ordinate of Ni was held constant to fix the origin. Refinement of the parameters for the inverted structure gave R = 0.0349 and wR = 0.0355. Data collection: Kuma KM-4 software. Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP*II (Johnson, 1976).

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71745 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1070]

References

Alcock, N. W., Kemp, T. J. & Leciejewicz, J. (1991). *Inorg. Chim. Acta*, **184**, 203-207.

Charbonnier, F., Petit-Ramel, M., Faure, R. & Loiseleur, H. (1984). *Rev. Chim. Miner.* **21**, 601-610.

Gilmore, C. J., Mallinson, P. R. & Speakman, J. C. (1983). *Acta Cryst.* C**39**, 1111-1113.

John, I. G., Ritchie, G. L. D. & Radom. L. (1977). *J. Chem. Soc. Perkin Trans.* 2, p. 1601.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kozioł, A. E., Brzyska, W., Klimek, B., Król, A., Palenik, G. J. & Stepniak, K. (1989). *J. Coord. Chem.* **20**, 57-67.

Kozioł, A. E., Brzyska, W., Klimek, B., Król, A. & Stepniak, K. (1987). *J. Coord. Chem.* **15**, 367-382.

Sheldrick, G. M.(1976). *SHELX76. Program for Crystal Structure Determination.* Univ. of Cambridge, England.

Smith, G., O'Reilly, E. J. & Kennard, C. H. L. (1982). *Inorg. Chim. Acta*, **62**, 241-246.

Walker, N. & Stuart, D. (1983). *Acta Cryst.* A**39**, 158-166.

Acta Cryst. (1994). C**50**, 686–688

Polyol Metal Complexes. VI.† Structure of Lithium Bis[methyl α-L-rhamnopyranosid-(2,3)-ato(2−)]cuprate(II) Tetrahydrate

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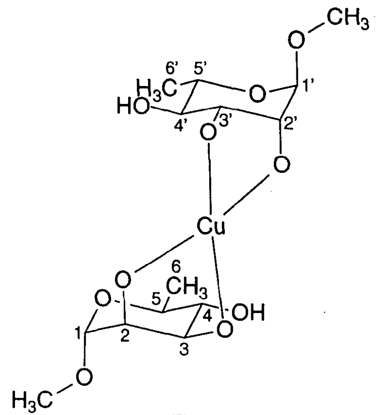
Abstract

Methyl α-L-rhamnopyranoside is deprotonated twice in the blue crystals of $Li_2[Cu(C_7H_{12}O_5)_2].4H_2O$. The sugar derivative acts as a chelate ligand in the homoleptic square-planar copper(II) complex. Furthermore, the alkoxide groups of the dianionic rhamnoside either bind to Li or act as acceptors in hydrogen bonds.

Comment

Only a few complexes of deprotonated carbohydrates with the later transition metals have been structurally characterized so far (Klaassen & Klüfers, 1993, and references therein; Fuchs, Habermann & Klüfers, 1993; Bhaduri, Sapre, Khwaja & Jones, 1992). We now report the crystal structure of the first coordination compound of a deprotonated rhamnose derivative.

Crystals of the title compound were grown from deep-blue aqueous solutions, which were prepared by the reaction of stoichiometric amounts of cupric nitrate, methyl α-L-rhamnopyranoside and excess lithium hydroxide. The X-ray structure determination reveals a square-planar homoleptic copper(II) complex, (I). The ligands are derived from the rhamnoside by deprotonation of the carbohydrate at O2 and O3, respectively. The resulting dianionic diolate ligand forms a five-membered chelate ring with the transition-metal ion. The planar geometry at the Cu atom is only slightly distorted [the dihedral angle between the planes Cu-O2-O3 and Cu-O2′-O3′ is 3.91 (13)°]. The conformational analysis of the copper chelate five-membered rings and of the pyranose rings is facilitated by the puckering parameters (Cremer & Pople, 1975): the conformation of the five-membered chelate ring Cu—O2′—C2′—C3′—O3′ [Q = 0.381 (3) Å, φ = 260.8 (3)°] is derived from a twist conformation $^4T_3$ with the metal ion as the pivot atom of the twist axis, distorted towards the E_3 conformation, *i.e.* an envelope conformation with C2′ as the out-of-plane atom (ideal φ values: 270° for $^4T_3$; 252° for E_3); the second five-membered ring Cu—O2—C2—C3—O3 [Q = 0.408 (3) Å, φ = 285.1 (3)°] has ^4E conformation (C3 as the out-of-plane atom, ideal φ = 288°). Each pyranose ring adopts an only slightly distorted $^1C_4$ conformation [for O5—C1—C2—C3—C4—C5—O5, Q = 0.557 (3) Å, θ = 173.0 (3)°, φ = 98 (2)°; for O5′—C1′—C2′—C3′—



(I)

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† Part V: Achternbosch & Klüfers (1994).

