Synthesis, Crystal Structure, and Reactivity of $Na_5[CuO_2](OH)_2$

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Abstract. $Na_5[CuO_2](OH)_2$ has been obtained as orange single crystals from mixtures of NaOH, Na_2O and Cu_2O in sealed Ag containers. The crystal structure has been refined from X-ray diffraction data (IPDS data, Pnma, Z = 4, a = 607.4(1) pm, b = 891.2(1) pm, c = 1201.0(2) pm, R_1 = 0.03). The characteristic unit is the bent $[CuO_2]^{3-}$ complex (∠(O–Cu–O) = 170°). The reactivity of $Na_5[CuO_2](OH)_2$ has been studied by DSC and *in situ* X-ray diffraction techniques. IR spectroscopy has been used for further characterization. The Madelung Part of the Lattice Energy (MAPLE) has been calculated as well.

Keywords: Copper; Cuprate; Crystal structure; IR spectroscopy

Darstellung, Kristallstruktur und Reaktivität von $Na_5[CuO_2](OH)_2$

Inhaltsübersicht. $Na_5[CuO_2](OH)_2$ wurde aus Gemengen von NaOH, Na_2O und Cu_2O in verschlossenen Ag-Containern in Form oranger Einkristalle erhalten. Die Kristallstruktur wurde anhand von Einkristalldaten bestimmt (IPDS-Daten, Pnma, Z = 4, a = 607,4(1) pm, b = 891,2(1) pm, c = 1201,0(2) pm, R_1 = 0,03). Die charakteristische Baueinheit, $[CuO_2]^{3-}$, liegt nicht linear vor (∠(O–Cu–O) = 170°). Die Reaktivität von $Na_5[CuO_2](OH)_2$ wurde thermoanalytisch (DSC) und mit *in-situ*-Röntgendiffraktometrie untersucht. Anhand von IR-Spektren erfolgte die weitergehende Charakterisierung. Der Madelunganteil der Gitterenergie, MAPLE, für $Na_5[CuO_2](OH)_2$ wird ebenfalls diskutiert.

1 Introduction

Several ternary oxides with monovalent copper in the systems A_2O/Cu_2O with A = Na–Cs have been reported. Apart from ACuO (Na–Cs) [1] no other phases of monovalent copper with sodium have been structurally characterized so far. It is interesting that only for A = K, Rb, Cs, another structure type in the copper rich part of the phase diagram, $A_3Cu_5O_4$ [2], and an alkaline rich phase, $A_3[CuO_2]$ (A = K, Rb) [3], is known. $Na_3[CuO_2]$ [4] has been reported not to crystallize isotypic with $Na_3[AgO_2]$ [5] and $A_3[CuO_2]$ [3]. Therefore, we have studied again the sodium rich part of the phase diagram A_2O/Cu_2O. We were not able to obtain any other compound than NaCuO. Since the system with sodium apparently reacts different from the heavier alkaline metals, which may be attested by the fact that a mixed-valent oxide, $NaCu_2O_2$ [6], and a divalent copper-hydroxide $Na_2[Cu(OH)_4]$ [7] have been described before, we have modified our synthesis by introducing additional anions, O_2^{2-} (Na_2O_2, for redox reactions) and OH^- (NaOH), respectively. The latter reaction has been successful: we obtained $Na_5[CuO_2](OH)_2$ – the first hydroxide of an oxocuprate(I).

2 Synthesis and Reactivity

$Na_5[CuO_2](OH)_2$ has been synthesized from Na_2O (from reactions of NaOH with sodium metal (98% Riedel-de Haën)) [8], NaOH (p. a. Merck) and Cu_2O (p. a. Aldrich) (molar ratio: 3 : 4 : 1). Reactions have been carried out in Ni (99.0% Goodfellow) and Ag (Degussa) containers under an inert gas atmosphere (Ar) and sealed in silica glass ampoules. The mixture has been annealed (600 °C, 5 d), then cooled down with a rate of 25 °C/d to 400 °C (3 d) and finally to 300 °C (5 d).

The mixture of the educts was studied by DSC experiments (STA 409, Netzsch, D) as well. We used self-made, air-tight silver containers and the following temperature program: heating rate 10 K/min, 25 °C → 600 °C, hold for 10 min, then cool to 200 °C. This cycle was repeated three times.

Fig. 1 shows the principal effects at 285/272 °C, which correspond to the phase transition α-NaOH ↔ β-

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NaOH and at 310/305 °C to the m. p. of NaOH [9], respectively. The third effect at 295/289 °C corresponds to the eutectic temperature of the binary phase diagram NaOH/Na_2O (13 wt-% Na_2O) [9]. At 408/384 °C we observe an additional reversible effect in the DSC. It is interesting to note that we always detected the presence of NaCuO by X-ray diffraction afterwards. Therefore, we investigated the reaction with the previously mentioned technique in the temperature range 25 °C → 400 °C → 25 °C, Fig. 2. In this case we used a Bühler camera (E. Bühler, D; Θ-Θ diffractometer, Stoe & Cie, D) which represents a quasi open system. The whole equipment is set up for protection against moisture in a dry glove box (Braun, D).

