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On the basics of carbohydrate–metal chemistry: complexes of palladium(II) with hydroxyaldehyde and -ketone hydrates☆

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Abstract—In this work, we present novel complexes of hydroxyaldehydes and ketones with palladium(II). The compounds are studied by two-dimensional NMR spectroscopy in solution (COSY, HMQC, HMBC). Glycolaldehyde, D-glyceraldehyde, glyoxal and 2,4-*O*-ethylidene-D-erythrose were used as aldehydes, D-erythrulose was used as an α-hydroxyketone. Although different species are present in solution, only the hydrated forms of the aldehydes can coordinate to the metal centre. These complexes are stable at 4 °C in aqueous solution. The crystal structure of a complex formed by mesoxalic acid and palladium(II) is reported and shows coordination by both hydroxy groups of the hydrated ketone.

Keywords: Carbohydrates; Bioinorganic chemistry; Coordination chemistry; Transition metals

1. Introduction

Palladium(II) is a convenient metal for the coordination of carbohydrates and polyhydroxy compounds. Due to its diamagnetic properties, its coordination compounds can be studied by NMR spectroscopy in solution.[2–6] Depending on chelate ring size, the coordination of palladium(II) leads to a coordination induced shift (CIS) of about 2–10 ppm downfield at the carbon atom connected to the coordinating oxygen atom, thus the coordinating groups of the ligand can be identified.[2–6]

In the case of the reducing sugars, palladium(II)-containing solutions are prone to react in a Fehling-type way. Both NMR spectroscopic investigations and crystallisation experiments must be conducted at low temperature.[2–6]

Recently the structure of a D-erythrose complex with palladium(II), which is the first crystal structure of the highly reducing tetrose D-erythrose to be identified as yet, could be obtained. Palladium(II) was used in the form of [Pd(*R*,*R*-chxn)(OH)$_2$] (*R*,*R*-chxn = 1*R*,2*R*-diaminocyclohexane). The NMR spectra in solution show up to five different metallated species. By the variation of pH and metal concentration, some of the species could be enriched or degraded. Two of the species were assigned to dimetallated open-chain forms of D-erythrose hydrate (unpublished data). The open-chain forms of monosaccharides are usually the isomers with the least abundance in solution. The free aldehydes and hydrates of aldopentoses and hexoses comprise only up to 0.1% of all the isomers in solution.[7,8] In the case of the tetroses, the hydrate amounts to 11% in solution.[9] Through metallation with palladium(II), the concentration of the open-chain forms of D-erythrose in equilibrium could be nearly doubled.

Since hydroxyaldehyde and hydroxyketone functions are the most significant functional groups of a reducing sugar, the unexpected finding of erythrose's open-chain ligation to a metal centre motivated us to conduct a systematic study on the coordination chemistry of these functional groups.

Aside from playing a role in coordination chemistry, hydroxyaldehydes in aqueous solution react in numerous ways. Thus many different species are observed in

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NMR spectra of the free aldehydes. They form hydrates, endiolates and there is the possibility to form acetals and to react with amines, the most important co-ligands in our studies under Amadori conditions. The following experiments were thus performed to unravel the metal-binding properties of these particularly reactive potentially oxygen-donor ligands.

2. Results and discussion

2.1. Glycolaldehyde

Glycolaldehyde is the simplest α-hydroxyaldehyde. In aqueous solution the main species is the monomeric aldehyde hydrate; various dimeric acetals comprise the minor species (Chart 1).[10] In a ^{13}C NMR spectrum of free glycolaldehyde the signal for C-1 lies at 89.7 ppm, for C-2 at 64.6 ppm. In comparison to reducing sugars, glycolaldehyde is a highly reducing compound, reducing copper(II) to copper metal in a Fehling-type reaction. In solution it readily reacts with oxygen to form glycolic acid. On reaction with an equimolar amount of [Pd(*R*,*R*-chxn)$(OD)_2$] in ice-cold D_2O a clear yellow solution with a pH of 12.5 was obtained. The solution was stable for about 2 h, then palladium metal precipitated. During this stable period NMR spectroscopic measurements were performed.

A ^{13}C NMR spectrum of the reaction mixture shows only two signals (Fig. 1). A CIS of 9.2 ppm is observed for C-1 and 10.1 ppm for C-2, thus the only solution species in considerable quantity is the palladium-bonded monomeric aldehyde hydrate (Chart 2). Double deprotonation of the chelating ligand is assumed in accordance with structural work on Pd^{II}–polyol complexes.

As illustrated in Chart 2, two isomers were expected according to the configuration at C-1. However, neither the ^{13}C nor the ^{1}H NMR spectra showed their signals separated. Particularly, the expected difference of the $^{3}J_{1,2}$ coupling constants in the latter was hidden due to signal broadening.

