The Crystal Structure of Bis[1-(2-thiazolylazo)-2-naphtholato]-cobalt(III) Perchlorate

Masayasu KURAHASHI

National Research Institute for Metals, 3-12, 2-Chome, Nakameguro, Meguro-ku, Tokyo 153

(Received May 14, 1976)

The crystal structure of bis[1-(2-thiazolylazo)-2-naphtholato]cobalt(III) perchlorate, $[Co^{III}(C_{13}H_8N_3OS)_2]ClO_4$ was determined from X-ray reflection data collected by counter methods. The crystals are monoclinic, space group $P2_1/c$, with $a=10.348(2)$, $b=21.066(5)$, $c=13.072(5)$ Å, $\beta=112.35(3)°$, and $Z=4$. The structure was determined by the heavy-atom method and refined by the least-squares technique to give an R value of 0.051 for 2696 observed reflections. The cobalt atom is six-coordinate and exhibits octahedral coordination. The 1-(2-thiazolylazo)-2-naphtholato group is coordinated as a terdentate ligand with the cobalt atom through the phenolic oxygen atom, the azo nitrogen atom adjacent to the naphthol ring and the thiazole nitrogen atom giving two five-membered chelate rings. Short intraligand contacts of 2.24(6) and 2.28(6) Å are observed between the azo nitrogen and naphthol hydrogen atoms.

1-(2-Thiazolylazo)-2-naphthol (Htan) was first used for the detection of metals by Boni and Hemmeler in 1958.[1] Since then, a number of applications of this dye as a spectrophotometric reagent or a complexometric indicator have been reported.[2-6] The proposed structures for some tan complexes with divalent metals were confirmed by X-ray analysis.[7-10] For the cobalt(III)–tan complex, however, there was an ambiguity concerning the structure.[3,4] X-Ray analysis was therefore carried out, a preliminary letter of the work being reported.[11]

Experimental

Single crystals of $[Co^{III}(tan)_2]ClO_4$ were grown from an ethanol solution by slow evaporation. The crystal data are given in Table 1. The unit-cell dimensions were determined by the least-squares technique using the 2θ angles of 11 reflections measured by a diffractometer. The density was determined by flotation in an aqueous solution of sodium iodide.

TABLE 1. CRYSTAL DATA
$[Co^{III}(C_{13}H_8N_3OS)_2]ClO_4$, F.W. 667.0

Monoclinic	Space group $P2_1/c$
$a=10.348(2)$ Å	$D_m=1.67$ g cm^{-3}
$b=21.066(5)$ Å	$D_x=1.68$ g cm^{-3}
$c=13.072(5)$ Å	$Z=4$
$\beta=112.35(3)°$	$\mu=9.9$ cm^{-1} (for Mo $K\alpha$)
$V=2635.4$ Å^3	

The intensity data were collected on a Rigaku automated four-circle diffractometer with Mo $K\alpha$ radiation monochromated with a graphite plate. The dimension of the crystal was $0.2\times0.2\times0.15$ mm. The ω-2θ scan technique was employed with a scan speed of 4°/min in ω. Scan range was calculated by the formula $1.5°+0.8°\times\tan\theta$. Measurement was automatically repeated until $\sigma(|F|)/|F|$ became less than 0.03, where $\sigma(|F|)$ is the standard deviation of $|F|$ due to the counting statistics. The maximum number of repetition was limited to four. The intensities of independent reflections

TABLE 2. POSITIONAL AND THERMAL PARAMETERS
(a) Fractional atomic coordinates for the non-hydrogen atoms.

