The Vibrational and NMR Spectra of Bidentate EDTA Complexes of Palladium(II)

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The vibrational spectra of $H_4EDTAPdCl_2 \cdot 5H_2O$ and its aqueous solutions indicate that EDTA acts as a bidentate ligand. NMR spectra of the D_2O solutions at varying pD support the formulation of the solution species as hydrolysis products, involving aquo and hydroxy species, in which EDTA is exclusively bidentate.

Introduction

EDTA adopts a wide range of stereochemistries and coordination numbers in its complexes with metals[1]. Amongst the most interesting of these are the compounds H_4YMCl_2 (where Y = EDTA, and M = Pd, or Pt); in these complexes X-ray structure determination[2] has shown that EDTA is bidentate through two nitrogen metal bonds, with the usual square planar arrangement around Pd(II) and Pt(II) completed by two metal–chlorine bonds. There are in addition four protonated carboxyl groups in the molecule. In contrast to the well defined solid state structure there is disagreement as to the nature of the corresponding solution species. In an initial NMR paper Sawyer[3] reported the spectra of solutions prepared in situ. Subsequently NMR spectra of solutions of both the palladium complex and of H_2YPd were reported by Sawyer[4]. This latter complex is considered to contain tetradentate EDTA, and was first characterised by Busch and Bailar[5], who also reported the preparations of H_2YPt and the two chlorides H_4YMCl_2. The infrared spectrum recorded by Sawyer for H_4YPdCl_2 was however different from that reported for the initial preparation. His NMR data were interpreted on the basis of the interconversion of two, three and four coordinate EDTA species, corresponding to an interpretation of UV–visible and electrophoresis data proposed by MacNevin and Kreige[6]; in contrast Ezerskaya *et al.* concluded from UV–visible and polarographic data that there was no evidence for an increase in the coordination number of EDTA when the palladium chloride complex dissolved in aqueous solution[7].

The interpretation of the NMR data postulated that the Pd–Cl bonds played a significant part in determining the mode of coordination of EDTA. In contrast, our initial comparison of the Raman spectrum of solid H_4YPdCl_2 and its solution over the pH range 2–12 showed that the Pd–Cl bond hydrolysed above pH 3, thus partially invalidating the argument advanced by Sawyer. Accordingly we have examined the vibrational and NMR spectra of H_4YPdCl_2 solutions in an attempt to reconcile the various reported data.

Experimental

After some initial difficulty it was found possible to repeat the preparations reported by Busch and Bailar[5] for H_4YMCl_2 and H_2YM, and to obtain the complexes with properties identical with those reported. We note however that heating $H_4YPdCl_2 \cdot 5H_2O$, even at temperatures less than 80°C, results in decomposition, as evidenced by the growth of an additional carboxyl infrared band at about 1630 cm^{-1}. A solid of this nature was used by Sawyer for his second NMR study.

Preparations of H_2YPd when isolated from aqueous solutions proved to have variable spectra dependent upon the temperature of isolation; the product of hot concentration corresponded to that previously reported, but isolation at room temperature resulted in products with a characteristic additional carboxyl region infrared band. The vibrational and NMR spectra of these forms of H_2YPd differed considerably, are of considerable complexity, and are the subject of further investigation. We note however that the NMR spectra of the corresponding solutions always includes a quartet, with chemical shifts (5.43, 5.6, 6.98, 7.16 ppm with respect to TMS) which are nearly invariant with change of pH, and which also is found in the NMR spectra of solutions of partially decomposed $H_4YPdCl_2 \cdot 5H_2O$. The data reported in this paper correspond with the solid compounds:

		Calc.	Obs.
$H_4YPdCl_2 \cdot 5H_2O$	C	21.4	21.47
	H	4.64	4.67
	N	5.0	5.05
	Cl	12.67	12.75
$H_4YPtCl_2 \cdot 5H_2O$	C	18.5	18.36
	H	4.02	4.12
	N	4.33	4.46
	Cl	10.95	11.0

$H_2YPd \cdot 3H_2O$	C	26.6	26.54
	H	4.43	4.45
	N	6.2	6.98
$H_2YPt \cdot 3H_2O$	C	22.25	22.15
	H	3.71	3.73
	N	5.19	5.35

All four compounds have infrared spectra identical to those reported by Busch and Bailar.

