Copper(II) and Palladium(II) Complexes of the Reducing Sugar Lyxose[‡]

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The reaction of the reducing aldopentose lyxose towards the metal centres in the copper-based cellulose solvents Schweizer's reagent (cupric hydroxide in aqueous ammonia) and Cu-en (cupric hydroxide in aqueous ethylenediamine) was investigated. Crystals of the trinuclear complexes $[(NH_3)_4\text{-}Cu_3^{II}(\beta\text{-}D\text{-}Lyxp1,2,3H_{-3})_2(H_2O)_2]\cdot4H_2O$ (**1**) and $[(en)_2Cu_3^{II}(\beta\text{-}D\text{-}Lyxp1,2,3H_{-3})_2(H_2O)_2]\cdot4H_2O$ (**2**) (Lyxp = lyxopyranose) were grown upon preventing Fehling-type aldose oxidation. One of the three cupric centres is coordinated by two chelating diolato ligands only, hence both ammonia and ethylenediam-ine are displaced from Cu^{II} by a carbohydrate ligand. A bi-nuclear lyxose-palladium(II) complex is formed on reaction of lyxose with Pd-en ($[(en)Pd(OH)_2]$ in water), which is another cellulose solvent of the coordinating type. From racemic mix-tures of the lyxose enantiomers, crystals of $[(en)_2Pd_2^{II}(\beta\text{-}rac\text{-}LyxpH_{-4})]\cdot7H_2O$ (**3**) were obtained. ^{13}C NMR spectra reveal the bimetallated lyxose tetraanions to be the main species in palladium-rich solutions.

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Introduction

Reducing Sugars as Ligands

Metal complexation of reducing sugars is a particularly challenging field of carbohydrate-metal complexation be-cause of the characteristic reactivity of aldoses and ketoses. While nonreducing sugars and sugar derivatives such as sugar alcohols, on- and ar-acids or glycosides have fixed configurations and hence a limited capability to match their oxygen-atom pattern with the binding sites of a metal ion, reducing sugars can isomerize to the various furanose and pyranose anomers. For the aldopentose D-lyxose, for ex-ample, Scheme 1 depicts the O-atom patterns of the anom-eric α- and β-forms of D-lyxofuranose and -pyranose, the latter as the $^4C_1$ conformers. Structural information con-cerning how a reducing sugar is bound to a particular transition metal in a specified oxidation state is rare. The few structural analyses available are due to the pioneering work of Taylor and Waters on a binuclear molybdenum(VI) complex of D-lyxose in its β-furanose form,[1] a series of binuclear β-D-mannofuranose complexes of trivalent metals (V, Cr, Fe, Mn),[2a,2b] and a palladium(II) complex of the most important aldose, D-glucose, in its α-pyranose form.[3] Despite its significance as a metal for catalysis, there is no structural information on any copper complex of a reducing sugar. The main experimental difficulty when investigating
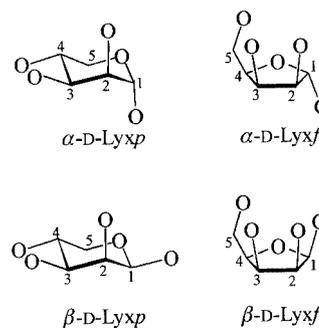
Scheme 1. Oxygen-atom patterns of the anomeric D-lyxofuranoses (right) and -pyranoses (left), the IUPAC-recommended abbrevi-ations, and the atom numbering used throughout the text; NB the β anomers (bottom) provide two diol moieties of suitable torsion angle for metal complexation each, but not the α forms (top)

complexes of this kind is the ease of the Fehling reaction. However, the oxidation of a carbohydrate may be sup-pressed for prolonged periods of time by cooling to about 5 °C and avoidance of local or short-term temperature in-creases when preparing the solutions. We report here the first structural analyses of crystals obtained from lyxose so-lutions in the well-known cellulose solvents Schweizer's re-agent (ammonia as a co-ligand) and Cu-en (ethylenediam-ine as the additional ligand).

