Crystal Structure of Chloro-1-(2-thiazolylazo)-2-naphtholatopalladium(II) Dioxane Solvate

Masayasu Kurahashi

Chemistry Division, National Research Institute for Metals, Meguro-ku, Tokyo 153

(Received January 29, 1974)

The crystals of chloro-1-(2-thiazolylazo)-2-naphtholatopalladium(II) dioxane solvate, [PdCl(TAN)]·$C_4H_8O_2$, are orthorhombic and of space group Pbcm, with unit cell dimensions: a=8.44(2), b=30.97(4) and c=6.82(2) Å and Z=4. The structure was determined by the heavy-atom method and refined by the least-squares procedure to give an R value of 0.097 for 1392 observed reflections. The crystallographic mirror plane normal to the c-axis coincides with the molecular plane of [PdCl(TAN)]. The 1-(2-thiazolylazo)-2-naphtholato group, *i.e.*, TAN, is a terdentate ligand; the phenolic oxygen atom, azo nitrogen atom and thiazole nitrogen atom are coordinated to the palladium atom to form two five-membered chelate rinsgs. The fourth coordination position is occupied by a chlorine atom.

Since Cheng and Bray used 1-(2-pyridylazo)-2-naphthol, "H-PAN", as an analytical reagent for metals in 1955,[1] a number of heterocyclic azo dyes have been prepared, their application to chemical analysis being studied by many researchers. 1-(2-Thiazolylazo)-2-naphthol (abbr. H-TAN) was found to be a useful and frequently used reagent for the spectrophotometric and titrimetric determination of metal ions as well as for their separation by solvent extraction techniques. In view of the lack of information on the structures of the metal chelate of H-TAN, a systematic X-ray investigation has been undertaken. This paper describes the structure of chloro-1-(2-thiazolylazo)-2-naphtholatopalladium(II) dioxane solvate.[2] This complex has been selected because its coordination configuration might be planar and it would differ from the configuration of iron(II)-, cobalt(II)- and nickel(II)-complexes. It is also of interest to see whether or not the thiazole sulfur atom takes part in the chelate ring formation.

Experimental

Green-colored and needle-like crystals were obtained by slow diffusion of aqueous palladium(II) chloride into dioxane solution of H-TAN. The crystal data are given in Table 1. The unit-cell dimensions were determined by oscillation and Weissenberg photographs.

From systematic absences, the space group was found to be Pbc2 or Pbcm, the latter being more probable from the positive result of intensity statistics for centrosymmetry.

Table 1. Crystal data

$[PdCl(C_{13}H_8N_3OS)]\cdot C_4H_8O_2$
F. W. = 484.2
Orthorhombic
$a = 8.44\pm0.02$ Å
$b = 30.97\pm0.04$ Å
$c = 6.82\pm0.02$ Å
$V = 1783$ Å^3
$Z = 4$
$D_m = 1.8\ g\cdot cm^{-3}$
$D_x = 1.80\ g\cdot cm^{-3}$
$\mu = 111\ cm^{-1}$ (for Cu$K\alpha$)
Space group: Pbcm

The three dimensional data of hk(0—5) were collected from the equi-inclination Weissenberg photographs taken with Cu$K\alpha$ radiation. The intensities of reflections were measured visually by comparison with a standard scale, and corrected for the usual Lorentz and polarization factors. No absorption and extinction corrections were applied. The absolute scale of each layer were obtained at a later stage of refinement by correlation with the calculated values.

Structure Determination and Refinement

The positions of the palladium, sulfur, and chlorine atoms were readily deduced from three-dimensional Patterson maps. The Fourier synthesis of electron density phased on the positions of these heavy atoms revealed the location of the remaining atoms of the complex molecule. A difference synthesis was then carried out and 1,4-dioxane molecule was found to be trapped in the lattice. The structure thus obtained was refined by the block-diagonal least-squares method with the use of individual isotropic thermal factors. Unit weight was given to all the observed reflections. At the final stage of refinement, anisotropic temperature factors were introduced for all the non-hydrogen atoms and the R factor was reduced to 0.097 for 1392 non-zero reflections. The atomic scattering factors were taken from International Tables for X-ray Crystallography. The atomic coordinates and anisotropic thermal parameters along with their estimated standard deviations are given in Table 2, and the observed and calculated structure factors in Table 3*.

