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The Crystal Structure of Bis[1-(2-thiazolylazo)-2-naphtholato]-iron(II)-Chloroform(2/3)

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Synopsis. The crystals of bis[1-(2-thiazolylazo)-2-naphtholato]iron(II)-chloroform (2/3) are triclinic, with unit-cell dimensions of: $a=12.509(7)$, $b=11.911(6)$, $c=10.460(4)$ Å, $\alpha=86.97(3)$, $\beta=97.24(4)$, and $\gamma=103.48(7)°$, $Z=2$ for $[\mathrm{Fe^{II}(C_{13}H_8N_3OS)_2}]\cdot 1.5\mathrm{CHCl_3}$, space group $P\bar{1}$. The complex is diamagnetic, and the iron atom is surrounded octahedrally by two terdentate ligands in the *mer* configuration.

The analytical use of heterocyclic azo dyestuffs, such as 1-(2-pyridylazo)-2-naphthol (Hpan) and 1-(2-thiazolylazo)-2-naphthol (Htan), has been the subject of a considerable number of papers; however, few crystallographic studies have been reported. We, therefore, have begun a systematic study of the structures of the metal chelates of these analytically important dyestuffs. It was thought that the determination of the crystal structures would be of great help in the design of new analytical reagents. The tan-complexes rather than the pan-complexes were selected because the coordination property of the thiazole ring appeared to be more interesting than that of pyridine. Thus far, the structures of Pd(II)-, Ni(II)-, Cu(II)-, and Co(III)-tan chelates have been determined.[1-4)]

This note will deal with the structure of the Fe(II)-tan chelate, bis[1-(2-thiazolylazo)-2-naphtholato]iron(II) (abbr. as $[\mathrm{Fe^{II}(tan)_2}]$). A preliminary work based on the photographic data has been published.[5)]

Experimental

The single crystals of $[\mathrm{Fe^{II}(tan)_2}]\cdot 1.5\mathrm{CHCl_3}$ were obtained by recrystallization from a chloroform solution of $[\mathrm{Fe^{II}(tan)_2}]$ by the slow evaporation of the solvent. The crystal data are: triclinic, $a=12.509(7)$, $b=11.911(6)$, $c=10.460(4)$ Å, $\alpha=86.97(3)$, $\beta=97.24(4)$, and $\gamma=103.48(7)°$, $V=1503.0$ Å^3, $D_m=1.63$, $D_x=1.64\ \mathrm{g\cdot cm^{-3}}$, $Z=2$ for $[\mathrm{Fe^{II}(tan)_2}]\cdot 1.5\mathrm{CHCl_3}$, $\mu=95.7\ \mathrm{cm^{-1}}$ (for Cu$K\alpha$), space group $P\bar{1}$. The specimen crystal had the dimensions of *ca.* $0.15\times0.3\times0.35$ mm. Both the determination of the cell constants and the collection of the intensity data were carried out on a Rigaku automated four-circle diffractometer using Cu$K\alpha$ radiation monochromatized with a graphite plate. The ω-2θ scan technique was employed at a scan rate of 4°/min in ω. Weak reflections with $|F|$ values less than $3\sigma(|F|)$ were omitted from the data, and a total of 1864 non-zero reflections ($\pm h$, $\pm k$, $l\geq0$) were recorded in the range of $0°<2\theta<120°$. The intensities were corrected for the Lorentz and polarization factors, but not for absorption.