Results and Discussion

Lyxose Complexes in Schweizer's Reagent and Cu-en

Blue, monoclinic crystals of $[(NH_3)_4Cu_3^{II}(\beta\text{-}D\text{-}Lyxp1,2,3H_{-3})_2(H_2O)_2]\cdot4H_2O$ (**1**) were obtained from D-lyxose solutions in ice-cold Schweizer's reagent (cupric hy-

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droxide dissolved in aqueous ammonia) in a large range of molar ratios of the components (Cu:Lyx from 0.5:1 to 2:1). To inhibit progress of the autocatalytic sugar oxidation in the course of crystallization, the solutions were filtered after preparation to remove small amounts of cuprous oxide. In the crystals of **1**, two bridging lyxose ligands adopt the β-pyranose form in C_2 symmetrical, trinuclear molecules; they are each threefold deprotonated along the *cis-cis* sequence of the hydroxy groups with C1, C2, and C3 (Figure 1). The coordination chemistry of the cupric centres is normal i.e. the bis-diolato-bonded Cu1 atom is square-planar coordinated with no further ligands, whereas Cu2, which is coordinated by a diolato ligand derived from the anomeric and the epimeric hydroxy groups, is surrounded by a square pyramid consisting of the two alkoxy oxygens, two ammine ligands and a water ligand at a longer distance. Intramolecular hydrogen bonds are established from N2−H donors and O3 acceptors. Also as usual in polyolato-metal compounds, the alkoxo atoms O1 and O3 are acceptors of two hydrogen bonds each; the acceptor capability of the bridging O2 atoms is weakened by an almost planar arrangement of its substituents (angle sum: 359.2°).

The capability of a polyolato ligand to replace ammine ligands is a prerequisite for the formation of **1**. To gain more insight into whether the molecular arrangement in **1** is unique to Schweizer's reagent, attempts were made to crystallize an analogous lyxose-copper complex in the related Cu(OH)$_2$/en/D-lyxose system with ethylenediamine instead of ammonia. Again, the stoichiometry was varied between half- and bimetallation of the saccharide. Blue, monoclinic crystals of [(en)$_2$Cu$_3^{II}$(β-D-Lyx$p$1,2,3H$_{-3}$)$_2$(H$_2$O)$_2$]·4H$_2$O (**2**) were obtained by the same procedure as with **1**, and also in all the Cu:Lyx ratios

Figure 2. The structure of the [(en)$_2$Cu$_3$(β-D-Lyx$p$1,2,3H$_{-3}$)$_2$(H$_2$O)$_2$] molecules in **2** projected down the twofold axis of space group $C2$; thermal ellipsoids are drawn at 40% probability; distances (Å) from Cu1 to: O3 1.936(2), O2 1.940(2); from Cu2 to: O2 1.943(2), O1 1.946(2), N2 1.998(3), N1 2.004(3), O91 2.350(3); C1−O1 1.378(4), C1−O5 1.437(5), C2−O2 1.430(4), C3−O3 1.412(4), C4−O4 1.436(4), C5−O5 1.425(5), C1−C2 1.523(5), C2−C3 1.527(4), C3−C4 1.522(5), C4−C5 1.522(6); bond angles (°): O3−Cu1−O2 86.53(9), O2−Cu2−O1 86.07(9); torsion angles (°): O1−C1−C2−O2 47.5(4), O5−C1−C2−O2 −71.6(3), O2−C2−C3−O3 −47.1(4), O3−C3−C4−O4 −71.0(4), C2−C3−C4−O4 167.4(3), O4−C4−C5−O5 179.1(3); puckering parameters of the lyxopyranose ring: Q = 0.546(4) Å, θ = 11.7(4)°, φ = 327(2)°

chosen. The molecular structure (Figure 2) resembles that in the ammine complex, including the detail of intramolecular hydrogen bonding from amine donors to alkoxide acceptors. The structure determination demonstrates that the stronger ethylenediamine ligand is also replaced by the lyxose anions. Both **1** and **2** crystallize in space group $C2$; however, despite the similarities in the lattice constants, the packing of the molecules is different. The lattice constants are therefore related according to $a_1 = 2c_2$, $b_1 = -b_2$, $2c_1 = a_2$, $\beta_1 = \beta_2$.

