Palladium(II) Complexes of the Reducing Sugars D-Arabinose, D-Ribose, *rac*-Mannose, and D-Galactose**

Peter Klüfers* and Thomas Kunte[a]

Abstract: The cellulose solvent Pd-en, an aqueous solution of $[(en)Pd^{II}(OH)_2]$ (en = ethylenediamine), reacts with the monosaccharides D-arabinose (D-Ara), D-ribose (D-Rib), *rac*-mannose (*rac*-Man), and D-galactose (D-Gal) under formation of dimetalated aldose complexes, if the molar ratio of Pd and sugar is 2:1 or larger. In the Pd_2 complexes, the aldoses are tetra-deprotonated and act as bisdiolato ligands. Two crystalline pentose complexes were isolated: $[(en)_2Pd_2(\beta\text{-D-Ara}p1,2,3,4H_{-4})]\cdot 5H_2O$ (**1**) and $[(en)_2Pd_2(\beta\text{-D-Rib}p1,2,3,4H_{-4})]\cdot 6.5H_2O$ (**2**), along with two hexose complexes. With *rac*-Man, the major solution species is crystallized as the 9.4-hydrate $[(en)_2Pd_2(\beta\text{-}rac\text{-Man}p1,2,3,4H_{-4})]\cdot 9.4H_2O$ (**3**). From the respective D-Gal solutions, $[(en)_2Pd_2(\beta\text{-D-Gal}f1,3,5,6H_{-4})]\cdot 5H_2O\cdot C_2H_5OH$ (**4**), with the sugar tetraanion in its furanose form, is crystallized though it is not the major species, rather the second most abundant in purely aqueous solutions. The Gal*f* species is enriched in the mother liquors to the extent of 25% of total sugar content. Substitution of the en ligand by two molecules of ammonia, methylamine, or isopropylamine, respectively, results in the formation of different solution species. With the bulkiest ligand, isopropylamine, monometalation of the aldoses in the 1,2-position is exclusively observed.

Keywords: carbohydrates · coordination modes · palladium · monosaccharides

Introduction

Despite their significance both as renewable resources and ubiquitous reactants in metabolic pathways, the information available regarding the metal-binding sites of monosaccharides is scant. The reason for the absence of a body of knowledge is clearly down to the characteristic reactivity of aldoses and ketoses. Nonreducing sugars, particularly sucrose, and sugar derivatives such as sugar alcohols, on- and ar-acids, or glycosides have fixed configurations and hence limited capability to match their oxygen-atom pattern with the binding sites of a metal ion. However, reducing sugars (including the uronic acids) can isomerize to the various furanose and pyranose anomers. As a result, metal–monosaccharide interactions are hard to predict when, for example, the binding of an aldose to a carbohydrate-directed metalloenzyme or the design of catalytic transformations are considered.

As a prerequisite for the evaluation of transition-metal-catalyzed transformations of the carbohydrates, we have started a program to investigate the metal-binding sites of the monosaccharides by combined X-ray and NMR methods. Crystal-structure determinations of transition-metal complexes of monosaccharides are sparse. The first crystal structure of this type was described in 1981 by Taylor and Waters for an oxodimolybdate(VI) featuring an entirely deprotonated D-lyxose ligand.[1] One-and-a-half decades later, entirely deprotonated β-D-mannofuranose has been found as the only ligand in homoleptic dimetalates of the trivalent metals vanadium, chromium, and iron,[2] as well as in manganese complexes with Mn_2^{III} and $Mn^{III}Mn^{IV}$ couples.[3] Recently, D-glucose[4] and *rac*-lyxose[5] complexes with fourfold deprotonated aldose ligands have been characterized, each bound to two ethylenediamine–palladium(II) moieties, and threefold deprotonated D-lyxose has been shown to be the ligand in two cupric complexes with ammonia and ethylenediamine as additional ligands, respectively[5] To sum up, there are, to the best of our knowledge, only ten crystal structure determinations in the whole area of transition-metal complexes of monosaccharides. This fact is intriguing since knowledge of the metal-binding sites of a monosaccharide appears to be a prerequisite for a rational design of catalytic routes in a carbohydrate-based branch of green chemistry.[6]

Herein, we report on the synthesis and characterization of palladium(II) complexes of the aldoses arabinose, ribose, mannose, and galactose. The palladium agent used was the cellulose solvent "Pd-en", which has been recognized as a

[a] Prof. Dr. P. Klüfers, Dr. T. Kunte
Department Chemie der Ludwig-Maximilians-Universität München
Butenandtstrasse 5-13, 81377 München (Germany)
Fax: (+49) 089-2180-77407
E-mail: kluef@cup.uni-muenchen.de

[**] Polyol Metal Complexes, Part 42; For Part 41, see reference [10].

 DOI: 10.1002/chem.200204342

suitable agent for the complexation of the reducing sugars, though, of course, the solutions are prone to Fehling-type reactions.[4]

Results and Discussion

Solution equilibria: The focus of this work was on palladium-rich solutions to attempt maximum metalation of the respective monosaccharide. As a result, dimetalation was observed throughout a series of aldo-pentoses and hexoses by NMR spectroscopy when the respective sugars were dissolved in 1M Pd-en in a 3:1 Pd:aldose molar ratio. Almost identical spectra were obtained when only a stoichiometric amount of palladium(II) for dimetalation was used. Even in solutions with a 2:1 ratio, neither monometalated nor free sugars were detected, which indicates the high stability of the Pd_2 complexes. However, the relatively highly concentrated solutions that have been used for spectroscopy showed signals of decomposition products when stored for a few hours at 5 °C (note the much lower concentrations in the crystallization batches).

