Nickel–Nickel Bond in the Binuclear Structure of Bis(dithiophenylacetato)nickel(II)

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Summary *X*-Ray determination of the crystal structure of bis(dithiophenylacetato)nickel(II) shows evidence of a nickel–nickel bond in a bridging acetate-cage binuclear complex.

IN connection with the problem of the structure of metal carboxylates, monothiocarboxylates, and dithiocarboxylates, and the chemical and spectrochemical investigations carried out in parallel by Furlani and co-workers,[1] we have undertaken an *X*-ray analysis of bis(dithiophenylacetato)nickel(II), to compare its structure with that of the previously studied bis(dithiobenzoato)nickel(II).[2]

The results show the complex to be binuclear with a bridging acetate cage structure and a nickel–nickel bond; this structure is very different from that of the bis(dithiobenzoato)nickel(II), which consists of a trimeric association of complex molecules wherein bidentate ligands form four-membered rings.

Crystals of $C_{32}H_{28}Ni_2S_8$ are red-brown orthorhombic prisms: $a = 9{\cdot}232 \pm 0{\cdot}003$, $b = 29{\cdot}420 \pm 0{\cdot}007$, $c = 12{\cdot}097 \pm 0{\cdot}001$ Å, $U = 3286$ Å^3; $D_m = 1{\cdot}59 \pm 0{\cdot}02$ g. cm.$^{-3}$ (by flotation); $Z = 8$, $D_c = 1{\cdot}591$ g. cm.$^{-3}$; space group $Iba2$ (C_{2v}^{21}, No. 45) from systematic absences and structure determination. Data are taken from Weissenberg photographs, using Cu-K_α ($\lambda = 1{\cdot}5418$ Å) radiation.

The structure was solved by Patterson and Fourier methods, using 1337 independent reflections. Co-ordinates and isotropic temperature factors were refined by least-squares to the present set of values, corresponding to $R = 9{\cdot}0\%$.

The structure consists of binuclear molecules of composition $(PhCH_2CS_2)_4Ni_2$ (see Figure), with intermolecular contacts greater than 3·49 Å. The molecule has a binary symmetry axis, passing through the two nickel atoms, which are chemically (but not crystallographically) equivalent. Each nickel atom has five neighbours, *i.e.* four sulphur atoms and one nickel atom. The four sulphur atoms form a plane (maximum deviation of 0·02 Å) from which the nickel atom is displaced by about 0·13 Å, in order to approach the other nickel atom to a distance of 2·56 Å ($\sigma = 0{\cdot}005$ Å). Therefore, each nickel is five-coordinate and its geometry is that of a tetragonally-distorted square-pyramid, with the four Ni–S bonds in the range 2·21—2·23 Å ($\sigma = 0{\cdot}005$ Å).

The planes of the phenyl groups are approximately orthogonal to each other. As the shape of the molecule clearly shows, the nickel–nickel distance of 2·56 Å must be considered structure-determining and, therefore, a real nickel–nickel bond.

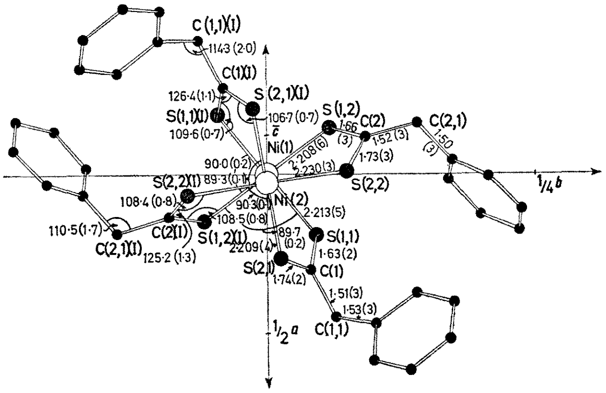

FIGURE. *Projection of the molecule on* (10$\bar{4}$), *with bond lengths in* Å *and angles in degrees* (*standard deviations in parentheses*).

Nickel–nickel bonds of the same order of magnitude were found in two acetato-bridged binuclear complexes of nickel, *i.e.* in bis-1-3-diphenyltriazenidonickel(II) (2·38 Å)[3] and in bis(monothiobenzoato)nickel(II) (2·49 Å).[4]

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[1] C. Furlani and M. L. Luciani, *Inorg. Chem.*, 1968, **7**, 1586; C. Furlani, M. L. Luciani, and R. Candori, *J. Inorg. Nuclear Chem.*, 1968, **30**, 3121; M. Bossa, *J. Chem. Soc.*, in the press.

[2] M. Bonamico, G. Dessy, and V. Fares, *Chem. Comm.*, 1969, 324.

[3] M. Corbett and B. F. Hoskins, *Chem. Comm.*, 1968, 1602.

[4] M. Bonamico, G. Dessy, and V. Fares, *Chem. Comm.*, 1969, 697.