Solid and Solution Vibrational Spectra

Raman spectra were recorded using a Cary 81 spectrometer with He/Ne excitation using standard sampling methods. The aqueous solutions were weak scatterers and only the strongest features which were readily seen in the solid spectra could be reliably identified in solution. Infrared spectra were recorded on Perkin–Elmer 337, and 125 spectrometers, from the solids as mulls, and from 0.1 mm thick D_2O solutions held between CaF_2 plates. Far infrared spectra were recorded on a Beckman FS 620 interferometer and FTC 100 computer from samples dispersed in polythene.
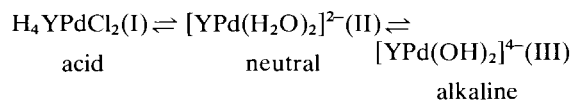
NMR Spectra

A Perkin–Elmer R 14, 100 MHz spectrometer operating at 35° C was used to record spectra in D_2O and deuteroacetone. Resonances are referred to TMS as standard.

The pH of the unbuffered solutions were measured using an EIL 23 Meter. Quoted pD in D_2O are obtained according to: pD = meter reading in pH + 0.4[8].

Results and Discussion

Ezerskaya concluded that dilute solutions of H_4YPdCl_2, and also solutions prepared from EDTA and palladium salts, contained three main pH dependent species, in all of which EDTA was bidentate[7]. In the dilute solutions used in that study formation of one species present in the mid pH range could be suppressed by addition of chloride. MacNevin and Kreige[6] concluded that as the pH of solution became more alkaline, increasingly negatively charged species were formed. Possible species corresponding to these observations are:

$$H_4YPdCl_2(I) \rightleftharpoons [YPd(H_2O)_2]^{2-}(II) \rightleftharpoons$$
$$\text{acid} \qquad\qquad \text{neutral} \qquad [YPd(OH)_2]^{4-}(III)$$
$$\text{alkaline}$$

It is clear however that since (I) is an acid, ionisation will occur, and that in addition intermediate monochloro, and mono-hydroxy species will be present. Addition of chloride ion will depress the concentration of the aquo complex in dilute solutions, but at the concentration required for obtaining Raman and NMR spectra results in the precipitation of the parent chloride.

Infrared Spectra

When $H_4YPdCl_2 \cdot 5H_2O$ is dissolved in D_2O, thin film solution infrared spectra over the range pD 2–5 show the presence of two types of acetate arm[9]. One band at 1720 cm^{-1} corresponds to that observed in the solid where it is assigned to a protonated carboxyl group, the second, new band, at 1610 cm^{-1} corresponds to an ionic carboxylate group. At more alkaline pD the band at 1720 cm^{-1} disappears leaving the lower frequency band only. In contrast, the solid formulated as H_2YPd which contains both coordinated carboxylate groups (νCO at 1625 cm^{-1}) and protonated carboxyl groups (νCO at 1742 cm^{-1}) dissolves in D_2O to give a series of pD dependant spectra which always include a band at 1630 cm^{-1}, characteristic of coordinated carboxylate. These solutions, derived from H_2YPd, which contain two or more species, at least one of which has EDTA tetradentate, also have NMR spectra with the quartet we consider to be characteristic of coordinated acetate arms, a feature subsequently discussed.

