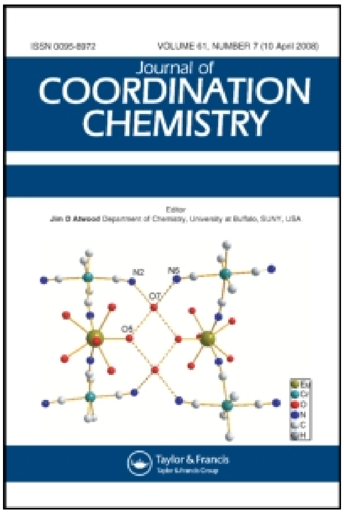


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

COPPER(II) COMPLEXATION BY 1,4-DIAMINO-2*R*, 3*R*-BUTANEDIOL AND ITS 2*R*, 3S-DIASTEREOISOMER. SPECTROSCOPIC AND POTENTIOMETRIC STUDIES

Henryk Kozłowski[a]; Barbara Radomska[a]; Tamas Kiss[b]; Andrzej Temeriusz[c]; Janusz Stepiáski[c]
[a] Institute of Chemistry, University of Wroclaw, Wroclaw, Poland [b] Department of Inorganic and Analytical Chemistry, University of Debrecen, Debrecen, Hungary [c] Faculty of Chemistry, University of Warsaw, Warszawa, Poland

To cite this Article Kozłowski, Henryk , Radomska, Barbara , Kiss, Tamas , Temeriusz, Andrzej and Stepiáski, Janusz(1993) 'COPPER(II) COMPLEXATION BY 1,4-DIAMINO-2*R*, 3*R*-BUTANEDIOL AND ITS 2*R*, 3S-DIASTEREOISOMER. SPECTROSCOPIC AND POTENTIOMETRIC STUDIES', Journal of Coordination Chemistry, 30: 3, 215 — 219
To link to this Article: DOI: 10.1080/00958979308022753
URL: http://dx.doi.org/10.1080/00958979308022753

J. Coord. Chem., 1993, Vol 30, pp. 215–219
Reprints available directly from the publisher
Photocopying permitted by license only

COPPER(II) COMPLEXATION BY 1,4-DIAMINO-2*R*, 3*R*-BUTANEDIOL AND ITS 2*R*, 3S-DIASTEREOISOMER. SPECTROSCOPIC AND POTENTIOMETRIC STUDIES

HENRYK KOZŁOWSKI, BARBARA RADOMSKA,

Institute of Chemistry, University of Wroclaw, F. Joliot-Curie 14, 50383 Wroclaw, Poland

TAMAS KISS,

Department of Inorganic and Analytical Chemistry, University of Debrecen, 4010 Debrecen, Hungary

ANDRZEJ TEMERIUSZ and JANUSZ STĘPIŃSKI

Faculty of Chemistry, University of Warsaw, Pasteura 1, 02–093 Warszawa, Poland

(Received January 28, 1993)

Potentiometric and spectroscopic studies of the binding ability of two diastereoisomers of 1,4-diamino-2, 3-butanediol have shown that these amino-alcohols form very stable and specific dimeric complexes with Cu(II) involving both amino nitrogen and hydroxyl oxygen atoms. Chirality at the C(2), C(3) centres has a distinct influence on the stability of complexes formed.

KEYWORDS: Amino-alcohols, Cu(II) complexes, stability constants

INTRODUCTION

Amino-alcohols are potentially very efficient ligands for binding transition metal ions, especially Cu(II). The amino group usually acts as an anchor, allowing deprotonation of the vicinal hydroxyl function and formation of stable chelates. For example, aminosugars (cyclic ligands) bind Cu(II) very effectively although the position of the coordinating hydroxyl group may have an important impact on complex structure and stability.[1–3] Diamino-alcohols are potentially multidentate ligands with the possibility of involvement of two nitrogen donors in metal ion binding. 1,3-Diamino-2-propanol is not able to involve both nitrogen donors in formation of monomeric species due to steric effects, but it forms oligomeric di- and trinuclear complexes in which the amino groups act as anchor binding sites and the deprotonated alcoholate groups act as bridging donors.[4,5]

1,4-Diamino-2, 3-butanediols may differ considerably from 2-propanol derivatives as they are potentially able to bind two metal ions (even in monomeric complexes) involving each terminal amino group. Such coordination may promote deprotonation of vicinal hydroxyl function with formation of two 5-membered chelate rings.

EXPERIMENTAL

Chemical synthesis

1,4-Diamino-2R, 3R-butanediol dihydrochloride was synthesized from D-tartaric acid (Aldrich) in the same way as described by Kiely *et al.*[6] for the *L*-enantiomer. Analytical data: m.p. 219–221°C; $[\alpha]_D^{20}$ +29.9° (c = 1, water); ^{13}C NMR δ 42.65 ppm (CH_2), 68.9 ppm (CH): *anal.* calc. for $C_4H_{14}Cl_2N_2O_2$: C, 24.88; H, 7.31; Cl, 36.72; N, 14.51%; found: C, 25.2; H, 7.4; Cl, 36.7; N, 15.2%.

