C_{4v} symmetry belong to different symmetry species (A_1 for 1581 cm^{-1} and B_1 for 1558 cm^{-1}), but they belong to the same symmetry species (A_1) for Fe(OEC)Br with C_{2v} symmetry. Therefore it seems very likely that vibrational coupling of two A_1 modes causes a large splitting of the two $C_\beta C_\beta$ stretching modes for Fe(OEC)Br. The so-called oxidation-state marker (ν_4) is seen at 1371 cm^{-1} in the RR spectrum of Fe(OEC)Br.

The middle spectrum of Fig. 1 was obtained by dissolving Fe(OEC)Br in a 1:1 mixture (V/V) of CH_2Cl_2/Me_2SO. The RR spectrum resembles that of $Fe(OEP)(Me_2SO)_2$ regarding the frequencies of the methine bridge stretching modes [5], suggesting that ferric chlorin forms the hexa-coordinated high-spin complex with dimethyl sulfoxide at two axial positions as in the case of porphyrin.

Upon the high- to low-spin conversion of ferric chlorins all the RR bands above 1450 cm^{-1} showed large upward shifts. The ν_{10}, ν_{19}, and ν_3 modes of $Fe(OEC)(Im)_2Br$ were observed at 1640, 1580, and 1508 cm^{-1}, respectively. These frequencies are again close to those of the corresponding modes of $Fe(OEP)(Im)_2Br$.

The reduction of the iron atom resulted in numerous changes in both positions and intensities of RR bands. However, the frequency shift of the ν_4 mode was rather small (*ca.* 4 cm^{-1}) compared with porphyrins (7-17 cm^{-1}) [3,4]. The frequency decrease of the ν_4 mode upon the change from Fe^{3+} to Fe^{2+} has been attributed to the increased π-back donation of d_π electrons to porphyrin π^* orbital [3,4]. Therefore, the relatively small frequency shift of ν_4 mode indicates that π-back donation is less significant in ferrous chlorins than in ferrous porphyrins.

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PS5.36 — MO

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PALLADIUM(II) DERIVATIVES OF SOME 1,4-BENZODIAZEPIN-2-ONES

The reaction of $PdCl_2$ and $Na_2[PdCl_4]$ with two 1,4-benzodiazepin-2-ones, L, (DIAZEPAM and PRAZEPAM) has been investigated. Complexes of the types trans-*$(L)_2PdCl_2$, $[(L-H)PdCl]_2$, $(L-H)(Ph_3P)PdCl$ and (L-H)Pd(acac) have been characterized by IR and NMR spectroscopy. An X-ray structure determination of $(PRAZEPAM)_2PdCl_2$ has shown that the ligand is coordinated to the metal through the 4-nitrogen atom.*

RESULTS

Previously we have shown that the reaction of some 1,4-benzodiazepin-2-ones, (L) (*e.g.* DIAZEPAM, PRAZEPAM, NIMETAZEPAM, LORAZEPAM, NITRAZEPAM) with gold(III) chloride affords 1:1 adducts $(L)AuCl_3$. For the complex $(PRAZEPAM)AuCl_3$ the coordination mode of the ligand has been ascertained by an X-ray structure determination and found to occur through the 4-nitrogen atom [1].

We report now some preliminary results on the interaction of $PdCl_2$ and $Na_2[PdCl_4]$ with DIAZEPAM and PRAZEPAM (scheme I):

1) $PdCl_2 + nL \xrightarrow{CHCl_3} trans\text{-}(L)_2PdCl_2$
$n = 1,2,3$

2) $Na_2[PdCl_4] + L \longrightarrow [(L\text{-}H)PdCl]_2 +$
$+ (L\text{-}H)(L)PdCl$

3) $[(L\text{-}H)PdCl]_2 +$
$2\ Ph_3P \longrightarrow 2\ (L\text{-}H)(Ph_3P)PdCl$

4) $[(L\text{-}H)PdCl]_2 +$
$+ 2\ Tl(acac) \longrightarrow 2\ (L\text{-}H)Pd(acac) + 2\ TlCl$

Reaction 1) was carried out in mild conditions (room temperature, $CHCl_3$): in any case only 1:2 adducts were obtained, even when excess ligand was employed. The *trans*-arrangement of the ligands was assigned on the basis of the IR and X-ray data. The complex $(PRAZEPAM)_2PdCl_2$ exists in two crystalline modifications: one of them is pictured in Fig. 1. The ligand is bonded to the metal through the 4-nitrogen atom: the overall geometry to the organic molecule [2] does not appear to be remarkably affected by the complexation to the metal, as observed previously in the gold(III) complex and in a copper(II) derivative, $(DIAZEPAM)_2CuCl_2$ [3], the only complexes of these ligands so far investigated by X-ray analysis. Reaction 2) gave, as the main product, the species $[(L\text{-}H)PdCl]_2$ plus a small amount of (L-H)(L)PdCl. The former are dinuclear complexes where the benzodiazepine ligand is likely to be coordinated through the 4-nitrogen atom and the *ortho*-carbon atom of the phenyl ring, to give a five-membered cyclometallated system. The dinuclear species are easily split by classical reactions such as 3) and 4) [4]. At the best of our knowledge these are the first complexes where a 1,4-benzodiazepin-2-one acts as an anionic chelating ligand.

