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# Interaction of 1,6-anhydro derivatives of amino sugars with copper(II) ions †

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## ABSTRACT

The synthesis of 2-amino-1,6-anhydro-2-deoxy-4-*O*-methyl-β-D-mannopyranose (**3**) is described. Potentiometric and spectroscopic methods were used to evaluate the equilibria and the complex structures in systems containing Cu(II) ions and **3**, and two other 1,6-anhydro derivatives. The results showed that no mannosamine derivative is able to form dimeric species found earlier for 1,6-anhydro-glucosamine ligands. The correlation between complex formation and sugar structure is discussed.

## INTRODUCTION

Aminodeoxy sugars, as has been shown earlier, co-ordinate copper(II) ions in a bidentate manner[2–8]. The resulting chelate ring contains an amino nitrogen acting as an anchor site and a favorably situated deprotonated hydroxyl donor. The configuration as well as the conformation of these ligands can affect critically their complex structure and stability, and in some cases may also promote the formation of dimeric species.

1,6-Anhydro derivatives of aminodeoxy sugars have limited flexibility in comparison with their parent compounds[9]. Studies of the binding abilities of a series of 1,6-anhydro derivatives of amino sugars containing a nitrogen atom in positions 2 or 4 have shown[1] that those ligands possessing an additional 1,3-dioxolane ring were able to form very specific dimeric complexes of the type $Cu_2L_4$ in neutral solutions. However, for a ligand containing an amino group in position 3, this is not the case. Instead, this particular sugar molecule has a tendency to adopt a boat conformation and is only able to form monomeric complexes. Although the

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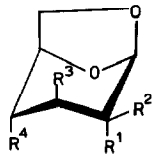
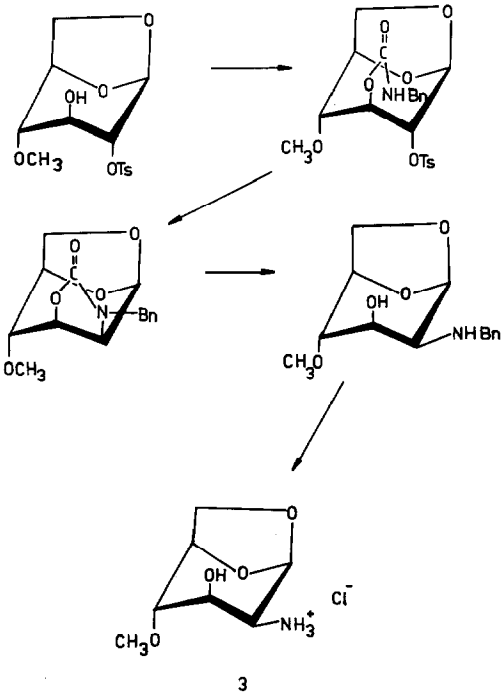


1 $R^1 = NH_2$ $R^2 = H$ $R^3 = OH$ $R^4 = OPhCH_2$
2 $R^1 = H$ $R^2 = NH_2$ $R^3 = OH$ $R^4 = H$
3 $R^1 = H$ $R^2 = NH_2$ $R^3 = OH$ $R^4 = OCH_3$

Scheme 1.

formation of the binuclear complexes appears to be well supported by both spectroscopic and potentiometric data[1], their structure and the reason for their formation is still unclear. In order to obtain further information about the nature of dimer formation, we have synthesized three further aminodeoxy derivatives of 1,6-anhydrohexoses (Scheme 1), including the analogue 2-amino-1,6-anhydro-2-deoxy-4-*O*-methyl-β-D-mannopyranose (**3**), and performed potentiometric and spectroscopic studies on their $H^+$ and Cu(II) complexes.



3

Scheme 2.

2-Amino-1,6-anhydro-4-*O*-benzyl-2-deoxy-β-D-glucopyranose (**1**) was prepared from 1,6:2,3-dianhydro-4-*O*-benzyl-β-D-mannopyranose by the action of ammonia in EtOH[10], and 2-amino-1,6-anhydro-2,4-dideoxy-β-D-*lyxo*-hexopyranose (**2**) was obtained as described[11]. For the synthesis of **3**, a method based on intramolecular cyclization of a urethane followed by hydrolysis of an oxazolidinone ring with sodium hydroxide was used (Scheme 2).