	x	y	z		x	y	z
Co	0.0510(1)	0.0674(1)	0.2312(1)	N(1′)	−0.0205(3)	0.0919(2)	0.0817(5)
S	−0.1067(1)	0.1600(1)	0.4501(2)	N(2′)	−0.1250(3)	0.0611(2)	0.0124(4)
O	0.1827(2)	0.0112(2)	0.2133(4)	N(3′)	−0.0931(3)	0.0048(2)	0.1758(5)
N(1)	0.1296(3)	0.0442(2)	0.3807(5)	C(1′)	0.0521(4)	0.1383(2)	0.0577(6)
N(2)	0.0858(3)	0.0709(2)	0.4512(4)	C(2′)	0.1645(3)	0.1586(3)	0.1543(6)
N(3)	−0.0615(3)	0.1191(2)	0.2842(5)	C(3′)	0.2583(4)	0.2049(3)	0.1453(6)
C(1)	0.2327(4)	0.0014(3)	0.4048(6)	C(4′)	0.2457(4)	0.2264(3)	0.0447(7)
C(2)	0.2562(4)	−0.0151(3)	0.3065(6)	C(5′)	0.1349(4)	0.2701(3)	−0.0546(6)
C(3)	0.3608(4)	−0.0613(3)	0.3131(6)	C(6′)	0.1274(4)	0.2310(3)	−0.1552(7)
C(4)	0.4336(4)	−0.0889(3)	0.4107(7)	C(7′)	0.0183(5)	0.2127(3)	−0.2512(7)
C(5)	0.4134(4)	−0.0735(3)	0.5104(6)	C(8′)	−0.0816(4)	0.1717(3)	−0.2472(7)
C(6)	0.4944(4)	−0.1036(3)	0.6116(7)	C(9′)	−0.0769(4)	0.1455(3)	−0.1491(6)
C(7)	0.4749(4)	−0.0880(3)	0.7067(6)	C(10′)	0.0338(4)	0.1631(2)	−0.0495(6)
C(8)	0.3798(4)	−0.0429(3)	0.7060(7)	C(11′)	−0.1621(4)	0.0150(3)	0.0683(6)
C(9)	0.2996(4)	−0.0125(3)	0.6098(6)	C(12′)	−0.2590(4)	−0.0713(3)	0.1359(7)
C(10)	0.3135(4)	−0.0274(3)	0.5103(6)	C(13′)	−0.1468(4)	−0.0450(3)	0.2130(7)
C(11)	−0.0182(4)	0.1127(3)	0.3933(6)	Cl	0.5762(1)	0.3043(1)	0.4394(2)
C(12)	−0.2055(4)	0.1887(3)	0.3212(7)	O(1)	0.5593(5)	0.3566(4)	0.4935(10)
C(13)	−0.1666(4)	0.1622(3)	0.2444(6)	O(2)	0.7128(4)	0.2841(3)	0.4847(6)
S′	−0.3002(1)	−0.0358(1)	0.0105(2)	O(3)	0.4857(6)	0.2627(4)	0.4409(13)
O′	0.1789(2)	0.1344(2)	0.2489(4)	O(4)	0.5423(7)	0.3133(6)	0.3273(8)

b) Anisotropic thermal parameters for the non-hydrogen atoms($\times 10^4$). The anisotropic thermal parameters are in the form $\exp\{-(h^2B_{11}+k^2B_{22}+l^2B_{33}+hkB_{12}+hlB_{13}+klB_{23})\}$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	76(1)	16(1)	40(1)	−5(1)	48(1)	−8(1)
S	116(2)	25(1)	66(1)	9(2)	94(3)	−11(1)
O	80(5)	22(1)	45(3)	6(4)	46(7)	−5(3)
N(1)	73(6)	18(1)	53(4)	−5(5)	52(8)	−4(4)
N(2)	96(6)	22(1)	40(4)	10(6)	53(8)	−3(4)
N(3)	87(6)	18(1)	39(4)	−1(5)	38(8)	−3(4)
C(1)	85(7)	19(2)	51(5)	0(6)	61(10)	−8(5)
C(2)	73(8)	22(2)	66(5)	−11(6)	48(10)	−6(5)
C(3)	113(8)	27(2)	63(5)	−14(7)	73(11)	−18(6)
C(4)	79(8)	28(2)	86(6)	0(6)	51(12)	−12(5)
C(6)	73(7)	24(2)	70(5)	−4(6)	52(10)	−7(6)
C(6)	99(9)	26(2)	91(6)	27(7)	24(13)	16(6)
C(7)	131(9)	36(3)	59(5)	−8(8)	43(12)	19(6)
C(8)	123(9)	34(2)	62(6)	−2(7)	71(12)	0(6)
C(9)	106(9)	26(2)	49(5)	19(7)	49(11)	14(5)
C(10)	80(7)	20(2)	53(5)	−2(6)	39(10)	1(5)
C(11)	107(8)	20(2)	55(5)	−7(6)	80(10)	−7(5)
C(12)	118(9)	27(2)	89(6)	28(7)	100(13)	7(6)
C(13)	102(8)	21(2)	78(6)	0(7)	76(12)	−4(5)
S′	113(2)	23(1)	75(1)	−37(2)	48(3)	−16(1)
O′	88(5)	18(1)	48(3)	−14(4)	54(7)	−11(3)
N(1′)	91(6)	20(1)	45(4)	−13(5)	64(8)	−15(4)
N(2′)	92(6)	18(1)	52(4)	−19(5)	42(8)	−10(4)
N(3′)	100(7)	18(1)	54(4)	−16(5)	60(8)	−7(4)
C(1′)	86(7)	19(2)	47(5)	−22(6)	60(10)	−9(4)
C(2′)	88(8)	19(2)	57(5)	−9(6)	68(10)	−13(5)
C(3′)	102(8)	24(2)	61(5)	−5(6)	49(11)	−10(5)
C(4′)	104(9)	20(2)	81(6)	−17(6)	70(12)	−5(5)
C(5′)	105(8)	18(2)	53(5)	−2(6)	50(11)	6(5)
C(6′)	142(10)	18(2)	96(6)	−14(7)	102(14)	14(5)
C(7′)	168(12)	25(2)	44(5)	6(8)	23(13)	10(5)
C(8′)	171(11)	21(2)	63(6)	−25(7)	81(13)	−3(6)
C(9′)	128(9)	25(2)	59(5)	−18(7)	72(11)	−4(5)
C(10′)	112(8)	15(2)	50(5)	6(6)	75(11)	2(5)
C(11′)	114(9)	21(2)	39(5)	−22(6)	45(11)	−11(5)
C(12′)	111(9)	25(2)	111(6)	−44(7)	121(12)	−32(6)
C(13′)	117(9)	20(2)	81(6)	−11(6)	102(12)	−10(5)
Cl	111(3)	42(1)	132(2)	−8(2)	53(4)	−32(2)
O(1)	239(12)	84(3)	319(12)	146(11)	−106(20)	−172(11)
O(2)	157(9)	84(3)	141(7)	65(9)	15(13)	−88(8)
O(3)	447(21)	93(4)	619(24)	−223(16)	821(40)	−120(17)
O(4)	461(23)	176(7)	145(8)	22(19)	−14(22)	91(13)

