Journal of

The Chemical Society,

Chemical Communications

NUMBER 4/1975 19 FEBRUARY

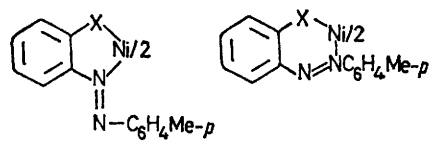
X-Ray Crystal Structures of Bis-(2-mercapto-4′-methylazobenzene)nickel(II) and Bis-(2-hydroxy-4′-methylazobenzene)nickel(II): Five-membered Metallocycle in the Former Complex

By Oleg A. Dyachenko,* Lev O. Atovmyan, and Sergei M. Aldoshin

(*Chemical Physics Institute of the Academy of Sciences, Chernogolovka, U.S.S.R.*)

Summary *X*-Ray structural data for the bis-azobenzenenickel(II) complexes (I) and (II) show that the donor atom X influences the size of the metallocycle and the bonding arrangement around nickel; in (I) (X = S) the metallocycle is five-membered, whereas in (II) (X = O) it is six-membered.

It has been reported[1] that the nickel(II) complexes bis-(2-mercapto-4′-methylazobenzene)nickel (I) and bis-2-hydroxy-4′-methylazobenzene)nickel (II) contain six-membered metallocycles. We report here an X-ray examination of



(I) X = S (II) X = O

compounds (I) and (II) as part of a study of the effect of the donor atom X on the structure of the metallocycle. We find that, while complex (II) does contain a six-membered metallocycle, the metallocycle in (I) is five-membered.

Crystal data: Compound (I): $C_{26}H_{22}N_4NiS_2$, M = 513·34, monoclinic, a = 13·615(3), b = 13·454(3), c = 13·575(5) Å, γ = 107°23′(3), U = 2373·1 Å^3, D_c = 1·445 g/cm^3, Z = 4, space group $B2/b$. Compound (II): $C_{26}H_{22}O_2N_4Ni$, M = 481·21, monoclinic, a = 11·880(3), b = 8·847(2), c = 11·992(4) Å, γ = 118°06′(3), U = 1111·8 Å^3, D_c = 1·445 g/cm^3, Z = 2, space group $P2_1/b$.

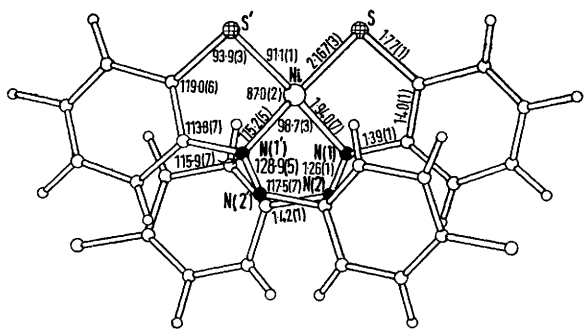


FIGURE 1. Structure of complex (I) showing bond lengths (Å) and bond angles in the chelate ring (e.s.d.'s in parentheses).

Intensities of 1412 (I) and 1660 (II) independent non-zero reflections $hk0$–$hk10$ and $hk0$–$hk13$ for (I) and (II), respectively, were measured on a DAR-UM automatic *X*-ray diffractometer by the layer registration technique using Mo-K_α radiation. Absorption corrections were not applied.

The structures were solved by direct methods. Refinement by full-matrix least-squares with isotropic temperature factors proceeded to R values of 0·111 for (I) and 0·068 for (II). Hydrogen atoms were located by a difference

Fourier map. Figures 1 and 2 show the structure, the principal bond lengths, and valency angles of the complexes (I) and (II).

Comparison of the structural data for complexes (I) and (II) has confirmed that the donor atom X influences the structure of the metallocycle. Complex (I) has a five-membered metallocycle in contrast to the six-membered metallocycle of complex (II). As far as we know, complex (I) is the first example of a compound in which one of the two multiply bonded atoms of the azo-group does not enter the metallocycle. Nevertheless the distance Ni · · · N(2) in both molecules is practically the same: 2·91 for (I) and 2·85 Å for (II). The structures of the co-ordination sphere in both molecules are different. Complex (I) has a tetrahedrally distorted square-planar arrangement of the ligands around the Ni atom with the two S atoms in *cis*-positions. Complex (I) has C_2 symmetry such that the Ni atom lies on a crystallographic two-fold axis. Complex (II) has exact C_i symmetry and shows an undistorted square-planar arrangement of the ligands around the Ni atom with the two oxygens in *trans* positions.

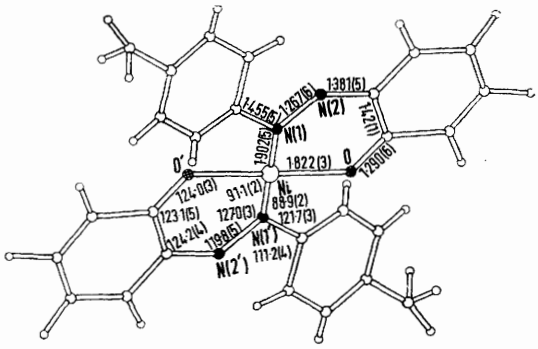


FIGURE 2. Structure of complex (II) showing bond lengths (Å) and bond angles in the chelate ring (e.s.d.'s in parentheses).

We thank Professor O. A. Osipov, and Drs. V. A. Kogan and S. G. Kochin for a gift of the crystals.

(*Received, 9th September* 1974; Com. 1142.)

[1] O. A. Osipov, V. I. Minkin, A. D. Garnovskii, V. A. Kogan, V. P. Kurbatov, L. E. Nivorozkin, L. S. Minkina, I. Ya. Kvitko, and S. G. Koshin, XV Mezdunarodnaya konferentsiya po koordinatsionnoi khimii, Tezisy dokladov, Moscow, 1973, p. 160.