## EXPERIMENTAL

*General methods.*—Melting points were determined with a Boëtius micro melting-point block and are uncorrected. Optical rotations were measured at 22 ± 2°C with a Perkin–Elmer Model 241 polarimeter. Elemental analyses were performed on a Perkin–Elmer 240 C instrument. IR spectra were recorded with a Perkin–Elmer 5808 spectrometer. The $^1$H NMR spectra were recorded with a Bruker WM 270 spectrometer for solutions in $CDCl_3$ (internal $Me_4Si$) and $D_2O$–sodium 4,4-dimethyl-4-silapentanesulfonate. Reactions were monitored by TLC on Kieselgel $60F_{254}$ (Merck 5554) with detection by charring after spraying with $H_2SO_4$. Kieselgel G was used for short column chromatography. The positive-ion FAB spectrum of the hydrochloride of **3** was recorded using $Me_2SO$–glycerol as the ionization matrix and atoms of Xe as bombarding particles.

*1,6-anhydro-3-O-(N-benzylcarbamoyl)-4-O-methyl-2-O-toluene-p-sulfonyl-β-D-glucopyranose* (**5**).—To a solution of 1,6-anhydro-4-*O*-methyl-2-*O*-toluene-*p*-sulfonyl-β-D-glucopyranose[12] (**4**; 10 g, 0.03 mol) in toluene (100 mL) was added benzyl isocyanate (6 g, 0.045 mol). The mixture was refluxed under Ar for 7 h (TLC; 9:1 benzene–acetone). The solvents were evaporated at 40°C and the residue was dried under vacuum (2 Pa) for 3 h. Crystallization from EtOH gave **5** (9.38 g, 67%); mp 117–118°C; $[\alpha]_D$ + 2.5° (*c* 0.8, $CHCl_3$). $^1$H NMR data (270 MHz, $CDCl_3$): δ 2.42 (m, 3 H, $CH_3Ar$), 3.13 (bs, 1 H, H-4), 3.43 (s, 1 H, $OCH_3$), 3.72 (dd, 1 H, $J_{6,6}$ 7.5, $J_{6,5}$ 5.6 Hz, H-6*exo*), 3.90 (bd, 1 H, $J_{6,6}$ 7.5, $J_{6,5}$ 0 Hz, H-6*endo*), 4.35 (d, 2 H, $J_{CH,NH}$ 5.6 Hz, $CH_2N$), 4.46 (bs, 1 H, H-2), 4.60 (bd, 1 H, $J_{5,6exo}$ 5.6 Hz, H-5), 4.85 (quintet, 1 H, $J_{3,1} = J_{3,2} = J_{3,4} = J_{3,5} = 1.6$ Hz, H-3), 5.17 (t, 1 H, $J_{NH,CH_2}$ 5.6 Hz, NH), 5.39 (b, 1 H H-1), 7.33–7.82 (m, 9 H, 2 Ph). IR spectrum (KBr pellet): 1177, 1190, 1373 ($SO_2$–O), 1510, 1732 (N–C–O), 3445 $cm^{-1}$ (NH). Anal. Calcd for $C_{22}H_{25}NO_8S$ (463.49): C, 57.01; H, 5.43; N, 3.02; S, 6.92. Found: C, 56.90; H, 5.28; N, 3.17; S, 6.70.

*3-Benzyl-(1,6-anhydro-2,3-dideoxy-4-O-methyl-β-D-mannopyrano)-[2,3-d]-2-oxazolidinone* (**6**) — To a solution of urethane **5** (5.5 g, 0.0119 mol) in $Me_2SO$ (50 mL) under Ar was slowly added a solution of potassium *tert*-butoxide (1.4 g) in $Me_2SO$ (15 mL). The mixture was stirred for 90 min at room temperature (TLC; 15:2:1 ethyl ether–toluene–EtOH), neutralized with aq 10% $H_2SO_4$, poured onto crushed ice, and extracted three times with chloroform. After drying with $CaCl_2$ and evaporation of the solvent, the residue was kept under vacuo (1 Pa) for 1 h. The syrupy-like residue was crystallized from acetone–hexane, yielding **6** (2.35

g, 68%); mp 99–104°C; $[\alpha]_D$ −77° (*c* 0.70 $CHCl_3$). IR spectrum (KBr pellet): 1759 (N–C–O), 1234 $cm^{-1}$ ($NR_3$). Anal. Calcd. for $C_{15}H_{17}NO_5$ (291.34): C, 61.85; H, 5.88; N, 4.81. Found: C, 62.07; H, 5.92; N, 4.86.

