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The Crystal Structure of Bis(1-(2-thiazolylazo)-2-naphtholato)nickel(II)

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Synopsis. The crystals of bis(1-(2-thiazolylazo)-2-naphtholato)nickel(II), [Ni(TAN)$_2$], are triclinic with unit-cell dimensions: a=12.38(6), b=12.72(6), c=8.41(4) Å, α=78.9(5), β=95.0(5) and γ=115.1(5)°, Z=2, space group P$\bar{1}$. The TAN is terdentate, one nickel atom being surrounded octahedrally by two ligand anions in the *mer* configuration.

As part of studies on the structures of metal chelates of 1-(2-thiazolylazo)-2-naphthol (abbr. as H-TAN), the X-ray determination of bis(1-(2-thiazolylazo)-2-naphtholato)nickel(II), [Ni(TAN)$_2$], has been carried out.[1] The aim of the present investigation is to establish the configuration around the nickel atom. Two terdentate ligands in the complex were expected to be coordinated to the central metal atom as in the case of iron(II)-chelate, [Fe(TAN)$_2$];[2] however, the crystal of [Ni(TAN)$_2$] is not isomorphous with that of [Fe(TAN)$_2$] even though they are recrystallized from the same solvent (chloroform), the former giving diffuse diffraction spots. It was thus desirable to establish the structure of [Ni(TAN)$_2$]. It is of interest to compare the structure of this compound with that of the palladium(II)-TAN complex, [PdCl(TAN)],[3] since the electronic configuration is of d^8 for both metal ions.

Experimental

The crystals of [Ni(TAN)$_2$] were obtained by slow evaporation of a chloroform solution. Unit-cell dimensions were determined by the oscillation and Weissenberg photographs around the a-, b-, and c-axes. The density was measured by the flotation method in an aqueous NaI solution. The crystal data are shown in Table 1. Owing to the poor crystallinity of the specimens, the diffraction spots were markedly diffuse. With the use of Cu$K\alpha$ radiation, intensities of 795 independent non-zero reflections were determined visually from multiple film Weissenberg photographs of the layers (0—6)kl, $h0l$, and $hk0$. The usual Lorents and polarization factors were applied to the observed intensities, no correction being made as regards absorption effect. All the intensities were then placed on a common scale. Since there are two complex molecules in a unit cell, the space group P$\bar{1}$ was assumed. This was justified by the subsequent smooth refinement.

TABLE 1. CRYSTAL DATA FOR [Ni(C$_{13}$H$_8$N$_3$OS)$_2$] (F.W.=567.3)

Triclinic, Space group P$\bar{1}$	
a=12.38±0.06 Å	V=1177 Å^3
b=12.72±0.06 Å	Z=2
c=8.41±0.04 Å	D_m=1.55 g·cm^{-3}
α=78.9±0.5°	D_x=1.60 g·cm^{-3}
β=95.0±0.5°	μ=32.7 cm^{-1} (for Cu$K\alpha$)
γ=115.1±0.5°	

Structure Determination and Refinement

The structure was determined by the heavy-atom method. The coordinates of the nickel and two sulfur atoms were deduced from the three dimensional Patterson maps. The remaining atomic positions were obtained by successive Fourier syntheses. The least-squares calculations were carried out with the use of isotropic temperature factors for all non-hydrogen atoms the R factor converging to 0.19. The anisotropic temperature factors were then applied to the nickel and two sulfur atoms, and the R index was improved to 0.16 after three cycles of refinement. The weighting scheme used was w=1.0 for $|F_o| \geqq 11.0$, and w=0.0 for $|F_o| < 11.0$. The diffraction data were so poor that no attempt was made to locate the hydrogen atoms. The structure thus obtained is chemically acceptable with satisfactory bond lengths and angles. The final atomic coordinates and thermal parameters of non-hydrogen atoms are shown in Table 2. The observed and calculated structure factors are listed in Table 3.*

Description of the Structure and Discussion

A perspective view of the molecule is shown in Fig. 1 along with the numbering of the atoms. The bond distances and angles are listed in Table 4 with their standard deviations. The TAN is present as a terdentate ligand; the thiazole nitrogen atom, the azo nitrogen atom adjacent to the naphthol ring and the phenolic oxygen atom are involved in chelate ring formation. The nickel atom is surrounded octahedrally by two ligand anions in the *mer* configuration. The features of the coordination of TAN to Ni(II)-, Fe(II)-, Pd(II)- and Cu(II)-atoms are common in their TAN-complexes. The configuration of [Ni(TAN)$_2$] coincides with that found in the crystals of [Fe(TAN)$_2$],[2] but differs from that of palladium(II)-chelate, [PdCl(TAN)],[3] or copper(II)-chelate, [Cu(TAN)(H$_2$O)$_2$]$^+$,[3] in which the coordination configuration is square-planar or square-pyramidal, respectively. Both TAN anions are planar within the deviation ±0.2 Å. The bond angles of O–Ni–N(1), N(1)–Ni–N(3), O′–Ni–N′(1) and N′(1)–Ni–N′(3) are 80, 79, 80 and 76°, respectively, being fairly deviated from 90°. This is the characteristic feature which can be always seen in the TAN-complexes.