1,4-Diamino-2*R*, 3*S*-butanediol dihydrobromide was obtained from 1,4-dichloro-1,4-dideoxyerythritol[7] following the procedure given by Feit and Nielsen.[8] Analytical data: m.p. 260° (decomp). ^{13}C NMR δ 42.4 (CH_2), 69.7 (CH); *anal.* calc. for $C_4H_{14}Br_2N_2O_2$: C, 17.04; H, 5.00; Br, 56.67: N, 9.93%; found: C, 17.1; H, 5.1; Br, 56.6; N, 9.9%.

Melting points were determined in a Bëtius block and are uncorrected. Optical rotation was measured on a Perkin Elmer 241 polarimeter. ^{13}C NMR spectra were recorded from solutions in D_2O (internal standard dioxan) with a JEOL FX90Q NMR spectrometer.

Spectroscopic studies

Solutions of copper ion (0.005 mol dm^{-3}) with 1:1, 1:2 and 1:4 metal ion to ligand molar ratio were used in spectroscopic studies. Absorption spectra were recorded on a Beckman UV5240 spectrophotometer and circular dichroism (c.d.) spectra on a JASCO J-600 automatic recording spectropolarimeter. All c.d. spectra are expressed in terms of $\Delta\varepsilon = (\varepsilon_l - \varepsilon_r)$. Electron spin resonance (e.s.r.) spectra of water-glycol solutions were obtained using a Radiopan SE/X2543 spectrometer at liquid nitrogen temperatures, at 9.13 GHz.

Potentiometric studies

The stability constants of the proton and Cu(II) complexes of the ligands were determined by pH-metric titration of 5 cm^3 samples in the pH range 3–11. The ligand concentration was 0.004 mol dm^{-3}, the metal to ligand ratios were 0:4, 1:4, 2:4 and 4:4 and the ionic strength was adjusted to 0.1 mol dm^{-3} with KNO_3. Titrations were performed with KOH solution of known concentration (*ca* 0.1 mol dm^{-3}). These measurements were made on a Tacussel LPH 400T instrument. The electrode system was calibrated to hydrogen ion concentration by the method of Irving *et al.*[9] The concentration stability constants $\beta_{pqr} = [M_pA_qH_r]/[M]^p[A]^q[H]^r$ were calculated from pH-metric titration curves by means of the PSEQUAD computer program.[10]

RESULTS AND DISCUSSION

1,4-diamino-2,3-butanediols behave as LH_2 ligands having two amino groups able to dissociate protons in basic solution. The stepwise log K values differ by about one log unit from each other (Table 1) due to statistical reasons and changes in charge on the ligand after losing the first proton. Stereochemistry of the ligand has almost no effect on the protonation constants of the amino groups (Table 1).

Both ligands coordinate to Cu(II) above pH 5 and the lack of EPR spectra above pH 5.5 indicates the formation of oligomeric species, most likely dimers. In the case of 2R,3R diastereoisomer, (D-2R,3R-B) the dimeric complex exhibits a clear CD spectrum as shown in Table 1.

The energy of the d-d transitions observed around 620–630 nm (Table 1) correspond well to the metal ion bound *via* two nitrogens.[1,2,11] The CD spectra obtained for (D-2R,3R-B) indicate a strong band around 260 nm characteristic of $NH_2 \Rightarrow Cu(II)$ charge transfer.[1,11]

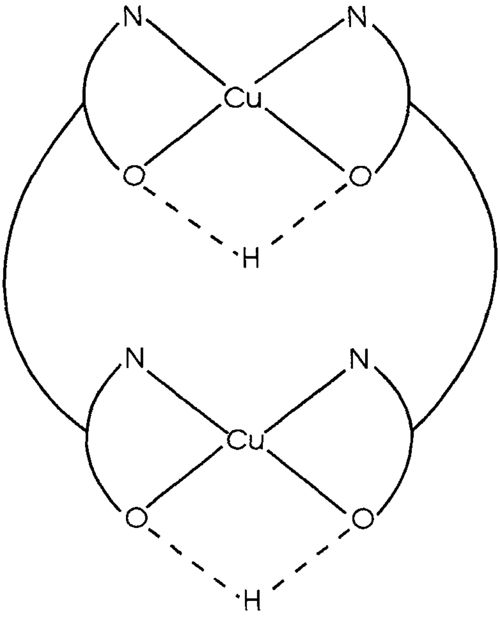
The titration curves obtained for Cu(II) with both ligands show very strong base consumption from pH 5. Then, there is a sudden pH jump from pH~6 to pH~10 with liberation of three protons per metal ion independently of extent of ligand excess. In the complex formation, each H_2L^{2+} loses three protons, two from terminal NH_3^+ groups and one presumably from the coordinating hydroxyl group. This suggests the formation of a single major species in the pH range 5–10 with composition $Cu_n(LH_{-1})_n$.