Work is in progress to collect X-ray evidence of such a behaviour.

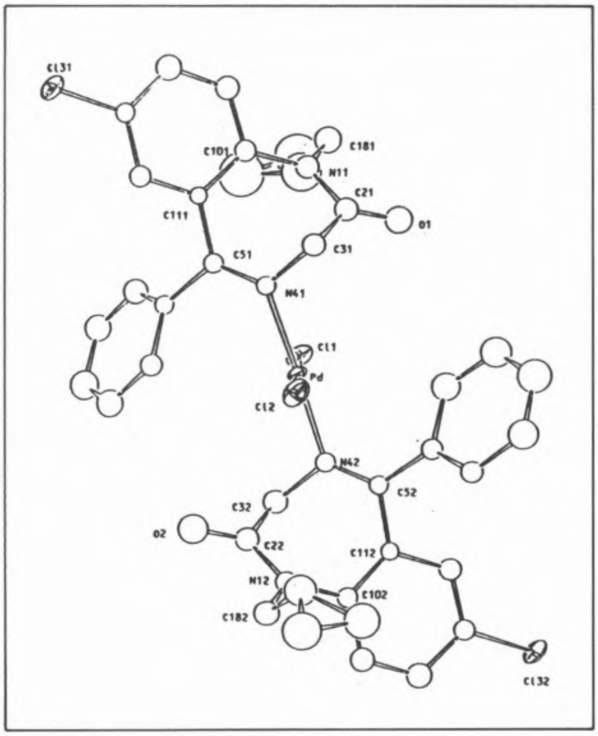

Fig. 1

ORTEP view of compound $(PRAZEPAM)_2PdCl_2$. The hydrogen atoms have been omitted for clarity.

Pd-Cl(1) 2.299(5), Pd-Cl(2) 2.310(4), Pd-N(41) 2.026(12), Pd-N(42) 2.024(12), C(51)-N(41) 1.293(18), C(52)-N(42) 1.281(18), N(41)-C(31) 1.487(19), N(42)-C(32) 1.418(18) Å

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PS5.37 — TU

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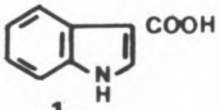
COPPER(II) COMPLEXES OF SOME INDOLIC ACIDS

Indolecarboxylic acids are a class of plant auxins which are responsible for metal complex formation in plant tissues [1]. As a continuation of our previous studies on the metal complexes of indolic auxins [2], we report here the synthesis and the characterization of the copper(II) complexes formed by the following ligands: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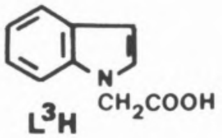
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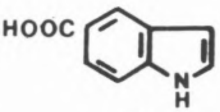
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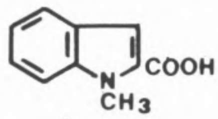
L^4H

The complexes obtained, along with their solid-state magnetic properties and electronic absorption data, are listed in Table I.

Table I
Magnetic properties and electronic absorption data

Compound		λ_{max} (nm)
$Cu(L^1)_2 \cdot H_2O$	dimer	685
$Cu(L^2)_2 \cdot 1.5\ H_2O$	dimer	690
$Cu(L^3)_2 \cdot 2\ CH_3OH$	dimer	700
$Cu(L^3)_2$	dimer	685
$Cu(L^4)_2 \cdot 1.5\ H_2O$	dimer	710
$Cu(L^4)_2 \cdot 2\ H_2O$	monomer	700

Indole-3-carboxylic and indole-5-carboxylic acids yield compounds having formulae $Cu(L^1)_2 \cdot H_2O$ and $Cu(L^2)_2 \cdot 1.5\ H_2O$, respectively, which exhibit spectral properties typical of tetracarboxylate-bridged dimers of the copper(II) acetate monohydrate-type.

Also indole-*N*-acetic acid yields dimeric compounds, $Cu(L^3)_2 \cdot 2CH_3OH$ and $Cu(L^3)_2$, the latter one exhibiting an ESR powder spectrum supportive of interdimeric exchange interactions as is often the case of anhydrous copper(II) carboxylates.

On the other hand, *N*-methyl-indole-2-carboxylic acid yields, in addition to the dimeric complex $Cu(L^4)_2 \cdot 1.5\ H_2O$, a monomeric compound, $Cu(L^4)_2 \cdot 2\ H_2O$, whose spectral properties are consistent with a tetragonally elongated coordination involving two water molecules and two bidentate carboxylate groups behaving in a strongly asymmetrical fashion.

By taking into account also the results obtained previously for the complexes of indole-3-acetic, -3-butanoic, -3-propanoic and -2-carboxylic acids [2], it may be suggested that indolic acids behave as simple carboxylic ligands and that monomeric arrangements for the copper(II) complexes are allowed only when the carboxylic group is in *ortho* to the ring nitrogen atom.

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