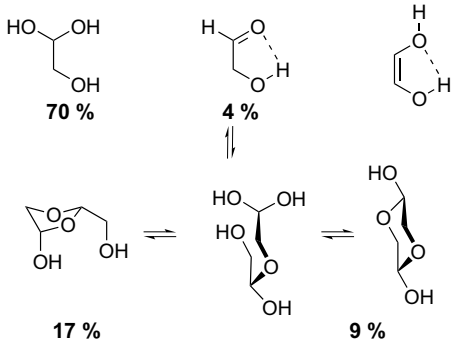

Chart 1. Isomers of glycolaldehyde in solution. Adapted from Yaylayan et al.[10]

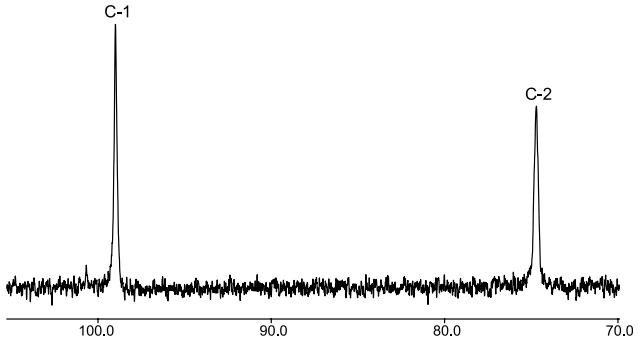

Figure 1. ^{13}C NMR spectrum of the reaction mixture of [Pd(*R*,*R*-chxn)$(OD)_2$] with glycolaldehyde (1:1) in D_2O ($c(Pd^{II}) = 0.5$ mol L^{-1}). In a ^{13}C NMR spectrum of free glycolaldehyde the signal for C-1 lies at 89.7, for C-2 at 64.6 ppm.

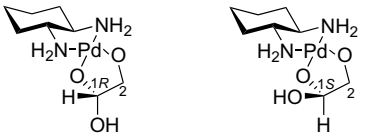

Chart 2. The two possible isomers of the metallated glycolaldehyde hydrate.

2.2. Glyoxal

Glyoxal is the simplest dialdehyde. It is provided as a colourless solid, which consists of the hydrate of the glyoxal trimer. Upon dissolution in water, the trimeric acetal is degraded to the monomeric dihydrate (Chart 3).

Since glyoxal can be metallated twice, the ^{13}C NMR spectra were recorded both at a molar ratio of 1:1 and 1:2 glyoxal hydrate and [Pd(*R*,*R*-chxn)$(OD)_2$]. The reaction of equimolar amounts of glyoxal and [Pd(*R*,*R*-chxn)$(OD)_2$] still needs further investigations. The ^{13}C NMR spectrum showed only one signal in the carboxylate region, indicating oxidation of the dialdehyde to oxalic acid. This might be due to different pH values of the solutions with 1:1 and 1:2 molar ratios.

The ^{13}C NMR spectrum of the 1:2 (metal:ligand) mixture shows one single signal at 109.3 ppm (Fig. 2). Thus it is clear that the hydrate is the coordinating species. The CIS is 18.7 ppm relative to the hydrate, which is about double the size of the usual shift.

A CIS of about 20 ppm appears to indicate dimetallation. To confirm the assumption of a doubled CIS at double metallation, we investigated the coordination of oxalic acid with [Pd(*R*,*R*-chxn)$(OD)_2$] at different stoichiometric ratios. It could be shown that the CIS is

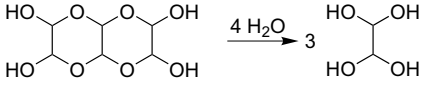

Chart 3. Hydrolysis of the dihydrate of the glyoxal trimer.

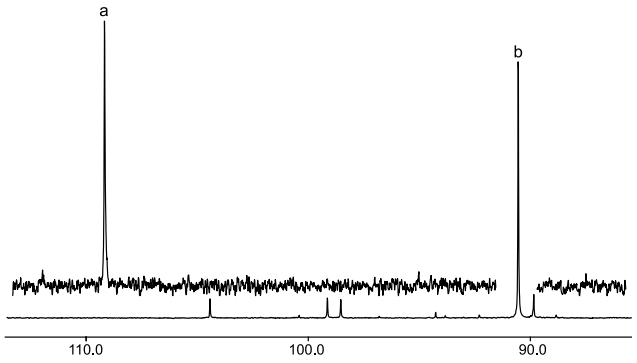

Figure 2. (a) ^{13}C NMR spectrum of the reaction of [Pd(*R*,*R*-chxn)$(OD)_2$] with glyoxal (2:1) in D_2O ($c(Pd^{II}) = 0.5$ mol L^{-1}). (b) ^{13}C NMR spectrum of the reaction of glyoxal in D_2O.

actually doubled when 2 equiv of [Pd(*R*,*R*-chxn)$(OD)_2$] are allowed to react with 1 equiv of oxalic acid. The signal of a monometallated complex at 168.1 ppm in the ^{13}C NMR spectrum showed a CIS of 6.7 ppm, while the signal of a dimetallated compound at 173.3 ppm was shifted downfield by 11.8 ppm.

In the case of glyoxal, two isomers can be expected as well (Chart 4). Isomer **II** in Chart 4, however, enforces torsion angles of 60° for the chelating O–C–C–O fragment—a value that is unsuitably large for a stable chelate ring. The only solution species was thus the dimetallated isomer **I**.