(c) Positional and thermal parameters for the hydrogen atoms.

	x	y	z	B
H(3)	0.372(3)	−0.073(2)	0.247(5)	3.8(13)
H(4)	0.508(3)	−0.119(2)	0.413(5)	4.2(14)
H(6)	0.574(4)	−0.133(3)	0.605(6)	4.7(15)
H(7)	0.507(5)	−0.113(3)	0.777(7)	11.4(21)
H(8)	0.372(3)	−0.037(2)	0.785(5)	2.2(11)
H(9)	0.227(3)	0.018(2)	0.602(5)	4.0(14)
H(12)	−0.288(4)	0.222(3)	0.314(6)	7.4(16)
H(13)	−0.209(3)	0.174(2)	0.158(5)	5.4(14)
H(3′)	0.339(3)	0.224(2)	0.211(5)	4.6(14)
H(4′)	0.300(4)	0.260(2)	0.039(6)	2.6(14)
H(6′)	0.198(3)	0.258(2)	−0.154(5)	2.7(13)
H(7′)	0.017(3)	0.236(2)	−0.319(6)	6.5(15)
H(8′)	−0.162(3)	0.149(3)	−0.323(6)	6.0(15)
H(9′)	−0.145(3)	0.120(2)	−0.142(5)	2.8(13)
H(12′)	−0.324(4)	−0.109(3)	0.148(6)	6.7(16)
H(13′)	−0.094(3)	−0.058(2)	0.293(5)	3.5(12)

with $2\theta \leq 55°$ were measured and weak reflections with $|F| < 3\sigma(|F|)$ were excluded. A total of 2696 independent reflections were obtained and used for the structure determination. The intensities were corrected for Lorentz and polarization effects, but not for absorption because of the small size of the crystal.

Solution of the Structure and Refinement

The structure was determined by the heavy-atom method. The location of the cobalt and two sulfur atoms was determined by the Patterson method. A Fourier map phased on these atoms yielded the positions of all the non-hydrogen atoms. Structural parameters were refined by the block-diagonal least-squares calculations, until $R(=\sum||F_o|-|F_c||/\sum|F_o|)$ was reduced to 0.083. The function minimized was $w(|F_o|-|F_c|)^2$, where w equals unity. 15 of 16 hydrogen atoms were clearly detected on a difference Fourier map, the remaining hydrogen position (H(7)) being evaluated by calculation. After inclusion of the hydrogen atoms, a final set of least-squares calculations was carried out, and the R value reached 0.051 for the 2696 observed reflections. Atomic scattering factors for the non-hydrogen atoms were taken from the International Tables for X-ray Crystallography,[12] and those for the hydrogen atom from Stewart, Davidson and Simpson.[13] Table 2 gives the final atomic parameters together with their estimated standard deviations. Observed and calculated structure factors are compared in Table 3.*

Description of the Structure and Discussion

The thermal ellipsoids and the numbering of atoms are given in Fig. 1. The complex cation, $[Co^{III}(tan)_2]^+$, has approximately C_2 symmetry. The cobalt atom is surrounded octahedrally by two ligand anions (referred to as A, unprimed atoms and B, primed atoms) in the mer configuration. The configuration coincides with that of $[Fe^{II}(tan)_2]$[7] and $[Ni^{II}(tan)_2]$[8] but differs from that of $[Cu^{II}(tan)(H_2O)_2]^+$,[9] or $[Pd^{II}Cl(tan)]$.[10]

The 1-(2-thiazolyazo)-2-naphtholato group (tan) acts as a terdentate ligand, being coordinated to the metal through the phenolic oxygen atom, the azo nitrogen atom adjacent to the naphthol ring and the thiazole nitrogen atom to form two five-membered chelate rings. Such mode of coordination is commonly observed in all the tan-complexes studied. No participation of the thiazole sulfur atom in metal binding has been found.