The species distribution in aqueous solutions of the monosaccharides investigated in this work is given in Table 1, the corresponding configurations and conformations of the carbohydrate ligands are depicted in Scheme 1 for the pyranose forms. Previous results on glucose[4] and lyxose[5] are included as well. The individual ^{13}C NMR shifts of the complexes of the aldoses investigated in this work are collected in Table 2. The signals have been assigned by means of HMQC and COSY techniques and by using H-H coupling constants.

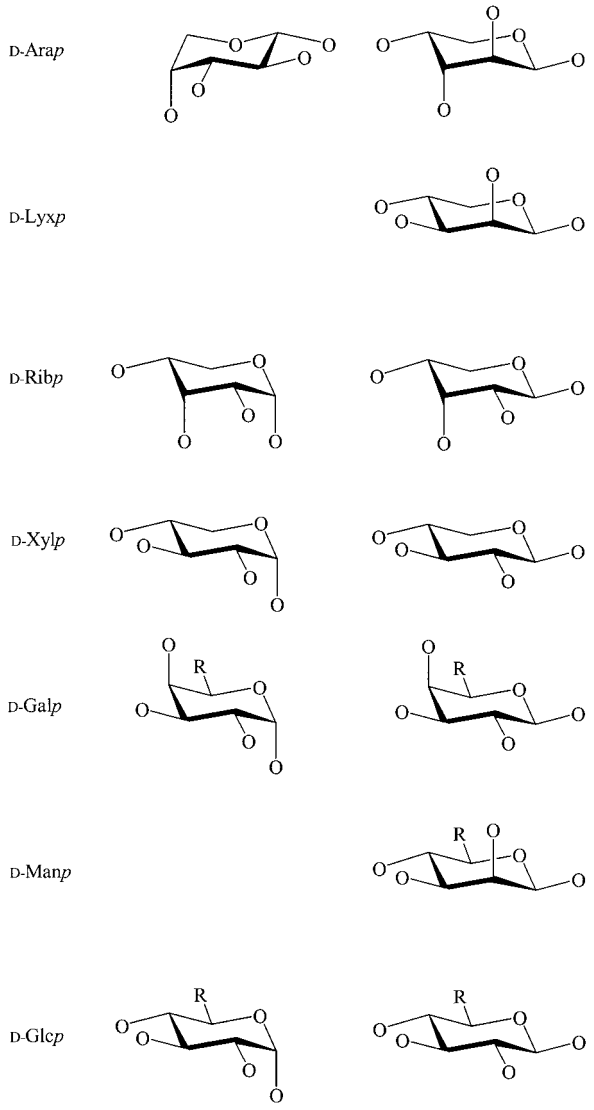
Since no indication was found for palladium complexation of the primary hydroxy group of a hexose (the one at C6), the palladium-bonding capability may be assessed based on the stereochemistry at the pyranose backbone. Formation of dimetalated pyranoses requires two diol functions that are not *trans*-diaxial. Hence, for lyxopyranose and its homologue mannopyranose, only the β-anomer in its $^4C_1$ conformation can be dimetalated. The major dimetalated species in solutions of ribose and galactose can be predicted as well, since the most stable form of the free sugars in aqueous solution (Table 1) provides two diol functions that are well-suited for palladium bonding without rearrangement. The same appears to hold true at first glance for the xylose/glucose pair. However, the actual anomer distribution deviates from that of the free sugars by a shift of the concentrations towards the α-anomer (compare the factors leading to the "anomeric effect"[7a]).

The bonding modes of dimetalated arabinopyranoses cannot be predicted. Suitable bisdiol conformations are adopted for the β-anomer both in its $^1C_4$ and $^4C_1$ conforma-

Table 1. Percentage composition of the cyclic forms of monosaccharides in aqueous solution.[a]

		α-p	*β-p*	*α-f*	*β-f*
arabinose	Pd_2	20	**80**		
	free	60	35.5	2.5	2
lyxose[b]	Pd_2		**100**		
	free	70	28	1.5	0.5
ribose	Pd_2	30	**70**		
	free	21.5	58.5	6.5	13.5
xylose	Pd_2	65	35		
	free	36.5	63	< 1	< 1
galactose	Pd_2	20	55		**25**
	free	30	64	2.5	3.5
mannose	Pd_2		**100**		
	free	64.9	34.2	0.6	0.3
glucose[c]	Pd_2	**65**	35		
	free	38	62		0.14

[a] In each entry, the first line denotes the amount of dimetalated aldose in 1M Pd-en (Pd:aldose molar ratio: 3:1); the isomer that is the ligand in crystalline bispalladium complexes is printed in boldface. The second line shows the respective values for the free aldose according to reference [7b]. The entries in the Pd_2 rows are less precise than for the free monosaccharides because of decomposition products in the concentrated solutions used for NMR spectroscopy (see text). In the table header, *p* and *f* denote the pyranose and furanose forms, respectively. [b] Ref. [5]; [c] Ref. [4]



Scheme 1. The pyranose bisdiolate ligands in binuclear complexes as detected by NMR spectroscopy (charges omitted; R = CH_2OH, left: α-pyranoses, right: β-pyranoses; the conformation is $^4C_1$ except for α-D-Ara*p* (top left), which has to adopt the $^1C_4$ conformation in its Pd_2 derivative). Relative quantities are given in Table 1. Note the close resemblance of the lyxose/mannose and the xylose/glucose pairs. See also entries in Table 1.