Structure Determination and Refinement

The centrosymmetric space group was indicated by the intensity statistics and has been used throughout. The structure was solved by the heavy-atom method. The analysis of a three-dimensional Patterson map gave the coordinates of Fe, S, and S′. The positions of the remaining non-hydrogen atoms were obtained from the successive Fourier and difference syntheses. After several cycles of least-squares refinement with isotropic temperature factors, anisotropic thermal parameters were introduced for Fe, S, S′, Cl(1), Cl(2), and Cl(3). At the final stage of the refinement, the calculated hydrogen positions and the isotropic temperature factor of 5.0 Å^2 were included in the structure factor calculations, but were not refined; the R value reached

TABLE 1. AVERAGE BOND DISTANCES AND ANGLES

Bond distances (Å)		Bond angles (°)	
Fe -O	1.97(1)	O -Fe -N(1)	84(1)
Fe -N(1)	1.88(2)	N(1) -Fe -N(3)	80(1)
Fe -N(3)	1.95(2)	C(11)-S -C(12)	90(1)
S -C(11)	1.71(2)	Fe -O -C(2)	110(1)
S -C(12)	1.72(2)	Fe -N(1) -N(2)	121(1)
O -C(2)	1.31(2)	Fe -N(1) -C(1)	115(1)
N(1) -N(2)	1.31(2)	N(2) -N(1) -C(1)	123(2)
N(1) -C(1)	1.40(2)	N(1) -N(2) -C(11)	107(2)
N(2) -C(11)	1.39(3)	Fe -N(3) -C(11)	111(2)
N(3) -C(11)	1.32(2)	Fe -N(3) -C(13)	139(2)
N(3) -C(13)	1.41(3)	C(11)-N(3) -C(13)	111(2)
C(1) -C(2)	1.39(3)	N(1) -C(1) -C(2)	110(2)
C(1) -C(10)	1.44(3)	N(1) -C(1) -C(10)	127(2)
C(2) -C(3)	1.45(3)	C(2) -C(1) -C(10)	122(2)
C(3) -C(4)	1.37(3)	O -C(2) -C(1)	122(2)
C(4) -C(5)	1.39(3)	O -C(2) -C(3)	118(2)
C(5) -C(6)	1.44(3)	C(1) -C(2) -C(3)	120(2)
C(5) -C(10)	1.44(3)	C(2) -C(3) -C(4)	117(2)
C(6) -C(7)	1.35(4)	C(3) -C(4) -C(5)	124(2)
C(7) -C(8)	1.41(4)	C(4) -C(5) -C(6)	121(2)
C(8) -C(9)	1.40(3)	C(4) -C(5) -C(10)	121(2)
C(9) -C(10)	1.41(3)	C(6) -C(5) -C(10)	117(2)
C(12)-C(13)	1.33(3)	C(5) -C(6) -C(7)	122(2)
CH -Cl(1)	1.71(6)	C(6) -C(7) -C(8)	121(2)
CH -Cl(2)	1.83(6)	C(7) -C(8) -C(9)	120(2)
CH -Cl(3)	1.81(6)	C(8) -C(9) -C(10)	121(2)
		C(1) -C(10)-C(5)	115(2)
		C(1) -C(10)-C(9)	125(2)
		C(5) -C(10)-C(9)	120(2)
		S -C(11)-N(2)	124(2)
		S -C(11)-N(3)	115(2)
		N(2) -C(11)-N(3)	122(2)
		S -C(12)-C(13)	113(2)
		N(3) -C(13)-C(12)	113(2)
		Cl(1) -CH -Cl(2)	106(3)
		Cl(1) -CH -Cl(3)	110(3)
		Cl(2) -CH -Cl(3)	104(3)

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0.124 for 1864 observed reflections. A unit weight was given to each reflection. The atomic scattering factors were taken from International Tables for X-ray Crystallography.[6] The final atomic parameters and the list of structure factors are kept as Document No. 7618 at the Chemical Society of Japan.

Description of the Structure and Discussion

The perspective view of the molecules and the numbering of atoms are given in Fig. 1, while the electron density map is shown in Fig. 2. The iron atom is six-coordinated, surrounded octahedrally by two terdentate ligands in the *mer* configuration. The ligand, 1-(2-thiazolylazo)-2-naphtholato (tan) group coordinates to the iron atom through the phenolic oxygen, the azo nitrogen adjacent to the naphthol ring and the thiazole nitrogen atoms giving two five-membered chelate rings. This mode of attachment of the tan to the metal is common in all the tan-complexes studied.[1–5] The metal environment of the $[Fe^{II}(tan)_2]$ complex is just the same as those of $[Ni^{II}(tan)_2]$ and $[Co^{III}(tan)_2]^+$, but differs from those of $[Pd^{II}Cl(tan)]$ and $[Cu^{II}(tan)(H_2O)_2]^+$.

