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Palladium Complexes Involving Tetronic Acid Derivatives

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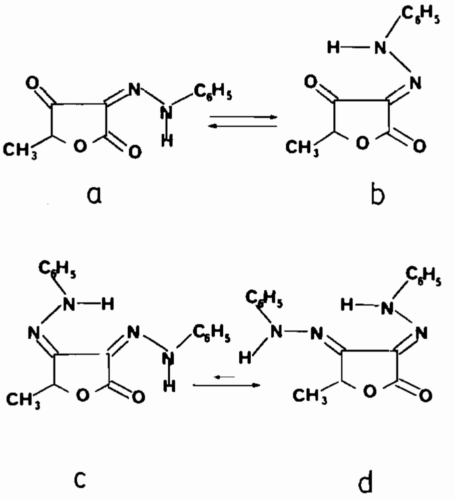

Fig. 1. Equilibrating Structures of the Tetronic Acids.

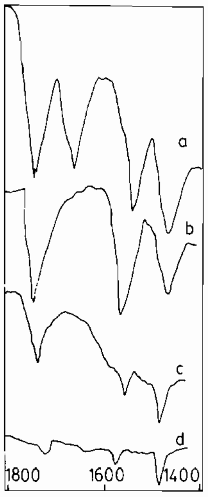

Fig. 2. Infrared Spectra in the 1800 cm^{-1} to 1400 cm^{-1} region of a) 'pht', b) $[Pd(pht)_2]$, c) 'dpht' and d) $[Pd(dpht)_2(NH_3)_2]$, in nujol.

The discovery that *cis*-dichlorodiammineplatinum(II) is a suitable anticancer agent has stimulated the growth in the synthesis of new platinum complexes [1]. Other group VIII metals have been used with some limited success [2]. Attention has focused on the pyrimidine and purine bases and their derivatives [3–5]. The arylhydrazonotetronic acids should also possess excellent ligating properties with several sites available for coordination. It is surprising therefore, that their complex chemistry has been largely ignored. We report here the synthesis of two palladium complexes and an infrared study of their structure.

Experimental

The tetronic acids, 3-phenylhydrazono-5-methyl tetronic acid, 'pht' (I), 3,4-di(phenylhydrazono)-5-methyl tetronic acid, 'dpht' (II), [6] and the palladium starting material, *trans*-$[Pd(NH_3)_2(NO_2)_2]$ [7] were separated by methods described in the literature. The complexes were prepared by dissolving the palladium compound in hot acidified ethanol and adding the ligand, previously dissolved in a similar solution. Both 1:1 and 1:2 ratios were tried but only one type of each complex was ever isolated. The mixed solution was refluxed for three hours and then evaporated at reduced pressure until the solid began to precipitate out. It was then cooled, filtered and washed with cold ether. The crystals were then recrystallised from ethanol. Analytical results were consistent with the formulae, $[Pd(pht^-)_2]$ and $[Pd(dpht^-)_2(NH_3)_2]$.

Results and Discussion

Several structures of the acid II have been postulated as shown in Fig. 1. It is possible for the phenylhydrazono group to occupy a position close to either the lactone (1a) or to the carbonyl oxygen (1b). Alternatively tautomeric structures are possible, involving a nitrogen–nitrogen double bond. Using ^{13}C NMR it has been demonstrated that the acid exists as a 45–55% mixture of the former tautomers, 1a and 1b. The second acid, 'dpht', II, occurs as an equilibrating mixture of the two isomers, 1c and 1d, [8, 9].

Both acids exhibit lactone bands in the region 1760 cm^{-1} to 1750 cm^{-1} but only I exhibits the

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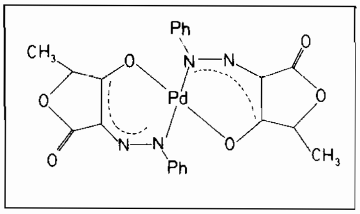

Fig. 3. Proposed structure for [Pd(pht)$_2$].

additional ketone band at 1655 cm^{-1}, Fig. 2. In the complex [Pd(pht)$_2$] there is a marked broadening of the lactone band, while the carbonyl band almost disappears. Assuming square planar symmetry and the expulsion of the hydrazono proton, coordination will take place through the nitrogen and the carbonyl oxygen. The negative charge can be easily delocalised within the six member palladium ring that results, Fig. 3. The ν(C=N) will still be present in the complex but should be reduced in intensity. In practice this is difficult to detect as there will be some overlap of the ν(C=C) and the δ(N–H) in the same region. Rearrangement does occur as is shown by the shift in the original C=N band from 1538 cm^{-1} to 1560 cm^{-1}. Broadening is also evident with shoulders appearing at 1550 cm^{-1} and 1535 cm^{-1}. Another significant change is observed in the skeletal stretching vibrations; in hydrazine, phenylhydrazine and their derivatives, complex formation causes shifts of between 50 cm^{-1} and 100 cm^{-1} [10]. In the acid the strong band at 810 cm^{-1} is reduced in intensity and lowered to 775 cm^{-1}. The bands observed at 1200 cm^{-1} and 1157 cm^{-1}, due to ν(C–C(=O)–O) [11] are both reduced in intensity, again showing the strength of the carbonyl coordination. In the complex involving the second acid, [Pd(dpht)$_2$(NH$_3$)$_2$], the lactone band is much reduced in intensity and drops to 1730 cm^{-1}, in contrast to the monophenylhydrazono substituted acid where the two bands are virtually the same. Again we observe a shift in the ν(C–C(=O)–O) bands at 1260 cm^{-1} and 1248 cm^{-1} indicating that some form of oxygen coordination is present. The presence of two moles of ammonia in the complex completes the coordination sphere.

The results presented show that both the lactone and ketone oxygen atoms are capable of coordination, and can do so in combination with the hydrazono nitrogen. This is similar behaviour to that found in some of the uracil complexes.

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