SHORT COMMUNICATIONS

Crystal Structures of 1-(2-Thiazolylazo)-6-bromo-2-naphthol and Bis(1-(2-thiazolylazo)-2-naphthol)iron(II)

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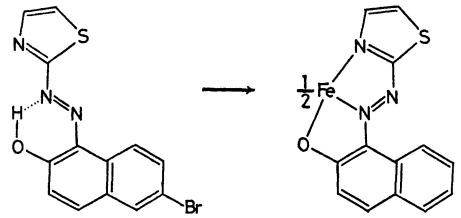
The crystal structures of 1-(2-thiazolylazo)-6-bromo-2-naphthol(TAN-Br) and bis(1-(2-thiazolylazo)-2-naphthol)iron(II) ([Fe[TAN)$_2$]) have been determined by X-ray diffraction. Our main interest lies in the reactions of thiazolylazo-naphthol(TAN) with various metal ions as an analytical reagent. 6-Bromo-derivative of TAN was chosen for the elucidation of structure by the heavy atom method.

The crystals of TAN-Br were grown by sublimation of crude materials. Crystal data are: $C_{13}H_8N_3OSBr$, M.W. 334.2, mp 189°C, orthorhombic, $a=19.07\pm0.03$, $b=32.08\pm0.05$, $c=4.22\pm0.01$ Å. $Dm=1.72$g·cm^{-3}, $Z=8$, $Dx=1.72$ g·cm^{-3}; space group $P2_12_12_1$. Intensities of the three-dimensional reflections were measured visually from equi-inclination Weissenberg photographs for 0—3 layers around the c-axis and 0th layer around the a-axis. In total, 2074 independent reflections were collected and converted into $|F|$ values in the usual way. The structure was solved by the heavy atom method. Parameters were refined by the least-squares method and the R value was reduced to 0.12.

Crystal data of [Fe(TAN)$_2$] are: [Fe($C_{13}H_8N_3OS$)$_2$]·$CHCl_3$·C_2H_5OH·H_2O, F.W. 784.0, triclinic, $a=12.63$, $b=11.97$, $c=10.52$ Å, $\alpha=87°12'$, $\beta=99°36'$, $\gamma=104°46'$. $Dm=1.63$ g.cm^{-3}, $Z=2$, $Dx=1.64$ g.cm^{-3}; space group $P\bar{1}$. Using Cu$K\alpha$ radiation, 3318 intensity data were collected by photographic method for 0—8 layers around the c-axis and 0—2 layers around the a-axis. The structure was solved by the heavy atom method and refined by the block-diagonal least-squares method. R factor was found to be 0.18.

The two crystallographically independent TAN-Br molecules are similar in shape and size. They are planar within a deviation of ±0.03 and ±0.15 Å. Both molecules conform to the chemical formula presented in Fig. 1a. The N···O distance of 2.50 Å suggests an intramolecular hydrogen bonding between N and O atoms as indicated in Fig. 1a.

The structure of [Fe(TAN)$_2$] is shown in Figs. 1b and 2. The TAN acts as a terdentate ligand. One Fe(II) ion is bonded octahedrally to two phenolic oxygens, two azo nitrogens adjacent to the naphthol ring and two thiazole nitrogens to form four five-membered chelate rings. The ligand molecules are very nearly planar and the mean planes of the ligands are perpendicular to each other. The two ligands are in *mer* coordination. Thus the structure determined from the measurement of stability constant and absorption spectra has been verified. Since the structure of TAN-Br and probably also of TAN is as shown in Fig. 1a, 180° rotation around the two N–C bonds should occur in chelate ring formation and turn the structure into that shown in Fig. 1b.



a TAN-Br b [Fe(TAN)$_2$]

Fig. 1. Comparison between TAN-Br and [Fe(TAN)$_2$].

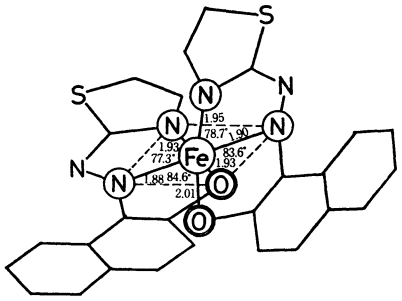


Fig. 2. The Structure of Fe(II) chelate [Fe(TAN)$_2$].

The general feature of coordination of TAN to Fe(II) is very similar to that of 1-(2-pyridylazo)-2-naphthol(PAN) observed in crystals of [Cu(PAN)-H_2O]·ClO_4.[1]

1) S. Ooi, D. Carter, and Q. Fernand, *Chem. Commun.*, **1967**, 1301.