Semiconductivity in Single Crystals of Bisdimethylglyoximatonickel

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SEVERAL recent papers[1-4] have shown that certain transition metal complexes, in which there exists the possibility of direct metal–metal bonding, possess semi-conducting properties. Much of this work was carried out using compressed-powder discs which precluded the measurement of the anisotropic conduction in these compounds. We now report, from studies on single crystals of bisdimethylglyoximatonickel (Ni dmg_2), the first measurement of a comparatively high conductivity along the axis of metal–metal interaction for a first row transition metal complex.

All measurements were made in an atmosphere of dry nitrogen using silver-paste electrodes and a specially constructed cell which will be described in a further communication. Compressed-powder discs were made at a pressure of 20,000 p.s.i. D.c. conductivities were obtained by applying a potential of between 0 and 350 v across the crystal or disc and a standard resistor connected in series, and measuring the potential across the resistor using a vibrating reed electrometer (E.I.L.33B2 coupled to E.I.L. B33B resistance box). The smallness of the crystals (average size $0{\cdot}5 \times 10^{-2} \times 10^{-2}$ mm.) only allowed measurements of the conductivity along the needle axis to be made.

Ni dmg_2 is orthorhombic,[5] with the nickel atoms 3·25 Å apart and stacked above one another in the line of the *c*-axis, which is also the needle axis of the crystal. An ohmic relationship was observed between the current and the applied voltage along this axis. The conductivity (σ) was $3{\cdot}8 \times 10^{-10}$ ohm^{-1} cm.$^{-1}$ at 50°, and increased with increasing temperature showing the complex to be a semiconductor. This value is comparable to that observed by Collman and co-workers[1] for the conductivity of single crystals of dicarbonylacetylacetonatorhodium. The conductivity of compressed-powder discs of Ni dmg_2 was, however, only $5{\cdot}2 \times 10^{-15}$ ohm^{-1} cm.$^{-1}$, in agreement with that reported previously.[2,4] The activation energy (Q) for conduction along the needle axis of the single crystals, calculated from the expression $\sigma = \sigma_0 e^{-Q/RT}$ was found to be 0·57 ev.

The conductivity along the *c*-axis of single crystals of Ni dmg_2 is 10^5 greater than that of the discs, suggesting some delocalisation of electrons along the line of the metal–metal stacking. Several workers have suggested the possibility of interaction between adjacent nickel atoms to account for the insolubility[6] and unusual dichroism[7] of this complex, although both these properties can be explained[8] without invoking the concept of any metal–metal bond. Indeed, until the present measurements, no direct evidence for electron delocalisation has been observed in Ni dmg_2.

Molecular orbital calculations[9] have suggested that, although little nickel–nickel interaction is probable in the ground state, a consideration of $4p_z$–$4p_z(\sigma)$ overlap[8] does indicate the possibility of some degree of delocalisation in the excited state. The behaviour of this compound as a semiconductor, rather than as a metallic conductor, indicates that excitation of an electron from a fully occupied to an unoccupied molecular orbital is necessary before conduction can take place. The energy difference between the excited state in which conduction occurs and the ground state can be obtained from the activation energy (*i.e.* band gap, $\Delta E = 2Q$), and is about 9200 cm.$^{-1}$. This corresponds to a spectroscopically observed transition which stretches from 7000 to 11,500 cm.$^{-1}$ in the spectrum of single crystals of Ni dmg_2.[10]

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