New High-conductivity Salts of Bis(dicyanoethylenedithiolato) Complex Monoanions

By Evelio A. Perez-Albuerne,* Lawrence C. Isett, and Robert K. Haller
(*Research Laboratories, Eastman Kodak Company, Rochester, New York* 14650)

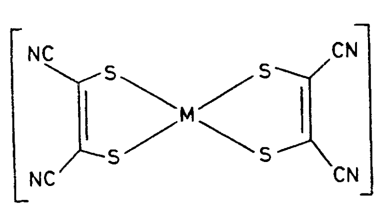
Summary Several salts of bis(dicyanoethylenedithiolato)-nickel (**1**) and -palladium (**2**) monoanions show high compressed-powder conductivity, and some have magnetic susceptibility typical of organic 'metals.'

Semiconducting salts of planar 'metal dithiolene' bis complex anions $[M(S_2C_2R_2)_2]^{n-}$ (M = Ni, Pd, Pt, Cu, Co, or Fe; R = CN, Me, H, CF_3, or C_4H_4) with a variety of cations have been reported to have relatively low levels of conductivity[1] [σ_{RT} (compressed powder) $<10^{-4}\ \Omega^{-1}\ cm^{-1}$]. Higher values have been reported in a few cases,[2,3] but always for salts in which the cations are either expected or known to be primarily responsible for the conductivity. We report here the first observation of high levels of conductivity in salts of bis(dicyanoethylenedithiolato) (mnt) complex monoanions (**1**) and (**2**) with cations of such a nature that electronic conduction must be attributed to transport between the mnt complex anions. Evidence of 'metallic' behaviour has also been obtained for one of the highly conducting compounds.

Table. Conductivity of salts of (**1**) and (**2**)

Salt	Cation	Anion	σ_{RT} (compressed pellet)/Ω^{-1} cm^{-1}
(**3**)	NEt_4^+	(**1**)	$1{\cdot}0 \times 10^{-8}$
(**4a**)	NH_4^+	(**1**)	$4{\cdot}0 \times 10^{-4}$
(**4b**)			$1{\cdot}0$
(**5a**)	Na^+	(**1**)	$4{\cdot}0 \times 10^{-4}$
(**5b**)			$2{\cdot}5 \times 10^{-1}$
(**6**)	NEt_4^+	(**2**)	$2{\cdot}5 \times 10^{-8}$
(**7**)	NH_4^+	(**2**)	$1{\cdot}1$
(**8**)	Na^+	(**2**)	$4{\cdot}0 \times 10^{-1}$

Six salts (**3**)—(**8**) (Table) of the complex anions were prepared by closely following published procedures[4] and their conductivity (σ_{RT}) was determined on compressed pellets by standard two- and four-probe d.c. techniques. The non-ionic nature of the conductivity was established by charge exhaustion experiments. Of particular interest are the small-cation salts (**4b**), (**5b**), (**7**), and (**8**), which show compressed-powder conductivity levels comparable to those of highly conducting 'metallic' salts of the well known organic species tetracyanoquinodimethane (TCNQ), tetrathiafulvalene (TTF), and naphthaceno[5,6-*cd*-11,12-*c'd'*]bis-[1,2]dithiole (TTT).



(**1**); M = Ni
(**2**); M = Pd

Salts (**4**) and (**5**) were found to occur in two forms of different conductivity. The i.r. spectra of forms (**4b**) and (**5b**) are dominated by a broad absorption (ν_{max} 1800 cm^{-1}) characteristic of other highly conducting organic solids.[5] A more extensive characterization of (**4a**) and (**4b**) by elemental and thermogravimetric analyses and *X*-ray powder diffraction established that (**4a**) is essentially anhydrous while (**4b**) is a hydrated form corresponding to the formula $NH_4[Ni(mnt)_2]{\cdot}1{\cdot}15H_2O$. It was possible reversibly to interconvert (**4a**) and (**4b**) by changes in ambient humidity. Since rigorous exclusion of H_2O was not attempted, the values of σ_{RT} reported for (**4a**) and (**5a**) are possibly higher than those of the completely water-free crystal.[3]

A plot of magnetic susceptibility *vs.* temperature (χ *vs.* T) shows that (**4a**) follows the Curie–Weiss law [χ (300) = $1{\cdot}10 \times 10^{-8}$ and χ (100) = $3{\cdot}97 \times 10^{-8}$ m^3 mol^{-1}], while (**4b**) has a near-temperature-independent paramagnetism at higher temperatures followed by a transition (at *ca.* 50 K) to a nonmagnetic semiconductor state [χ (300) = $2{\cdot}76 \times 10^{-9}$, χ (100) = $1{\cdot}88 \times 10^{-9}$, and χ (40) = $6{\cdot}28 \times 10^{-10}$ m^3 mol^{-1}]. This behaviour is typical of 1*d*-Peierls solids[6] (*e.g.*, TTF–TCNQ). By analogy with TCNQ, TTF, and TTT systems,[7] and based on the crystal structure of other salts of mnt complex monoanions,[8] it would be expected that the present mnt-based conductors would be quasi-unidimensional, with conduction occurring only along the anion stacks. Solution-grown single crystals of (**4a**) were of poor quality, but provided an upper limit for σ_{RT} (single crystals) (10^{-1} Ω^{-1} cm^{-1}). Crystals of the 'metallic' form (**4b**) have not been grown yet, but the high value of σ_{RT} (compressed pellet)† and the χ *vs.* T behaviour are clear indications that a new family of highly conducting 'metallic' salts based on the organometallic mnt complex monoanions has been discovered.

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† Crystals of (**4b**) would be expected to show the usual anisotropic conductivity typical of other known organic conductors: σ (highest conductivity axis)/σ (compressed powder), *ca.* 10^2—10^3.

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