The structures of the copper-lyxose complexes show that the retardation of Fehling-type reactions is not caused by a lack of contacts between the central copper atoms and the hemiacetal function of the monosaccharide. As should be expected from the acidities of the lyxose hydroxy groups, the OH group at C1 (as the most acidic one) is deprotonated and bonded to a copper ion. The high tendency of formation of **1** and **2** shows the difficulty in deriving rules for copper complexation in these ternary systems. Neither simple monometallated species of the kind [(N-ligand)$_m$Cu(D-LyxH$_{-2}$)] nor bimetallated complexes of the type [(N-ligand)$_n$Cu$_2$(D-LyxH$_{-4}$)] have been isolated despite the use of suitable molar ratios. One of the reasons for the formation of the more complicated structures of **1** and **2** is the higher stability of polyolato over am(m)ine complexes in solutions of sufficiently high pH, as has been shown for simple diolates,[4] possibly together with a particular stability of Cu$_2$-μ-triolate(3−) assemblies, which are known for glycerol complexes.[5]

Figure 1. The structure of the [(NH$_3$)$_4$Cu$_3$(β-D-Lyx$p$1,2,3H$_{-3}$)$_2$(H$_2$O)$_2$] molecules in **1** projected down the twofold axis of space group $C2$; thermal ellipsoids are drawn at 60% probability; distances (Å) from Cu1 to: O3 1.932(3), O2 1.970(3); from Cu2 to: O1 1.930(2), N2 1.972(4), O2 1.983(3), N1 2.002(3), O91 2.427(4); C1−O1 1.372(5), O2−C2 1.417(5), O3−C3 1.410(5), O4−C4 1.430(5), O5−C5 1.429(5), O5−C1 1.459(6), C1−C2 1.526(6), C2−C3 1.523(6), C3−C4 1.521(6), C4−C5 1.527(6); torsion angles (°): O1−C1−C2−O2 48.2(5), O2−C2−C3−O3 −47.3(4), O3−C3−C4−O4 −71.9(4); puckering parameters of the lyxopyranose ring: Q = 0.555(4) Å, θ = 11.9(4)°, φ = 349(2)°
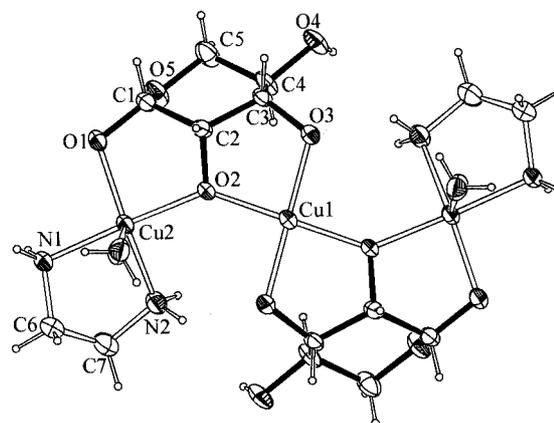
Lyxose Complexes of Palladium(II)

The experiments with the copper-based cellulose solvents suggest that monosaccharide complexation should follow simpler rules if the spectator ligand is chosen such that the stabilities of the competing complexes are not in the same order of magnitude. Maintaining lyxose as the sugar component, this may be demonstrated by replacing Cu-en with Pd-en {as an aqueous solution of [(en)Pd^{II}(OH)$_2$]}, which is also a cellulose solvent.[6] The ethylenediamine ligand at the central palladium atoms is not prone to substitution by polyolato ligands. Thus Pd-en can only act as a diol-coordinating agent (the typical reactions following hydroxide addition to cellulose solutions in Schweizer's reagent — in particular cross-linking of polysaccharide strands due to bis-diolato-cuprate formation — are therefore missing with Pd-en.) On reaction with lyxose, the lowest number of species was found for Pd/lyxose molar ratios of 2:1 and higher. ^{13}C NMR spectra of the diamagnetic complexes reveal bimetallated lyxopyranose ligands by the typical "coordination induced shift" (CIS) of the carbon atoms 1−4. Crystals of the complex formed from D-lyxose and Pd-en could not be isolated, although yellow, centrosymmetric, triclinic crystals of [(en)$_2$Pd$_2^{II}$(β-rac-LyxpH$_{-4}$)]·7H$_2$O (3) were obtained from rac-lyxose solutions, which can be prepared easily due to the availability of both D- and L-lyxose. The structure of the complex molecules agrees well with the expectation that: (1) only diol moieties are bound to palladium, and (2) due to the high thermodynamic stability of the complexes, the maximum number of palladium atoms should be bonded to the monosaccharide. Scheme 1 shows that only two isomers are able to bind two palladium atoms for steric reasons: the β-pyranose form in its $^4C_1$ conformation, and the β-furanose form when 1,3-diolato complex formation is taken into consideration as well as 1,2-bonding. Figure 3 shows the actual structure with the lyxose ligands in the β-pyranose form. In agreement with the NMR spectra, O1−4 are deprotonated and bonded to the central palladium atoms. Hydrogen bonding is as usual with polyolato-metallates: each alkoxide O atom accepts two hydrogen bonds, mostly from water donors (2 N−H···O- and 14 O−H···O- contacts are established by the 16 lone pairs of
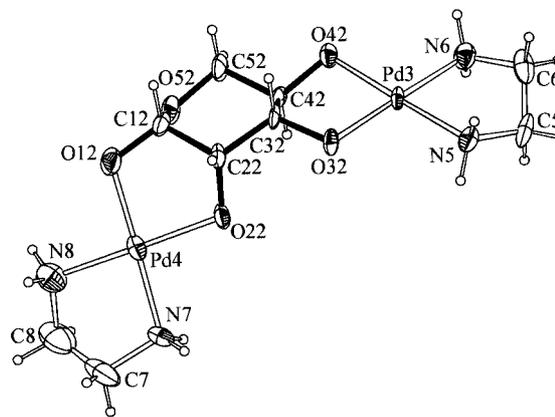

