron-donating groups (*e.g.* alkyl) on the other hand render iodine oxidation easier.

The central metal atoms seem to have a smaller effect on the conductivity. In fact, comparison of a series of metal tetraaza[14]annulenes showed approx. the same conductivities of the iodinated products when the metal atom only was varied [10]. First oxidation potentials of complexes with the same tetraaza[14]annulene ligand but different central atoms are very similar [11], indicating that the oxidation is mainly ligand-centered. Thus, electrons are not removed from metal-centered orbitals such as d_{z^2} (as might be desirable) but from the ligand π-system. This should result in a lengthening of the bonds in the ligand and a shortening of the interplanar distance in the crystal which are indeed observed in the oxidized complexes Ni(dbtaa)I_2 and Pd(dbtaa)I_2. Bond lengthening in the ligand system of

Table 2. *Room temperature conductivities of iodinated tetraaza-14-annulenes* ($[\Omega \mathrm{cm}]^{-1}$)

Compound	Powder	Single crystal	Compound	Powder	Single crystal
$Ni(dbtaa)I_{1.66}$[b])	$2 \cdot 10^{-1}$		$H_2(hmdbtaa)I_2$[a])		2
$Ni(dbtaa)I_2$[a])		115	$H_2(hmdbtaa)I_{2.45}$[b])		56
$Pd(dbtaa)I_{1.55}$[c])	$4 \cdot 10^{-2}$		$Ni(hmdbtaa)I_{2.69}$[c])	$2 \cdot 10^{-3}$	
$Pd(dbtaa)I_{8.07}$[c])	$2 \cdot 10^{-2}$		$Ni(hmdbtaa)I_x$[b])[d])		6
$Pd(dbtaa)I_2$[a])		10	$Ni(dpdbtaa)I_{4.01}$[c])	$7 \cdot 10^{-2}$	
$Ni(dmdbtaa)I_{6.83}$[c])	$4 \cdot 10^{-4}$		$Ni(dtdbtaa)I_{3.44}$[c])	$2 \cdot 10^{-1}$	
$Ni(dmdbtaa)I_2$[b])	$3 \cdot 10^{-4}$		$Ni(dtdbtaa)I_{2.55}$[c])	$8 \cdot 10^{-2}$	
$H_2(dmdbtaa)I_{1.45}$[c])	$2 \cdot 10^{-3}$		$Ni(dtdbtaa)I_{2.6}$[b])		64

[a]) From cosublimation. [b]) From solution. [c]) From iodine vapor exposure. [d]) No elemental analysis.

$Ni(dbtaa)I_2$ averages 0.02 Å. The reason for this apparently rather small effect is that iodine is present in the form of I_3^--units; the total charge removed per molecule is only 0.66 and 0.028 e^- are removed per bond upon oxidation. The interplanar separation is reduced by 0.08 Å to 3.21 Å for the oxidized nickel complex. A possible ligand-centered oxidation was originally deduced from the fact that metalfree tetraaza[14]annulenes also form highly conducting oxidation products with iodine *(Tab. 2)*. A predominantly ligand-centered oxidation was also observed in the case of the partially oxidized metal phthalocyanines and porphyrins [2] [3] and had already been suggested by *Marks et al.* for the metal tetraaza[14]annulenes [4].

The effects of the stoichiometry are different in powders and in single crystals. In powders, the iodine content may vary within a broad range without much influence on the conductivity. When the iodine content x in Pd(dbtaa) I_x-powders

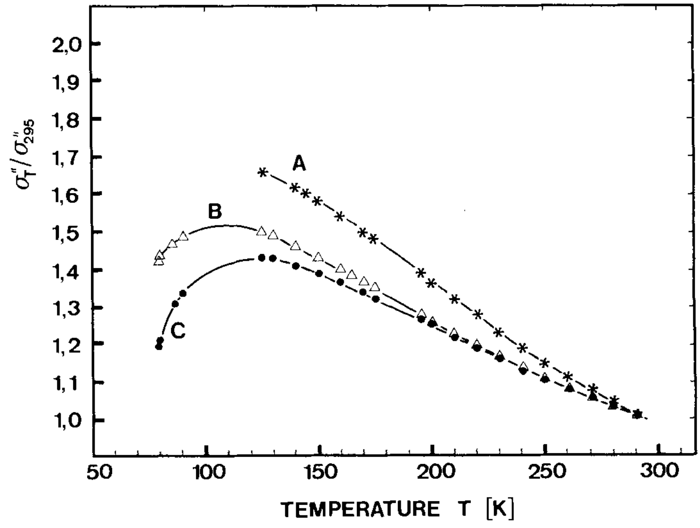


Fig. 1. *Temperature dependence of the conductivity ratio* $\sigma_\parallel(T)/\sigma_\parallel$ *(297 K) for three* $Ni(dbtaa)I_2$ crystals with the following room temperature conductivities: A = 42, B = 37 and C = 20 $[\Omega \mathrm{cm}]^{-1}$.

