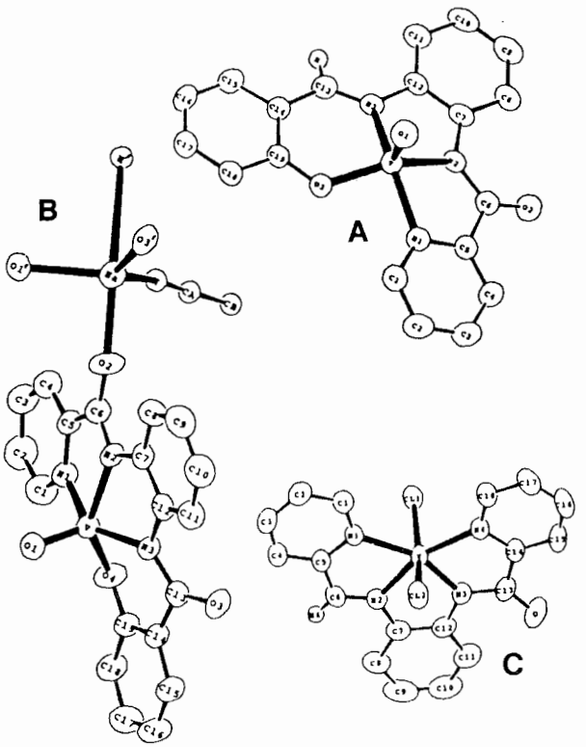

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1,4-BENZODIAZEPINE COMPLEXES INVESTIGATION. CRYSTAL AND MOLECULAR STRUCTURE OF NIMETAZEPAM COPPER DERIVATIVE

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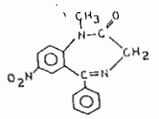
Following our studies in the chemical behaviour of 1,4-benzodiazepines as ligands owing to their biological applications, we report the preparation, the spectroscopic characterization, crystal and molecular structure of the copper(II) chloride derivative of nimetazepam,



nimetazepam
(nmz)

Figure 1

7-nitro-1,3-dihydro-5-phenyl-1-methyl-2H-1,4-benzodiazepin-2-one as shown in Figure 1.

The copper(II) derivative, of the type $Cu(nmz)_2Cl_2 \cdot 2nmz$, belongs to the triclinic space group $\overline{P}_1$ with $a = 9.860(2)$, $b = 10.670(2)$ and $c = 16.115(3)$ Å, $\alpha = 91.46(2)$, $\beta = 102.26(2)$, $\gamma = 115.54(2)$ deg, and $z = 2$. The structure was solved by the heavy-atom method and refined by full-matrix least square techniques to a final R = 0.049 (R_w = 0.052) for 5051 collected reflections.

A stereoview of the molecule is shown in Figure 2. The copper ion is in a planar environment by conditions of crystallographic symmetry. This unusual perfect planarity could be explained taking into account the perturbation which could be induced by the proximity of the hydrogen atoms on the C(15) and its centrosymmetric which are close enough to warrant special attention, Cu···H = 2.64(2) Å. The crystal packing consists of $\pi - \pi$ interactions, involving also the two other non-bonded molecules of ligands present in the lattice.

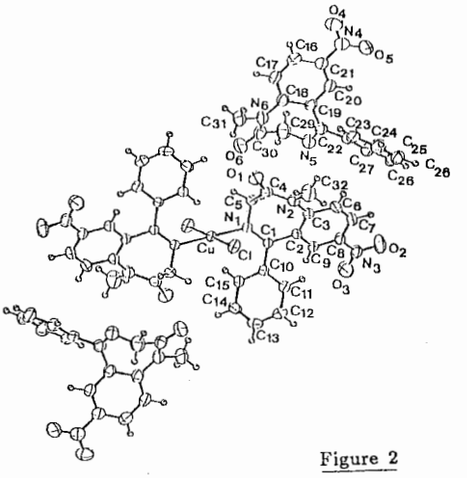


Figure 2

PS-07.04.18 STRUCTURES OF METAL COMPLEXES DERIVED FROM THE TETRAAZATHIAPENTALENE DERIVATIVE. By N. Manabe*, M. Yasui, S. Yoshida, S, Shimamoto and F. Iwasaki, Dept. of Applied Physics and Chemistry, The Univ. of Electro-Communications, Chofu, Tokyo 182, Japan.

6α-Thiatetraazapentalene derivative (I) which contains a hypervalent sulfur atom (Iwasaki, F., et al. (1991) Acta Cryst. C47, 998-1003) was found to give some novel metal complexes (II-IV) with metalapentalene frameworks by treating with metal triphenylphosphines (Yasui, M., et al. (1992) AsCA Inaugural Conference, 15U-57). In this paper we describe structures of a new type copper complex (V) and a palladium complex with a pyridine ligand (VI). The Cu complex (V) was synthesized by the reaction of (I) with $Cu(ClO_4)_2$. X-Ray study has revealed that four S atoms of the thiocarbonyl group from four molecules of (I) coordinate to the Cu atom and that the rest of the thiocarbonyl S atoms coordinate to another Cu atom. Thus the Cu atom is four-coordinated with tetrahedral arrangement and the molecular chain extends over the whole unit cell. In this complex, two pairs of pentalene frameworks are facing parallel to each other. The Pd complex (II) was treated with 18% HCl aq. to give the complex without triphenylphosphine, and then treated with pyridine to give complex (VI). The metalapentalene framework sill remains in complex (VI). The Pd atom is consequently four coordinated square-planar as in (II). The two molecules in the asymmetric unit are chemically equivalent. Bond lengths are Pd-S 2.28Å and Pd-C 1.944Å that are slightly shorter than the sum of covalent radii. The length of Pd-N (2.106Å) is longer than the sum of covalent radii.

	(V)	(VI)
Color	Yellow	Yellow
Fw	683.77	414.9
Crystal System	monoclinic	monoclinic
Space group	P2₁/n	P2₁/n
a/Å	17.693(2)	16.155(2)
b	9.848(1)	23.092(3)
c	16.085(2)	8.901(1)
β/°	11.82(1)	105.72(1)
Z	4	8
measured	6377	7820
observed	4696	5627
R	0.039	0.035