Figure 3. The structure of the [(en)$_2$Pd$_2$(β-D-LyxpH$_{-4}$)] isomer from the racemic mixture in 3 projected with almost the same view of the carbohydrate ligand as in the copper complexes; thermal ellipsoids are drawn at 60% probability; distances (Å) and angles (°) (the first entry is the specified distance, the second entry is the corresponding distance in the L-configured isomer): Pd3−O42 2.004(4), 2.006(4), Pd3−O32 2.024(4), 2.027(4), Pd4−O22 2.011(4), 1.990(4), Pd4−O12 1.993(5), 2.004(4), C12−O12 1.374(8), 1.372(7), C12−O52 1.434(9), 1.432(8), C22−O22 1.418(8), 1.414(8), C32−O32 1.421(7), 1.427(6), C42−O42 1.424(7), 1.414(8), C52−O52 1.424(8), 1.425(8), C12−C22 1.542(8), 1.551(8), C22−C32 1.529(8), 1.527(9), C32−C42 1.514(9), 1.509(9), C42−C52 1.517(8), 1.525(8); mean of eight Pd−N distances: 2.034 Å, standard deviation of the mean: 0.007 Å, mean standard deviation: 0.006 Å; torsion angles: O12−C12−C22−O22 49.8(7), −47.2(7), O22−C22−C32−O32 −55.6(8), 52.8(8), O32−C32−C42−O42 −55.9(6), 58.0(6); puckering parameters of the lyxopyranose ring: Q = 0.574(7), 0.579(7) Å, θ = 6.2(7), 173.0(7)° (the conformation is close to an ideal chair, hence no φ value is given)

the eight alkoxo ligands of the asymmetric unit). The water donors are incorporated in cooperative hydrogen bond sequences, which often start with an N−H donor.

In the ^{13}C NMR spectra, the aforementioned CIS is a maximum for C2. Though data on aldoses are scarce, this seems to be biased towards the axial substitution of the epimeric carbon atom to some extent.[7] At the concentrations given in Table 1, the binuclear [(en)$_2$Pd$_2^{II}$(β-D-LyxpH$_{-4}$)] complex is the main species at high palladium:lyxose ratios. Monometallated species occur in only small amounts, although they become the main species at a

Table 1. Signal positions in the ^{13}C NMR spectrum of solutions of D-lyxose in 1 M Pd-en; in addition to the chemical shift the "coordination induced shift" ("CIS", defined as $\delta_{complex} − \delta_{reference}$) is tabulated; the reference is an approx. 0.6 M solution of D-lyxose in D$_2$O;[a] signals of the en ligand are omitted; Δδ values that indicate a CIS are printed in **boldface**; in the last two columns, a rough estimate of the species distribution as derived from ^{13}C signal heights is given for different molar ratios: a "+" sign represents about one fifth of the tetraol, whereas a "−" sign accounts for less than about 10%; an unidentified form of lyxose (abundance: "−" at 2:1, "+" at 1:1 molar ratio) exhibits signals at δ = 90.6, 71.3, 68.7, 66.8, 56.6; from the fact that signal height closely corresponds to that of the monometallated form on Pd/Lyx ratio variation, the unidentified species may be another monometallated derivative, possibly with a lyxofuranose ligand