2.3. 2,4-*O*-Ethylidene-D-erythrose

2,4-*O*-Ethylidene-D-erythrose is an intermediate product in the synthesis of D-erythrose.[11,12] It can be isolated as a white solid, mainly consisting of the dimeric 1,1′:1′,3-cyclic acetal bis(2,4-*O*-ethylidene-D-erythrose). Various modifications of this solid with various melting points are known.[13]

Due to the presence of isomeric forms (Chart 5), a large number of signals are observed in the ^{13}C NMR spectra on dissolution of 2,4-*O*-ethylidene-D-erythrose in water. However, after a few hours, only the six signals of the monomeric hydrate are left. This hydroxyaldehyde hydrate is ideally suited to study whether or not six-ring chelates are formed upon coordination of palladium(II). In the ^{13}C NMR spectrum of 2,4-*O*-ethylidene-D-erythrose and [Pd(*R*,*R*-chxn)$(OD)_2$] (1:1) in D_2O, three sets of signals with different intensities were observed (Fig. 3). The set with the lowest intensities could be identified as free 2,4-*O*-ethylidene-D-erythrose, whereas the other two sets could be assigned to two complex isomers (Chart 6).

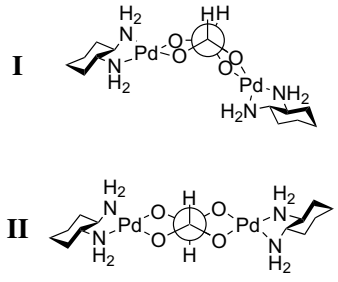

Chart 4. The two possible isomers of dimetallated glyoxal.

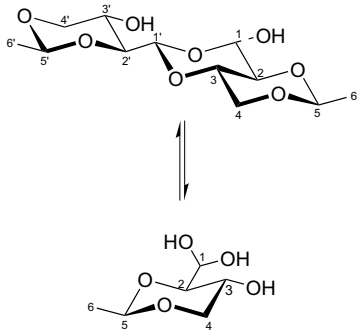

Chart 5. Dimer and monomer of 2,4-*O*-ethylidene-D-erythrose.

All signals were assigned by means of 2D NMR spectroscopy (Table 1). In contrast to glycolaldehyde and glyoxal, two C-1 isomers were resolved in the spectra. The two C-1 configurations determine the $^3J_{1,2}$ coupling constants in the ^1H NMR spectrum. The isomer with the

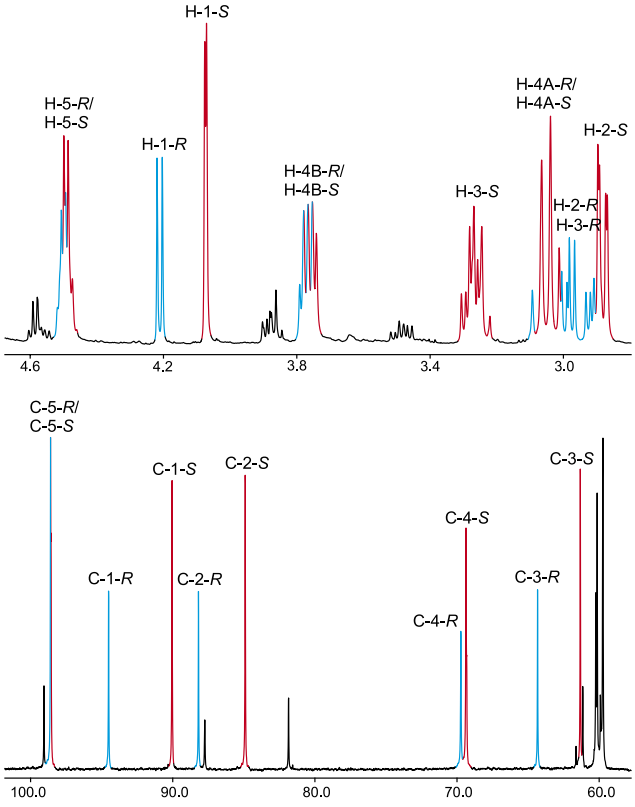

Figure 3. ^1H and ^{13}C NMR spectra of the reaction mixture of [Pd(*R*,*R*-chxn)$(OD)_2$] and 2,4-*O*-ethylidene-D-erythrose (1:1) in D_2O ($c(Pd^{II}) = 0.5$ mol L^{-1}).

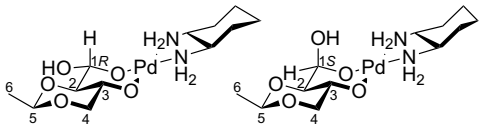

Chart 6. The two isomers of the reaction of [Pd(*R*,*R*-chxn)(OD)$_2$] and 2,4-*O*-ethylidene-D-erythrose. In the 1*R*-configurated isomer the free hydroxy group of the hydrate is in an equatorial position. In the 1*S*-configurated isomer the free hydroxy group is in an axial position, corresponding to H–C-1–C-2–H torsional angles of 180° and 60°, respectively.

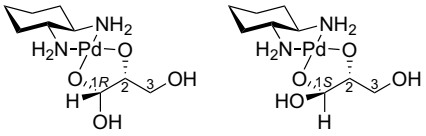

Chart 7. The two Isomers of the reaction of [Pd(*R*,*R*-chxn)(OD)$_2$] with D-glyceraldehyde.

R configuration at C-1 shows a $^3J_{1,2}$ coupling constant of 6.2 Hz which indicates a dihedral angle of about 150°, whereas the 1*S* isomer shows a coupling constant of 2.2 Hz corresponding to an angle of about 60°.