The thiazole sulfur atom is not involved in chelate ring formation because of (1) the positive charge on the thiazole sulfur atom, predicted by MO calculation for π-electron density of Htan,[14] the metal ion binding with the positively charged sulfur atom being unfavorable; and (2) the angular distortion of the chelate rings. Two possible molecular models for chelation, where the hybridization state of the ligating atoms was assumed to be sp^2, are shown in Fig. 2. The angular distortion of the chelate rings in model (a) is smaller than that in model (b). The difference arises from the fact that C(11)–S is longer than C(11)–N(3) by 0.4 Å and that C(11)–S–C(12) angle is less than C(11)–N(3)–C(13) by

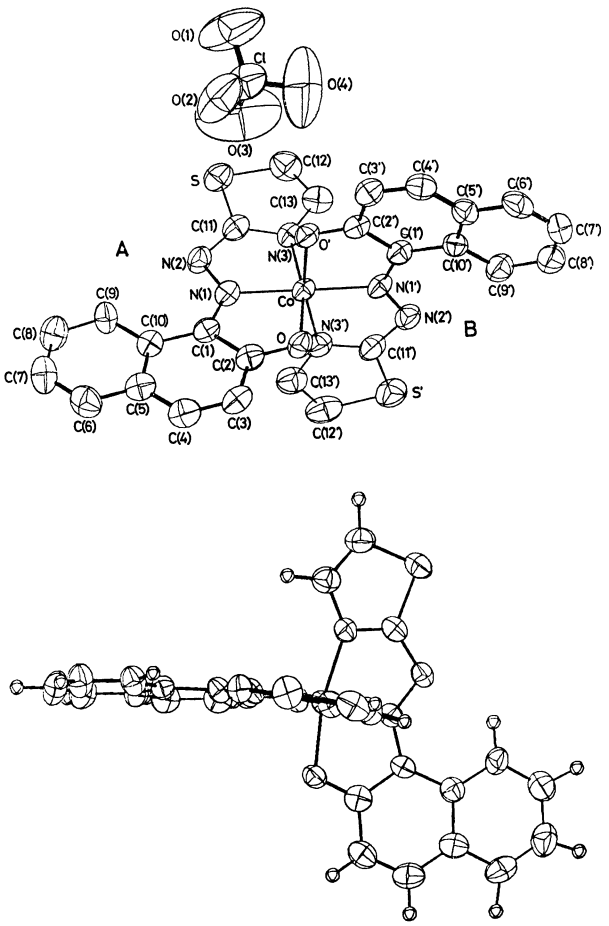


Fig. 1. (a) Thermals ellipsoids and numbering of atoms. The thermal ellipsoids are drawn at 50% probability. (b) The structure of the complex cation viewed perpendicular to the plane through Co and unprimed tan group.

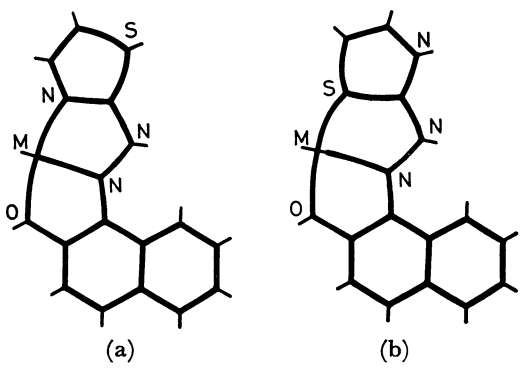


Fig. 2. Framework molecular models for the two linkage isomers.
(a) Coordination through O, N(1) and N(3). (Observed). (b) Coordination through O, N(1) and S. (Unobserved).

* Table 3 is kept as Document No. 7633 at the Chemical Society of Japan, 1-5, Kanada-Surugadai, Chiyoda-ku, Tokyo.

11°. If the hybridization state of the sulfur atom is not sp^2 and d-electron orbitals are involved in hybridization as indicated from the observed C(11)–S–C(12) angle of 90°, a larger angular distortion will occur, or chelation will not occur.[15]

The bond lengths and angles for the complex cation and the perchlorate anions are given in Table 4 with their e.s.d.'s. The geometries of the two moieties in the complex agree within the limit of three times their corresponding e.s.d.'s. The average Co–O distance of 1.888(4) Å is acceptable. The Co–N distances range from 1.874(5) to 1.918(6) Å, being significantly shorter than the Co–NH_3 distance observed in hexaamminecobalt(III) complex (1.972(1) Å).[16] The average O–Co–N(1) and N(1)–Co–N(3) angles are 85.0(2) and 81.4(2)° respectively, being compressed from the normal valence angles. On the other hand, average N(2)–N(1)–C(1), N(1)–C(1)–C(10), S–C(11)–N(2), and Co–N(3)–C(13) angles are enlarged to 125.7(5), 128.0(5), 124.6(5) and 139.0(4)°, respectively. Such an angular distortion is usually observed in the metal-tan complexes. The average N(1)–N(2), C(1)–N(1), and C(2)–O distances of 1.301(7), 1.349(8), and 1.291(8) Å, respectively, are between the corresponding single and double bonds. This will indicate the presence of some delocalization of π-electrons.