		C1	C2	C3	C4	C5	2:1	1:1
[(en)$_2$Pd$_2$(β-D-Lyxp1,2,3,4H$_{-4}$)]	δ	108.6	85.6	84.1	74.5	65.0	++++	−
	Δδ	**12.7**	**14.1**	**9.9**	**6.5**	−0.7		
[(en)$_2$Pd(β-D-Lyxp1,2H$_{-2}$)]	δ	107.2	82.8	72.9	70.4	64.8	−	++
	Δδ	**11.3**	**11.3**	−1.3	2.4	−0.9		
[(en)$_2$Pd(β-D-Lyxp2,3H$_{-2}$)]	δ	96.4	81.5	80.1	66.9	64.7	−	++
	Δδ	0.5	**10.0**	**5.9**	−1.1	−1.0		

[a] M. J. King-Morris, A. S. Serianni, J. Am. Chem. Soc. **1987**, 109, 3501−3508.

molar ratio of 1:1. Their concentration is governed by the relative acidities of the hydroxy groups of lyxose. The main species is the mononuclear [(en)Pd^{II}(β-D-Lyx$p$1,2H$_{-2}$)] complex with the most acidic hydroxy group at O1 being deprotonated, although almost the same concentration is reached by the [(en)Pd^{II}(β-D-Lyx$p$2,3H$_{-2}$)] species. A minor species in the 1:1 solutions has not been identified (cf. Table 1).

Attempts to synthesize a heteronuclear Pd$_2$Cu complex by reacting the [(en)Pd^{II}(β-D-Lyx$p$H$_{-2}$)] complexes with Cu(OH)$_2$ failed according to NMR spectroscopy. Instead of increasing signal widths at the suggested copper-binding site (C2, C3), the signals of the binuclear [(en)$_2$Pd$_2^{II}$(β-D-Lyx$p$H$_{-4}$)] complex emerge. Obviously, the dissolved cupric hydroxide forms homonuclear species of unknown com-

position that do not give rise to observable NMR signals and also consume lyxose.

Conclusion

Prior to undergoing redox chemistry, the aldose lyxose forms coordination compounds with copper atoms in alkaline aqueous solution. The compounds are prevented from Fehling-type reactions by cooling to 5 °C and removal of autocatalytically acting seeds of cuprous oxide. The most acidic hydroxy group at the anomeric carbon atom is involved in copper chelation. However, the prediction of a particular structure is complicated by the ability of diolato ligands to substitute nitrogen ligands at the cupric centres.

Table 2. Crystallographic data

	1	2	3
Empirical formula	C$_{10}$H$_{38}$Cu$_3$N$_4$O$_{16}$	C$_{14}$H$_{42}$Cu$_3$N$_4$O$_{16}$	C$_9$H$_{36}$N$_4$O$_{12}$Pd$_2$
M_r/g mol^{-1}	661.064	713.139	605.22
Crystal size/mm	0.30 × 0.16 × 0.08	0.27 × 0.06 × 0.02	0.52 × 0.35 × 0.10
T/K	200(2)	200(2)	200(2)
Radiation	Mo-K_α	Mo-K_α	Mo-K_α
	rotating anode	rotating anode	sealed anode
Diffractometer	Nonius Kappa CCD	Nonius Kappa CCD	Stoe IPDS
φ increment/°	1	1	1.2
Irradiation time	70 s deg^{-1}	60 s deg^{-1}	120 s plate^{-1}
Crystal system	monoclinic	monoclinic	triclinic
Space group	$C2$	$C2$	$P\bar{1}$
a/Å	21.1164(4)	19.7731(3)	9.6538(10)
b/Å	6.4130(2)	6.41900(10)	14.5600(15)
c/Å	9.4660(2)	12.3972(2)	15.6269(19)
α/°	90	90	77.008(13)
β/°	115.0241(12)	125.3170(10)	75.928(13)
γ/°	90	90	77.725(12)
V/Å^3	1161.55(5)	1283.92(3)	2046.9(4)
Z	2	2	4
Calcd. density/g cm^{-3}	1.89013(8)	1.84468(4)	1.9640(4)
μ/mm^{-1}	2.803	2.543	1.820
Absorption correction	numerical (9 faces)	numerical (8 faces)	numerical (10 faces)
Transmission factor range	0.6823−0.8207	0.6322−0.9675	0.5613−0.8490
Refls. measured	7104	11089	16223
R_{int}	0.025	0.038	0.059
Mean σ(I)/I	0.028	0.043	0.057
θ range/°	2.3−23.3	3.3−27.5	2.1−25.7
Observed refls.	1639	2695	5839
x, y (weighting scheme)	0.0340, 3.2527	0.0405, 1.2634	0.0648, 6.3502
Water-H refinement	[a]	[a]	[b]
Flack parameter	−0.03(2)	−0.02(2)	−
Refls. in refinement	1671	2887	7272
Parameters	183	191	573
Restraints	20	13	42
$R(F_{obs})$	0.025	0.031	0.047
$R_w(F^2)$	0.068	0.080	0.123
S	1.135	1.098	1.057
Shift/error$_{max}$	0.001	0.001	0.001
Max. diff. density/eÅ^{-3}	0.410	0.755	2.818
Min. diff. density/eÅ^{-3}	−0.765	−0.862	−1.352

