Copper(II) Salts of Metal Dithiolates

Geoffrey E. Holdcroft and Allan E. Underhill
Department of Chemistry and the Institute of Molecular and Biomolecular Electronics, University College of North Wales, Bangor, Gwynedd LL57 2UW

The preparation and electrical conduction properties of a series of copper(II) salts of metal dithiolates are described. Compounds of the types $Cu[M\{S_2C_2(CN)_2\}_2]\cdot 2H_2O$ (M = Ni, Pt, Pd, or Cu) and $Cu[M\{S_2C_2(CN)_2\}_2]_2\cdot H_2O$ (M = Ni, Pt, or Cu) all exhibit compressed pellet conductivities of $>10^{-6}$ S cm^{-1} at room temperature.

Metal dithiolates have been extensively studied since their discovery over twenty years ago because of their unusual redox properties and the recent synthesis of a one-dimensional metal based on the $[Pt\{S_2C_2(CN)_2\}_2]^{n-}$ anion has realised their potential as electronic conductors.[1] In this compound the high electrical conductivity arises from a non-integral charge on the anion resulting in a partially filled band and hence metallic properties. The majority of metal dithiolate salts possess an integral charge of -1 or -2 on the dithiolate anion and this results in semiconductor behaviour with a small value for the electrical conductivity at room temperature. These are typically 10^{-5}—10^{-8} S cm^{-1} for salts of monovalent cations such as $[NEt_4]^+$.[2,3] Manecke and Wohrle[4] carried out an extensive study of the preparation and electrical conduction properties of compounds of the general formula $M'[M''(mnt)_2]$ {where mnt = $[S_2C_2(CN)_2]^{2-}$ and M′ and M″ are divalent first-row transition metals}. They found that compounds which contained both copper and nickel exhibited a significantly higher conductivity than compounds containing other first-row transition metals and that the compound in which M′ = Cu and M″ = Ni had a conductivity of 5×10^{-2} S cm^{-1}. We have now studied a series of Cu^{II} salts of transition-metal dithiolates to investigate the factors which determine high conductivity in this class of compound.

Experimental

Preparation of Compounds.—The complexes $[NEt_4]_2[M(mnt)_2]$, where M = Cu, Ni, or Pt, were prepared by the method of Davison and Holm.[5] The preparation of the analgous Pd complex proved difficult and the $[NBu_4]^+$ salt was prepared instead. The dianion complexes were oxidised to the monoanion complexes using iodine in dimethyl sulphoxide but attempts to oxidise the Pd complex under similar conditions were unsuccessful.

Copper(II) octanoate, $[Cu\{OOC(CH_2)_6CH_3\}_2]$, was prepared in a two-phase reaction. Copper(II) acetate in a minimum volume of water was mixed with the same volume of chloroform and a stoicheiometric quantity of octanoic acid added dropwise with stirring to the mixture. A green-blue colour slowly developed in the chloroform layer and when the colour was fully developed the chloroform layer was separated from the almost colourless aqueous layer. The chloroform solution was rotary evaporated to dryness and the resulting green-blue residue was washed with water until the precipitate had become a hard solid. The product was recrystallised twice from methanol (see Table 1 for analysis).

The complexes $Cu[M(mnt)_2]$ and $Cu[M(mnt)_2]_2$ were prepared in acetone solution by mixing the stoicheiometric quantities of the N-alkyl salt with copper(II) octanoate. Very fine black precipitates were formed in every case. To increase the particle size the solvent was changed slowly from acetone to water and the mixture digested for about 4 h. The precipitate was then filtered off and washed with acetone to remove any unreacted starting material. Finally the precipitate was washed with hot water and air dried. Analyses of the complexes are shown in Table 1. If, with the exception of the Pd complex, the $[NBu_4]^+$ salts were treated in the same manner as the $[NEt_4]^+$ salts the C, H, and N analyses showed that only about 70% of the tetra-alkylammonium groups were replaced by Cu^{2+}.

Electrical Conductivity.—Four-probe d.c. electrical conductivity measurements were made on compressed pellets of the compounds using Agdag as the contact material. Aquadag gave inconsistent results with some samples, presumably due to contact problems. When a d.c. current was applied to a sample the voltage detected across the centre probes rose asymptotically and reached a steady reading after 10 min. Under these conditions the compressed pellet exhibited ohmic behaviour. The room-temperature values for the conductivities reported in Table 2 are the steady-state values. Variable-temperature measurements were obtained using a computer-controlled

Table 1. Elemental analyses (%)

	Theoretical			Found		
Compound	C	H	N	C	H	N
$[Cu\{OOC(CH_2)_6CH_3\}_2]$	54.90	8.65	0	55.00	8.60	0
$Cu[Ni(mnt)_2]\cdot 2H_2O$	21.95	0.90	12.80	22.10	1.00	11.85
$Cu[Pt(mnt)_2]\cdot 2H_2O$	16.70	0.70	9.75	17.05	0.70	8.45
$Cu[Pd(mnt)_2]\cdot 2H_2O$	19.75	0.85	11.50	20.00	0.80	11.85
$Cu[Cu(mnt)_2]\cdot 2H_2O$	21.65	0.90	12.65	22.75	0.80	12.05
$Cu[Ni(mnt)_2]_2\cdot H_2O$	25.35	0.25	14.75	24.95	0.30	14.60
$Cu[Pt(mnt)_2]_2\cdot H_2O$	18.60	0.20	10.85	20.00	0.25	10.00
$Cu[Cu(mnt)_2]_2\cdot H_2O$	25.00	0.25	14.55	24.65	0.25	13.95