*1,6-Anhydro-2-benzylamino-2-deoxy-4-O-methyl-β-D-mannopyranose* (**7**).—A solution of NaOH (2.8 g) in water (10 mL) was added to a stirred solution of oxazolidinone **6** (2 g, 0.0068 mol) in EtOH (50 mL) and refluxed for 5 h (TLC; 10:1 benzene–acetone). The mixture was neutralized with dil HCl and evaporated, and to the solid residue was added water (50 mL). The solution was extracted with $CH_2Cl_2$ (3 × 25 mL), and the combined extract was dried with $Na_2SO_4$ and evaporated. Flash chromatography of the residue gave **7** (1.63 g, 89%); which, after recrystallization from ether–hexane, had mp 69–71°C; $[\alpha]_D$ −59° (*c* 0.6, $CHCl_3$). Anal. Calcd for $C_{14}H_{19}NO_4$ (265.31): C, 63.38; H, 7.22; N, 5.28. Found: C, 63.53; H, 7.31; N, 5.23.

In addition to the main product, two other compounds were isolated. The substance (38 mg) with the highest $R_f$ value had: mp 55–57°C; $[\alpha]_D$ −40.2° (*c* 1.2, MeOH), and was identified as 1,6:2,3-dianhydro-4-*O*-methyl-β-D-mannopyranose, described earlier[13]. The more polar by-product (45 mg) with mp 167°C was identical with an authentic sample of *N,N'*-dibenzylurea.

*Hydrochloride of 2-amino-1,6-anhydro-2-deoxy-4-O-methyl-β-D-mannopyranose* (**3**).—The benzylamino derivative **7** (2 g, 0.0075 mol) was hydrogenolyzed in MeOH (80 mL) with 1.5 equiv of HCl in the presence of 10% Pd–C. The course of the reaction was monitored by TLC (20:20:2:2:1 $CHCl_3$–2-propanol–25% ammonia–water–EtOH); the starting material disappeared within 5 h. The catalyst was filtered off by passing through a 2 × 2 cm layer of Celite and the solution was evaporated. The excess of HCl was removed by three-fold evaporation with MeOH. Recrystallization from EtOH–ether gave **3** (1.43 mg, 89%); mp 217–220°C, $[\alpha]_D$ −109° (*c* 0.63, $H_2O$). MS spectrum (FAB, glycerol–$Me_2SO$ matrix, Xe): *m/z* 176 $[C_7H_{14}NO_4]^+$. $^1H$ NMR data (270 MHz, $D_2O$), δ 3.48 (dd, 1 H, $J_{2,1}$ 1.9, $J_{2,3}$ 5.8 Hz, H-2), 3.5 (s, 3 H, $OCH_3$), 3.59 (t, 1 H, $J_{4,3} = J_{4,5}$ = 1.9 Hz, H-4), 3.82 (dd, 1 H, $J_{6,6}$ 7.8, $J_{6,5}$ 6.0 Hz, H-6*exo*), 4.18 (dq, 1 H, $J_{3,4}$ 1.4, $J_{3,2}$ 5.8, $J_{4,5}$ 1.9, $J_{3,5}$ 1.6 Hz, H-3), 4.31 (dd, 1 H, $J_{6,6}$ 7.8, $J_{6,5}$ 1.2 Hz, H-6*endo*), 4.83 (dq, 1 H, $J_{5,6endo}$ 1.2, $J_{5,6exo}$ 6.0, $J_{5,4}$ 1.9, $J_{5,3}$ 1.6 Hz, H-5), 5.61 (t, 1 H, $J_{1,2}$ 1.9, $J_{1,3}$ 1.4 Hz, H-1). Anal. Calcd for $C_7H_{14}ClNO_4$ (211.65): C, 39.73; H, 6.67; N, 6.62; Cl, 16.64. Found: C, 39.81; H, 6.59; Cl, 16.64; N, 6.43.