Table 2. Signal positions of bispalladium species detected by ^{13}C NMR spectroscopy.[a]

		C1	C2	C3	C4	C5	C6
α-Arap[d]	δ	105.4	84.8	84.4	78.8	67.2	
	Δδ	**10.1**	**11.4**	**10.4**	**8.8**	−0.7	
β-Arap	δ	104.2	84.1	82.3	73.2	64.8	
	Δδ	**10.1**	**14.1**	**12.2**	**3.2**	0.8	
α-Ribp[e]	δ	106.2	83.5	83.9	83.9	67.0	
	Δδ	**11.2**	**12.0**	**13.2**	**15.1**	2.5	
β-Ribp	δ	101.7	82.0	83.9	77.4	66.3	
	Δδ	**6.4**	**9.5**	**13.5**	**8.7**	1.8	
α-Xylp	δ	102.3	83.3	86.4	78.8	63.8	
	Δδ	**8.6**	**10.3**	**12.1**	**7.9**	1.4	
β-Xylp	δ	106.8	85.3	87.2	80.1	65.6	
	Δδ	**8.7**	**9.8**	**9.9**	**9.4**	−1.1	
α-Galp	δ	101.9	83.0	79.1	80.9	70.6	62.2
	Δδ	**8.3**	**13.2**	**8.4**	**10.1**	−1.4	−0.5
β-Galp	δ	105.0	84.8	84.7	80.4	76.1	62.1
	Δδ	**7.1**	**11.4**	**10.4**	**10.2**	−0.5	−0.4
β-Galf	δ	105.0	81.0	87.6	78.3	79.4	72.7
	Δδ	**3.2**	−1.2	**11.0**	−4.5	**7.9**	**9.1**
β-Manp	δ	108.2	86.0	84.3	75.5	76.8	62.1
	Δδ	**13.0**	**13.3**	**9.8**	**7.4**	−0.8	−0.4

[a] In each second and fourth numeric row Δδ, defined by $\delta_{complex} - \delta_{reference}$, is tabulated; the reference is an approximately 0.6 M solution of the respective monosaccharide in D_2O.[b] Δδ values that indicate a "coordination induced shift" ("CIS") appear in boldface. The Δδ values for β-galactofuranose appear to be the least certain due to only a 3.5% abundance of this form in the reference sample.[c] [b] M. J. King-Morris, A. S. Serianni, *J. Am. Chem. Soc.* **1987**, *109*, 3501–3508. [c] K. Bock, C. Pedersen, *Adv. Carbohydr. Chem. Biochem.* **1983**, *41*, 27–66. [d] Ambigous assignment for C2 and C3, which may be subject to change. [e] Uncertain assignment of this minor component due to part decomposition of the solution

tions (two axial substituents in each case) and in its $^1C_4$-α-anomer, the latter and the $^4C_1$-β-anomer being handicapped by an anomeric effect if the findings in the xylose/glucose case are generalized. In fact, the spectra show the β-form is preferred. Contradicting considerations on an anomeric effect, the H2,H3-coupling constant of 2 Hz is consistent with the exclusive existence of the $^4C_1$-β-anomer (H2-C2-C3-H3 torsion angles: ca. 60° for $^4C_1$, 180° for $^1C_4$; a coupling constant of about 10 Hz is to be expected for the latter conformer).

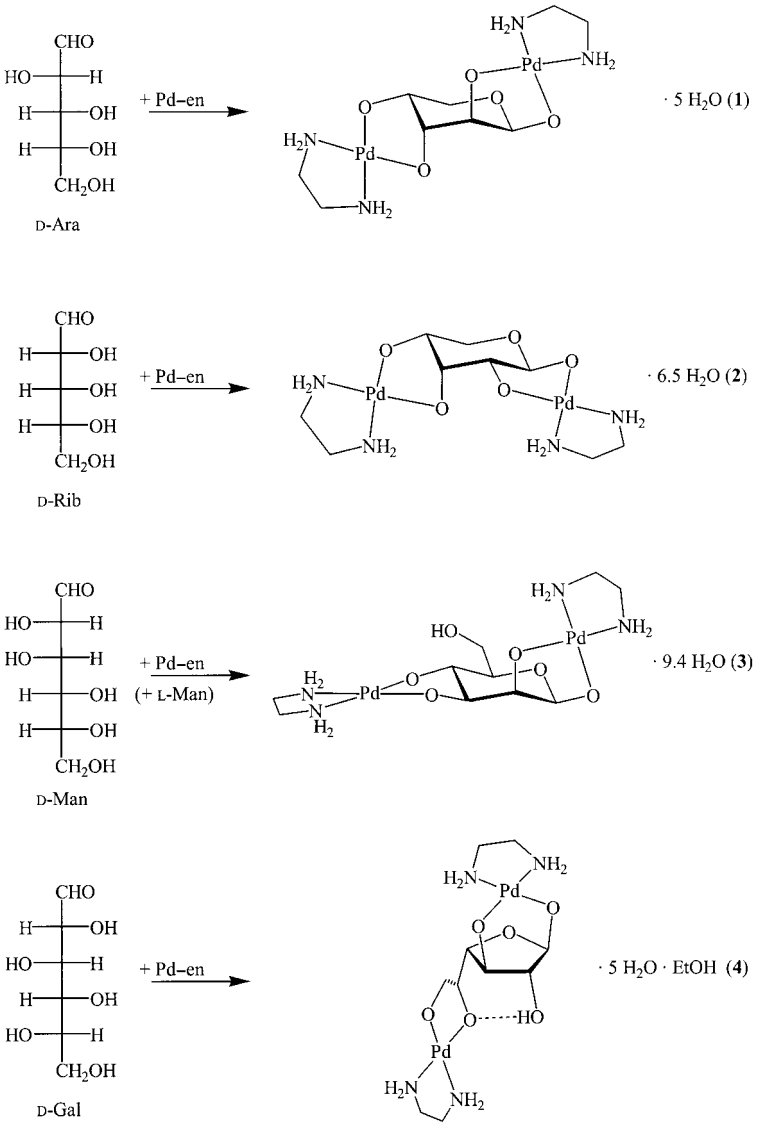
Generally, no dimetalated furanose forms are observed. The only exception in the aldose series has been found with galactose. Looking for the amount of furanoses in the aqueous equilibria of the free sugars, the galactofuranoses are the second most abundant furanose forms in the series of monosaccharides in this work (the ribofuranoses being the most abundant with a total amount of 20%). Galactose thus being a good candidate for furanose complexation, the 25% quantity of dimetalated galactofuranose, which resembles an eightfold enrichment, is astonishing and points towards a particularly stabilized metal derivative.