Table 2. Room-temperature electrical conductivities

Compound	$\sigma_{r.t.}$/S cm^{-1}
Cu[Ni(mnt)$_2$]·2H$_2$O	3×10^{-3} $5 \times 10^{-2\,a}$
Cu[Pt(mnt)$_2$]·2H$_2$O	1×10^{-2}
Cu[Pd(mnt)$_2$]·2H$_2$O	5×10^{-6}
Cu[Cu(mnt)$_2$]·2H$_2$O	1×10^{-5} $8 \times 10^{-6\,a}$
Cu[Ni(mnt)$_2$]$_2$·H$_2$O	1×10^{-2}
Cu[Pt(mnt)$_2$]$_2$·H$_2$O	2×10^{-4}
Cu[Cu(mnt)$_2$]$_2$·H$_2$O	5×10^{-6}

[a] From ref. 4.

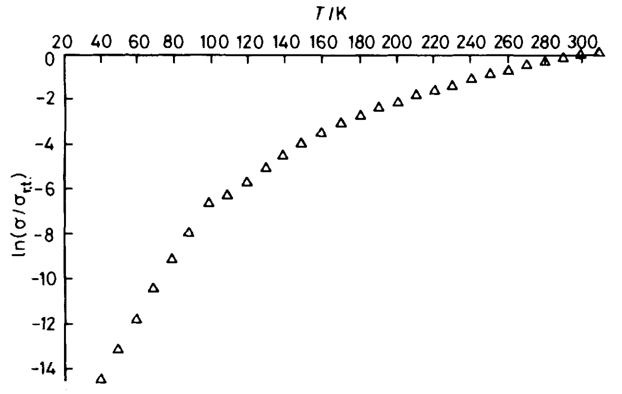

Figure 1. Variation of ln($\sigma/\sigma_{r.t.}$) with temperature for Cu[Ni{S$_2$C$_2$(CN)$_2$}$_2$]·2H$_2$O

apparatus in which the values of the conductivities were determined when the conductivity was changing by less than 2% per minute after an interval of at least 10 min at a given temperature.

Results and Discussion

The room-temperature electrical conductivities, $\sigma_{r.t.}$, of the dithiolate complexes are shown in Table 2. Duplicate measurements were made and the results between samples of the same material agreed to within 20%. This is typical for measurements on amorphous powders. Two of the complexes studied by Manecke and Wohrle[4] were re-examined in this work and, as can be seen from Table 2, there is agreement to within an order of magnitude.

It has previously been observed that the salts of the monoanions are considerably more conducting than either the corresponding neutral complexes or the dianions.[2,3] This was attributed to the relative ease of the disproportionation reaction required for carrier formation. For the present series of compounds no pattern is apparent. Whereas for the nickel complexes the monoanion is more conducting than the dianion salt the reverse is observed for the platinum complexes. However, the much higher conductivities observed for the Cu^{II} salts compared with other metal salts of mono- or di-anions suggest that the Cu^{II} ions play an important role in the conduction process. The most obvious possibility is the reduction of some of the Cu^{II} ions to Cu^{I} with the corresponding oxidation of either [M(mnt)$_2$]$^{2-}$ to [M(mnt)$_2$]$^-$ or [M(mnt)$_2$]$^-$ to [M(mnt)$_2$]. Either process will produce carriers on the anions leading to enhanced conductivity and without the necessity for any disproportionation reaction. There is no obvious correlation between the redox properties of the metal dithiolate anions and the observed conductivities in Table 2.[6] This suggests that the conductivity is mobility dominated rather than dependent on the carrier concentration which would be related to the redox properties. Without detailed structural properties and conductivity results obtained on single crystals further speculation is pointless.

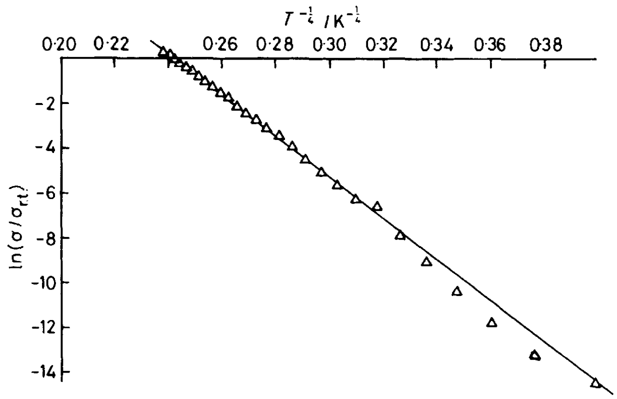

Figure 2. Variation of ln($\sigma/\sigma_{r.t.}$) with $T^{-\frac{1}{4}}$ for Cu[Ni{S$_2$C$_2$(CN)$_2$}$_2$]·2H$_2$O

A graph of ln($\sigma/\sigma_{r.t.}$) *versus* T for Cu[Ni(mnt)$_2$]·2H$_2$O is shown in Figure 1 and is typical of the temperature dependence of the conductivities of all the compounds studied. For amorphous semiconductors the dimensionality of the conduction pathway can be estimated by the variation of the function ln($\sigma/\sigma_{r.t.}$) with T^{-n}.[7] For one-, two-, or three-dimensional conductors n is expected to be 2, 3, or 4. It is found that for most of the compounds a plot of ln($\sigma/\sigma_{r.t.}$) against $T^{-\frac{1}{4}}$ gave the best approximation to a straight line (see Figure 2) suggesting that they behave as isotropic amorphous semiconductors in compressed pellet form.

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