C4′—C5′—O5′, Q = 0.558 (3) Å, θ = 170.7 (3)°, φ = 118 (2)°]. All puckering amplitudes are normal.

The Li atoms are chelated by the O4—C4—C3—O3 and O4′—C4′—C3′—O3′ moieties [puckering parameters for C3—O3—C4—O4—Li1 ($1-x, y-\frac{1}{2}, \frac{1}{2}-z$) are Q = 0.498 (4) Å, φ = 46.9 (4)°, and those for C3′—O3′—C4′—O4′—Li2 are Q = 0.502 (4) Å, φ = 64.1 (4)°, indicating a distorted twist conformation with the twist axis running through the Li atom (ideal φ = 54°)]. The deprotonated atoms O3 and O3′ act as bridging ligands. Water molecules complete a distorted tetrahedral and a 4 + 1 coordination geometry for Li1 and Li2, respectively.

In the title compound, the alkoxide O atoms act as acceptors in a partially cooperative hydrogen-bonding system, which is depicted in Fig. 2. The crystal packing of the complex dianions closely resembles that of the related methyl α-D-mannopyranoside compound lithium [methyl α-D-mannopyranosid-(2,3)-ato(2−)][methyl α-D-mannopyranosid-(2,3,4)-ato(3−)]cuprate(II) pentahydrate (Habermann, Jung, Klaassen & Klüfers, 1992), although the two compounds differ in their hydrogen-bonding systems as a result of further deprotonation of one ligand and the presence of OH groups at the 6 position in the mannose derivative.

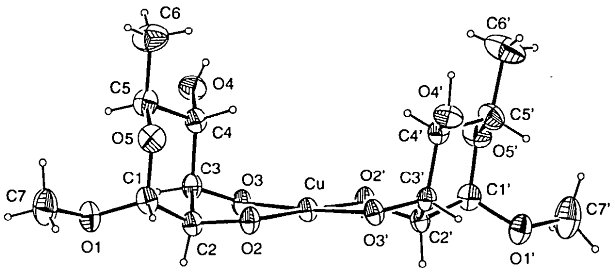

Fig. 1. The structure of the dianionic bis(methyl α-L-rhamnopyranosidato) cuprate moiety showing 50% probability displacement ellipsoids.

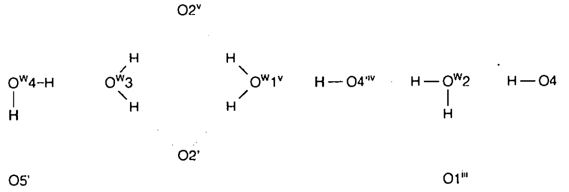

Fig. 2. The hydrogen-bonding structure. Symmetry codes: (iii) $x-1, y, z$; (iv) $-x, y-\frac{1}{2}, -z$; (v) $1-x, y-\frac{1}{2}, -z$. The U_{ij} values of the OW4 site indicate disorder. The appropriate H atoms have not been localized.

Experimental

25 ml ethanol and 25 ml diethyl ether were added to a solution of 0.40 g (16.5 mmol) cupric nitrate trihydrate, 0.66 g (37 mmol) methyl α-L-rhamnopyranoside, 2.6 ml 5 M LiOH and 5 ml water (nitrogen atmosphere). Blue platelets of the title compound were formed at 277 K.

Crystal data

$Li_2[Cu(C_7H_{12}O_5)_2].4H_2O$
M_r = 501.826
Orthorhombic
$P2_12_12_1$
a = 8.011 (6) Å
b = 12.205 (10) Å
c = 22.336 (13) Å
V = 2183.9 (27) Å^3
Z = 4
D_x = 1.526 (2) Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 14 reflections
θ = 2.5-12.5°
μ = 1.066 mm^{-1}
T = 293 (2) K
Platelet
0.40 × 0.30 × 0.08 mm
Blue

Data collection

Stoe Stadi-4 diffractometer
ω/θ scans
Absorption correction: empirical
T_{min} = 0.681, T_{max} = 0.820
8929 measured reflections
3856 independent reflections
3345 observed reflections [$I > 2\sigma(I)$]

R_{int} = 0.0325
θ_{max} = 25.00°
$h = -9 \rightarrow 9$
$k = -14 \rightarrow 14$
$l = -26 \rightarrow 26$
3 standard reflections
frequency: 120 min
intensity variation: 5%