It is of interest to see the structural changes on chelate ring formation. Figure 3 shows a comparison of the structures of Htan and $[Co^{III}(tan)_2]^+$. Since there exist two crystallographically independent tan groups in an asymmetric unit, average values for bond lengths and angles are given. There is a notable difference in the conformation about the azo group; the two ring systems attached to the central azo group are rotated

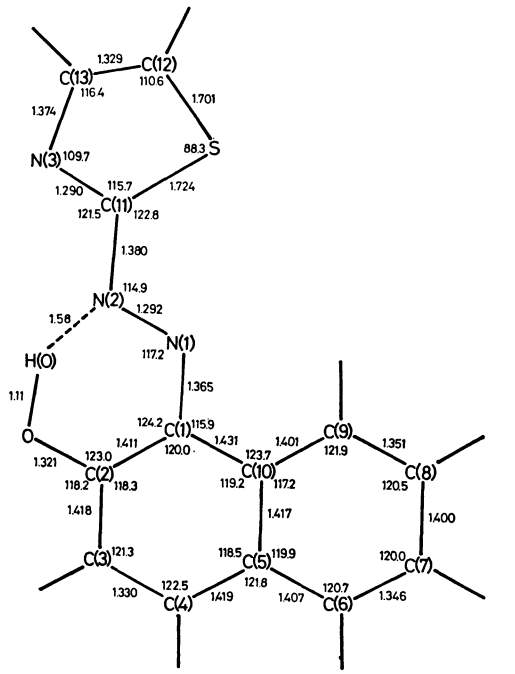
TABLE 4. BOND LENGTHS AND ANGLES

(a) Bond lengths (l/Å).

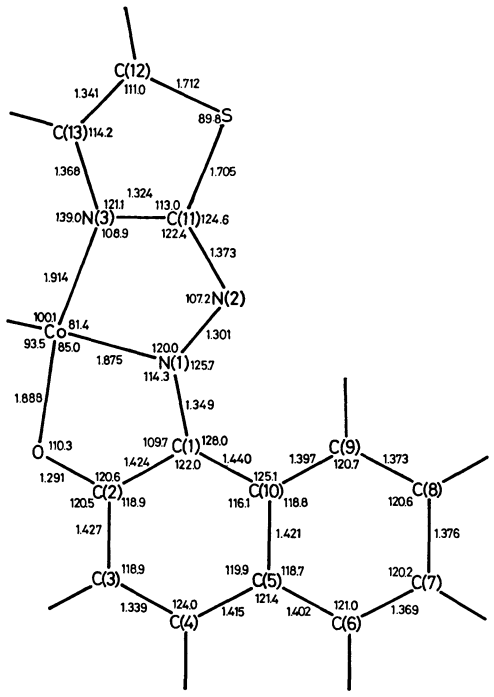
		Unprimed atoms	Primed atoms
Co	–O	1.886(4)	1.889(4)
Co	–N(1)	1.874(5)	1.875(5)
Co	–N(3)	1.909(5)	1.918(6)
S	–C(11)	1.703(7)	1.706(7)
S	–C(12)	1.709(8)	1.715(8)
O	–C(2)	1.291(8)	1.291(8)
N(1)	–N(2)	1.307(7)	1.294(7)
N(1)	–C(1)	1.347(8)	1.350(8)
N(2)	–C(11)	1.377(8)	1.369(9)
N(3)	–C(11)	1.323(8)	1.324(9)
N(3)	–C(13)	1.367(9)	1.368(9)
C(1)	–C(2)	1.432(9)	1.416(9)
C(1)	–C(10)	1.441(9)	1.438(9)
C(2)	–C(3)	1.436(10)	1.417(9)
C(3)	–C(4)	1.337(10)	1.341(10)
C(4)	–C(5)	1.412(10)	1.418(10)
C(5)	–C(6)	1.417(10)	1.387(10)
C(5)	–C(10)	1.414(9)	1.428(10)
C(6)	–C(7)	1.376(11)	1.361(12)
C(7)	–C(8)	1.369(11)	1.383(12)
C(8)	–C(9)	1.370(10)	1.375(11)
C(9)	–C(10)	1.394(9)	1.400(10)
C(12)	–C(13)	1.344(11)	1.338(11)
Cl	–O(1)	1.369(12)	
Cl	–O(2)	1.380(9)	
Cl	–O(3)	1.296(16)	
Cl	–O(4)	1.390(15)	
C(3)	–H(3)	0.98 (5)	1.04 (6)
C(4)	–H(4)	1.05 (6)	1.02 (6)
C(6)	–H(6)	1.05 (6)	1.02 (5)
C(7)	–H(7)	1.03 (7)	1.05 (6)
C(8)	–H(8)	1.06 (5)	1.08 (6)
C(9)	–H(9)	1.01 (6)	0.97 (5)
C(12)	–H(12)	1.11 (6)	1.10 (6)
C(13)	–H(13)	1.05 (6)	1.05 (5)

(b) Bond angles (φ/°).