Description of the Structure and Discussion

The crystal consists of palladium(II)-complex and dioxane molecule. The bond lengths and angles are given in Table 4 together with their standard deviations. The thermal ellipsoids are shown in Fig. 1 with numbering of atoms.

The palladium(II)-complex is exactly planar, having a mirror symmetry fulfilling the requirement of the space group. The configuration around the palladium atom is square-planar. The 1-(2-thiazolylazo)-2-naphtholato group TAN is present as a terdentate

---

* Table 3 is kept as Document No. 7418 at the Chemical Society of Japan, 1—5, Kanda, Surugadai, Chiyoda-ku, Tokyo.

TABLE 2. ATOMIC PARAMETERS AND THEIR ESTIMATED STANDARD DEVIATIONS[a] ($\times 10^4$)
Temperature factors are of the form: $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$

	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pd	1815(2)	1792(1)	2500(*)	113(2)	12(0)	349(6)	−6(1)	0(*)	0(*)
Cl	364(7)	1160(2)	2500(*)	127(8)	12(1)	461(26)	−12(4)	0(*)	0(*)
S	6974(7)	1663(2)	2500(*)	110(8)	15(1)	430(26)	1(4)	0(*)	0(*)
O (1)	34(22)	2233(5)	2500(*)	95(21)	16(2)	482(68)	−10(12)	0(*)	0(*)
N (1)	3047(24)	2316(6)	2500(*)	84(23)	15(3)	449(81)	−16(13)	0(*)	0(*)
N (2)	4670(27)	2260(7)	2500(*)	122(30)	22(4)	380(81)	−29(18)	0(*)	0(*)
N (3)	3975(23)	1519(6)	2500(*)	129(28)	10(2)	415(78)	17(13)	0(*)	0(*)
C (1)	2337(28)	2706(7)	2500(*)	130(34)	11(3)	414(97)	2(16)	0(*)	0(*)
C (2)	591(27)	2628(7)	2500(*)	172(38)	5(2)	448(98)	−1(14)	0(*)	0(*)
C (3)	−450(33)	3000(9)	2500(*)	113(34)	26(5)	226(82)	−1(21)	0(*)	0(*)
C (4)	184(34)	3378(9)	2500(*)	223(50)	16(4)	247(83)	13(22)	0(*)	0(*)
C (5)	1874(30)	3430(7)	2500(*)	73(26)	18(3)	366(89)	−7(17)	0(*)	0(*)
C (6)	2433(29)	3898(8)	2500(*)	192(42)	11(3)	332(87)	−19(18)	0(*)	0(*)
C (7)	4070(29)	3969(8)	2500(*)	275(56)	10(3)	313(88)	−13(20)	0(*)	0(*)
C (8)	5175(33)	3644(9)	2500(*)	167(42)	29(5)	157(75)	4(25)	0(*)	0(*)
C (9)	4609(28)	3222(8)	2500(*)	202(42)	7(2)	348(84)	−10(17)	0(*)	0(*)
C (10)	2824(31)	3135(8)	2500(*)	291(60)	8(2)	307(88)	−17(19)	0(*)	0(*)
C (11)	5141(27)	1854(7)	2500(*)	207(43)	7(2)	304(80)	−18(16)	0(*)	0(*)
C (12)	6350(36)	1151(9)	2500(*)	177(46)	26(5)	332(98)	53(26)	0(*)	0(*)
C (13)	4676(30)	1120(8)	2500(*)	136(36)	18(4)	292(85)	0(19)	0(*)	0(*)
O (2)	9295(22)	4657(6)	2500(*)	156(29)	16(2)	523(77)	41(14)	0(*)	0(*)
O (3)	6287(23)	5054(6)	2500(*)	180(31)	14(2)	559(83)	0(13)	0(*)	0(*)
C (14)	8371(24)	4641(6)	757(38)	210(33)	19(3)	483(83)	34(16)	−134(91)	−74(25)
C (15)	7252(23)	5043(6)	742(34)	193(33)	21(3)	477(89)	1(16)	114(86)	72(27)

a) Standard deviations are given in parentheses. * Parameter constrained by symmetry requirements.