Refinement

Refinement on F^2
$R(F)$ = 0.0288
$wR(F^2)$ = 0.0643
S = 1.054
3856 reflections
400 parameters
All H-atom parameters refined
Calculated weights $w = 1/[\sigma^2(F_o^2) + (0.0409P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max}$ = 0.464 e Å^{-3}
$\Delta\rho_{min}$ = −0.341 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: x = 0.000 (13) (Flack, 1983)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Cu	0.51246 (4)	0.38561 (2)	0.244540 (13)	0.02288 (9)
O1	0.8477 (3)	0.4015 (2)	0.43907 (9)	0.0361 (5)
O2	0.6257 (3)	0.47211 (15)	0.30405 (8)	0.0277 (4)
O3	0.5867 (2)	0.25732 (14)	0.28870 (8)	0.0240 (4)
O4	0.3841 (4)	0.2048 (2)	0.38575 (11)	0.0344 (5)
O5	0.5725 (3)	0.4654 (2)	0.43481 (9)	0.0344 (5)
C1	0.7273 (4)	0.4582 (2)	0.40484 (13)	0.0291 (6)
C2	0.7153 (4)	0.4039 (2)	0.34398 (12)	0.0256 (6)
C3	0.6229 (4)	0.2947 (2)	0.34746 (12)	0.0246 (6)
C4	0.4604 (4)	0.3108 (2)	0.38176 (12)	0.0266 (6)
C5	0.4920 (4)	0.3607 (2)	0.44342 (12)	0.0327 (6)
C6	0.3328 (6)	0.3833 (4)	0.4771 (2)	0.0509 (10)
C7	0.8921 (6)	0.4581 (4)	0.4932 (2)	0.0531 (10)
O1′	0.2479 (3)	0.3642 (2)	0.03896 (9)	0.0380 (5)
O2′	0.4078 (3)	0.29889 (15)	0.18405 (8)	0.0302 (5)
O3′	0.4268 (2)	0.51415 (14)	0.20302 (9)	0.0255 (4)
O4′	0.0918 (3)	0.5830 (2)	0.19750 (10)	0.0339 (5)
O5′	0.0825 (3)	0.3137 (2)	0.12049 (10)	0.0359 (5)
C1′	0.2434 (4)	0.3124 (2)	0.09429 (13)	0.0294 (6)
C2′	0.3729 (4)	0.3669 (2)	0.13452 (12)	0.0251 (6)
C3′	0.3168 (4)	0.4785 (2)	0.15736 (12)	0.0230 (6)

C4′	0.1388 (4)	0.4720 (2)	0.18109 (13)	0.0262 (6)
C5′	0.0237 (4)	0.4225 (2)	0.13404 (14)	0.0349 (7)
C6′	−0.1566 (5)	0.4092 (5)	0.1553 (3)	0.0621 (12)
C7′	0.1496 (8)	0.3106 (4)	−0.0059 (2)	0.0642 (12)
O*W*1	0.7656 (3)	0.6345 (2)	0.24869 (12)	0.0351 (5)
O*W*2	0.0495 (4)	0.2220 (3)	0.3969 (2)	0.0657 (9)
O*W*3	0.6116 (3)	0.1296 (2)	0.17145 (11)	0.0376 (5)
O*W*4	−0.0628 (6)	0.1078 (5)	0.1632 (3)	0.178 (3)
Li1	0.5746 (6)	0.6378 (4)	0.1928 (2)	0.0339 (11)
Li2	0.2965 (6)	0.6337 (4)	0.2463 (3)	0.0368 (11)
HO4	0.3038 (41)	0.2131 (25)	0.3888 (14)	0.007 (9)
HO4′	−0.0108 (60)	0.5919 (38)	0.2180 (20)	0.084 (14)

Table 2. *Selected geometric parameters* (Å, °)

Cu—O2′	1.910 (2)	O3′—C3′	1.416 (3)
Cu—O2	1.925 (2)	O4′—C4′	1.453 (4)
Cu—O3	1.944 (2)	O5′—C1′	1.416 (4)
Cu—O3′	1.947 (2)	O5′—C5′	1.442 (4)
O1—C1	1.412 (4)	C1′—C2′	1.524 (4)
O1—C7	1.438 (4)	C2′—C3′	1.523 (4)
O2—C2	1.416 (3)	C3′—C4′	1.524 (4)
O3—C3	1.419 (3)	C4′—C5′	1.523 (4)
O4—C4	1.433 (4)	C5′—C6′	1.529 (5)
O5—C1	1.412 (4)	Li1—O4^{i}	1.964 (6)
O5—C5	1.444 (3)	Li1—O3^{i}	1.991 (6)
C1—C2	1.516 (4)	Li1—O3′	1.932 (5)
C2—C3	1.527 (4)	Li1—O*W*1	1.975 (5)
C3—C4	1.523 (4)	Li1—Li2	2.529 (8)
C4—C5	1.527 (4)	Li2—O3^{i}	1.940 (6)
C5—C6	1.507 (5)	Li2—O*W*3^{i}	1.979 (6)
O1′—C1′	1.388 (4)	Li2—O3′	2.039 (6)
O1′—C7′	1.433 (5)	Li2—O4′	2.064 (5)
O2′—C2′	1.411 (3)	Li2—O*W*4^{ii}	2.772 (9)
O2—Cu—O3	86.97 (9)	O3^{i}—Li2—O*W*3^{i}	102.4 (2)
O2′—Cu—O3′	87.42 (10)	O3^{i}—Li2—O3′	96.8 (3)
O3′—Li1—O4^{i}	122.3 (3)	O*W*3^{i}—Li2—O3′	103.4 (2)
O4^{i}—Li1—O*W*1	116.3 (3)	O*W*3^{i}—Li2—O4′	141.1 (3)
O3′—Li1—O3^{i}	98.7 (3)	O3′—Li2—O4′	86.6 (2)
O4^{i}—Li1—O3^{i}	89.4 (2)		
O2—C2—C3—O3	48.4 (3)	O3′—C3′—C4′—O4′	63.2 (3)
O2′—C2′—C3′—O3′	46.5 (3)	O4—C4—C5—C6	−64.4 (3)
O3—C3—C4—O4	62.9 (3)	O4′—C4′—C5′—C6′	−63.4 (4)