Crystallization of the major solution species: arabinose, ribose, and mannose: Scheme 2 summarizes the successful attempts to crystallize some of the solution species. As has been observed with glucose and lyxose, dimetalated forms of arabinose, ribose, and mannose that are the major solution species are the ones that precipitate in the crystallization batches. This indicates that, as a rule of thumb, the solubilities of the various forms are almost the same for a given aldose, hence nucleation is determined simply by the concentration of a particular species. Attempts to obtain well-grown crystals of the complexes of the pure D-configured pyranoses were successful for D-arabinose. Structural analysis on the yellow crystals of $[(en)_2Pd_2(\beta\text{-D-Arap}1,2,3,4H_{-4})]\cdot 5H_2O$ (**1**) confirms the NMR assignment of a $^4C_1$ conformer (Figure 1). The tetra-deprotonated β-D-arabinopyranose ligand is the only one in this work that exhibits two axial alkoxy functions.

With D-ribose, thin platelets of $[(en)_2Pd_2(\beta\text{-D-Ribp}1,2,3,4H_{-4})]\cdot 6.5H_2O$ (**2**) were obtained, but the quality of the diffraction data was low. Hence, no attempts were made to locate the hydrogen atoms of water molecules. Moreover, since thermal parameters refined unsatisfactorily, Figure 2 shows only a sketch of the structure as a preliminary result.

Although NMR spectra show a single solution species, crystallization was hampered with D-mannose. In this case we took advantage of the experience that the corresponding racemic species, which may crystallize in a centrosymmetric space group now and then, shows a higher tendency to form crystals. In fact, a 1:1 mixture of D- and L-mannose yielded yellow crystals of $[(en)_2Pd_2(\beta\text{-}rac\text{-Manp}1,2,3,4H_{-4})]\cdot 9.4H_2O$ (**3**) (Figure 3).

Crystallization of a metalated furanose: galactose: The significance of secondary interactions that may stabilize a particular configuration of the ligand can be derived from experiments with galactose. NMR spectra of the monosaccharide in Pd-en in a Pd:Gal ratio of 3:1 show three dimetalated species, which can be attributed to the Pd_2(α-Galp), the Pd_2(β-Galp), and the Pd_2(β-Galf) complex. The latter species is present up to an amount of one quarter of all galactose-containing species in pure aqueous solutions prior to addition of any precipitating agents. Coordination-induced shift (CIS) values (Table 2) do not allow us to establish a substantiated structural model but, fortunately, the furanose complex crystallizes as the only solid product after addition of ethanol. Yellow crystals of $[(en)_2Pd_2(\beta\text{-D-Galf}1,3,5,6H_{-4})]\cdot 5H_2O\cdot C_2H_5OH$ (**4**) are obtained by allowing ethanol vapors to diffuse into the aqueous reaction mixtures. The factor that is responsible for an increase of the β-furanose quantity of about one order of magnitude in the equilibrium mixture (Table 1) is made strikingly clear by the molecular structure (Figure 4). Contrary to the other aldose structures with Pd(en) moieties, a strong intramolecular hydrogen bond of the O–H···O$^-$ type is established with O2–H as the donor and O5 as the acceptor (the same bond may be responsible for the decreased solubility of this species by decreasing the hydrogen-bond donor and acceptor number for interactions with the solvent). One of the palladium atoms is coordinated by a 1,3-diolato(2−) ligand. Though this bonding mode is unusual, it is not unique, since levoglucosane (1,6-anhydro-β-D-glucose) binds to palladium(II) in a similar way.[8] The question may arise why the O2–H···O5 bond, which of course may also be established in free galactose, causes furanose enrichment after metalation. However, the free galactofuranoses are enriched compared with the other hexoaldoses. Nevertheless, strengthening of the bond by



Scheme 2. Reaction scheme for the four crystalline compounds **1**–**4**.

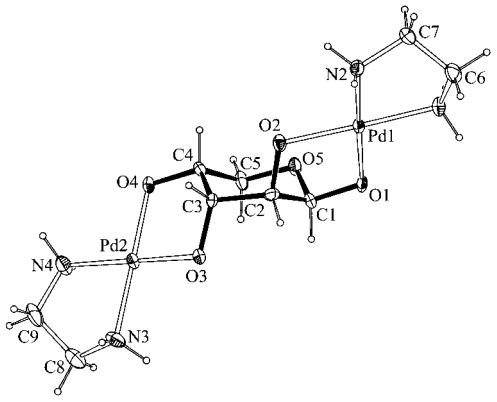


Figure 1. The molecular structure of one of two symmetrically independent molecules of $[(en)_2Pd_2(\beta\text{-D-Ara}p1,2,3,4H_{-4})]$ in crystals of the pentahydrate **1** (40% probability ellipsoids). Distances [Å] and angles [°]: from Pd1 to: O1 2.003(6), O2 2.008(5), N2 2.043(7), N1 2.052(6); from Pd2 to: O4 2.002(5), O3 2.007(5), N3 2.038(7), N4 2.056(7); torsion angles: O1-C1-C2-O2 45.4(8), O2-C2-C3-O3 −159.5(6), O3-C3-C4-O4 44.8(8); add the digit "2" to each atomic label to obtain the appropriate label in the Crystallographic Information File.