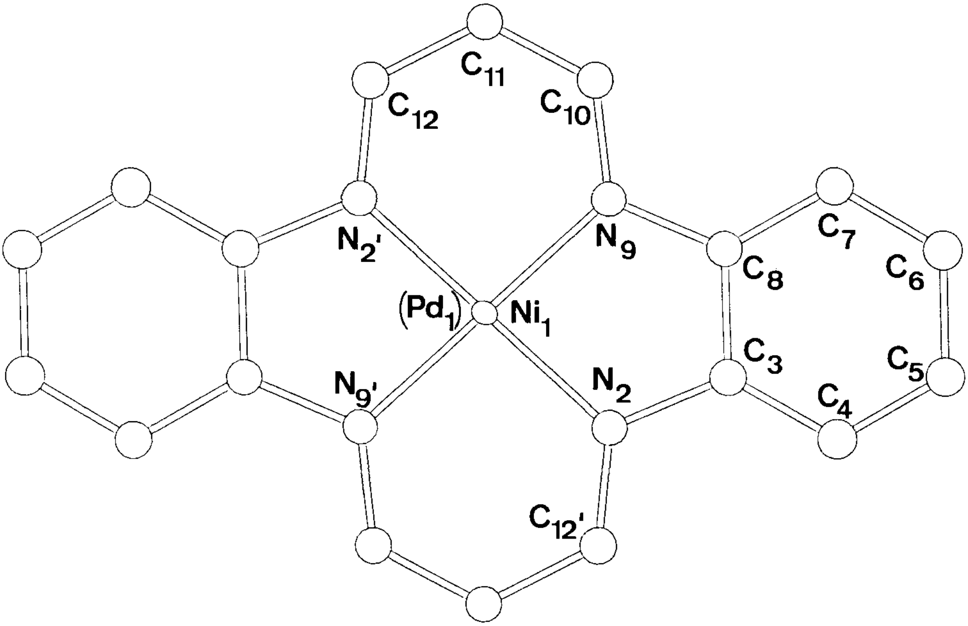


Fig. 2. *Labeling scheme for M(dbtaa)-complexes,* hydrogen atoms omitted. Shown are the thermal ellipsoids at 20% probability for the Ni(dbtaa)I_2 structure.

was varied between 1 and 8 the conductivity remained around $3 \cdot 10^{-2}$ $[\Omega cm]^{-1}$. This is in agreement with the observations of *Marks et al.* on Ni(dbtaa)I_x [4].

Apart from crystal quality, stoichiometry is, however, a critical parameter for high electrical conductivity in single crystals [12]. *Marks et al.* reported semiconducting behaviour for single crystals of Ni(dbtaa)$I_{1.80}$ [4]. In our own experiments, single crystals grown by co-sublimation with an iodine content of 2.1-2.2 were also semiconducting. However, when the iodine concentration in the vapour phase was lowered, a phase with the stoichiometry Ni(dbtaa)I_2 was isolated, which showed metallic conductivity *(Fig. 1)* down to ca. 110 K (at this point it became a semiconductor). Whether this transition is first order as required by the *Landau* theory [13] for 2/3 charge transfer will need further investigations. The maximum value for the ratio $\sigma_{\|}(T)/\sigma_{\|}(RT)$ is currently 1.7. More precise stoichiometry and better crystals will probably lead to a steeper increase in conductivity with decreasing temperature¹).

Single crystals of the other complexes (see *Tab. 2*) have not shown a metallic behaviour so far, probably because the iodine content has not been optimized yet.

Description of the structures of Ni(dbtaa)I_2 and Pd(dbtaa)I_2: (Fig. 2) shows the labeling scheme for the macrocyclic complexes. Bond lengths and angles are given

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¹) *Footnote added in proof:* Single crystals of a new batch prepared in the meantime show room temperature conductivities up to 240 $(\Omega cm)^{-1}$ and a metal to semiconductor transition centered at 100K with $\sigma_{\|}(T)/\sigma_{\|}(RT) = 1.9$.