*Potentiometric studies.*—The stability constants of the $H^+$ and $Cu^{2+}$ complexes were calculated from the pH titration data (NaOH) obtained at 25°C with a Radiometer PHM84 pH meter, using total volumes of 3 mL. A Radiometer ABU 80 autoburette and a Russell CMAWL combined electrode, calibrated in concentrations by titrations of diluted $HNO_3$[14], were used. All solutions were prepared with 0.1 M $KNO_3$, $3 \cdot 10^{-3}$ M ligand, and 1:3, 1:4, and 1:6 metal-to-ligand ratios. Stability constants were calculated with the aid of the SUPERQUAD program[15]. The standard deviations reported are those given by SUPERQUAD and refer to random errors only. They give, however, a good indication of the importance of the particular species in the equilibrium.

*Spectroscopic measurements.*—Absorption spectra were recorded on a Beckman UV 5240 spectrometer. EPR spectra were obtained on a Radiopan SE/X 2543 spectrometer at 9.15 GHz at 130 K. For these spectra, samples were dissolved in 3:1 water–ethylene glycol in order to obtain a better glass. CD spectra were recorded on a Jasco J-600 automatic spectropolarimeter. The concentration of $Cu^{2+}$ was $3 \cdot 10^{-3}$ M and the metal-to-ligand ratio was fixed at 1:4.

## RESULTS AND DISCUSSION

Protonation constants of all the ligands studied and their complex stabilities (log $\beta$) are given in Table I. Spectroscopic properties for complexes are collected in Table III. The species distribution curves for **3** are given in Fig. 1. CD spectra for the complexes of this ligand are shown in Fig. 2.

*2-Amino-1,6-anhydro-4-O-benzyl-2-deoxy-β-D-glucopyranose* (**1**).—It can be seen that the protonation constant is virtually identical to that of 2-amino-1,6-anhydro-2-deoxy-β-D-glucopyranose[1], a molecule which differs only by the absence of the benzyl group. This indicates that there is no interaction between the nitrogen and the aromatic ring in **1**.

The CuL species is the only detectable complex found for this ligand. Its spectroscopic parameters (values of $A_{\parallel}$ and $g_{\parallel}$, energies of *d–d* transitions in absorption and CD spectra) are typical for a species with one nitrogen atom co-ordinated to Cu(II) (1 N)[1,5]. The presence of a charge transfer band in CD spectra at ca. 290 nm ($NH_2 \rightarrow Cu$)[2–6] also supports the formation of a Cu–N bond.

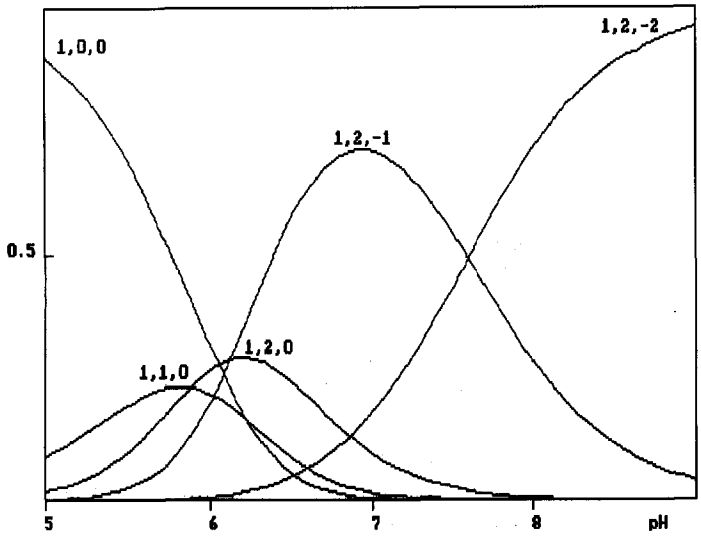



Fig. 1. Species distribution curves for Cu(II)–4-Me-AManN complexes: $C_{Cu} = 0.003$ mol dm$^{-3}$, $C_L : C_{Cu} = 4:1$, (1,0,0) corresponds to free metal ion.