The signals with the highest intensity belong to the 1*S*-configured complex [Pd(*R*,*R*-chxn)((1*S*)-2,4-*O*-MeCH-D-Ery*h*1,3H$_{-2}$)], which was the main solution species with 60% abundance at equilibrium. The $\Delta\delta$ pattern of the six-membered chelates was in agreement with known patterns and differs, as usual, markedly from the typical patterns of 1,2-diolato chelation. Interestingly the CIS in [Pd(*R*,*R*-chxn)((1*R*)-2,4-*O*-MeCH-D-Ery*h*1, 3H$_{-2}$)] is bigger than all the known CIS values in chelate six rings and seems to depend only on the position of the uncoordinated hydroxyl group (axial or equatorial). This, and the fact that the main solution species was the one with the sterically inconvenient axial hydroxyl group, is due to an anomeric effect at C-1.

2.4. D-Glyceraldehyde

In solution, the main isomer of D-glyceraldehyde is the monomer's hydrate. Due to its four hydroxy groups the formation of various metallated isomers was expected. In contrast to the simple hydroxyaldehyde hydrates presented above, D-glyceraldehyde can form five- and six-membered chelate rings, as well as mixed dimetallated complexes. Moreover, the 2,3-diol function may be metallated, leaving the hydrate hydroxyl groups uncoordinated.

In fact, on the reaction of [Pd(*R*,*R*-chxn)(OD)$_2$] with D-glyceraldehyde in D_2O only the two O-1,O-2-monometallated isomers shown in Chart 7 were observed in solution. The hydroxyl group at C-3 remained uncoordinated in these main species (Table 2).

Table 2. ^{13}C NMR data of the observed solution species after the reaction of D-glyceraldehyde with [Pd(*R*,*R*-chxn)(OD)$_2$]; atom numbering according to Chart 7

	C-1	C-2	C-3
D-Glyceraldehyde	89.6	73.8	61.7
[Pd(*R*,*R*-chxn)((1*R*)-D-Gld*h*1,2H$_{-2}$)]	99.1	83.6	64.0
$\Delta\delta$	**9.5**	**9.8**	2.3
[Pd(*R*,*R*-chxn)((1*S*)-D-Gld*h*1,2H$_{-2}$)]	99.1	83.3	61.3
$\Delta\delta$	**9.5**	**9.5**	−0.4

The signals of the ancillary ligand are omitted. $\Delta\delta$ values that indicate a CIS are in boldface. δ values refer to the TMS standard.

The main species in solution (70%) shows a $^3J_{1,2}$ coupling constant of 4.8 Hz in the ^{1}H NMR spectrum. According to the Karplus equation, this value derives from a dihedral angle of 40°. The $^3J_{1,2}$ coupling constant for the minor species has a value of less than 1 Hz indicating a dihedral angle of 60–120°. The expected value for the dihedral angle of the 1*R* isomer is about 40° or less, whereas the dihedral angle of the 1*S* isomer is expected to be over 60°. Thus the main species can be assigned as the 1*R* configured isomer (Fig. 4).

2.5. D-Erythrulose

The tetrose, D-erythrulose, is the corresponding ketose to the tetroaldoses, D-erythrose and D-threose. In aqueous solution this reducing monosaccharide usually occurs as the free ketone. The hydrated ketone is not observed in solution in terms of NMR spectra. During the first 30 min upon reaction with 2 equiv of [Pd(*R*,*R*-chxn)(OD)$_2$] in D_2O, still no hydrate was formed, although coordination had already taken place. Due to the significant CIS of the C-3 and C-4 signals (see Fig. 5a, Table 3), it was obvious that D-erythrulose coordinates to palladium(II) by the C-3/C-4-diol group thus

Table 1. ^{13}C NMR data of the observed solution species after the reaction of 2,4-*O*-ethylidene-D-erythrose with [Pd(*R*,*R*-chxn)(OD)$_2$]; atom numbering according to Chart 6

	C-1	C-2	C-3	C-4	C-5	C-6
2,4-*O*-Ethylidene-D-erythrose	88.1	81.2	61.4	69.6	99.6	19.5
[Pd(*R*,*R*-chxn)((1*R*)-2,4-*O*-MeCH-D-Ery*h*1,3H$_{-2}$)]	94.5	88.2	64.3	69.7	98.6	19.3
$\Delta\delta$	**6.4**	7.0	**2.9**	0.1	−1.0	−0.2
[Pd(*R*,*R*-chxn)((1*S*)-2,4-*O*-MeCH-D-Ery*h*1,3H$_{-2}$)]	90.1	84.9	61.3	69.4	98.6	19.3
$\Delta\delta$	**2.0**	3.7	**−0.1**	−0.2	−1.0	−0.2

The signals of the ancillary ligand are omitted. $\Delta\delta$ values that indicate a CIS are in boldface. δ values refer to the TMS standard.

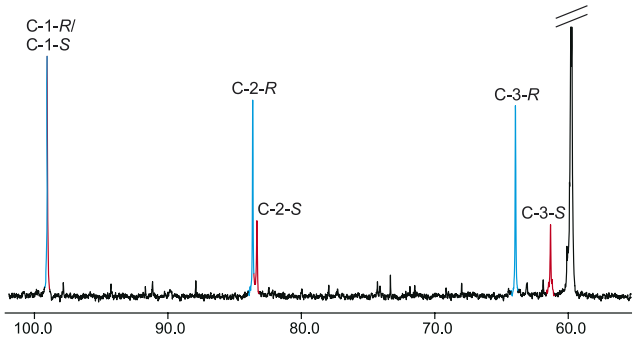

Figure 4. ^{13}C NMR spectrum of the reaction of [Pd(*R*,*R*-chxn)(OD)$_2$] and D-gylceraldehyde (1:1) in D_2O.

