

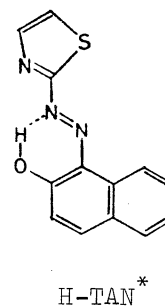
THE MOLECULAR STRUCTURES OF PALLADIUM(II), COPPER(II) AND NICKEL(II)
CHELATE OF 1-(2-THIAZOLYLAZO)-2-NAPHTHOL

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The structures of palladium(II), copper(II) and nickel(II) chelate of 1-(2-thiazolylazo)-2-naphthol have been determined by X-ray analysis. The coordination configuration around the metal atom has been found to be square-planar, square-pyramidal and octahedral for palladium, copper and nickel, respectively.

The compound, 1-(2-thiazolylazo)-2-naphthol (=H-TAN; $C_{13}H_9N_3OS$), is a complexing agent used in the spectrophotometric and titrimetric determination of metal ions as well as in their separation by solvent extraction technique. Applications of this reagent in analytical chemistry have been investigated in detail¹⁾; however, the structure of the metal chelates has not been established²⁾. In view of the lack of information on the structures of metal chelates of this analytically important azo-dyestuff, systematic investigations on the structure of the metal chelates have been attempted. The main interest lies in looking for the configuration around the metal atom and, furthermore, in seeing whether or not the thiazole sulfur atom takes part in chelate ring formation.



The crystals of palladium(II) complex, I, were obtained by slow diffusion of aqueous palladium(II) chloride into dioxane solution of H-TAN. The chelate is green and insoluble in water. Blue needle crystals of 1:1 copper(II)-TAN complex, II, were obtained from a dioxane-water solution. The crystals of nickel(II) chelate, III, were grown from a chloroform solution by slow evaporation; they have the visual appearance of metallic copper but the complex is violet in organic solutions. The crystal data of the metal chelates I, II and III are summarized in Table 1.

Table 1 The crystal data for TAN-complexes of Pd(II), Cu(II) and Ni(II).

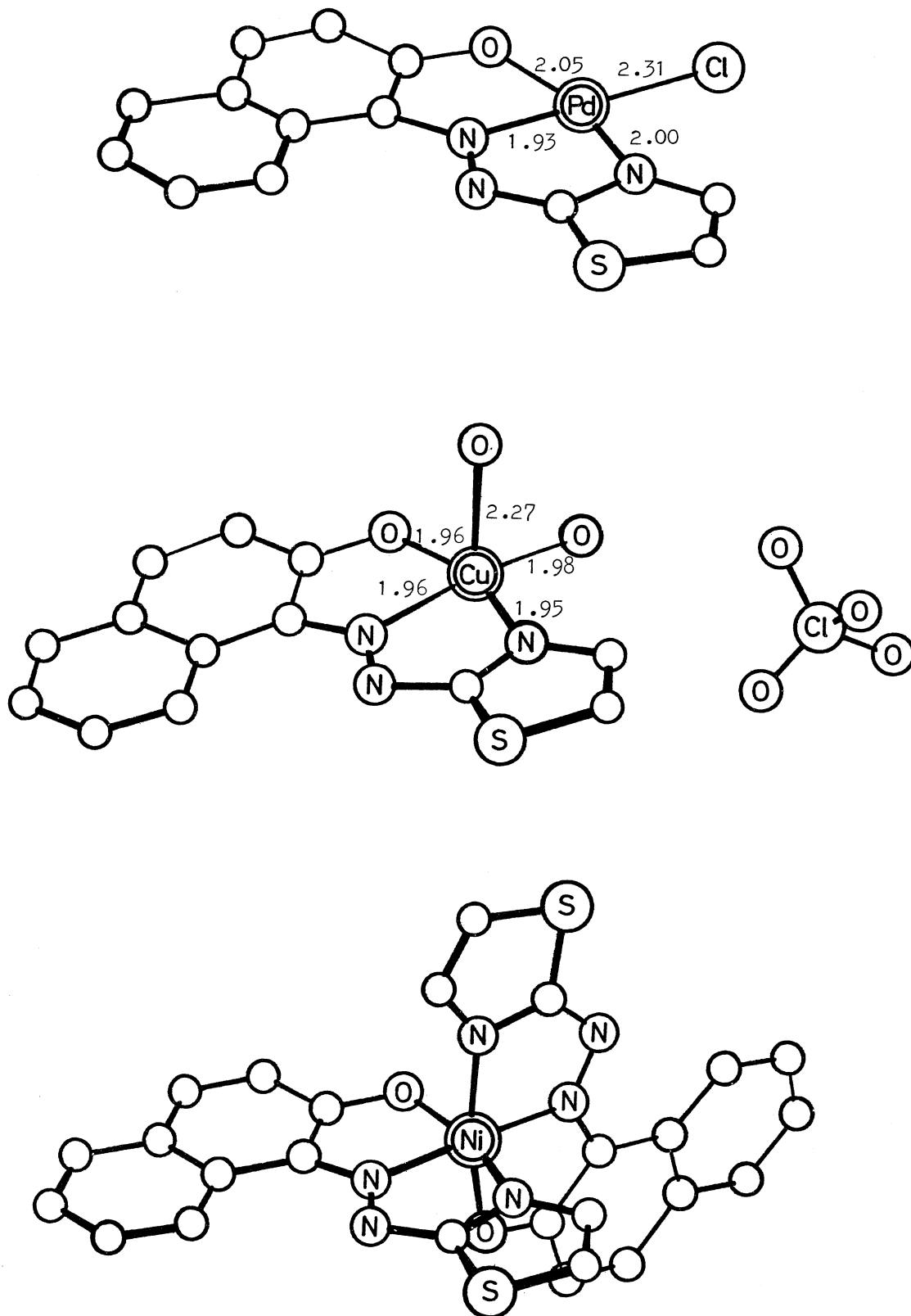
Compound	[PdCl(TAN)]·C ₄ H ₈ O ₂ I	[Cu(TAN)(H ₂ O) ₂]·ClO ₄ II	[Ni(TAN) ₂] III
Molecular weight	484.2	453.3	567.3
Crystal system	Orthorhombic	Monoclinic	Triclinic
Space group	Pbcm	P2 ₁ /c	P $\bar{1}$
a	8.44(2)	13.477(5)	12.38(6) Å
b	30.97(4)	8.059(3)	12.72(6) Å
c	6.82(2)	15.304(5)	8.41(4) Å
α	90°	90°	78.9(5)°
β	90°	95.58(4)°	95.0(5)°
γ	90°	90°	115.1(5)°
V	1782.7	1654.4	1176.8 Å ³
Z	4	4	2
D _m	1.8	—	1.55 g/cm ³
D _x	1.80	1.819	1.60 g/cm ³
μ	111.3(CuK α)	17.0(MoK α)	32.7(CuK α) cm ⁻¹