[a] C- and N-bonded H atoms fixed; O−H and H−H distance fixed for water-H atoms at 0.83 and 1.31, respectively; one common U for all H atoms. [b] C- and N-bonded H atoms fixed; one common O−H distance refined for water-H atoms (0.94), H−H distance fixed to the 1.57-times that of O−H thus forcing a 105° bonding angle; one common U for all H atoms.

The latter characteristic does not hold for palladium(II) centres, to which nitrogen ligation is clearly favoured over alkoxide bonding. (en)Pd fragments thus bind to diol groups without loss of the ethylenediamine ligand. Hence the rules of carbohydrate-metal coordination appear to be less complicated in the palladium(II) case. For this metal, the maximum number of palladium atoms is bonded to as many diol groups as are needed for chelation in terms of the torsion angle (i.e. no axial-axial diols in pyranoses and no *trans*-diols in furanoses).

Experimental Section

D- and L-lyxose were purchased from the Institute of Chemistry, Bratislava. Ethylenediamine, ammonia and sodium hydroxide were purchased from Fluka. Cupric hydroxide was synthesized from cupric sulfate pentahydrate (Merck). Pd-en was stored under nitrogen at 4 °C before use. All experiments with Pd-en were carried out under nitrogen. NMR measurements were performed either with a Jeol EX 400 or a Jeol GSX 270 NMR spectrometer.

1: D-Lyxose (450 mg, 3.00 mmol) and cupric hydroxide (195 mg, 2.00 mmol) were stirred in 5 mL aqueous ammonia (25%) at 4 °C for 2 h. The dark blue solution was filtered off from excess cupric hydroxide. Blue platelets of **1** formed during the course of one week upon diffusing acetone vapours into the solution. Solutions kept at room temperature had decomposed after two days.

2: The entire procedure was conducted at a temperature of 4 °C: D-lyxose (300 mg, 2.00 mmol) and cupric hydroxide (195 mg, 2.00 mmol) were stirred in 5 mL water for 5 min. Sodium hydroxide (8 mg, 0.2 mmol) was then added and stirring was continued for a further 5 min, after which time ethylenediamine (120 mg, 2.00 mmol) was added. After stirring for 1 h, the dark blue solution was filtered. Blue platelets of **1** formed during the course of one week upon diffusing acetone vapours into the solution. Decomposition of the solutions at room temperature proceeds in the same way as with **1**.

3: Pd-en was prepared as described earlier.[6] *rac*-Lyxose (74 mg, 0.50 mmol) was dissolved in 5 mL of an aqueous 0.2 M Pd-en solution (1.0 mmol) and stirred for 24 h at 0 °C. Diffusion of acetone−water vapours (4:1) caused the formation of yellow platelets within one week.

X-ray Structure Determinations: Details of the structure analyses are summarized in Table 2. Disordered positions for hydrogen attached to two (**1**) or one (**2**) water-oxygen atoms were allowed for to account for hydrogen bonding between symmetry-related oxygen atoms.

CCDC-170697 (**1**), -170696 (**2**) and -170960 (**3**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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