A New Synthetic Metal, Cu(di-2-pyridylamine)$_2$·(tetracyanoquinodimethane)$_2$

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Metallic electrical conduction was found in the single crystals of [Cu(di-2-pyridylamine)$_2$]$^+$-[(tetracyanoquinodimethane)$_2$]$^-$; this complex was characterized by e.s.r. experiments.

In the search for new 'synthetic metals', the development of new donors and acceptors is of great current interest. As part of these efforts, we have reported that some copper chelates can act as donors with TCNQ (7,7,8,8-tetracyanoquinodimethane) to form charge-transfer complexes having high electrical conductivity.[1] An advantage of the metal chelate donors is that the electrical conductivity of their TCNQ salts can be easily and widely changed by replacing the co-ordinated ligands. Some Cu–TCNQ complexes show high powder conductivity comparable with that of synthetic metals already reported. Unfortunately, however, metallic conduction has not been confirmed in the complexes because their single crystals have not been obtained. We report here a new Cu–TCNQ complex with di-2-pyridylamine,

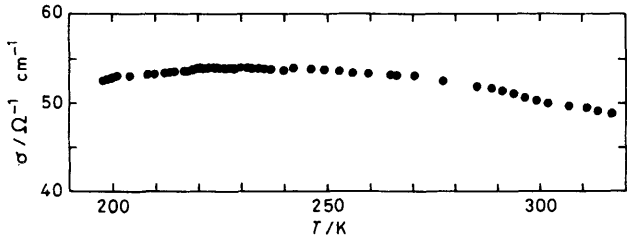

Figure 1. Variation with temperature (T) of the electrical conductivity (σ) of a single crystal of Cu(di-2-pyridylamine)$_2$·(TCNQ)$_2$.

$Cu(dpa)_2(TCNQ)_2$, which provides single crystals exhibiting metallic conductivity.

The single crystals were grown by diffusing together $[Cu(dpa)_2]^{2+}$ [from $Cu(dpa)_2(NO_3)_2 \cdot 2H_2O$] and $TCNQ^-$ (from LiTCNQ) in a methanol–acetonitrile (1 : 1) solution of neutral TCNQ. Black needles were obtained. The number of TCNQ molecules in the compound formula was confirmed by observation of the 842 and 394 nm bands in the solution electronic absorption spectrum of the complex.[2]

The obtained crystals were so thin that the conductivity was determined only along the needle axis on five samples by the standard four-probe method. The electrical contact was made with Aquadag. The single-crystal conductivity was *ca.* 50 Ω^{-1} cm^{-1} at 300 K. Figure 1 shows the typical temperature dependence of the conductivity: it increases with decreasing temperature until a very broad maximum is reached at around 230 K, and decreases below this temperature without showing any appreciable phase transition. This metallic behaviour resembles that of quinolinium(TCNQ)$_2$.[3]

The single crystals exhibited a narrow e.s.r. signal (peak-to-peak width *ca.* 0.6 G†) whose g value was angle-dependent. The principal components of the crystal g tensor were equal to 2.0035, 2.0030, and 2.0027. The axis of the smallest g component lay along the needle axis, which is a probable TCNQ-stack direction. The observed e.s.r. signal is ascribed to $TCNQ^-$ ions. An e.s.r. signal attributable to Cu^{II} ions was not detected: the $[Cu(dpa)_2]^{2+}$ chelates employed as donors are reduced to the corresponding diamagnetic Cu^{I} chelates in forming the TCNQ complex. The formula of the new complex can be given as $[Cu(dpa)_2]^+[(TCNQ)_2]^-$.

The results of this study demonstrate that use of metal chelates as donors is a versatile way to prepare a variety of synthetic metals.

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† 1 G = 10^{-4} T.