# Mixed Nickel Co-ordination in a Binuclear Complex with a Short Nickel–Nickel Bond

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THE co-ordination behaviour of carboxylic anions is quite varied and the compounds of carboxylic acid derivatives have been divided by structure into five groups.[1] When the two terminal atoms of the ligand bond with two metal atoms, the ligand forms the syn–syn configuration giving a bridged structure [like copper(II) acetate monohydrate[2]]. There is no known nickel complex with this type of structure; however, a binuclear complex of nickel(II)bis-1,3-diphenyltriazenide,[3] in which the NNN-group closely resembles the OCO-group, has been reported.

We report the preliminary results of an *X*-ray analysis on nickel monothiobenzoate which is found to be a binuclear complex with a bridging acetate cage structure. The two nickel atoms are separated by 2·49 Å, and one is co-ordinated by a molecule of ethyl alcohol. Our interest in this compound is related to our structural studies on metal dithiocarboxylates[4,5,6] and the *X*-ray analysis was undertaken in conjunction with the parallel research of Furlani and co-workers[7] on their spectrochemical and magnetic behaviour.

Crystals of $C_{30}H_{26}Ni_2O_5S_4$ are red–brown triclinic prisms; $a = 10{\cdot}465 \pm 0{\cdot}010$, $b = 11{\cdot}644 \pm 0{\cdot}010$, $c = 12{\cdot}680 \pm 0{\cdot}010$ Å $\alpha = 91°40'$, $\beta = 93°5'$, $\gamma = 93°10'$, $U = 1540$ Å$^3$; $D_m = 1{\cdot}54 \pm 0{\cdot}02$ g.cm.$^{-3}$ (by flotation); $Z = 2$, $D_c = 1{\cdot}536$ g.cm.$^{-3}$; space group $P\bar{1}$($C_i^1$, No. 2). Data are taken from Weissenberg photographs, using Cu-$K_\alpha$ ($\lambda = 1{\cdot}5418$ Å) radiation.

The structure was determined by Patterson and Fourier methods using 2096 independent reflections. Co-ordinates and anisotropic temperature factors were refined by least squares to the present set of values, corresponding to $R = 0{\cdot}09$. The structure consists of binuclear molecules of composition $(PhCOS)_4Ni_2{\cdot}C_2H_5OH$, a pair of which, related by a centre of symmetry, forms a dimer through Ni–S interactions (Figure).

The two nickel atoms Ni(1) and Ni(2) appear to be different. Ni(1) is planar and bonded to four oxygen atoms belonging to four different thioacetate groups; its co-ordination is completed by the oxygen atom of ethyl alcohol and the other nickel atom. Ni(2) also has six neighbours: it lies in the plane of the four sulphur atoms of the thioacetate groups and forms short bonds with a sulphur atom belonging to the centrosymmetrically related molecule and with Ni(1). The co-ordination for Ni(1) is tetragonally distorted octahedral. The five Ni–O bond lengths are in the range 2·00—2·09 Å ($\sigma = 0{\cdot}009$ Å) which is a typical

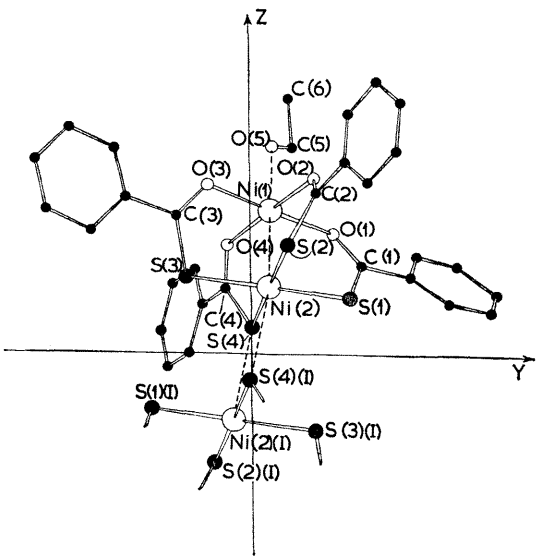


FIGURE. [100] *projection, on the* y-z *plane. One molecule is shown in total, and only a part of the centrosymmetrically related molecule is shown. Adjacent oxygen atoms subtend with* Ni(1) *angles near* 90°, *the same as do sulphur atoms in the plane with* Ni(2). *The average value for* Ni(1)–$\widehat{O}$–C *is* 123°, *for* Ni(2)–$\widehat{S}$–C 105°, *and for* O–$\widehat{C}$–S 123°.

range for Ni–O bonds in octahedral structures, and the nickel–nickel distance of 2·49 Å ($\sigma = 0{\cdot}004$ Å) is equal to that found in metallic nickel.[8] For Ni(2), instead, the four closest sulphur atoms are in the range 2·22—2·23 Å ($\sigma = 0{\cdot}004$ Å), a range typical of Ni–S bonds in tetra-co-ordinated complexes of nickel. However, the Ni–Ni interaction and the fifth Ni–S bond length of 2·82 Å ($\sigma = 0{\cdot}005$ Å) in the near axial positions complete a distorted six-co-ordination.

The phenyl groups are not completely coplanar with respect to the O–C–S groups, 15° being about the average angle between them, and the average C–phenyl group distance is 1·50 Å. These results appear to be in agreement with the interpretation of the u.v. spectra of the free ligand.[9]

Only one nickel–nickel bond length of the same order of magnitude (2·38 Å) has been found until now.[3] Although it is difficult to decide if the metal–metal interaction is structure-determining, in this case we consider that the contribution of the nickel–nickel interaction is decisive because the two intersecting rings bridging the nickel atoms appear to be twisted in order to permit the nickel–nickel separation of 2·49 Å.

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