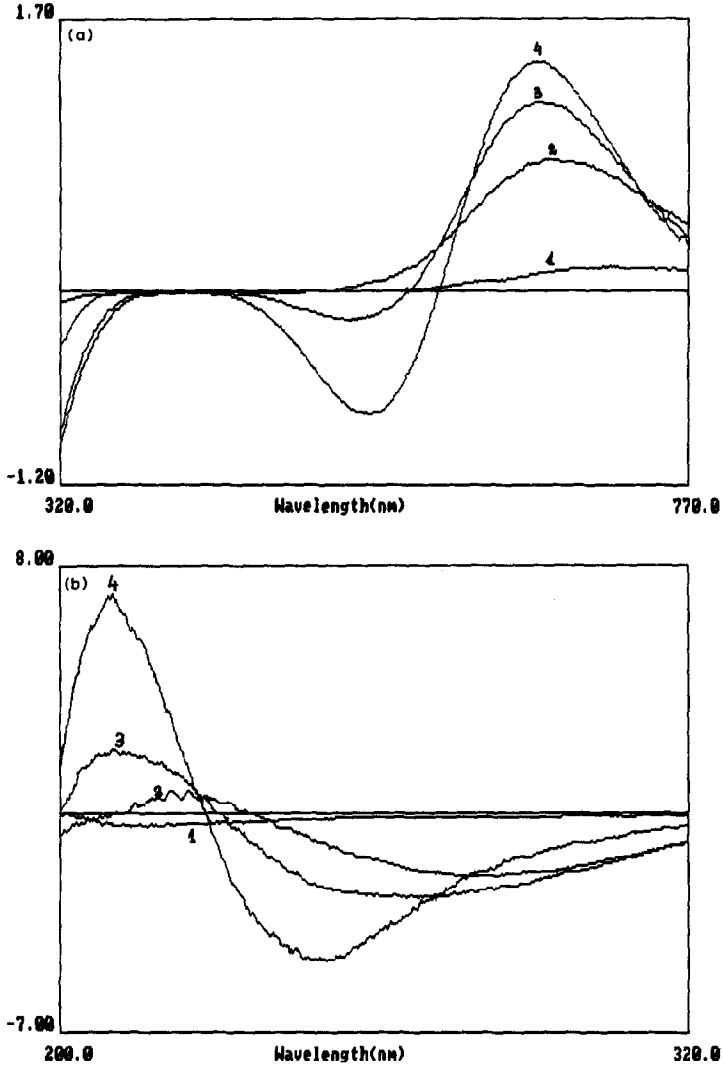



Fig. 2. CD spectra for Cu(II)–4-Me-AManN solutions: $C_{Cu} = 0.003$ mol dm$^{-3}$, $C_L : C_{Cu} = 4:1$; at pH 5.32 (1), 6.06 (2), 7.10 (3), and 10.08 (4); a, $d$–$d$ bands; b, UV region.

No oxygen-related transition could be detected. The only other band observable down to 190 nm is the $L_a$ transition of the phenyl ring at 215 nm (the $L_b$ transition, expected at ca. 270 nm, is usually of a magnitude at least 100 times smaller and thus contributes to the 290-nm band instead of manifesting itself separately). The stability of the CuL species is rather low: the calculated complex formation at pH 6.5 and 4:1 L:Cu(II) ratio is only 50% of total Cu(II). Consequently, copper(II) precipitates as hydroxide above pH 7. The low stability of the CuL species and the spectroscopic evidence indicate that there is no $CuL_2$ or chelate formation by this

TABLE I

Stability constants (log $\beta$) for $H^+$ and $Cu^{2+}$ complexes of 1,6-anhydro derivatives of glucosamine and mannosamine, and ManN and $\alpha$-ManN-OMe.

| Species | 1 | 3 | 2 | ManN [a] | $\alpha$ManN-OMe [a] |
|---|---|---|---|---|---|
| LH | 7.058 (6) | 7.485 (7) | 7.820 (3) | 7.59 | 7.47 |
| CuL | 3.40 (1) | 3.88 (3) | 4.60 (2) | | 4.81 |
| $CuL_2$ | | 8.01 (2) | 8.21 (2) | 9.68 | |
| $CuL_2H_{-1}$ | | 1.88 (1) | 1.65 (1) | 2.72 | 2.91 |
| $CuL_2H_{-2}$ | | −5.72 (1) | −6.95 (1) | −3.66 | −4.29 |
| $CuL_2H_{-3}$ | | | | −13.00 | −13.4 |
| $CuL_2H_{-4}$ | | | | | −23.7 |