			Unprimed atoms	Primed atoms
O	–Co	–N(1)	85.4(2)	84.6(2)
N(1)	–Co	–N(3)	81.3(2)	81.5(2)
C(11)	–S	–C(12)	89.6(3)	90.0(3)
Co	–O	–C(2)	110.1(4)	110.4(4)
Co	–N(1)	–N(2)	120.3(4)	119.7(4)
Co	–N(1)	–C(1)	114.4(4)	114.1(4)
N(2)	–N(1)	–C(1)	125.2(5)	126.1(5)
N(1)	–N(2)	–C(11)	106.7(5)	107.8(5)
Co	–N(3)	–C(11)	109.3(4)	108.5(4)
Co	–N(3)	–C(13)	138.1(4)	139.8(4)
C(11)	–N(3)	–C(13)	112.5(5)	111.7(5)
N(1)	–C(1)	–C(2)	109.2(5)	110.2(5)
N(1)	–C(1)	–C(10)	128.7(5)	127.2(5)
C(2)	–C(1)	–C(10)	122.1(5)	122.4(5)
O	–C(2)	–C(1)	121·1(5)	120.7(5)
C(1)	–C(2)	–C(3)	118.7(6)	119.0(5)
C(2)	–C(3)	–C(4)	118.8(6)	119.0(6)
C(3)	–C(4)	–C(5)	124.1(6)	123.8(6)
C(4)	–C(5)	–C(6)	121.4(6)	121.4(6)
C(4)	–C(5)	–C(10)	120.1(6)	119.7(6)
C(6)	–C(5)	–C(10)	118.5(6)	119.0(6)
C(5)	–C(6)	–C(7)	120.8(6)	121.1(7)
C(6)	–C(7)	–C(8)	119.8(6)	120.7(7)
C(7)	–C(8)	–C(9)	121.2(6)	120.0(7)
C(8)	–C(9)	–C(10)	120.9(6)	120.5(6)
C(1)	–C(10)	–C(5)	116.2(5)	116.0(5)
C(1)	–C(10)	–C(9)	125.0(6)	125.3(6)
C(5)	–C(10)	–C(9)	118.8(6)	118.7(6)
S	–C(11)	–N(2)	124.5(5)	124.7(5)
S	–C(11)	–N(3)	113.2(5)	112.8(5)
N(2)	–C(11)	–N(3)	122.3(5)	122.5(6)
S	–C(12)	–C(13)	111.1(5)	110.9(5)
N(3)	–C(13)	–C(12)	113.6(6)	114.7(6)
O(1)	–Cl	–O(2)	109.8(5)	
O(1)	–Cl	–O(3)	108.0(7)	
O(1)	–Cl	–O(4)	114.0(7)	
O(2)	–Cl	–O(3)	114.9(7)	
O(2)	–Cl	–O(4)	107.7(6)	
O(3)	–Cl	–O(4)	102.4(8)	
O	–Co	–N(1′)	93.5(2)	
N(3)	–Co	–N(1′)	99.7(2)	
O′	–Co	–N(1)	93.4(2)	
N(3′)	–Co	–N(1)	100.4(2)	



(a)



(b)

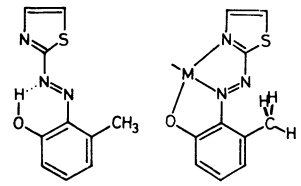
Fig. 3. Comparison of the structures between Htan and $[Co^{III}(tan)_2]^+$.
(a) Htan. (b) $[Co^{III}(tan)_2]^+$.

by 180° around the N(1)–C(1) and N(2)–C(11) bonds. As for the bond length distribution, all the corresponding distances in Htan and $[Co^{III}(tan)_2]^+$ agree within ± 0.03 Å.

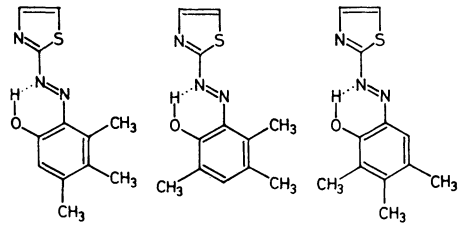
Comparison of N(1)–C(1)–C(10), C(1)–N(1)–N(2) and N(1)–N(2)–C(11) angles in Htan and $[Co^{III}(tan)_2]^+$ indicates that these angles are distorted by chelate ring formation. If these angles in $[Co^{III}(tan)_2]^+$ are the same as those observed in Htan, the N(2)···H(9) distance will be less than 1.8 Å. The observed distances are 2.24(6) and 2.28(6) Å for A and B, respectively. It is apparent that the tan deforms so as to relieve the N(2)···H(9) repulsion on chelate ring formation. Using the following potential function proposed by Giglio,[17]

$$V(r) = \{52100 \exp(-2.04r)\}/r^6 - 132/r^6$$

the N···H interaction energies $V(r)$ were calculated, and the values of 35.1 kcal/mol for $r=1.8$ Å and 2.3 kcal/mol for $r=2.3$ Å were obtained. This may indicate that the repulsion energy present in the complex is not too large; however, the steric effect would play an important role on chelate ring formation. A similar intraligand repulsion occurs in a complex of 2-(2-thiazolylazo)-3-methylphenol (I), as can be seen in I'.