Potentiometric data calculations as well as EPR spectra strongly suggest the formation of a dimeric species $Cu_2L_2H_{-2}$ at pH above 5 as the only major complex present in the systems studied. The coordination involves two amino groups

Table 1 Stability constants (log β) and spectroscopic parameters for Cu(II) complexes with 1,4-diamino- 2*R*, 3*R*-butanodiol and 1,4-diamino-2*R*, 3*S*-butanodiol at 25°C, ionic strength 0.1 M (KNO_3).

species M L H	log β	absorption λ[nm] (ε) [$M^{-1}cm^{-1}$]	CD λ[nm] [$\Delta\varepsilon$) [$M^{-1}cm^{-1}$]
D-2R,3S-B			
0 1 2	8.53 (1)[a] (log K_1)		
0 1 1	18.29 (1) (log β_2)		
	9.76 (1) (log K_2)		
2 2 -2 ($Cu_2L_2H_{-2}$	9.64(5)	617(89)	
2 2 -3 ($Cu_2L_2H_{-3}$)	-0.55(5)	620(85)	
D-2R, 3R-B			
0 1 2	8.57 (1) (log K_1)		
0 1 1	18.24 (1) (log β_2)		
	9.67 (1) (log K_2)		
2 2 -2 ($Cu_2L_2H_{-2}$)	10.90(4)	625(53)	652(+ 0.50)[b] 260(- 2.08)[c]
2 2 -3 ($Cu_2L_2H_{-3}$)	0.12(9)	617(70)	720(- 0.23)[d] 587(+ 0.42)[b] 260(- 1.20)[c]

[a]Standard deviation. [b](B + E) d-d transition. [c]$NH_2 \Rightarrow Cu(II)$ charge transfer transition. [d](A) d-d transition.



(suggested by CD spectra, Table 1) which act as the anchors for two Cu(II) ions. One of the two hydroxyl groups undergoes deprotonation to from a chelate ring. The $Cu_2L_2H_{-2}$ stoichiometry results from coordination of two amino nitrogens, one deprotonated hydroxyl and one protonated hydroxyl oxygen atom to each metal ion, *i.e.*, the binding mode is **2** × {$\mathbf{NH_2,O^-,OH,NH_2}$}. The very high stability of the dimeric species suggests that both oxygens are equivalent in metal ion binding and that the proton forms a bridge between two *cis*-coordinated hydroxyl oxygens (see above).

Molecular models indicate that 1,4-diamino-2*R*, 3*S*-butanediol, forming dimeric species, may coordinate to Cu(II) only in the *cis* mode as shown above. In the case of 2*R*, 3*R* diastereoisomers, both *cis* and *trans* arrangements of donor atoms are possible. This may underlie the fact that the dimeric complex of 1,4-diamino-2*R*, 3*R*-butanediol is distinctly more stable than that of 1,4-diamino-2*R*, 3*S*-butanediol (Table 1).

Above pH 10, deprotonation of the dimer takes place and the species $Cu_2L_2H_{-3}$ becomes a major complex above pH 11. This is indicated in the CD spectra which show the d-d transition shift from 652 nm ($Cu_2L_2H_{-2}$) to 587 nm ($Cu_2L_2H_{-3}$) for the chiral ligand. A weaker band is observed also at 720 nm (A transition).

Base consumption above pH 10 can be equally well described by the formation of a monomeric complex, $CuLH_{-2}$. The almost complete lack of EPR signals even at pH~12, however, allows only structures with strongly coupled Cu(II)-Cu(II) centres. Thus, the dimeric coordination mode is also proposed for the deprotonated species. It can be assumed that the proton dissociates from an alcoholic hydroxyl group, and the remaining single proton may form a multi-centre hydrogen bond.

Acknowledgements

This work was supported by the Polish Committee of Scientific Research (KBN 2.2614.92.03).

References

1. M. Jezowska-Bojczuk, H. Kozlowski, P. Decock, M. Cerny and T. Trnka, *Carbohydr. Res.*, **216,** 453 (1991).
2. H. Kozlowski, P. Decock, I. Olivier, G. Micera, A. Pusino and L.D. Pettit, *Carbohydr. Res.*, **197,** 109 (1990).
3. J. Urbanska and H. Kozlowski, *J. Coord. Chem.* **21,** 175 (1990).
4. T. Kiss, C. Simon and Z. Vachter, *J. Coord. Chem.*, **16,** 225 (1987).
5. J.-Ch. Zheng, R.J. Rousseau and S. Wang, *Inorg. Chem.* **31,** 106 (1992).
6. D.E. Kiely, J.L. Navia, L.A. Miller and T.H. Lin, *J. Carbohydr. Res.*, **5,** 183 (1986).
7. S. Przybytek, *Ber.*, 1091 (1884).
8. P.W. Feit and O.T. Nielsen, *J. Med. Chem.*, **10,** 697 (1967).
9. H. Irving, M.G. Mills and L.D. Pettit, *Anal. Chim. Acta*, **38,** 475 (1967).
10. L. Zékány and I. Nagypál, in " *Computational Methods for the Determination of Stability Constants*," D. Leggett, ed., (Plenum Press, New York, 1985).
11. L.D. Pettit, J. Gregor and H. Kozlowski, in "*Perspectives on Bioinorganic Chemistry*", R.W. Hay, J.R. Dilworth and K.B. Nolan, eds., (JAI Press, London, 1991), Vol. 1, pp. 1-41.