[a] Ref 6.

sugar ligand. In the Cu(II) simple amino sugar systems studied earlier (see, e.g., ref 5), formation of the CuL species is readily followed by that of the $CuL_2$ complex, which prevents hydroxide precipitation. In the case of **1**, O-4 benzyl protection prevents any distinct interaction between O-4 and the metal ion; thus, metal hydrolysis occurs before the formation of any further complex species. The HO-3 group cannot be involved in metal chelation with the $NH_2$ group because of the unfavorable sugar ring conformation ($NH_2$ is axial while HO-3 is equatorial).

The 1,3-dioxolane ring seems to have no effect on complex formation at lower pH.

*2-Amino-1,6-anhydro-2-deoxy-4-O-methyl-β-D-mannopyranose* (**3**) *and 2-amino-1,6-anhydro-2,4-dideoxy-β-D-lyxo-hexopyranose* (**2**).—In contrast to glucose derivatives[1], 1,6-anhydro-mannosamine derivatives form only monomeric species similar to those formed by mannosamine and its methyl glycoside ($\alpha$-ManN-OMe)[6]. Like $\alpha$-ManN-OMe, both anhydro derivatives form CuL complexes, which therefore suggests the involvement of the same donor sets in Cu(II) ion binding (i.e., N-2 and possibly weak interaction with HO-3[6]).

Increase in pH leads to formation of a chelate species involving the amino nitrogen (equatorial) and also the favorably situated deprotonated C-3–$O^-$ donor (Table I, species $CuL_2H_{-1}$ and $CuL_2H_{-2}$).

Complexes formed by the anhydro derivatives of mannosamine are 1.5 to almost 4 log units less stable than those of mannosamine or $\alpha$-ManN-OMe[6] (see log*$K$ values in Table II) and this suggests that the rigidity of the anhydro-ligand is an

TABLE II

Log *$K$ values for some of the systems studied

| | [a] log *$K_{CuL}$ | log *$K_{CuL_2}$ | log *$K_{CuL_2H_{-1}}$ | log *$K_{CuL_2H_{-2}}$ |
|---|---|---|---|---|
| **3** | −3.61 | −6.97 | −13.10 | −20.70 |
| **2** | −3.22 | −7.43 | −13.99 | −22.59 |
| ManN [b] | | −5.50 | −12.46 | −18.84 |
| $\alpha$-ManN-OMe [b] | −2.66 | | −12.03 | −19.23 |

[a] log *$K$ = log($\beta_{complex}$) − log ($\beta_{XHL}$), x = number of bound ligand molecules; this stability constant includes compensation for different basicities of the ligands studied. [b] Ref 6.

important factor in determining complex stability. The considerable effect observed for the monodentate CuL and $CuL_2$ complexes having protonated hydroxyl groups may support the involvement of the Cu-(HO-3) interaction in complex stabilization.

The spectroscopic parameters observed are typical for these types of complexes[2–8] and they support the formation of the species proposed from evaluation of the potentiometric data (Tables I and III).

TABLE III

Spectroscopic data for the $Cu^{2+}$ complexes of the 1,6-anhydro sugar derivatives