Table 3. *Bond lengths and bond angles, Å and deg respectively*

Atoms	$Ni(C_{18}H_{14}N_4)I_2$	$Pd(C_{18}H_{14}N_4)I_2$	Atoms	$Ni(C_{18}H_{14}N_4)I_2$	$Pd(C_{18}H_{14}N_4)I_2$
Ni(Pd)–N(2)	1.880(8)	1.972(5)	C(3)–N(2)–C(12)′	119(1)	124(1)
Ni(Pd)–N(9)	1.875(7)	1.976(5)	N(2)–C(3)–C(4)	127(1)	126(1)
N(2)–C(3)	1.43(1)	1.42(1)	N(2)–C(3)–C(8)	113(1)	115(1)
N(2)–C(12)′	1.32(1)	1.32(1)	C(4)–C(3)–C(8)	120(2)	119(2)
C(3)–C(4)	1.39(1)	1.41(1)	C(3)–C(4)–C(5)	121(2)	119(2)
C(3)–C(8)	1.42(1)	1.44(1)	C(4)–C(5)–C(6)	119(2)	122(1)
C(4)–C(5)	1.40(1)	1.38(1)	C(5)–C(6)–C(7)	122(2)	120(1)
C(5)–C(6)	1.40(1)	1.42(1)	C(6)–C(7)–C(8)	119(2)	118(2)
C(6)–C(7)	1.40(1)	1.41(1)	C(7)–C(8)–C(3)	120(2)	122(2)
C(7)–C(8)	1.40(1)	1.40(1)	C(7)–C(8)–N(9)	126(1)	123(1)
C(8)–N(9)	1.42(1)	1.45(1)	C(3)–C(8)–N(9)	114(1)	113(1)
N(9)–C(10)	1.33(1)	1.34(1)	Ni(Pd)–N(9)–C(8)	114(1)	113(1)
C(10)–C(11)	1.40(2)	1.39(2)	Ni(Pd)–N(9)–C(10)	126(1)	122(1)
C(11)–C(12)	1.42(2)	1.39(1)	C(8)–N(9)–C(10)	120(1)	125(1)
N(2)–Ni(Pd)–N(9)	85.2(6)	84.2(4)	N(9)–C(10)–C(11)	124(1)	127(1)
N(2)–Ni(Pd)–N(9)′	94.8(6)	95.8(4)	C(10)–C(11)–C(12)	124(2)	126(2)
Ni(Pd)–N(2)–C(3)	114(1)	113(1)	C(11)–C(12)–N(2)′	123(2)	127(2)
Ni(Pd)–N(2)–C(12)′	127(1)	123(1)			

in *Table 3*. As the two complexes are isomorphous, only the structure of the nickel complex is described.

Figure 3 shows a projection of the crystal structure on the *a, b*-plane. The macrocyclic molecules are stacked on top of each other perpendicular to the *c*-axis. The molecules at 0 0 ½ and ½ ½ ½ are rotated by an angle of 59° (54° for Pd) in

