Heteronuclear *versus* Homonuclear Electron Transfer Mechanisms in the Conductivity of Solid Dithiolate Mixtures with Methylene Blue or Tetraethylammonium as Cations

By DAVID R. ROSSEINSKY and RICHARD E. MALPAS
(*Department of Chemistry, The University, Exeter* EX4 4QD)

Summary In $[M^+]_z$ $[Ni(mnt)_2]^{z-}$ salts the conductivity is higher with methylene blue (MB^+) as cation than with $NEt_4{}^+$, indicating for MB^+ salts heteronuclear ('charge transfer') interaction in the electron-transfer process; by contrast, in compacted mixtures of salts with $z = 1$ and $z = 2$, the conductivity is enhanced across the 5—95% mixture region in the $NEt_4{}^+$- containing series but not in the MB^+, indicating homonuclear ('intervalence') anionic interaction in the former.

IN solids conduction often proceeds by electron hopping[1] involving transfer from one particular atomic or ionic centre to another. When the centres are chemically identical apart from charge, or at least comprise the same element, the process is termed a homonuclear intervalence transfer,[2] whereas the involvement of two different centres is a heteronuclear charge-transfer (CT) interaction.[2,3] We now report a graphic illustration of the contrasting effects of the two interactions, in the composition dependences of the conductivities of compacted mixtures of the salts of $[Ni(mnt)_2]^-$ and $[Ni(mnt)_2]^{2-}$ (mnt = dicyanoethylenedithiolato). In one series of mixtures the cation employed was methylene blue (MB^+) (which demonstrates an electron acceptor capacity by its reducibility to the *leuco* form MB°). In the other series use of the inert cation $NEt_4{}^+$ should enforce solely anion–anion interaction in the electron-transfer mechanism.

The dithiolate salts were prepared following ref. 4 except that MB^+ or $NEt_4{}^+$ were used in the place of $NBu^n{}_4{}^+$, the products giving satisfactory elemental analyses. Compacted mixtures of copper(I,II) chlorides[5] and of organic redox systems[6] have been shown to give satisfactorily reproducible intervalence enhancement of conductivity as demonstrated by a minimum in the resistivity–composition curve. Two-probe resistance measurements with 5 V applied potential were found satisfactory as before,[7] according with four-probe values when taken. The least variation (*ca.* 3-fold max.), with near-Ohmic behaviour, was obtained with mercury contacts, in a Teflon cell of a design allowing mercury to be driven along contact channels to the compacted disc by means of a screw.

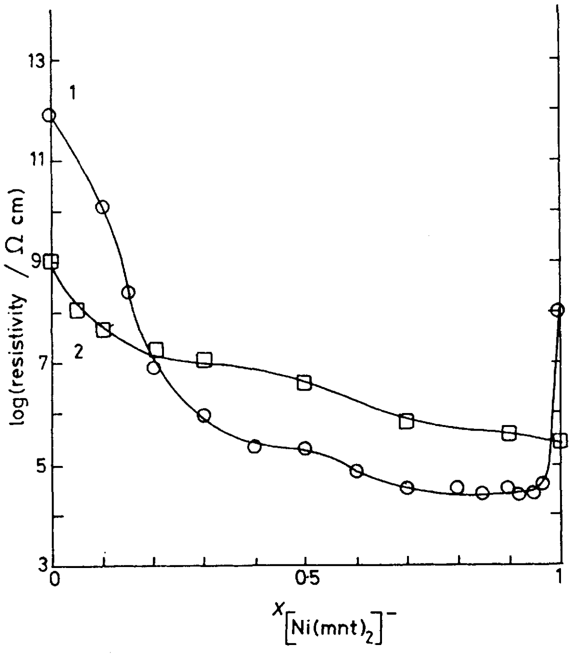

FIGURE. Variation of log of resistivity/Ω cm of intervalence mixtures $[Ni(mnt)_2]^-$ and $[Ni(mnt)_2]^{2-}$ with composition. Curve 1, $NEt_4{}^+$ as cation; curve 2, MB^+ as cation. x is the mole fraction of the monoanion $[Ni(mnt)_2]^-$.

The dependence of the resistivity of compacted mixtures of $[NEt_4][Ni(mnt)_2]$ and $[NEt_4]_2[Ni(mnt)_2]$ on composition is shown by curve 1 of the Figure. A markedly unsymmetrical curve is shown, the conductivity being enhanced by 3×10^3 fold in the best-conducting mixture relative to the more conductive single salt.

For the MB^+ salts the resistivity values in curve 2 show no minimum, only slight curvature. The pure-salt conductivities of the MB^+ salts are enhanced compared with the $NEt_4{}^+$ salts by 400 fold for $[Ni(mnt)_2]^-$ and by 10^3 fold for $[Ni(mnt)_2]^{2-}$; *cf.* the similar[7] $[Fe(mnt)_3]^{2-}$ salts, 10^5 fold enhancement for MB^+ compared with $PPh_4{}^+$. Facilitation of the electron-transfer process afforded by anion–cation CT interaction with MB^+ is thus already present in the pure MB^+ salts, and the middle composition range offers no advantages. Here the two mechanisms give conductivities within *ca.* tenfold; quantitative differences should not be overemphasized, since somewhat differing lattices are involved. Commensurately, the slight plateaus at about 50 : 50 composition in both curves are probably insignificant.

Two further conclusions can be drawn. The planarity, alone, of MB^+, appears ineffective in promoting conductivity by allowing the dithiolate anions closer proximity, as tentatively mooted in ref. 7. Secondly, to generalise the present result, the prospect of increasing the conductivity of an originally pure salt, by intervalence enhancement resulting from the admixture of a different valency,[5] seems promising only if the conductivity of the pure salt does not already proceed largely by CT interaction between juxtaposed moieties, *e.g.* MB^+ and dithiolate here.

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