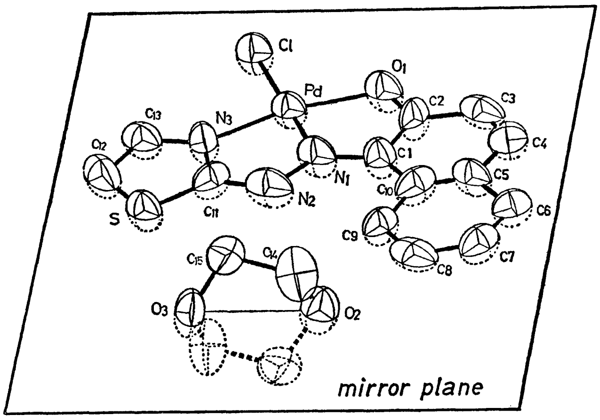

Fig. 1. Perspective drawing of [PdCl(TAN)] and dioxane.
The thermal ellipsoids are drawn at the 50% probability level. The diagram has been produced by the DEAM program.**

ligand; the phenolic oxygen atom, the azo nitrogen atom and the thiazole nitrogen atom are coordinated jointly to the palladium atom to form two five-membered chelate rings. The fourth coordination position is occupied by a chlorine atom. The feature of coordination of TAN to the palladium atom is quite common to those found in iron(II)-,[3] nickel(II)-[2] and copper(II)-TAN[2] chelates, although it is not the case with the configuration around the metal.

The structure of the palladium(II)-TAN chelate bears a close resemblance to that of the 1 : 1 copper(II)-PAN chelate observed in the crystals of $[Cu(PAN)H_2O]\cdot ClO_4$.[4] Distances of Pd-Cl(2.31 Å), Pd-O(1) (2.03 Å) and Pd-N(2.01 Å) are all normal, but the central bond in the chelate, Pd-N(1)(1.93 Å), is slightly shorter than the normal Pd-N distance(2.02 Å). Bond angles around the palladium atom, O(1)-Pd-N(1) and N(1)-Pd-N(3), are compressed to 80° and 82°, respectively.

The crystal structure of H-TAN recently has been determined by the present author.[5] There are two crystallographically independent molecules in an asymmetric unit. Both molecules are in concordance with the chemical formula presented in Fig. 2a, although the details of their molecular structures differ from each other. A comparison of the structure of H-TAN with that of TAN in the form of [PdCl(TAN)] (Fig. 2) shows that both of the two ring systems of H-TAN attached to the central azo group are rotated by 180° around the two N-C single bonds in the case of chelate ring formation.

The crystal structure, as projected along the c-axis, is shown in Fig. 3 together with intermolecular distances less than 3.75 Å. Successive [PdCl(TAN)] molecules lie above one another along the c-axis to form columns. The interplanar distance is 3.41 Å. The molecular columns are held together by the van der Waals forces, constructing layers parallel to the (010) plane. Diox-

---

** A. Takenada, "Schematic Drawing of Crystal and Molecular Structures Containing Atomic Thermal Motions", APPLY 270/23—503—001, Tokyo, Fujitsu Ltd.