| Species | EPR | | Absorption | CD |
|---|---|---|---|---|
| | $A_{\parallel}$ [G] | $g_{\parallel}$ | λ[nm] (ε) | λ[nm] (Δε) |
| **1** | | | | |
| CuL | 138 | 2.35 | 735 (27) | 730 (+0.15) [a] |
| | | | | 290 (−0.03) [b] |
| | | | | 215 (+1.2) [d] |
| **3** | | | | |
| CuL | 143 | 2.32 | 780 (23) | 710 (+0.15) [a] |
| | | | | 214 (−0.37) [d] |
| $CuL_2$ | | | | 675 (+0.82) [a] |
| | | | | 280 (−2.02) [b] |
| | | | | 222 (+0.77) [d] |
| | | | | 197 (−0.71) [d] |
| $CuL_2H_{-1}$ | 182 | 2.24 | 625 (42) | 665 (+1.18) [a'] |
| | | | | 528 (−0.18) [a''] |
| | | | | 284 (−2.35) [b] |
| | | | | 250 (−2.41) [b'] |
| | | | | 210 (+2.10) [d] |
| | | | | 195 (−2.7) [d] |
| $CuL_2H_{-2}$ | 191 | 2.23 | 585 (63) | 662 (+1.42) [a'] |
| | | | | 542 (−0.77) [a''] |
| | | | | 250 (−4.67) [c] |
| | | | | 210 (+7.16) [d] |
| **2** | | | | |
| CuL | 141 | 2.33 | 755 (27) | 700 (+0.18) [a] |
| | | | | sh240 (−0.75) [c] |
| | | | | 215 (−1.05) [d] |
| $CuL_2$ | | | | 675 (+0.48) [a] |
| | | | | sh272 (−0.86) [b] |
| | | | | 211 (−1.43) [d] |
| $CuL_2H_{-1}$ | 180 | 2.24 | 623 (51) | 668 (+1.17) [a] |
| | | | | 276 (−2.99) [b] |
| | | | | 224 (+0.55) [d] |
| | | | | 198 (−5.0) [d] |
| $CuL_2H_{-2}$ | 192 | 2.22 | 580 (56) | 660 (+1.17) [a'] |
| | | | | 540 (−0.78) [a''] |
| | | | | 246 (−4.94) [c] |
| | | | | 190 (−4.0) [d] |

[a] *d–d* transitions ([a] B+E, [a'] B, [a''] E); [b] $NH_2 \Rightarrow Cu(II)$ charge transfer transition; [b'] $O^- \Rightarrow Cu(II)$ CT transition; [c] overlapped charge transfer transitions; [d] intraligand transitions.

$CuL$, $CuL_2$, and $CuL_2H_{-1}$ complexes are characterized by a single CD $d$–$d$ band at 710–675 nm (B + E). This splits into two transitions (B and E) for $CuL_2H_{-2}$ species due to a decrease in the effective symmetry around the metal ion (Fig. 2, Table III).

In the UV region, two CT bands associated with $NH_2 \rightarrow Cu$ and $O^- \rightarrow Cu$ bonds are observed (Fig. 2) and are centered at ~280 and ~250 nm, respectively[1,16].

The O-4 oxygen even in the methoxy form has a considerable impact on the binding ability of **3** when compared to **2** (Tables I and II). The $CuL_2H_{-2}$ complex of the former ligand is distinctly more stable (about 2 orders of magnitude) than that of the latter one. This suggests the involvement (possibly axial) of methoxy oxygen in the interaction with the metal ion. It should also be mentioned that in the case of mannosamine and $\alpha$-ManN-OMe[6], the formation of $CuL_2H_{-3}$ suggests direct interaction of the Cu(II) ion with the HO-4 group.

Comparison of the stabilities (log $\beta$) of the CuL and $CuL_2$ species shows that ligand (**2**) follows the statistical rules expected for planar Cu(II) complexes quite well. The statistical value, $\Delta K$, is evaluated[17] as $\log K_{ML} - \log K_{ML_2} = 1.2$, while for this ligand it is equal to 1.0; the $\Delta K$ value for **3** is $-0.25$. This latter value suggests the existence of a cooperative effect, favoring the co-ordination of a second ligand molecule. This may result from interlined interactions in the $CuL_2$ complex involving the MeO-4 group.

It is also interesting to note that none of the mannosamine derivatives studied here are able to form the dimeric species found earlier with 1,6-anhydro-glucosamines[1]. All those ligands, 2-amino-1,6-anhydro-2-deoxy-$\beta$-D-glucopyranose, its *N*-methyl derivative, and 4-amino-1,6-anhydro-4-deoxy-$\beta$-D-glucopyranose, form binuclear species and coordinate ligand via C-4 and C-2 donors, forming a 6-membered chelate ring[1]. Both mannosamine derivatives, **3** and **2**, as well as the previously studied 3-amino-1,6-anhydro-3-deoxy-$\beta$-D-glucopyranose, involve two donors at C-3 and C-2 or C-4 sites and form 5-membered chelates. No dimeric complexes are found in these systems.

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