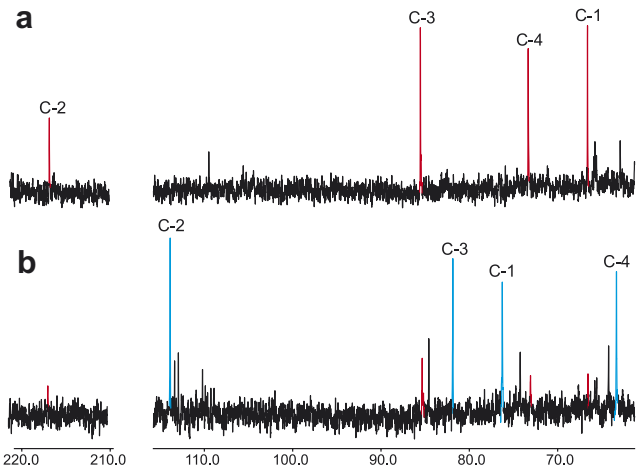

Figure 5. ^{13}C NMR spectra of the reaction of [Pd(*R*,*R*-chxn)(OD)$_2$] and D-erythrulose in D_2O. (a) [Pd(*R*,*R*-chxn)(OD)$_2$]/D-erythrulose 2:1 after 0.5 h. (b) [Pd(*R*,*R*-chxn)(OD)$_2$]/D-erythrulose 2:1 after 2 h.

Table 3. ^{13}C NMR data of the observed solution species on the reaction of D-erythrulose with [Pd(*R*,*R*-chxn)(OD)$_2$]; atom numbering according to Chart 8

	C-1	C-2	C-3	C-4
D-Erythrulose	65.5	211.9	75.5	62.6
[Pd(*R*,*R*-chxn)(D-Eru3,4H$_{-2}$)]	66.6	216.4	85.5	73.3
$\Delta\delta$	1.1	4.5	**10.0**	**10.7**
[Pd(*R*,*R*-chxn)(D-Eru*h*1,2;2,3H$_{-4}$)]	76.3	113.9	81.9	63.3
$\Delta\delta$	**10.8**	**23.0**	**6.4**	0.7

The signals of the ancillary ligand are omitted. $\Delta\delta$ values that indicate a CIS are in boldface. δ values refer to the TMS standard.

forming a five-membered chelate, including the metal centre (Chart 8).

In the course of two more hours, the ^{13}C NMR spectrum of the reaction mixture changed significantly. Now a new species, with three signals shifted with respect to free erythrulose, contributed the most intense signal set. The signal of the free ketone disappeared completely and a new signal at 113.9 ppm occurred indicating the ketone hydrate. According to the CIS values of C-1,

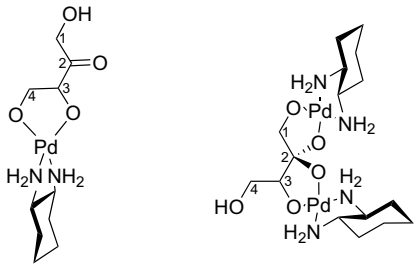

Chart 8. Products of the reaction of [Pd(*R*,*R*-chxn)(OD)$_2$] with D-erythrulose.

C-2 and C-3, two palladium(II) atoms are coordinated by the alkoxy oxygens at C-1 and C-3 and the two hydroxyl oxygen atoms of the hydrated keto group forming two five-membered chelate rings. Due to the lack of a ^{13}C NMR spectrum of erythrulose hydrate, the CIS values were estimated at 10.8 ppm (C-1), 23.0 ppm (C-2) and 6.4 ppm (C-3), thus indicating double metallation of C-2 (Chart 8).

Since the dimetallated erythrulose hydrate complex is derived from a minor solution species, the conclusions drawn from the NMR spectra deserve confirmation. Fortunately, a matching NMR result and a crystal structure analysis were obtained for the related mesoxalato ligand.

2.6. The crystal structure of [(*R*,*R*-chxn)$_4$Pd$_4$(C_3O_6)(μ-OH)](NO_3)$_3$·8H_2O

Due to the inductive and mesomeric effects of the two carboxylate groups in mesoxalic acid (dihydroxymalonic acid), its keto group is hydrated in aqueous solution as well as in the solid.

Attempts to support the conclusions made from NMR assignments by crystallisation of any of the metallised species have failed until now. Experiments include variation of the nitrogen ligand as well as the molar ratios of metal and sugar-type ligand, and the ratio of base equivalents and metal. This latter parameter was fixed at 2:1 in all the NMR experiments reported above by the use of a palladium agent of the (L)Pd(OH)$_2$ type. Experiments conducted at a lower base/metal ratio included D-threose. The palladium-bonded forms are of similar instability towards oxidative degradation as are the solutions of the reactive molecules dealt with herein. One of the decomposition products identified in D-threose–palladium batches was the anion of mesoxalic acid, O=C(COOH)$_2$, which was found as a ligand in a crystalline compound of the formula [(*R*,*R*-chxn)$_4$Pd$_4$(C_3O_6)(μ-OH)](NO_3)$_3$·8H_2O (**1**), the nitrogen ligand being the (*R*,*R*)-enantiomer of 1,2-diaminocyclohexane (chxn). Though the mesoxalato complex was not the attempted product, its structure contributes to the quest for the answer to whether or

not a ketone hydrate may act as a ligand as formulated for erythrulose. (Attempts to synthesize **1** from the respective palladium reagent and mesoxalic acid always resulted in the rapid formation of a fine powder of sparingly soluble **1**, hence no NMR data are given; note that crystallisation from decomposing threose-containing solutions corresponds to homogenous precipitation conditions.)