Table 4. Bond lengths and angles

Bond lengths (Å)		Bond angles (°)	
Pd-Cl	2.31(1)	Cl-Pd-O(1)	100(1)
Pd-O(1)	2.03(2)	Cl-Pd-N(3)	98(1)
Pd-N(1)	1.93(2)	O(1)-Pd-N(1)	80(1)
Pd-N(3)	2.01(2)	N(1)-Pd-N(3)	82(1)
S-C(11)	1.65(2)	C(11)-S-C(12)	92(1)
S-C(12)	1.68(3)	Pd-O(1)-C(2)	111(1)
O(1)-C(2)	1.31(3)	Pd-N(1)-N(2)	115(2)
N(1)-N(2)	1.39(3)	Pd-N(1)-C(1)	122(2)
N(1)-C(1)	1.34(3)	N(2)-N(1)-C(1)	123(2)
N(2)-C(11)	1.34(3)	N(1)-N(2)-C(11)	114(1)
N(3)-C(11)	1.42(3)	Pd-N(3)-C(11)	109(1)
N(3)-C(13)	1.38(3)	C(11)-N(3)-C(13)	111(2)
C(1)-C(2)	1.49(3)	N(1)-C(1)-C(2)	106(2)
C(1)-C(10)	1.36(4)	N(1)-C(1)-C(10)	137(2)
C(2)-C(3)	1.46(4)	C(2)-C(1)-C(10)	117(2)
C(3)-C(4)	1.32(4)	O(1)-C(2)-C(1)	121(2)
C(4)-C(5)	1.40(4)	O(1)-C(2)-C(3)	120(2)
C(5)-C(6)	1.51(4)	C(1)-C(2)-C(3)	119(2)
C(5)-C(10)	1.26(4)	C(2)-C(3)-C(4)	116(2)
C(6)-C(7)	1.42(4)	C(3)-C(4)-C(5)	122(3)
C(7)-C(8)	1.37(4)	C(4)-C(5)-C(6)	116(2)
C(8)-C(9)	1.41(4)	C(4)-C(5)-C(10)	124(3)
C(9)-C(10)	1.53(4)	C(6)-C(5)-C(10)	121(2)
C(12)-C(13)	1.40(4)	C(5)-C(6)-C(7)	118(2)
O(2)-C(14)	1.41(3)	C(6)-C(7)-C(8)	123(2)
O(3)-C(15)	1.46(3)	C(7)-C(8)-C(9)	117(2)
C(14)-C(15)	1.55(3)	C(8)-C(9)-C(10)	121(2)
		C(1)-C(10)-C(5)	123(2)
		C(1)-C(10)-C(9)	118(2)
		C(5)-C(10)-C(9)	120(2)
		S-C(11)-N(2)	128(2)
		S-C(11)-N(3)	113(2)
		N(2)-C(11)-N(3)	119(2)
		S-C(12)-C(13)	113(2)
		N(3)-C(13)-C(12)	112(2)
		O(2)-C(14)-C(15)	108(2)
		O(3)-C(15)-C(14)	111(2)

ane molecules are located between the layers of the chelate molecules.

Part of the calculation was carried out on the HITAC 5020F computer at the Computer Center of the National Aerospace Laboratory, using PAMI, HBLS-4 and SFR-5 programs in UNICS system.[6] The other calculations were performed on the NEAC 3100 computer at this Institute.

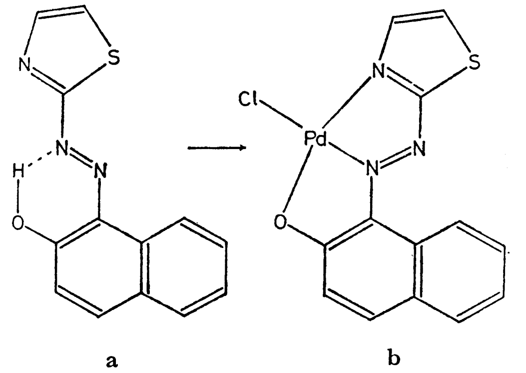

Fig. 2. Structure of [PdCl(TAN)] as compared with that of H-TAN.

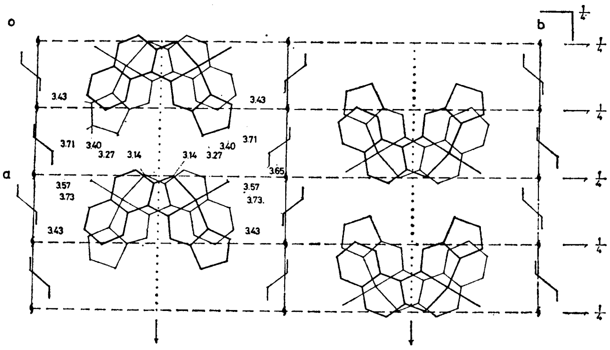

Fig. 3. The crystal structure projected along the *c*-axis.
Heavy lines indicate atoms at $z/c=1/4$, light line ones at $z/c=3/4$.

The author wishes to express his sincere thanks to Dr. A. Kawase for valuable discussions and advice.

References

1) K. L. Cheng and R. H. Bray, *Anal. Chem.*, **27**, 782 (1955).
2) A preliminary note; M. Kurahashi, *Chem. Lett.*, **1974**, 63.
3) M. Kurahashi, A. Kawase, K. Hirotsu, M. Fukuyo, and A. Shimada, This Bulletin, **45**, 1940 (1972).
4) S. Ooi, D. Carter, and Q. Fernando, *Chem. Commun.*, **1967**, 1301.
5) M. Kurahashi, *Chem. Lett.*, **1974**, 181.
6) "The Universal Crystallographic Computing System (I)", Japanese Crystallographic Association (1967).