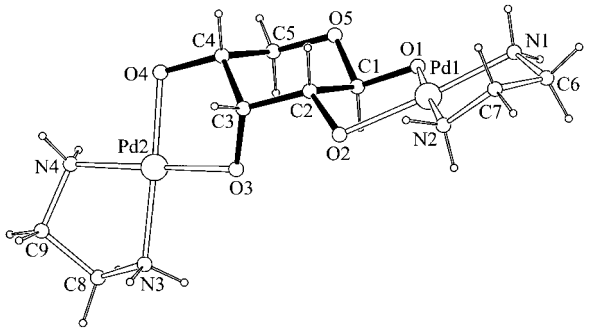


Figure 2. The structure of the dimetalated ribose complex $[(en)_2Pd_2(\beta\text{-D-Rib}p1,2,3,4H_{-4})]$ in a preliminary structure analysis of **2**. Mean distances [Å]: Pd–O 2.009, Pd–N 2.029; add the digit "2" to each atomic label in the Figure to obtain the label in the crystallographic information file (CIF).

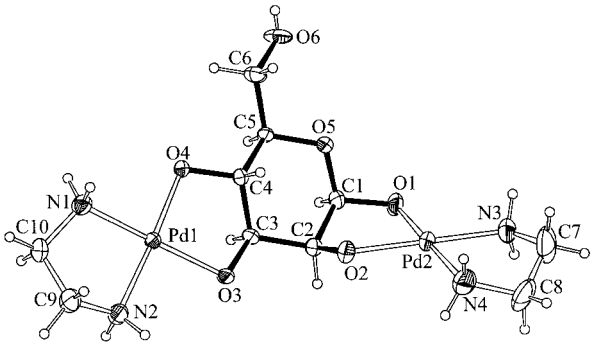


Figure 3. The molecular structure of the D enantiomer $[(en)_2Pd_2(\beta\text{-D-Man}p1,2,3,4H_{-4})]$ in crystals of the 9.4-hydrate **3**, which form as a racemic mixture with the L enantiomer (70% probability ellipsoids). Distances [Å] and angles [°]: from Pd1 to: O1 1.988(2), O2 2.008(2), N1 2.011(3), N2 2.042(3); from Pd2 to: O4 2.007(2), O3 2.016(2), N3 2.026(3), N4 2.033(3); torsion angles: O1-C1-C2-O2 −46.9(4), O2-C2-C3-O3 52.7(4), O3-C3-C4-O4 54.7(3).

deprotonation of the O5 acceptor is substantial in terms of energy[8] and appears to be the reason for the observed quantities of dimetalated furanose.

Hydrogen bonding in the solid state: The crystal structures of the title compounds are governed by hydrogen bonding. Two peculiarities that are typical for polyolato–metal structures are apparent: 1) an almost balanced donor:acceptor ratio, and 2) the predominance of cooperative hydrogen bond sequences. The structure of **4** may be analyzed as an example. Examination of Scheme 2 reveals 20 hydrogen donors (eight N-bonded, one galactose, one ethanol, and ten water hydrogen atoms), and 24 acceptor sites (that is, oxygen lone pairs = $2 \times \{6\,\text{galactose-O} + 5\,\text{water-O} + 1\,\text{ethanol-O}\}$). Note that a water molecule with its balanced hydrogen atom:lone-pair number does not alter a hydrogen or acceptor-site excess stemming from another constituent, but is able to support the formation of cooperative hydrogen bond sequences. Owing to a small acceptor-site excess in the structure of **4**, acceptor sites at three water molecules and at the ring oxygen atom are left without a matching donor. Distances and angles are normal; the mean value of the water-O to alkoxide distance is (2.77 ± 0.05) Å for example. An exception is the intramolecular bond O2–H···O5, which is rather short (Figure 4).

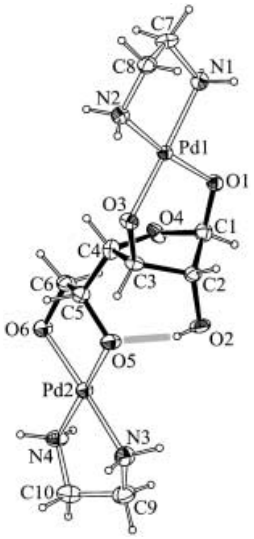


Figure 4. The structure of $[(en)_2Pd_2(\beta\text{-D-Gal}f1,3,5,6H_{-4})]$ molecules in crystals of **4** (50% probability ellipsoids). The intramolecular O2–H···O5 bond is shown as a gray bar. Distances [Å] and angles [°]: from Pd1 to: O1 2.010(2), O3 2.014(2), N2 2.040(3), N1 2.044(3); from Pd2 to: O6 1.992(2), O5 2.016(2), N4 2.026(3), N3 2.054(3); O1–C1 1.383(4), O2–C2 1.439(4), O3–C3 1.408(4), O4–C1 1.441(4), O4–C4 1.447(4), O5–C5 1.431(4), O6–C6 1.423(4), C1–C2 1.521(5), C2–C3 1.528(5), C3–C4 1.556(4), C4–C5 1.524(4), C5–C6 1.525(4); galactose bond angles with largest deviation from the tetrahedral angle: C1-C2-C3 101.6(3), C2-C3-C4 101.7(3); torsion angles: O1-C1-C2-O2 −160.0(3), O2-C2-C3-O3 160.0(3), O3-C3-C4-O4 98.0(3), O4-C4-C5-O5 71.0(4), O5-C5-C6-O6 49.6(4); intramolecular hydrogen bond: O2–H 0.91(4), H···O5 1.64(4), O2···O5 2.544(3) Å, O2–H···O5 172(4)°; puckering parameters[13] of the furanose ring O4–C1…: $Q_2 = 0.407(3)$ Å, $\phi_2 = 248.5(5)°$, the conformation therefore being close to E_{C2} (ideal ϕ_2: 252°).