Compound **1** crystallises in the triclinic space group *P*1 with two formula units in the unit cell (Table 4). The four metal centres in the tetranuclear complex trications are bridged by the geminal alkoxy functions of the entirely deprotonated ketone hydrate (Chart 9, Fig. 6). One oxygen atom of each carboxylate group coordinates to one metal centre. The two oxygen atoms of the hydrated keto group coordinate to two metal centres. The two palladium atoms that are not part of a chelate ring are bridged by a hydroxido ligand. This coordination mode is an extension of the metal coordination derived for D-erythrulose from spectral data and supports the suggestion that the hydroxy groups of the hydrate are able to coordinate to one metal centre each. The structure of a complex of mesoxalic acid coordinating

Table 4. Crystallographic data

	1
Net formula	$C_{27}H_{73}N_{11}O_{24}Pd_4$
M_r (g mol^{-1})	1367.02
Crystal size (mm)	$0.15 \times 0.11 \times 0.08$
ρ (g cm^{-3})	1.78355(6)
T (K)	200(2)
Radiation	Mo Kα
Crystal system	Triclinic
Space group	*P*1
a (Å)	12.8502(3)
b (Å)	14.3042(3)
c (Å)	14.6608(3)
α (°)	74.2946(11)
β (°)	84.3330(11)
γ (°)	79.2674(11)
V (Å^3)	2545.51(9)
Z	2
μ (mm^{-1})	1.477
Reflections measured	15,442
R_{int}	0.0000
Mean $\sigma I/I$	0.0295
θ Range	3.16–24.00
Observed reflection	14400
x,y (weighting scheme)	0.1091, 13.8811
Hydrogen refinement	Mixed
Flack parameter	0.02(4)
Reflections in refinement	15442
Parameters	939
Restraints	9
$R(F_{obs})$	0.0575
R_wF^2	0.1699
S	1.048
Shift/error$_{max}$	0.001
Maximum electron density (e Å^{-3})	1.751[a]
Minimum electron density (e Å^{-3})	−0.670

[a] Contributions from disordered nitrate.

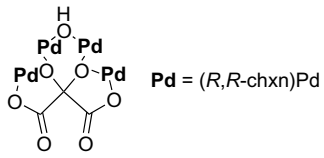

Chart 9. The structure of the complex cation in $[(R,R\text{-chxn})_4\text{-}Pd_4(C_3O_6)(\mu\text{-}OH)](NO_3)_3{\cdot}8H_2O$.

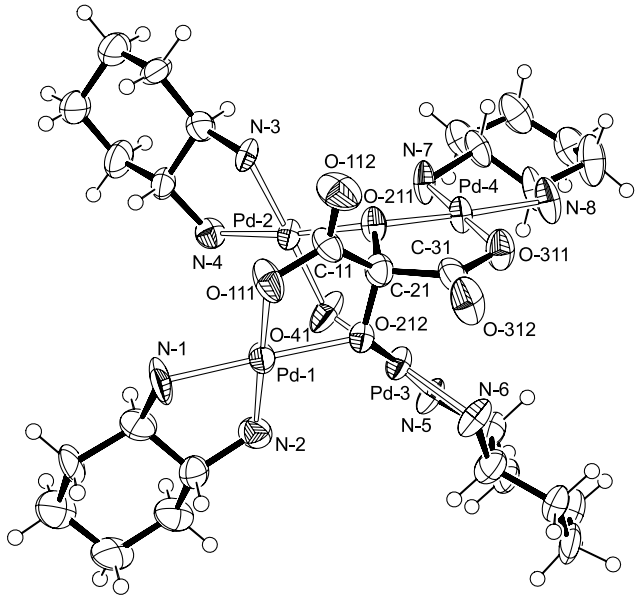

Figure 6. ORTEP-plot of the complex cation in $[(R,R\text{-chxn})_4\text{-}Pd_4(C_3O_6)(\mu\text{-}OH)](NO_3)_3{\cdot}8H_2O$. H atoms at all N atoms are omitted.

two manganese(II)-ions in a similar fashion substantiates this assumption.[14]

3. Conclusion

Both hydroxyaldehyde and hydroxyketone functions—the characteristic functionalities of the aldoses and ketoses—are able to form redox-labile complexes with the carbohydrate-binding palladium(II) central metal. In both ligand types, the actual metal-chelating site is a dianion derived from one of the two geminal hydroxyl functions of the carbonyl group's hydrate form and the vicinal hydroxyl groups on either side; a ligand results that is capable of binding at least two metal centres in a spiro-bis(chelate) way.