Symmetry codes: (i) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $-x, \frac{1}{2} + y, \frac{1}{2} - z$.

Table 3. *Hydrogen-bonding geometry* (Å, °)

D	H	*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O4	HO4	O*W*2	0.65 (3)	2.05 (3)	2.700 (5)	174 (4)
O4′	HO4′	O*W*1^{i}	0.95 (5)	1.99 (5)	2.921 (4)	168 (4)
O*W*1	H*W*11	O2	0.88 (4)	1.75 (3)	2.591 (4)	160 (3)
O*W*1	H*W*12	O2′^{ii}	0.71 (4)	2.17 (4)	2.866 (4)	165 (4)
O*W*2	H*W*21	O1	0.71 (6)	2.25 (6)	2.881 (5)	148 (7)
O*W*2	H*W*22	O4′^{iii}	0.73 (5)	2.23 (5)	2.933 (5)	161 (5)
O*W*3	H*W*31	O2^{iv}	0.72 (3)	2.08 (3)	2.758 (4)	157 (3)
O*W*3	H*W*32	O2′	0.76 (4)	1.91 (3)	2.648 (4)	162 (3)
O*W*4	-	O*W*3^{i}	-	-	2.628 (6)	-
O*W*4	-	O5′	-	-	2.929 (7)	-

Symmetry codes: (i) $x - 1, y, z$; (ii) $1 - x, \frac{1}{2} + y, \frac{1}{2} - z$; (iii) $-x, y - \frac{1}{2}, \frac{1}{2} - z$; (iv) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$.

Friedel opposites were not merged. Data collection: *DIF*4 (Stoe & Cie, 1988*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1988*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*92 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976); *PLATON* (Spek, 1982).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71692 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1071]

References

Achternbosch, M. & Klüfers, P. (1994). *Acta Cryst.* C**50**, 175–178.
Bhaduri, S., Sapre, N., Khwaja, H. & Jones, P. G. (1992). *J. Organomet. Chem.* **426**, C12–C15.
Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Fuchs, R., Habermann, N. & Klüfers, P. (1993). *Angew. Chem.* **105**, 895–897; *Angew. Chem. Int. Ed. Engl.* **32**, 852–854.
Habermann, N., Jung, G., Klaassen, M. & Klüfers, P. (1992). *Chem. Ber.* **125**, 809–814.
Klaassen, M. & Klüfers, P. (1993). *Z. Anorg. Allg. Chem.* **619**, 661–668.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* Univ. of Göttingen, Germany.
Sheldrick, G. M. (1993). *SHELXL92. Program for the Refinement of Crystal Structures.* Univ. of Göttingen, Germany.
Spek, A. L. (1982). *The EUCLID Package. Computational Crystallography*, edited by D. Sayre, p. 528. Oxford: Clarendon Press.
Stoe & Cie (1988*a*). *DIF4. Diffractometer Control Program.* Version 6.2. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1988*b*). *REDU4. Data Reduction Program.* Version 6.2. Stoe & Cie, Darmstadt, Germany.

Acta Cryst. (1994). C**50**, 688–690

Bis(1,1,1,5,5,5-hexafluoro-2,4-pentanedionato)(1,4,10,13-tetraoxa-7,16-diazacyclooctadecane)barium

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Abstract

In the title compound, $[Ba(C_5HF_6O_2)_2(C_{12}H_2N_2O_4)]$, the Ba^{2+} cation is ten-coordinated by four O and two N atoms from a crown ether, and by four O atoms from two β-diketone ligands. Ba—O and Ba—N distances range from 2.75 to 3.00 Å. The Ba atom is located near the center and 1.343 (1) Å above the mean plane of the crown ether. The two β-diketone ligands are located on the same side of