Monometalated aldoses with bulky nitrogen ligands: Aldoses always form dimetalated complexes when the required amount of Pd(en) moieties is provided (Pd:aldose molar ratios of 1:1 result in the formation of mononuclear species with aldos-1,2-*O*-diato ligands but, in addition, equal amounts of dimetalated and free sugar are observed). All these findings only hold true for ethylenediamine as the co-ligand. When en is replaced by increasingly bulky ligands, mononuclear aldos-1,2-*O*-diato complexes gain increasing importance as the only species detected by NMR methods even in metal-rich solutions. To demonstrate this dependence, aqueous solutions of the (probably trans-configured) palladium(II) complexes $[(NH_3)_2Pd(OH)_2]$,[5] $[(MeNH_2)_2Pd(OH)_2]$, and $[(i\text{PrNH}_2)_2Pd(OH)_2]$, are investigated. In the following, the nomenclature for cellulose solvents[9] is used for the aqueous solutions, that is, Pd-NH_3, Pd-$MeNH_2$, and Pd-iPrNH$_2$, respectively.

A particularly simple case is lyxose. Throughout the series of solvents, the β-anomer is the only one observed—simply the number of bound palladium atoms varies. As described, dimetalation is observed in Pd-en, both for a stoichiometric molar ratio or in excess Pd-en. Both monometalated and dimetalated lyxose is found in excess Pd-NH_3, whereas only 1,2-deprotonated β-lyxopyranose is detected in excess Pd-$MeNH_2$, and Pd-iPrNH$_2$.

A more complex case is glucose. Reaction with excess Pd-en yields the dimetalated pyranoses in a 2:1 α:β-ratio.[4] In Pd-NH_3, a 2:0.5:0.5 ratio of α-Pd_2:β-Pd_2:α-Pd is observed, that is, monometalated α-anomer is formed at the expense of the β-Pd_2 species. Finally, only mono-metalated glucopyranose is found in Pd-iPrNH$_2$ in a 3:1 α:β-ratio.

As has been demonstrated for galactofuranose, metal coordination may result in enrichment of a minor aldose isomer. That the aiding ligand is one of the parameters that may be used to select a particular isomer may be shown with ribose. Dissolution of ribose in Pd-iPrNH$_2$ results in the formation of a single species with the monometalated 1,2-deprotonated α-ribopyranose as the ligand. It is notable that α-ribopyranose has about a 20% abundance in aqueous ribose solutions only, whereas excess Pd-en yields 30% α-Rib*p* but 70% β-Rib*p*.

Conclusion

Pyranoses are relatively rigid in terms of torsion angles, which are restricted to values of about ±60 or 180° (only the 60° angle being relevant for a bidentate ligand). Hence, small central atoms that require chelating ligands with a small bite angle form stable diolato complexes with open-chain or, most efficiently, with furanoidic diols.[10] However, with the relatively large palladium(II) central atoms, the rather large O-C-C-O torsion angles of a pyranoidic diol do not affect complex stability. Hence amine–palladium moieties are able to form aldose–metal complexes with the monosaccharide in both the pyranose and the furanose form. Under the conditions of permetalation, the solution species may be predicted by considering those conformers that allow for maximum metal bonding. This principle is illustrated best for lyxose and mannose. Both sugars exhibit only one pyranose form that is capable of binding two metal atoms. Dissolution in Pd-en therefore transforms the former isomer mixture into a single-species solution.

In the case of galactose, an additional structure-determining factor becomes visible, which should be more important in di- and oligosaccharide complexes: The acceptor strength of an aldose-hydroxy group is increased after deprotonation and metal ligation. Hydrogen bonds are significantly strenghthened as a result. For entropic reasons, conformers with intramolecular hydrogen bonds are enriched.

Comment on nomenclature: In the framework of the IUPAC recommendations concerning coordination compounds on one side and carbohydrates[11] on the other, the following suggestions are made: ligands are usually abbreviated by lower-case letters ("en"). In the case of ligands derived from acids, the ligand, not the acid, bears the short symbol: compare $[Fe(ox)_3]^{3-}$ with H_2ox for oxalic acid. Carbohydrates are abbreviated by a three-character code, starting with an upper-case character, stereo descriptors being added in italics when required: Glc for glucose, D-Man*f* for D-mannofuranose, etc. As used throughout this work, it is suggested that both types of usage are combined, that is to use a coordination compound type symbol for a non-carbohydrate ligand but to switch to a carbohydrate-type abbreviation for the carbohydrate ligand. Missing protons are treated in the style of substituents. Hence, β-D-Gal*f*1,3,5,6H$_{-4}$ is β-D-galactofura-

nose, which is tetradeprotonated at the positions 1, 3, 5, and 6. The entirely deprotonated β-D-mannofuranose ligands referred to in the Introduction are simply abbreviated β-D-Man*f*H$_{-5}$. This procedure appears to be more reliable than strictly applying coordination chemistry nomenclature with newly designed names for well-known molecules; hence glcH$_5$ for glucose and β-D-gal*f*2H or something similar for the above-mentioned tetraanionic ligand is avoided.

Experimental Section

Preparation: Pd-en[8] and Pd-NH$_3$[12] were prepared as described earlier; Pd-MeNH$_2$ and Pd-*i*PrNH$_2$ were prepared by an analogous procedure as for Pd-NH$_3$.

^{1}H NMR: Complete ^{1}H NMR (400 MHz, D_2O, 25 °C) data sets of dimetalated aldose species in aqueous solution are given for β-D-arabinose and β-D-mannose; the data for galactose and ribose species are summarized without coupling constants, which have not been determined for the entire signal set of the respective sugar.