Intensity data of I and III were collected by multiple-film Weissenberg photographs taken with CuK α radiation. For II integrated intensities were measured on a Rigaku automated four-circle diffractometer with MoK α radiation monochromated by a graphite crystal. In total, 1392, 952 and 752 structure factors were obtained for I, II and III respectively and corrected for Lorentz and polarization effects as usual. The structures were solved by heavy atom method and refined by least-squares procedure. R values are 9.7, 7.7 and 16 % for I, II and III respectively; in the case of III, diffraction spots were markedly diffuse owing to the poor crystallinity of the compound and further refinement was impossible.

The molecular structures of I, II and III are shown in Fig. 1. In any of them, TAN acts as a terdentate ligand coordinating to the metal 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. The features of coordination of TAN to the metals are quite common in these three complexes.

The palladium complex, chloro-1-(2-thiazolylazo)-2-naphtholatopalladium(II) or [PdCl(TAN)], has an exact mirror symmetry by the requirement of the space group. The palladium atom is surrounded by one terdentate ligand and one chlorine atom, square-planar chelate being formed. In the crystal, dioxane molecules are trapped between the chelate molecules.

Fig. 1 The molecular structures of TAN-complexes of Pd(II), Cu(II) and Ni(II).



The crystals of copper complex are composed of a 1-(2-thiazolylazo)-2-naphtholatodiaquocopper(II) cation, $[\text{Cu}(\text{TAN})(\text{H}_2\text{O})_2]^+$, and a perchlorate anion, ClO_4^- . The copper atom has square-pyramidal coordination and is situated close to the center of the rectangle formed by three coordinating atoms of the TAN and a water oxygen atom, being slightly (0.17 Å) displaced toward the apical water oxygen atom. The TAN anion is planar within the deviations of ± 0.07 Å, while the two water oxygen atoms are deviated from the best plane of TAN by -0.40 and 2.15 Å.

The nickel complex, bis(1-(2-thiazolylazo)-2-naphtholato)nickel(II), $[\text{Ni}(\text{TAN})_2]$, has approximately C_2 symmetry. The nickel atom is surrounded octahedrally by two terdentate ligands in the mer configuration. TAN's are nearly planar and the mean planes of them are perpendicular to each other. This type of chelate with metal to ligand ratio of 1:2 has been observed in the crystals of TAN-complex compounds of iron(II)³⁾ and cobalt(III)⁴⁾. In addition, the crystal of TAN-chelate of zinc(II) was found to be isostructural with that of nickel(II).

Recently, the structure of the reagent, H-TAN, has been determined by the present author⁵⁾. A comparison of its structure with that of TAN in the form of metal chelate indicates that both of the two ring systems attached to the central azo group are rotated by 180° around the two N-C bonds in case of chelate ring formation.

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Footnotes and References.

*) TAN is a monovalent anion, $\text{C}_{13}\text{H}_8\text{N}_3\text{O}_2\text{S}$.

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3) M.Kurahashi, A.Kawase, K.Hirotsu, M.Fukuyo and A.Shimada, *Bull. Chem. Soc. Japan*, 45, 1940(1972).

4) M.Kurahashi, unpublished.

5) M.Kurahashi, to be published in *Chem. Lett.*

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