The crystal of Zn(II)–TAN chelate [Zn(TAN)$_2$] was found to be isostructural with that of [Ni(TAN)$_2$]. Both crystals have similar cell dimensions showing a

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* Table 3 is kept as Document No. 7419 at the Chemical Society of Japan, 1-5, Kanda-Surugadai, Chiyoda-ku, Tokyo,

TABLE 2. ATOMIC PARAMETERS AND THEIR STANDARD DEVIATIONS[a)]

Atom	x/a	y/b	z/c	B	Atom	x/a	y/b	z/c	B
Ni	0.198(1)	0.397(1)	0.329(1)						
S	0.101(1)	0.065(1)	0.690(2)		S′	0.875(1)	0.450(1)	0.154(2)	
O	0.276(3)	0.471(3)	0.110(4)	6.8(8)	O′	0.347(3)	0.483(2)	0.436(3)	6.0(8)
N(1)	0.225(4)	0.268(3)	0.281(5)	7.0(10)	N′(1)	0.169(4)	0.528(3)	0.366(5)	7.9(11)
N(2)	0.195(3)	0.171(3)	0.383(5)	6.8(10)	N′(2)	0.084(3)	0.554(3)	0.316(5)	6.6(10)
N(3)	0.138(3)	0.279(3)	0.535(4)	4.8(9)	N′(3)	0.048(3)	0.374(3)	0.224(4)	4.7(9)
C(1)	0.281(4)	0.282(3)	0.136(5)	4.2(10)	C′(1)	0.258(4)	0.617(4)	0.437(5)	5.8(12)
C(2)	0.302(5)	0.397(4)	0.043(6)	7.5(14)	C′(2)	0.353(4)	0.579(4)	0.473(5)	5.3(11)
C(3)	0.374(5)	0.443(5)	0.899(6)	8.8(15)	C′(3)	0.463(4)	0.648(4)	0.557(6)	6.7(13)
C(4)	0.402(4)	0.368(4)	0.845(6)	7.0(13)	C′(4)	0.475(5)	0.746(5)	0.607(7)	9.6(17)
C(5)	0.369(4)	0.247(4)	0.929(5)	5.9(12)	C′(5)	0.390(4)	0.791(4)	0.560(5)	5.9(12)
C(6)	0.409(5)	0.163(4)	0.874(6)	8.4(15)	C′(6)	0.400(5)	0.886(4)	0.618(6)	7.5(14)
C(7)	0.377(5)	0.050(4)	0.970(6)	8.7(15)	C′(7)	0.309(5)	0.931(4)	0.578(6)	8.3(15)
C(8)	0.304(5)	0.996(5)	0.101(7)	10.2(17)	C′(8)	0.197(4)	0.867(4)	0.501(5)	5.8(12)
C(9)	0.277(4)	0.084(4)	0.159(6)	6.5(12)	C′(9)	0.184(5)	0.771(5)	0.439(6)	8.7(15)
C(10)	0.309(4)	0.201(3)	0.068(5)	4.7(11)	C′(10)	0.268(5)	0.718(4)	0.489(6)	6.9(13)
C(11)	0.147(4)	0.166(4)	0.534(5)	6.0(12)	C′(11)	0.990(4)	0.449(4)	0.248(5)	5.9(12)
C(12)	0.074(5)	0.161(5)	0.787(7)	9.0(16)	C′(12)	0.858(5)	0.337(4)	0.081(6)	8.2(15)
C(13)	0.091(5)	0.253(4)	0.686(6)	8.3(15)	C′(13)	0.938(5)	0.293(5)	0.146(7)	9.8(17)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Ni	0.015(1)	0.017(1)	0.049(2)	0.023(2)	−0.007(3)	−0.022(2)
S	0.011(2)	0.017(2)	0.039(4)	0.021(3)	0.018(4)	−0.001(4)
S′	0.011(2)	0.020(2)	0.032(4)	0.019(3)	−0.009(4)	−0.017(4)

The anisotropic temperature factors are of the form:
$\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$

a) E.s.d.'s in parentheses are in units of least significant digit.

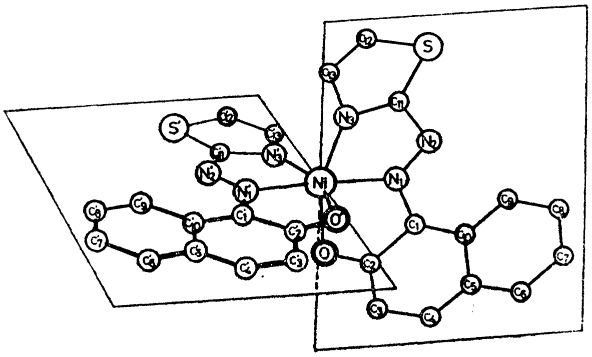

Fig. 1. Molecular structure of $[Ni(TAN)_2]$ and numbering of atoms.

