The Crystal and Molecular Structure of the Five-co-ordinate Complex Di-isothiocyanato-[*NN*-bis-(2-diethylaminoethyl)-2-diphenylarsinoethylamine]-nickel(II)

By M. DI VAIRA and L. SACCONI*

(*Istituto di Chimica Generale e Inorganica, Università di Firenze, Florence, Italy*)

COMPLEXES of nickel(II) and cobalt(II) with the "tripod-like" ligand *NN*-bis-(2-diethylaminoethyl)-2-diphenylarsinoethylamine (bddae), $(Et_2N{\cdot}CH_2{\cdot}CH_2)_2N{\cdot}CH_2{\cdot}CH_2{\cdot}AsPh_2$, which contains one arsenic and three nitrogen atoms as potential donor atoms, have been prepared.[1] Those with formula $M^{II}(NCS)_2$ bddae are found to be high-spin complexes and their electronic spectra are diagnostic for five-co-ordination. These compounds are monomeric and are non-conductors in solution. Hence both isothiocyanato-groups are bonded to the metal atom; the i.r. data indicate that the bonding is through nitrogen. It follows that one out of the four potential donor atoms is not bonded to the metal atom.[1] The reflectance spectrum and *X*-ray powder diagram of the $Ni(NCS)_2$ bddae complex are identical with those of the related complex $Ni(NCS)_2$ bddpe [bddpe = $(Et_2N{\cdot}CH_2{\cdot}CH_2)_2N{\cdot}CH_2{\cdot}CH_2{\cdot}PPh_2$]. This indicates that neither the arsenic or phosphorus atom is bonded to the metal atom in these two complexes.

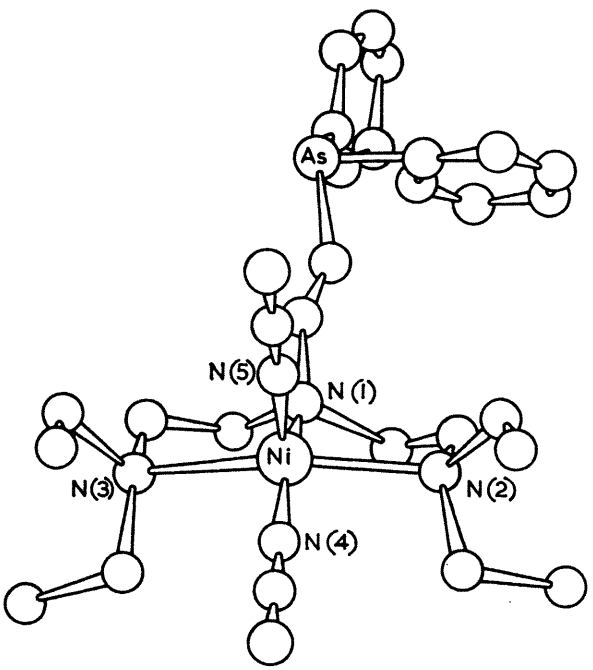

FIGURE. *A perspective view of the molecular configuration of* $Ni(NCS)_2$ bddae

A three-dimensional *X*-ray investigation has been undertaken on $Ni(NCS)_2$ bddae. Crystals of this compound are monoclinic, space group $P2_1/c$; $a = 15{\cdot}550 \pm 0{\cdot}013$, $b = 14{\cdot}552 \pm 0{\cdot}016$, $c = 18{\cdot}114 \pm 0{\cdot}015$ Å, $\beta = 127°\ 39' \pm 4'$; $D_m = 1{\cdot}31$, $Z = 4$, $D_c = 1{\cdot}32$ g.cm.$^{-3}$. Data were collected by means of the multiple-film equi-inclination Weissenberg technique, using Cu-K_α radiation.

The structure was solved by the heavy-atom method and refined by full-matrix least-squares with anisotropic temperature factors, to an *R* value of 7·3%, over 2171 observed reflections.

The structure consists of discrete $Ni(NCS)_2$ bddae molecules (Figure) in which the nickel(II) atom is in a five-co-ordinate environment of five nitrogen donor-atoms, three from the ligand molecule and two from the two isothiocyanate groups. The arsenic atom is not bonded to the metal, the Ni · · · As distance being 5·66 Å.

The co-ordination configuration can be described as a square pyramid with the metal atom 0·34 Å above the base. Distances and angles in the co-ordination polyhedron are: Ni–N(1) 2·08, Ni–N(2) 2·22, Ni–N(3) 2·18, Ni–N(4) 1·97, Ni–N(5) 1·95 Å, N(1)–Ni–N(5) 98·4, N(2)–Ni–N(5) 98·7,

N(3)–Ni–N(5) 99·6, N(4)–Ni–N(5) 100·3, N(1)–Ni–N(2) 82·6, N(1)–Ni–N(3) 82·5, N(2)–Ni–N(4) 93·9, N(3)–Ni–N(4) 94·9, N(1)–Ni–N(4) 161·2, N(2)–Ni–N(3) 157·8°; the average standard deviation is 0·01 Å for bond distances and 0·5° for angles.

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[1] L. Sacconi and R. Morassi, *Inorg. Nuclear Chem. Letters*, 1968, **4**, 449.