Raman Spectra

The infrared and Raman spectra of solid $H_4YPdCl_2 \cdot 5H_2O$ and its Pt analogue show similar features, and for clarity those of the former are discussed. There are numerous co-incidences in the infrared and Raman spectra of the complexes as is to be expected for the reported structure. The νC–O bands which are so informative a feature of the infrared spectra of carboxylates are however not strongly Raman active. We have observed however that in the Raman spectra of solid EDTA complexes bands between 950 and 890 cm^{-1} are a dominant feature[10]. In the previously reported spectra of aqueous solutions of EDTA complexes this feature was assigned to νC–C of the acetate group[11] and shown to vary with the nature of coordination present in the complex. We note that in the solid bidentate chloride one band only is observed at 890 cm^{-1}, while in H_2YPd there are two, at 900 and 916 cm^{-1}. In aqueous solutions of the chloride two bands are observed at low pH but only one, at about 930 cm^{-1}, above pH 3. Examination of this spectral region in the series of compounds H_6Y^{2+}, H_4Y, Na_4Y shows considerable complexity but an overall increase in frequency with deprotonation[10]. Thus our observation of two bands in the acid H_2O solutions of H_4YPdCl_2 agrees with the presence of both protonated carboxyl and ionized carboxylate groups, as was inferred from the infrared spectra at similar acidity in D_2O. The shift in frequency may be associated with the increased electron density on the ionized carboxylate group compared with the protonated group, thus corresponding to a general increase in bond order.

A second feature of the Raman spectrum of the solid chloride is a strong band at 320 cm^{-1} which is absent from the spectra of the H_2YM complexes. This we assign to νPd–Cl of the cis square planar complex,

both on the basis of its intensity and its frequency[12]. In solution in the pH range 1–3 the band is diminished in intensity relative to the νC–C vibrations and disappears above pH 3 from the spectrum. For H_4YPdCl_2 we have been able to follow the changing intensity of this feature as the solid crystallises from a super saturated solution. It is evident therefore that the metal–halogen bond is hydrolysed in solution, and that the complex exists substantially as the aquo complex in neutral solution, just as was suggested by Ezerskaya[7].

Comparison of the spectra of the solid H_4YMCl_2 and H_2YM complexes shows additional bands in the region 400–600 cm^{-1} for the latter series. It appears probable that these are associated with the metal–carboxylate bands present in the tetradentate complexes; in aqueous solution however, this region is complicated by the presence of a Raman active water band which makes our solution data indecisive.

H_4YPdCl_2 is also soluble in acetone and, though the Raman bands of acetone blank out most of the spectrum, the band we attribute to νPd–Cl may be positively identified in this solution.

NMR Spectra

The NMR spectra of EDTA complexes vary considerably in complexity but in general resonances corresponding to ethylenic, and methylenic (acetate) protons may be identified in D_2O solutions[13]. Though the spectra of EDTA–Pt complexes have been reported they are very complex[14] and we have re-examined only those derived from $H_4YPdCl_2 \cdot 5H O$ and various compounds of the type H_2YPd. Thus far we have not been able systematically to relate the NMR spectra of the latter to the method of preparation of the solution, nor are we able to explain completely the considerable changes in the NMR spectra which occur as a function of pD. We note however that in alkaline solution certain features of the spectra are coincident with those of solutions derived from the chloride. All the NMR spectra of this series include a quartet demonstrating the non-equivalence of methylenic protons, which we consider to be associated with coordination of the acetate arms (occupying the strained[15] girdle positions of a square planar tetradentate EDTA–Pd complex) since it shows by far the greatest splitting of all the features we observe in the spectra of both series, and the least dependance on pD. For any given solution this quartet shows no evidence of change of intensity with time and we are thus forced to the conclusion that in the pD range 2–12 the bidentate and tetradentate forms are not in equilibrium. With this qualification, we otherwise observe many of the individual features reported previously by Sawyer (Table).