Ethylenediamine-(β-D-arabinopyranos-1,2,3,4-*O*-tetraato)palladium(II) – water (1/5) (1): D-Arabinose (86 mg, 0.57 mmol) was dissolved in 0.8 M (2.5 mL, 2 mmol) Pd-en. After the mixture was stirred for 2 h at 0 °C under nitrogen, acetone vapours were allowed to diffuse into the solution at 4 °C. Yellow crystals of **1** formed within three days. The water-soluble crystals are stable in air but start to decompose with formation of palladium metal at room temperature within a few minutes, which generally is the behavior of the crystalline samples described here. ^{1}H NMR: $\delta = 3.24$ (ddd, ^3J(H,H) = 2.0 Hz, 11.0 Hz, 5.0 Hz, 1H; C4H), 3.28 (dd, ^3J(H,H) = 2.0 Hz, 2.0 Hz, 1H; C2H), 3.52 (dd, ^3J(H,H) = 2.0 Hz, 2.0 Hz, 1H; C3H), 3.58 (dd, ^3J(H,H) = 5.0 Hz, ^2J(H,H) = 11.0 Hz, 1H; C5H), 3.85 (dd, ^3J(H,H) = 11.0 Hz, ^2J(H,H) = 11.0 Hz, 1H; C5H), 4.32 (d, ^3J(H,H) = 2.0 Hz, 1H; C1H). Crystal data: $C_9H_{32}N_4O_{10}Pd_2$, $M_r = 569.21$ g mol^{-1}, triclinic (0.19 × 0.10 × 0.09 mm), *P*1, $a = 8.04970(10)$, $b = 8.18250(10)$, $c = 16.1659(3)$ Å, $\alpha = 85.9287(10)$, $\beta = 86.6638(11)$, $\gamma = 62.4320(7)°$, $V = 941.13(2)$ Å^3, $Z = 2$, $\rho = 2.00867(5)$ g cm^{-3}, $T = 200(2)$ K, $\mu(Mo_{K\alpha}) = 1.965$ mm^{-1}, numerical absorption correction, Enraf-Nonius KappaCCD, θ range = 3.69 – 27.50, 13685 reflections, 7652 independent, 7273 with $I = 2\sigma(I)$, $R_{int} = 0.0308$, mean $\sigma(I)/I = 0.0621$, C- and N-bonded H atoms fixed at idealized positions, O–H distance for water molecules refined as one variable, which refined to 0.88 Å, H···H distances in water molecules fixed to 1.57 × O–H distance, one common *U*(H) refined; 528 parameters, $R(F_{obs}) = 0.0287$, $R_w(F^2) = 0.0618$, $S = 1.041$, max./min. residual electron density: 0.664/ – 0.783 e Å^{-3}, shift/error$_{max}$ = 0.001.

Ethylenediamine-(β-D-ribopyranos-1,2,3,4-*O*-tetraato)palladium(II) – water (1/6.5) (2): D-Ribose (72 mg, 0.48 mmol) was dissolved in 0.3 M (4 mL, 1.2 mmol Pd) Pd-en and stirred for 2 h at 0 °C under nitrogen. The solution was covered with acetone at 4 °C. Yellow crystals of **2** formed in the course of one week. ^{1}H NMR: $\delta = 3.1$ (2H; C2H, C4H), 3.5 (1H; C5H), 3.9 (1H; C3H), 4.1 (1H; C5H), 4.7 ppm (1H; C1H). Crystal data: $C_9H_{35}N_4O_{11.50}Pd_2$, $M_r = 596.23$ g mol^{-1}, monoclinic (0.22 × 0.11 × 0.02 mm), $P2_1$, $a = 5.3270(5)$, $b = 16.4449(16)$, $c = 24.664(3)$ Å, $\beta = 94.385(13)°$, $V = 2154.3(4)$ Å^3, $Z = 4$, $\rho = 1.8383(3)$ g cm^{-3}, $T = 200(3)$ K, $\mu(Mo_{K\alpha}) = 1.726$ mm^{-1}, numerical absorption correction, Stoe-IPDS, θ range = 1.66 – 23.86, 10886 reflections, 6420 independent, 5151 with $I = 2\sigma(I)$, $R_{int} = 0.0613$, mean $\sigma(I)/I = 0.0715$, only C- and N-bonded H atoms considered in a riding model, *U*(H) coupled to *U* of the respective pivot atom, 478 parameters, $R(F_{obs}) = 0.0592$, $R_w(F^2) = 0.1554$, $S = 0.988$, max./min. residual electron density: 3.725/ – 1.913 e Å^{-3}, shift/error$_{max}$ = 0.001.

Ethylenediamine-(β-*rac*-mannopyranos-1,2,3,4-*O*-tetraato)palladium(II) – water (1/9.4) (3): D-Mannose (25 mg, 0.14 mmol) and L-mannose (25 mg, 0.14 mmol) were dissolved in 0.2 M (5 mL, 1 mmol) Pd-en under nitrogen. After the mixture was stirred at 0 °C for 2 h, acetone vapors were allowed to diffuse into the solution at 4 °C. Yellow crystals of **3** formed within three days. ^{1}H NMR: $\delta = 3.06$ (ddd, ^3J(H,H) = 7.5 Hz, 7.5 Hz, 1.5 Hz, 1H; C5H), 3.3 (m, 2H; C3H, C4H), 3.59 (dd, ^3J(H,H) = 7.5 Hz, ^2J(H,H) = 11.5 Hz, 1H; C6H), 3.76 (s, 1H; C2H), 3.78 (dd, ^3J(H,H) = 1.5 Hz, ^2J(H,H) = 11.5 Hz, 1H; C6H), 4.18 ppm (s, 1H; C1H). Crystal data: $C_{20}H_{85.6}N_8O_{30.8}Pd_4$, $M_r = 1357.02$ g mol^{-1}, triclinic (0.46 × 0.28 × 0.10 mm), $P\bar{1}$, $a = 8.1798(8)$, $b = 10.9038(11)$, $c = 14.3754(12)$ Å, $\alpha = 89.892(11)$, $\beta = 105.078(10)$, $\gamma = 90.389(12)°$, $V = 1238.0(2)$ Å^3, $Z = 1$, $\rho = 1.8202(3)$ g cm^{-3}, $T = 200(2)$ K, $\mu(Mo_{K\alpha}) = 1.525$ mm^{-1}, numerical absorption correction, Stoe-IPDS, θ range = 2.38 – 23.00, 6385 reflections, 3252 independent, 2912 with $I = 2\sigma(I)$, $R_{int} = 0.0344$, mean $\sigma(I)/I = 0.0378$, H atom refinement as with **1**, O–H = 0.76 Å; 379 parameters, $R(F_{obs}) = 0.0250$, $R_w(F^2) = 0.0629$, $S = 1.008$, max./min. residual electron density: 0.561/ – 0.555 e Å^{-3}, shift/error$_{max}$ = 0.001.