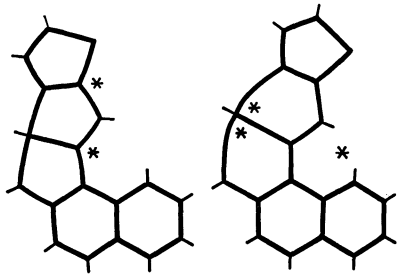
(I) (I')



(II) (III) (IV)

In the course of studying the extraction of nickel(II) chelates of 2-(2-thiazolylazo)-3,4,5-trimethylphenol (II), 2-(2-thiazolylazo)-3,4,6-trimethylphenol (III) and 2-(2-thiazolylazo)-4,5,6-trimethylphenol (IV) into benzene, Fujiwara and Kawase[18,19] found that stability constants, K, for the nickel chelates of II and III are lower than the values expected from the pK_a (acid dissociation constant) *vs* $\log K$ relation.[20] This implies a steric repulsion between the azo nitrogen and the methyl group at 3-position on the phenyl group.

It is likely that the magnitudes of the N(2)···H(9)



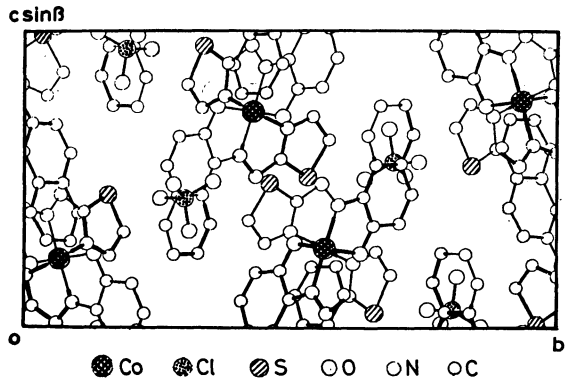
(a) (b)

Fig. 4. Framework molecular models for the tan-complex, showing that the magnitudes of the N(2)···H(9) repulsion and the angular distortion depend on the size of the central metal atom.
(a) Small metal ion. (b) Large metal ion.

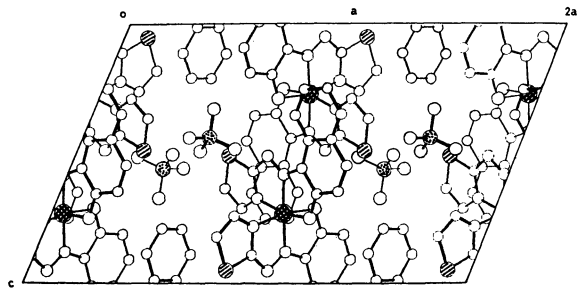
repulsion and the angular distortion depend on the size of the metal ion. Inspection of the molecular model (Fig. 4) reveals that in the complex of metal with small ionic radius the N(2)···H(9) repulsion and the angular distortion of O–M–N(1) and N(1)–M–N(3) will be small but the distortion of N(2)–N(1)–C(1) and S–C(11)–N(2) will be very large, whereas in the complex of metal with large ionic radius the former will be large and the latter small. This fact might be related to the selectivity of this reagent, that is, tan will not form a complex with metal having too small or too large ionic radius. It can be shown that the tan will not form a complex with metal whose coordination configuration is tetrahedral, so far as the tan acts as a planar terdentate ligand.[10]

A knowledge on structures may be useful for the prescription of a new analytical reagent. If one wishes to control the solubility, stability or absorbance of the complex, some functional groups are usually introduced in the ring system. In this case, it is important to take the effect of intramolecular repulsion into consideration. The present study revealed that the substitution of H(9) atom with a non-hydrogen atom or a large functional group will prevent the formation of a stable chelate ring. This means that it is unable to introduce a hydrophilic group or auxochromic group into 8-position (H(9) position) in the case of tan chelate. A similar argument holds for the substitution of H(13) atom (4-position of thiazole) with a large functional group.

The mean planes through Co and the unprimed tan



(a)



(b)

Fig. 5. (a) The crystal structure projected along the a axis.
(b) The crystal structure projected along the b axis.