At low pD the NMR of the solutions derived from the chloride show an ill defined quartet, centred at about 5.8 ppm and shifting slightly with pD; with increasing pD an off centre singlet appears in the

quartet and grows at the expense of the quartet. Simultaneously a strong singlet at 6.5 ppm, which has a side band at 6.6 ppm (pD 1.8) sharpens and shifts slightly down field and, the side band disappears as the pD increases. At pD 4.5 single resonances at 6.02 and 6.42 ppm are the sole features of the spectrum with the former twice the area of the latter. This last spectrum is typical of EDTA complexes in which methylenic protons are equivalent, and the two features may thus be assigned to methylenic and ethylenic protons respectively.

At low pD the methylenic proton quartet must correspond to a preferred configuration for the acetate arms. An indication of the mechanism by which this may be achieved is provided by the spectra of the compound in acetone. In this solvent the Raman spectrum indicates that the complex is in the chloride form, and cryoscopic measurements show that it is monomeric. The NMR spectrum in deutero acetone shows that the methylenic protons are non equivalent corresponding to a well defined quartet (5.16, 5.34, 5.83, 6.01 ppm), while the ethylenic resonance occurs at 6.52 ppm; an additional resonance attributable to carboxyl protons is at 7.9 ppm. Upon successive additions of D_2O the quartet shifts slightly, so that at 90% D_2O its centre is coincident with that observed in aqueous acid solutions. Since in aqueous solution the quartet reverts to a singlet with deprotonation we conclude that the acetate arms are held by the formation of carboxylic acid type dimers through hydrogen bonds[16]; which a study of models of the complex suggests is sterically feasible. In aqueous solution ionisation will result in a reduction in hydrogen bonding, thus explaining the asymmetry of the

TABLE. NMR Spectra of H_4YPdCl_2 Solutions.

H_4YPdCl_2/D_2O
Chemical Shift in ppm

pD	Methylenic		Ethyl-enic
1.8	5.55 5.71 5.87 6.03	5.77	6.5 6.6
3.4	5.73 5.9 5.96 6.13	5.96	6.46
4.5		6.02	6.42
7.9		6.02	6.42
9.5		6.0 6.17	6.45
11.2		5.78 5.95 6.16 6.33	6.60

$H_4YPdCl_2/Deuteroacetone$
Chemical Shift in ppm

%D_2O	Methylenic	Ethylenic	Carb-oxylate
0	5.16 5.34 5.83 6.01	6.52	7.9
90	[a] 5.56 5.94 6.12	6.55 6.68	7.9

[a] Obscured by HDO.

quartet and its subsequent collapse when complete ionisation occurs, and the acetate arms are no longer held in a preferred configuration.

With increasing alkalinity the methylenic quartet reappears, and at pD 11 is well defined; again hydrogen bonding provides a possible explanation for the adoption of a preferred configuration for the acetate arms, but in this instance through hydroxyl groups. pH titration[7] indicates that in solutions more alkaline than pH 9 two hydroxy groups are incorporated in the complex and thus one possible explanation is the formation of hydrogen bonds between the carboxylates and these groups.

It is apparent that the NMR spectra fall into three pD dependent sets which have features compatible with the presence of the postulated bidentate species. Only at low pD is there evidence of two distinct species, corresponding to the presence of two ethylenic resonances. These are apparently the chloride and aquo forms, in a relatively slowly interconverting equilibrium; though in more alkaline solutions other equilibria must exist they are presumably too rapidly exchanging to give rise to separate sets of NMR spectra, and in consequence the changing nature of the species present is represented by a continuous variation of resonance position and profile.

All the data obtained indicate however that solutions derived from H_4YPdCl_2 do not attain an equilibrium with a tetradentate species at room temperature over a period of several days. At low pH, in HCl solution where protonation of EDTA might be expected to displace the Pd(II), precipitation as the chloride occurs, while at high pH palladium black is formed before any detectable interconversion occurs. It appears therefore that there is a considerable energy barrier to the formation of tetradentate species in solution. This could be a result of the particular stability of square planar palladium complexes containing nitrogen ligands[17], coupled with the strain inherent in the formation of EDTA girdle ring coordination arrangements.

Acknowledgment

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