4. Experimental

4.1. General methods

$PdCl_2$, (1*R*,2*R*)-diaminocyclohexane (*R*,*R*-chxn), Ag_2O, KCl, NaOH, HNO_3 (2 M), concd HCl, D-glyceraldehyde and glycolaldehyde dimer were used as supplied

by Fluka. D_2O and D-erythrulose were supplied by Aldrich, glyoxal trimer-dihydrate was supplied by Sigma. 2,4-*O*-Ethylidene-D-erythrose was prepared by the literature methods.[11,12] Dilute NaOH (1 M) was prepared freshly before the reactions were performed.

4.1.1. [(*R*,*R*-chxn)Pd(Cl)$_2$].[15] To a suspension of $PdCl_2$ (5.00 g, 0.03 mol) in 50 mL of water, KCl (4.20 g, 0.06 mol) was added at 45 °C and stirred for 10 min until a clear brown soln was obtained. A soln of (1*R*,2*R*)-diaminocyclohexane (3.22 mL, 0.03 mol) in 5 mL of concd HCl and 95 mL of water was added. The mixture was stirred for 1 h at 45 °C. Afterwards dilute NaOH was added slowly to adjust a pH of 5.0–6.5. After a complete reaction time of 3 h the mixture was allowed to cool and the yellow solid filtered off. The yellow solid was washed with diethylether and dried under diminished pressure (7.81 g, yield 95%). Anal. Calcd for $C_6H_{12}N_2Cl_2Pd$: C, 24.72; H, 4.84; N, 9.61. Found: C, 24.71; H, 4.78; N, 9.59.

4.1.2. [(*R*,*R*-chxn)Pd(OD)$_2$]. [(*R*,*R*-chxn)$PdCl_2$] (3.64 g, 0.01 mol) and Ag_2O (3.02 g, 0.01 mol) were stirred in the dark under nitrogen in 25 mL of D_2O for 2 h at 4 °C. The slurry was allowed to cool and then filtered. The clear yellow soln which is 0.5 M referred to palladium was stored under nitrogen at 4 °C.

4.2. General procedure for the reaction of aldehydes and ketones with [(*R*,*R*-chxn)$PdCl_2$]

0.5 mmol of the respective aldehyde or ketone was dissolved in 1 mL (for equimolar ratios) or 2 mL (for molar ratios of 2:1 metal and ligand) of the 0.5 M [(*R*,*R*-chxn)Pd(OD)$_2$] soln under ice cooling. The clear yellow solns were stirred and ice-cooled for 1 h.

4.2.1. Glycolaldehyde

4.2.1.1. [(*R*,*R*-chxn)Pd($C_2H_4O_3$)]. ^{1}H NMR (D_2O): δ 4.54 (m, 1H, H-1), 2.92 (m, 1H, H-2a/b). ^{13}C NMR (D_2O): δ 99.0 (C-1), 74.7 (C-2).

4.2.2. Glyoxal

4.2.2.1. [(*R*,*R*-chxn)Pd($C_2H_2O_4$)]. ^{1}H NMR (D_2O): δ 4.17 (m, 1H). ^{13}C NMR (D_2O): δ 109.3.

4.2.3. 2,4-*O*-Ethylidene-D-erythrose

4.2.3.1. [Pd(*R*,*R*-chxn)((1*R*)-2,4-*O*-MeCH-D-Ery*h*1,3H$_{-2}$)]. ^{1}H NMR (D_2O): δ 4.50 (q, 1H, H-5, $^3J_{5,6}$ 5.1 Hz), 4.22 (d, 1H, H-1, $^3J_{1,2}$ 6.2 Hz), 3.77 (dd, 1H, H-4b, $^3J_{3,4b}$ 4.9 Hz, $^2J_{4a,4b}$ −9.9 Hz), 3.07 (dd, 1H, H-4a, $^3J_{3,4a}$ 9.9 Hz, $^2J_{4a,4b}$ 9.9 Hz), 2.98 (dd, 1H, H-2, $^3J_{1,2}$ 6.2 Hz, $^3J_{2,3}$ 9.1 Hz), 2.90 (ddd, 1H, H-3, $^3J_{2,3}$ 9.1 Hz, $^3J_{3,4a}$ 9.9 Hz, $^3J_{3,4b}$ 4.9 Hz), 1.02 (d, 3H, H-6, $^3J_{5,6}$ 5.1 Hz). ^{13}C NMR (D_2O): δ 98.6 (C-5), 94.5 (C-1), 88.2 (C-2), 69.7 (C-4), 64.3 (C-3), 19.3 (C-6).

4.2.3.2. [Pd(*R*,*R*-chxn)((1*S*)-2,4-*O*-MeCH-D-Ery*h*1,3H$_{-2}$)]. ^{1}H NMR (D_2O): δ 4.49 (q, 1H, H-5, $^3J_{5,6}$ 5.1 Hz), 4.07 (d, 1H, H-1, $^3J_{1,2}$ 2.2 Hz), 3.76 (dd, 1H, H-4b, $^3J_{3,4b}$ 5.1 Hz, $^2J_{4a,4b}$ −10.0 Hz), 3.26 (ddd, 1H, H-3, $^3J_{2,3}$ 9.3 Hz, $^3J_{3,4a}$ 10.0 Hz, $^3J_{3,4b}$ 5.1 Hz), 3.06 (dd, 1H, H-4a, $^3J_{3,4a}$ 10.0 Hz, $^2J_{4a,4b}$ −10.0 Hz), 2.87 (dd, 1H, H-2, $^3J_{1,2}$ 2.2 Hz, $^3J_{2,3}$ 9.3 Hz), 1.00 (d, 3H, H-6, $^3J_{5,6}$ 5.1 Hz). ^{13}C NMR (D_2O): δ 98.6 (C-5), 90.1 (C-1), 84.9 (C-2), 69.4 (C-4), 61.3 (C-3), 19.3 (C-6).