TABLE 5. INTERATOMIC DISTANCES LESS THAN 3.5 Å

		Symmetry operation	Distance (l/Å)
S	O(2)	1	3.34
O	N(2′)	2	3.17
O	C(9′)	2	3.50
C(2)	C(6)	3	3.47
C(3)	C(9′)	2	3.42
C(4)	C(10)	3	3.45
C(6)	O′	3	3.24
C(6)	O(3)	3	3.44
C(7)	C(12)	4	3.41
C(8)	C(12)	4	3.50
C(9)	C(13′)	4	3.48
C(12)	C(8′)	5	3.48
C(12)	O(2)	6	3.26
C(13)	O(1)	7	3.44
C(13)	O(2)	7	3.33
C(13)	C(7′)	5	3.26
S′	O(1)	8	3.49
O′	C(6′)	5	3.23
C(4′)	O(3)	9	3.27
C(5′)	C(12′)	2	3.44
C(6′)	O(3)	9	3.44
C(8′)	C(13′)	2	3.47
C(9′)	C(13′)	2	3.46
C(12′)	O(1)	8	3.28

Symmetry operations

1	$(-1+x$	y	$z)$	6 $(1+x$	y	$z)$
2	$(-x$	$-y$	$-z)$	7 $(-1+x$	$\frac{1}{2}-y$	$-\frac{1}{2}+z)$
3	$(1-x$	$y-$	$1-z)$	8 $(-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z)$
4	$(-x$	$-y$	$1-z)$	9 $(x$	$\frac{1}{2}-y$	$-\frac{1}{2}+z)$
5	$(x$	$\frac{1}{2}-y$	$\frac{1}{2}+z)$			

and through Co and the primed tan are roughly planar (the maximum deviations being 0.08 and 0.17 Å, respectively) and these planes make an angle of 89°. The large displacements from the planes are due partly to non-bonded N(2)···H(9) repulsion and partly to intermolecular interaction. The structure of the complex cation viewed normal to the plane through the Co and the primed tan is given in Fig. 1(b).

The crystal structures projected along the a and b axes are illustrated in Fig. 5. The intermolecular distances less than 3.5 Å are listed in Table 5. There is no indication of hydrogen bonding.

The author wishes to express his sincere thanks to Professor Yoshihiko Saito of the University of Tokyo for use of the X-ray diffractometer. He is also grateful to Dr. Akira Kawase of National Chemical Laboratory for Industry for his valuable discussions. Part of the calculations was carried out on the HITAC 5020F computer at the Computer Center of the National Aerospace Laboratory, using SFR-5 and HBLS-4 programs in UNICS system.[21] The other calculations were performed on the NEAC 3100 computer of this Institute. Figures 1 and 5 were produced by DEAM-4 program.[22]

References

1) I. E. Boni and A. Hemmeler, *Chimica(Milan)*, **34**, 443 (1958).

2) A. Kawase, *Bunseki Kagaku*, **11**, 628 (1962); **12**, 810 (1963); **13**, 553 (1964).
3) A. Kawase, *Bunseki Kagaku*, **12**, 904 (1963).
4) G. Nakagawa and H. Wada, *Nippon Kagaku Zgsshi*, **83**, 1185 (1962).
5) G. Nakagawa and H. Wada, *Nippon Kagaku Zasshi*, **85**, 202 (1964).
6) H. Wada and G. Nakagawa, *Bunseki Kagaku*, **14**, 28 (1965).
7) M. Kurahashi and A. Kawase, *Bull. Chem. Soc. Jpn.*, **49**, 1419 (1976).
8) M. Kurahashi, *Bull. Chem. Soc. Jpn.*, **47**, 2045 (1974).
9) M. Kurahashi, *Bull. Chem. Soc. Jpn.*, **47**, 2067 (1974).
10) M. Kurahashi and A. Kawase, *Bull. Chem. Soc. Jpn.*, **49**, 127 (1976).
11) M. Kurahashi, *Chem. Lett.*, **1974**, 1271.
12) "International Tables for X-ray Crystallography," Vol. III, Kynoch Press, Birmingham, England (1962).
13) R. T. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
14) K. Nishimoto, Private comunication.
15) M. Kurahashi, *Bull. Chem. Soc. Jpn.*, **49**, 2927 (1976).
16) M. Iwata and Y. Saito, *Acta Crystallogr.*, **B29**, 822 (1973).
17) E. Giglio, *Nature*, **222**, 339 (1969).
18) J. Fujiwara and A. Kawase, *Bunseki Kagaku*, **22**, 564 (1973).
19) J. Fujiwara and A. Kawase, Private communication.
20) J. G. Jones, J. B. Pooles, J. C. Tomkinson, and R. T. P. Williams, *J. Chem. Soc.* **1958**, 2001.
21) "The Universal Crystallographic Computing System (I)," ed. by T. Sakurai, The Crystallographic Society of Japan (1967).
22) A. Takenaka, "Schematic Drawing of Crystal and Molecular Structures Containing Atomic Thermal Motions," APPLY 270/30—503—001, Fujitsu Ltd., Tokyo (1972).