Ethylenediamine-(β-D-galactofuranos-1,3,5,6-*O*-tetraato)palladium(II) – water – ethanol (1/5/1) (4): D-Galactose (108 mg, 0.6 mmol) was dissolved in 0.5 M (3 mL, 1.5 mmol) Pd-en and stirred under nitrogen for 1 h at 4 °C. The solution was saturated with acetone at 0 °C, covered with ethanol and stored at 4 °C. Yellow crystals of **4** formed within three days. ^{1}H NMR: $\delta =$ 3.25 (1H; C6H), 3.27 (1H; C4H), 3.42 (1H; C2H), 3.56 (1H; C6H), 3.70 (1H; C5H), 4.20 (1H; C3H), 4.59 ppm (1H; C1H). Crystal data: $C_{12}H_{40}N_4O_{12}Pd_2$, $M_r = 645.31$ g mol^{-1}, orthorhombic (0.35 × 0.09 × 0.04 mm), $P2_12_12_1$, $a = 7.73980(10)$, $b = 15.10640(10)$, $c = 20.0460(2)$ Å, $V = 2343.79(4)$ Å^3, $Z = 4$, $\rho = 1.82878(3)$ g cm^{-3}, $T = 200(2)$ K, $\mu(Mo_{K\alpha}) =$ 1.596 mm^{-1}, numerical absorption correction, Stoe-IPDS, θ range = 3.59 – 27.49, 58511 reflections, 5317 independent, 4955 with $I = 2\sigma(I)$, $R_{int} =$ 0.0533, mean $\sigma(I)/I = 0.0274$, H atom refinement as with **1**, O-H = 0.91 Å; 310 parameters, $R(F_{obs}) = 0.0206$, $R_w(F^2) = 0.0677$, $S = 1.122$, max./min. residual electron density: 0.989/ – 1.027 e Å^{-3}, shift/error$_{max}$ = 0.001.

β*-D-Gal*p: ^{1}H NMR: $\delta = 2.86$ (1H; C3H), 3.53 (1H; C4H), 3.61 (1H; C5H), 3.70 (2H; C6H$_2$), 4.05 (1H; C2H), 4.26 ppm (1H; C1H).

α*-D-Gal*p: ^{1}H NMR: $\delta = 3.70$ (4H; C2H, C4H, C6H$_2$), 3.81 (1H; C3H), 4.01 (1H; C5H), 5.22 ppm (1H; C1H).

CCDC-188965 (**1**), CCDC-188968 (**2**), CCDC-188967 (**3**), and CCDC-188966 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.can.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336033; or deposit@ccdc.cam.ac.uk).

Acknowledgement

This work was supported by the Deutsche Forschungsgemeinschaft (grant no. Kl 624/5-2).

[1] G. E. Taylor, J. M. Waters, *Tetrahedron Lett.* **1981**, *22*, 1277 – 1278.
[2] J. Burger, C. Gack, P. Klüfers, *Angew. Chem.* **1995**, *107*, 2950 – 2951; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2647 – 2649.
[3] A. Geißelmann, P. Klüfers, B. Pilawa, *Angew. Chem.* **1998**, *110*, 1181 – 1184; *Angew. Chem. Int. Ed.* **1998**, *37*, 1119 – 1121.
[4] P. Klüfers, T. Kunte, *Angew. Chem.* **2001**, 113, 4356 – 4358; *Angew. Chem. Int. Ed.* **2001**, 40, 4210 – 4212.
[5] P. Klüfers, T. Kunte, *Eur. J. Inorg. Chem.* **2002**, *6*, 1285 – 1289.
[6] *Green Chemistry* (Eds.: P. Tundo, P. Anastas), Oxford University Press, Oxford, **2000**.
[7] a) P. Collins, R. Ferrier, *Monosaccharides,* Wiley, Chichester, **1995**, p. 25; b) P. Collins, R. Ferrier, *Monosaccharides,* Wiley, Chichester, **1995**, p. 41
[8] R. Ahlrichs, M. Ballauff, K. Eichkorn, O. Hanemann, G. Kettenbach, P. Klüfers, *Chem. Eur. J.* **1998**, *4*, 835 – 844.
[9] G. Kettenbach, P. Klüfers, P. Mayer, *Macromol. Symp.* **1997**, *120*, 291 – 301.
[10] K. Benner, P. Klüfers, M. Vogt, *Angew. Chem.* **2003**, *115*, 1088 – 1093; *Angew. Chem. Int. Ed.* **2003**, *42*, 1058 – 1062.
[11] IUPAC-IUBMB Joint Commission on Biochemical Nomenclature: Nomenclature of Carbohydrates (Recommendations 1996); www-version by G. P. Moss, http://www.chem.qmul.ac.uk/iupac/2carb/.
[12] X. Kästele, P. Klüfers, T. Kunte, *Z. Anorg. Allg. Chem.* **2001**, *627*, 2042 – 2044.
[13] D. Cremer, J. A. Pople, *J. Am. Chem. Soc.* **1975**, *97*, 1354—1358.

Received: August 14, 2002
Revised: December 23, 2002 [F4342]