4.2.4. D-Glyceraldehyde

4.2.4.1. [Pd(*R*,*R*-chxn)((1*R*)-D-Gld*h*1,2H$_{-2}$)]. ^{1}H NMR (D_2O): δ 4.35 (d, 1H, H-1, $^3J_{1,2}$ 4.8 Hz), 3.31 (dd, 1H, H-3b, $^3J_{2,3b}$ 5.3 Hz, $^2J_{3a,3b}$ −11.0 Hz), 3.25 (dd, 1H, H-3a, $^3J_{2,3a}$ 6.2 Hz, $^2J_{3a,3b}$ −11.0 Hz), 2.91 (ddd, 1H, H-2, $^3J_{1,2}$ 4.8 Hz, $^3J_{2,3a}$ 6.2 Hz, $^3J_{2,3b}$ 5.3 Hz). ^{13}C NMR (D_2O): δ 99.1 (C-1), 83.6 (C-2), 64.0 (C-3).

4.2.4.2. [Pd(*R*,*R*-chxn)((1*S*)-D-Gld*h*1,2H$_{-2}$)]. ^{1}H NMR (D_2O): δ 4.28 (d, 1H, H-1, $^3J_{1,2}$ 4.8 Hz), 3.33 (m, 1H, H-3a), 3.33 (m, 1H, H-2, $^3J_{1,2} < 1$ Hz), 3.15 (m, 1H, H-3b). ^{13}C NMR (D_2O): δ 99.1 (C-1), 83.3 (C-2), 67.8 (C-3).

4.2.5. D-Erythrulose

4.2.5.1. [Pd(*R*,*R*-chxn)(D-Eru3,4H$_{-2}$)]. ^{1}H NMR (D_2O): δ 4.84 (d, 1H, H-1b, $^3J_{1a,1b}$ −19.3 Hz), 4.42 (d, 1H, H-1a, $^3J_{1a,1b}$ −19.3 Hz), 3.72 (ddd, 1H, H-3, $^3J_{3,4a}$ 4.1 Hz, $^3J_{3,4b}$ 4.6 Hz), 3.40 (dd, 1H, H-4b, $^3J_{3,4b}$ 4.6 Hz, $^2J_{4a,4b}$ −10.5 Hz), 3.21 (dd, 1H, H-4a, $^3J_{3,4a}$ 4.1 Hz, $^2J_{4a,4b}$ −10.5 Hz). ^{13}C NMR (D_2O): δ 216.4 (C-2), 85.5 (C-3), 73.3 (C-4), 66.6 (C-1).

4.2.5.2. [Pd(*R*,*R*-chxn)(D-Eru*h*1,2;2,3H$_{-4}$)]. ^{1}H NMR (D_2O): δ 4.30 (dd, 1H, H-4b, $^3J_{3,4b}$ 8.7 Hz, $^2J_{4a,4b}$ −10.5 Hz), 3.22 (m, 1H, H-3), 3.41 (m, 1H, H-4a), 3.13 (d, 1H, H-1b, $^3J_{1a,1b}$ −10.3 Hz), 3.00 (d, 1H, H-1a, $^3J_{1a,1b}$ −10.3 Hz). ^{13}C NMR (D_2O): δ 113.9 (C-2), 81.9 (C-3), 76.3 (C-1), 63.3 (C-4).

4.2.5.3. [(*R*,*R*-chxn)$_4$Pd$_4$(C_3O_6)(μ-OH)](NO$_3$)$_3$·8H$_2$O (1). To 1 mL of a soln of D-threose (0.28 M) in water, 4 mL of a soln of [(*R*,*R*-chxn)Pd(OD)$_2$] (0.285 M) and 0.42 mL HNO_3 (2 M) were added under cooling and stirred for 2 h. The yellow soln was stored at 4 °C and eventually precipitating palladium metal was filtered off. Brown crystals of **1** were obtained within four weeks.

4.3. Crystal structure determination and refinement

Crystals suitable for X-ray crystallography were selected with the aid of a polarisation microscope, mounted on the tip of a glass fibre and investigated on a Nonius KappaCCD diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.71073$ Å). The structures

were solved by Direct Methods (SIR97, SHELXS) and refined by full-matrix least squares calculation on F^2 (SHELXL-97). Anisotropic displacement parameters were refined for all non-hydrogen atoms. CCDC 639611 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

4.4. NMR spectroscopy

All measurements were performed at 4 °C in 5 mm glass tubes on a Jeol EX-400, Eclipse 400 and Eclipse 500 with resonance frequencies of 400 and 500 MHz for ^{1}H and 100 and 125 MHz for ^{13}C. All ^{13}C NMR spectra were recorded proton decoupled (^{13}C{^{1}H}-experiment) with tetramethylsilane as an external standard. All ^{1}H NMR spectra were recorded with the remaining proton signal of D_2O as an internal standard. 2D NMR spectra (COSY, HMBC, HMQC) were measured with field gradient technique. δ values are given in ppm.

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