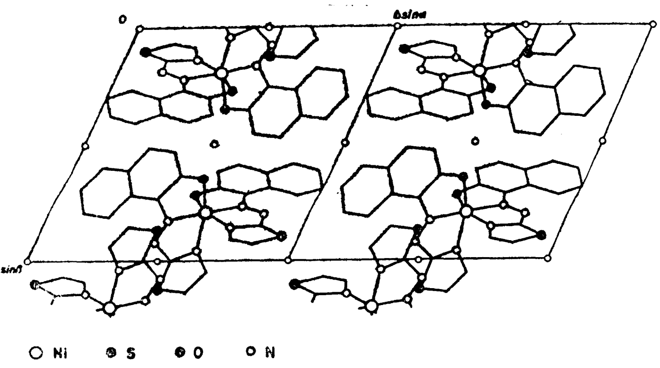

Fig. 2. The crystal structure of $[Ni(TAN)_2]$ as projected along the c-axis.

striking resemblance to each other in intensity distribution. It can thus be presumed that the molecular configuration of $[Zn(TAN)_2]$ is congruent with that of $[Ni(TAN)_2]$.

The crystal structure projected along the c-axis is shown in Fig. 2. No strong intermolecular interactions such as hydrogen bonding are observed in the structure. Since the positive charge of nickel(II) ion is neutralized by the coordination of the two bulky TAN ligands, the dominant force in the crystal should be essentially of the van der Waals type. Analogous packing of the chelate molecules can be observed in the crystals of $[Fe(TAN)_2]$ and $[Ni(TAN)_2]$, though vacant spaces are filled with solvent molecules in the former. Poor crystallinity of $[Ni(TAN)_2]$ might be related to the fact that some vacant spaces are retained in the crystal structure.

TABLE 4. AVERAGE BOND DISTANCES AND ANGLES

Bond lengths (Å)		Bond angles (°)	
Ni-O	1.98(4)	O-Ni-N(1)	80(2)
Ni-N(1)	1.93(5)	N(1)-Ni-N(3)	78(2)
Ni-N(3)	1.97(4)	C(11)-S-C(12)	90(3)
S-C(11)	1.59(6)	Ni-O-C(2)	113(3)
S-C(12)	1.68(6)	Ni-N(1)-N(2)	124(3)
O-C(2)	1.32(6)	Ni-N(1)-C(1)	118(3)
N(1)-N(2)	1.26(6)	N(2)-N(1)-C(1)	117(4)
N(1)-C(1)	1.40(6)	N(1)-N(2)-C(11)	113(4)
N(2)-C(11)	1.47(6)	Ni-N(3)-C(11)	116(3)
N(3)-C(11)	1.48(6)	Ni-N(3)-C(13)	149(4)
N(3)-C(13)	1.43(7)	C(11)-N(3)-C(13)	95(4)
C(1)-C(2)	1.44(7)	N(1)-C(1)-C(2)	107(4)
C(1)-C(10)	1.42(8)	N(1)-C(1)-C(10)	120(4)
C(2)-C(3)	1.46(8)	C(2)-C(1)-C(10)	120(4)
C(3)-C(4)	1.33(8)	O-C(2)-C(1)	120(4)
C(4)-C(5)	1.42(8)	O-C(2)-C(3)	118(5)
C(5)-C(6)	1.43(8)	C(1)-C(2)-C(3)	122(5)
C(5)-C(10)	1.44(8)	C(2)-C(3)-C(4)	118(5)
C(6)-C(7)	1.43(8)	C(3)-C(4)-C(5)	121(5)
C(7)-C(8)	1.41(8)	C(4)-C(5)-C(6)	121(5)
C(8)-C(9)	1.41(8)	C(4)-C(5)-C(10)	124(5)
C(9)-C(10)	1.46(8)	C(6)-C(5)-C(10)	114(5)
C(12)-C(13)	1.31(8)	C(5)-C(6)-C(7)	119(5)
		C(6)-C(7)-C(8)	127(5)
		C(7)-C(8)-C(9)	114(5)
		C(8)-C(9)-C(10)	121(5)
		C(1)-C(10)-C(5)	115(5)
		C(1)-C(10)-C(9)	121(5)
		C(5)-C(10)-C(9)	124(5)
		S-C(11)-N(2)	129(4)
		S-C(11)-N(3)	121(4)
		N(2)-C(11)-N(3)	108(4)
		S-C(12)-C(13)	109(5)
		N(3)-C(13)-C(12)	122(5)

Some of the calculations were carried out on the HITAC 5020F computer at the Computer Center of National Aerospace Laboratory, using the UNICS system programs.[4)] The other calculations were made on the NEAC 3100 computer at this Institute.

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References

1) A part of this study was reported in a preliminary communication; M. Kurahashi, *Chem. Lett.*, **1974**, 63.

2) M. Kurahashi, A. Kawase, K. Hirotsu, M. Fukuyo, and A. Shimada, This Bulletin, **41**, 1940 (1972).

3) M. Kurahashi, *Chem. Lett.*, **1974**, 63; This Bulletin, **47**, 2045 (1974).

4) "The Universal Crystallographic Computing System (I)," Japanese Crystallographic Association (1967).