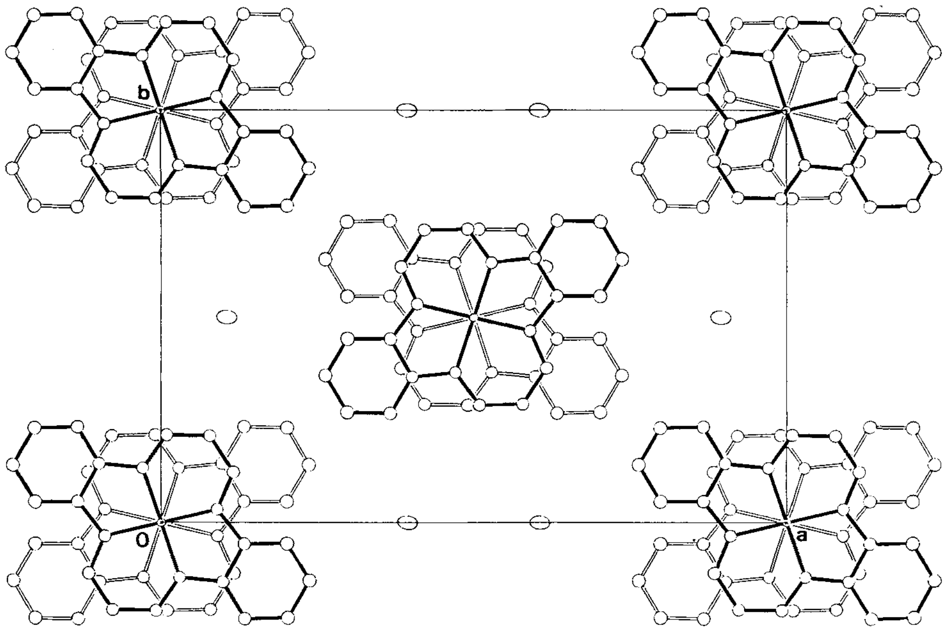

Fig. 3. *Projection of the Ni(dbtaa)I_2 structure on the* a, b*-plane.*

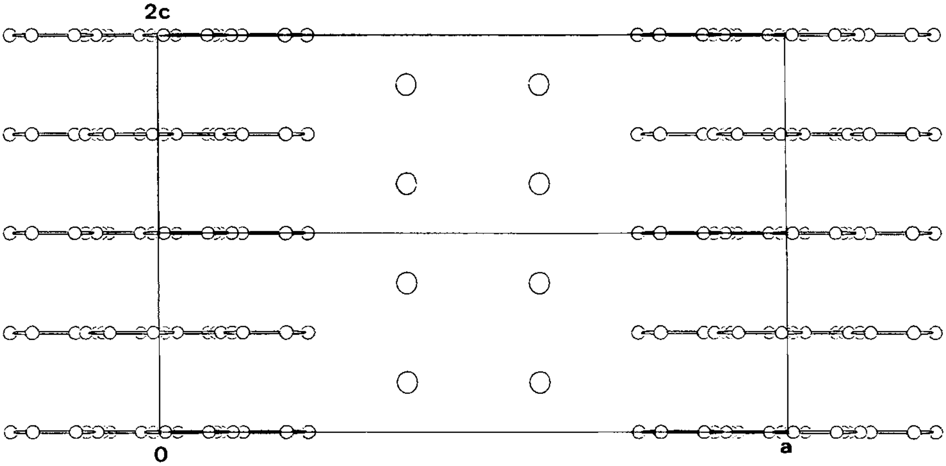

Fig. 4. *Projection of the Ni(dbtaa)I_2 structure on the* a,c*-plane illustrating flatness of molecules*

respect to the molecules in the *a, b*-plane. The complex molecules are exactly planar and separated by 3.208 Å (3.250 for Pd) *(Fig. 4)*. This is approx. 0.08 Å shorter than the interplanar separation in the orthorhombic modification of Ni(dbtaa) (3.29 Å). Metal-metal separations of 3.153 Å, 3.271 Å and 3.252 Å were reported for Ni$(bqd)_2I_{0.5}$ [14], Ni$(dpg)_2$I [15] and Ni(pc)I [2] (bqd = 1,2-benzoquinonedioximato, dpg = diphenylglyoximato). Iodine atoms are confined to the channels formed by the molecule stacks, with two chains of iodine per stack. The iodine atoms are displaced by $c/4$ in respect to the nickel macrocycle and lie on a twofold axis parallel to *a*. The mean I-I distance is half the *c*-axis or 3.208 Å (3.250 for Pd). This is remarkably shorter than twice the ionic radius for I^- of 2.51 Å [16] confirming the presence of I_3^-. The separation of two iodine chains is 4.288 Å (4.323 for Pd) and thus close to the sum of the *van der Waals* radii for I of 4.3 Å [16]. The thermal parameters of the iodine atoms show large values for both the *a*- and *c*-directions, indicating that the iodine chains might not be exactly linear and show some disorder. The latter is probably the cause for the diffuse scattering. The same conclusion was reached by other authors [2] [14] for similar structures.

4. Conclusion. - Partial oxidation of metal tetraaza[14]annulenes with iodine provides an interesting class of molecular conductors with the possibility of metallic conductivity as illustrated in the case of dihydrodibenzo[*b, i*]-1,4,8,11-tetraazacyclotetradecinenickel iodide. In the many systems where single crystal growing is successful, the optimization of the stoichiometry poses some formidable problems but will probably lead to more systems with metallic conductivity in the near future[2].

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[2] *Note added in proof:* In the meantime metallic conductivity was also found in single crystals of Ni(dtdbtaa) iodide. Conductivity-data collection and crystal-structure determination are currently in progress.

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