The Crystal Structure of Bis(methyl thiohydroxamate)nickel(II)

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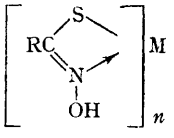
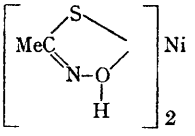
FOR the metal complexes of thiohydroxamic acid, Cambi, Bacchetti, and Paglia[1] in 1956, suggested the structure (I) in which the metal atom is linked to S and N atoms. Recently we have reported[2] that the nickel complex of methylthiohydroxamic acid forms a five-membered chelate ring (II), in which the metal co-ordinates with S and O atoms, and the chelate rings are *cis*.



(I)



(II)

The complexes were precipitated from nickel acetate and sodium acetothiohydroxamate in pH 6 buffer solutions and crystallized from methanol solutions. The following data were obtained using Cu-K_α radiation:

(*a*) from 100% MeOH, $Ni(C_2H_4ONS)_2$, $M = 239$ monoclinic, $a = 7{\cdot}52$, $b = 5{\cdot}79$, $c = 10{\cdot}20$ Å, $\beta = 103{\cdot}3$, $U = 432$ Å^3, $D_m = 1{\cdot}843$, $Z = 2$, $D_c = 1{\cdot}834$, space group $P2_1/c$

(*b*) from 90% MeOH, $Ni(C_2H_4ONS)_2$, $M = 239$ orthorhombic, $a = 15{\cdot}59$, $b = 5{\cdot}78$, $c = 9{\cdot}53$ Å, $U = 858$ Å^3, $D_m = 1{\cdot}823$, $Z = 4$, $D_c = 1{\cdot}849$, space group $P2_12_12_1$

(*c*) from 80% MeOH, $Ni(C_2H_4ONS)_2,H_2O$, $M = 257$ monoclinic, $a = 22{\cdot}13$, $b = 6{\cdot}09$, $c = 14{\cdot}20$ Å, $\beta = 95{\cdot}45°$, $U = 1905$ Å^3, $D_m = 1{\cdot}793$, $Z = 8$, $D_c = 1{\cdot}792$, space group $C2/c$ or Cc

The crystal structure of (*a*) has been now determined by *X*-ray diffraction methods, the structure of (*b*) has already been reported[2] by our *X*-ray group, and the analysis of structure (*c*) is in progress. The intensities of 1114 significantly non-zero reflections were measured with an automatic diffractometer (with Mo-K_α radiation) equipped with SrO–ZrO_2 balanced filters, and the structure determined from the Patterson functions was refined by the least-squares method using the full matrix and assuming independent isotropic temperature-factors for all atoms; the final *R*-value was 11·3% for the 1114 reflections used.

Bond distances and angles are shown in the Figure, the nickel atoms are required to be at symmetry centres and the bonds around the nickel atom are found to have a *trans*-configuration.

The standard deviations in intramolecular bond distances are $\sim 0{\cdot}005$ Å between Ni and light atoms and $\sim 0{\cdot}012$ Å between pairs of light atoms. Bisthiohydroxamatonickel(II) seems to be the first example of a nickel complex which can take either the *cis*- or *trans*-configuration according to experimental conditions.

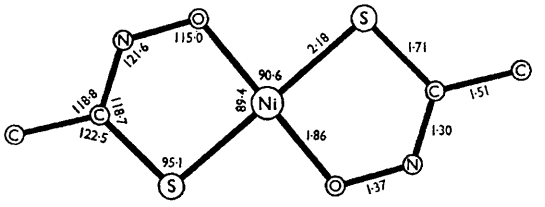


FIGURE. *Intramolecular bond distances* (Å) *and angles* (*degrees*).

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[1] L. Cambi, T. Bacchetti, and E. Paglia, *Istituto Lombardo* (*Rend. Sci.*), **1956**, **90**, 577.
[2] T. Sato, K. Nagata, M. Shiro, and H. Koyama, *Chem. Comm.*, 1966, 192.