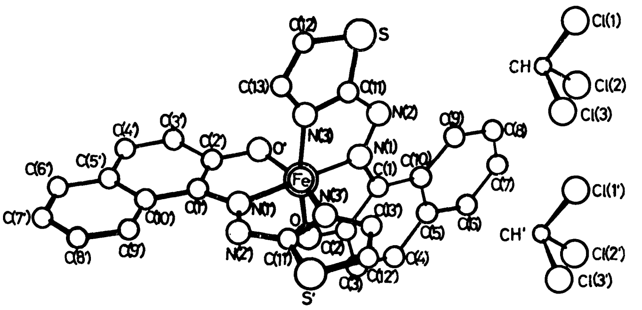

Fig. 1. Perspective view of the molecules and the numbering of atoms.

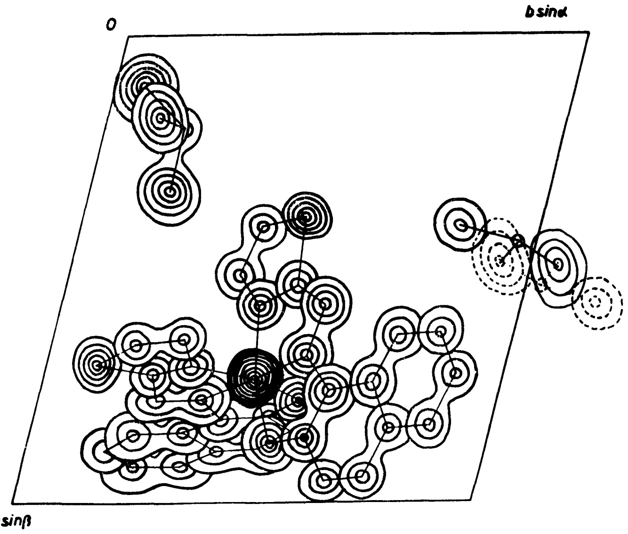

Fig. 2. Composite electron density map viewed down the c-axis. Contours are drawn at intervals of 2 e·Å^{-3} except for iron atom, the lowest contour being 2 e·Å^{-3}.

The average bond distances and angles, together with their e.s.d.'s, are given in Table 1. The bond angles around the metal, O–Fe–N(1) and N(1)–Fe–N(3), are compressed from the normal valence angles. This is attributable to the geometry of the tan ligand; a similar situation was observed for the other metal-tan complexes. The mean plane through Fe and the unprimed tan and that through Fe and the primed tan are roughly planar, and they are nearly perpendicular to each other.

It has been reported that the stability constants of metal chelates of tan and its analogues diminish in this order;[7]

$$Fe(II) > Ni(II) > Co(II) > Zn(II)$$

This order is the same as the stability series of Irving and Williams,[8] with the exception of Fe(II). This anomaly can be interpreted in terms of the orbital stabilization. Measurement of the magnetic moments confirmed that the iron atom utilizes d^2sp^3 orbitals, while the other three utilize sp^3d^2 orbitals.

The arrangment of the $[Fe^{II}(tan)_2]$ chelates is very similar to that observed in the crystals of $[Ni^{II}(tan)_2]$. However, the present crystal contains chloroform molecules (as a crystal solvent). One chloroform (CH, Cl (1), Cl (2), and Cl(3)) is in a general position, while the other chloroform (CH', Cl(1'), Cl(2'), and Cl(3'): half weight) is disordered and takes two possible orientations randomly and with equal probability about a center of symmetry at (1/2, 0, 0).

Calculations were carried out on the HITAC 5020F computer at the Computer Center of the National Aerospace Laboratory and on the NEAC 3100 computer at this Institute, using some UNICS programs.

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