Mixed Nickel Co-ordination revealed in a Crystallographic Study of Trimeric Bis(dithiobenzoato)nickel(II)

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CONTINUING our structural studies of metal dithiocarboxylates,[1,2] we have undertaken the *X*-ray analysis of bis(dithiobenzoate)nickel(II). Crystals of this complex exhibit unusual spectrochemical behaviour,[3] the interpretation of which would be facilitated by knowledge of the crystal and molecular structures.

B are similar but not identical. Each is nearly planar, the mean deviation being 0·08 Å, and the C–phenyl group distances of 1·47—1·48 Å indicate a partial double-bond character, consistent with planarity.

A trimer appears to be formed, resembling that found in bis(dithiobenzoate)Pd.[1] It contains one molecule of type

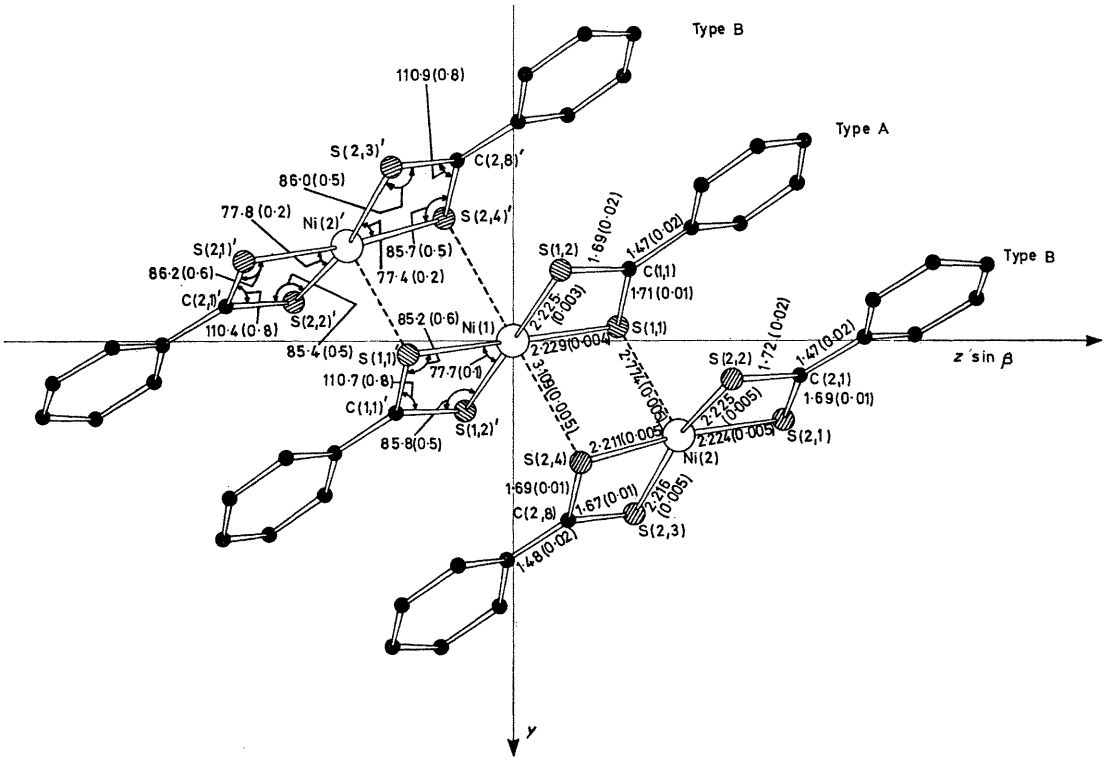

FIGURE. [100] *projection of the molecules with bond lengths (in* Å*) and angles (in degrees) (standard deviations in parentheses).*

Crystals of $(PhCS_2)_2Ni$ are deep blue monoclinic prisms, $a = 5{\cdot}809 \pm 0{\cdot}01$, $b = 17{\cdot}306 \pm 0{\cdot}005$, $c = 21{\cdot}392 \pm 0{\cdot}01$ Å; $\beta = 93° 56' \pm 10'$; $U = 2146$ Å^3; $D_m = 1{\cdot}69$ g.cm.$^{-3}$ (by flotation); $Z = 6$; $D_c = 1{\cdot}69$ g.cm.$^{-3}$; $F(000) = 1104{\cdot}5$; space group $P2_1/n$ from systematic absences. Data are taken from Weissenberg photographs, using Cu-K_α ($\lambda = 1{\cdot}5418$ Å) radiation. The intensities of 1621 independent reflections were visually estimated from equi-inclination Weissenberg photographs taken about the *a*-axis and precession photographs about the *b*-axis.

Since there are six molecules per unit cell, at least two (crystallographically equivalent) must be centrosymmetric (type A in the Figure). A three-dimensional Patterson synthesis showed that the other four (crystallographically equivalent) are in general positions (type B).

Atomic co-ordinates, determined by Fourier methods, and anisotropic temperature factors were refined by least-squares techniques to R 0·091. Molecules of types A and A, linked centrosymmetrically through short Ni–S bridges to two molecules of type B, the three molecules being closely parallel (see Figure). The Ni co-ordination in both A- and B-type molecules is essentially square planar with Ni–S distances in the range 2·21—2·23 Å ($\sigma = 0{\cdot}005$ Å), a range typical of Ni–S bonds in tetra-co-ordinated complexes of nickel. But, if the trimer bridges are included, Ni(1) in A should be regarded as having tetragonally distorted octahedral co-ordination [Ni(1) to both S(2,4) and S(2,4)' being 3·109 Å], and Ni(2) in B as being penta-co-ordinated [Ni(2)–S(1,1) = 2·774 Å]. No other atom outside the trimer is less than 4·0 Å from Ni(2). The trimer bridges are respectively 0·68 and 0·34 Å greater than the sum of the covalent radii (2·43 Å), but are proportionately considerably shorter than the corresponding bridges in the Pd complex, and are strong enough apparently to have induced more significant buckling of the molecules in the present structure. Thus, while Ni(1) and the four

S atoms in A are strictly coplanar, this group has been twisted with respect to the rest of molecule A to displace S(1,1) 0·34 Å towards molecule B. Similarly Ni(2) and S(2,4) are displaced from the mean plane of B by 0·38 and 0·28 Å toward A along their respective bridges. The evidence points, therefore, to bridging which is distinctly stronger in the Ni trimer than in the Pd analogue.

Comparison of the two complexes shows that, although the values of a and β match, the lengths of b and c differ markedly and the space groups differ ($P2_1/c$ for Pd). The fact that, despite these differences, similar trimers are found, though differently packed, confirms for both structures the importance of the intra-trimer bonds and the relative unimportance of the inter-trimer contacts.

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