

Structure of the Methylthiohydroxamic Acid Complex of Nickel

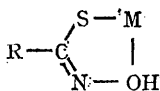
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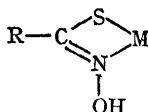
THERE are three possible structural formulae, (I), (II), and (III), for metal complexes of thiohydroxamic acid, of which (III) is ruled out by infrared-spectroscopic evidence.

Although Mizukami and Nagata¹ recently presumed on the basis of chemical evidence that metal complexes of thiohydroxamic acid consisted of a five-membered chelate ring (I) in which the metal

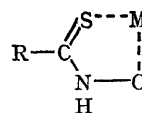
automatic diffractometer² (with Mo- K_{α} radiation) equipped with SrO-ZrO₂ balanced filters, and the structure was solved by the heavy-atom method. The later stages of refinement, by full-matrix least-squares analysis, were based on 431 reflections, those suspected of extinction or with count smaller than 150 having been rejected; the final *R*-value was 5.0%.



(I)



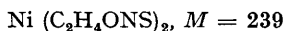
(II)



(III)

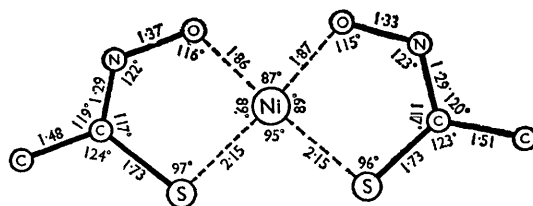
formed co-ordinate bonds with sulphur and oxygen atoms, structure (II), a four-membered ring with the metal co-ordinated to nitrogen and sulphur atoms, was not altogether ruled out. We have therefore carried out an *X*-ray-crystallographic study of the structure of the nickel complex of methylthiohydroxamic acid. The complex was prepared from nickel acetate and sodium aceto-thiohydroxamate, and was crystallised from 80% methanol.

The following data were obtained using Cu- K_{α} radiation:



Orthorhombic, $a = 15.59$, $b = 5.78$, $c = 9.53 \text{ \AA}$, $U = 858 \text{ \AA}^3$, $D_m = 1.823$, $Z = 4$, $D_c = 1.849$, space group $P2_12_12_1$ (No. 19). The intensities of 1050 significantly non-zero reflections were measured by

Details of the structure are shown in the Figure, the standard deviation of the bond lengths being ± 0.01 (Ni-S), ± 0.02 (Ni-O), ± 0.04 (C-S), and $\pm 0.04 \text{ \AA}$ (C-C, C-N, and N-O). The atoms of the five-membered chelate ring are coplanar with one another to within 0.01 \AA . This seems to be the first thiohydroxamate complex to have been studied by *X*-ray analysis.



(Received, February 1st, 1966; Com. 059.)

¹ T. Mizukami and K. Nagata, *Chem. and Pharm. Bull. (Japan)*, 1966, in the press.

² U. W. Arndt and D. C. Phillips, *Acta Cryst.*, 1961, **14**, 807.