Fig. 2 illustrates the principle reflection patterns as a function of temperature. The reactions occurring in the system NaOH/Na_2O/Cu_2O are:

1. $4\,NaOH_{(l)} + 3\,Na_2O_{(s)} + Cu_2O_{(s)} \rightarrow 2\,Na_5[CuO_2](OH)_{2(s)}$ (300 °C)

2. $Na_5[CuO_2](OH)_{2(s)} \rightarrow NaCuO_{(s)} + Na_2O_{(s)} + 2\,NaOH_{(l)}$ (400 °C)

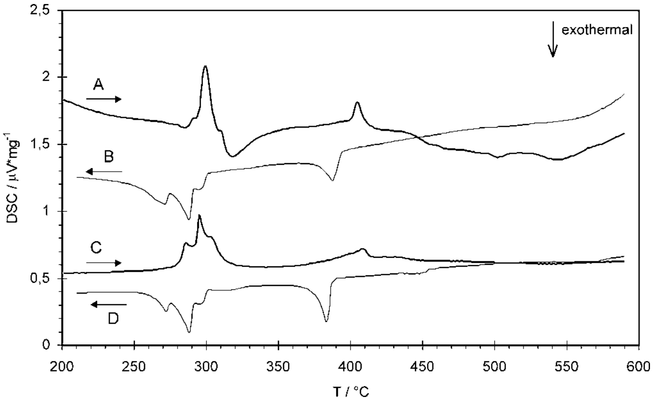

Fig. 1 DSC studies of the formation and decomposition of $Na_5[CuO_2](OH)_2$ under inert gas atmosphere in sealed Ag-containers.

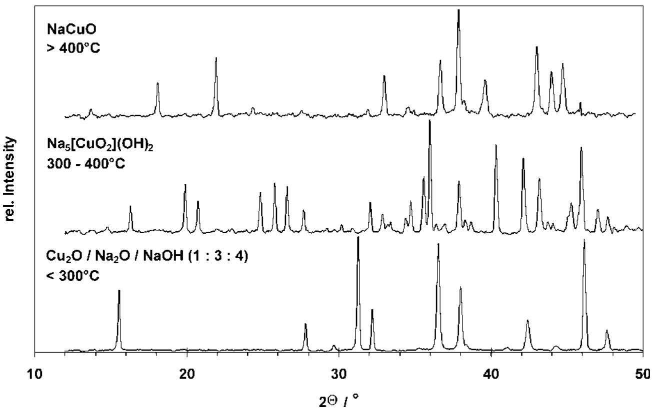

Fig. 2 *In situ* X-ray diffraction studies of the formation and decomposition of $Na_5[CuO_2](OH)_2$ under inert gas atmosphere.

No reflections of Na_2O at 400 °C were found. We assume that at somewhat lower temperature the mixture Na_2O/NaOH melts, with the corresponding thermal effect at 408/384 °C observed in the DSC. From the phase diagram NaOH/Na_2O [9] the melting point for a composition of 25 wt-% Na_2O in NaOH is approximately 420 °C. For preparative and DSC investigations we used closed reaction containers and ended up always with a mixture of NaOH, NaCuO and $Na_5[CuO_2](OH)_2$. From the Bühler camera experiments the formation of the latter compound, NaCuO and Na_2O were not observed by cooling below the m. p. of NaOH. The reflections of NaOH became too prominent (by a factor of 10). From these results we assume that $Na_5[CuO_2](OH)_2$ is stable up to 400 °C and is obtained via a peritectic reaction.

3 Crystal Structure of $Na_5[CuO_2](OH)_2$

The crystal structure of $Na_5[CuO_2](OH)_2$ has been determined from X-ray diffraction data. For details see Tab. 1 and 2. Fig. 3 shows a projection of the crystal structure.

The characteristic feature of the structure are the bent $[CuO_2]^{3-}$ complexes oriented in channels along [010]. Angles ∠(O–M–O) of 175°–180° are typical for $[MO_2]^{3-}$ anions with M = Fe, Co, Ni [10, 11], whereas we observe 170.14(8)° here. The two interatomic distances, d(Cu–O) are not equal, 178.8(2) pm and 181.7(2) pm. A similar effect upon bending has been reported for $KNa_2[NiO_2]$ as well [11].

The next nearest neighbours of the $[CuO_2]^{3-}$ complex are Na^+, d(Cu–Na) ≥ 285.2(1) pm and four hydroxide ions, which are orientated towards the monovalent metal (d(Cu–HO) = 315 pm and 332 pm) in the

Table 1 Crystallographic data and structure refinement for $Na_5[CuO_2](OH)_2$

Space group	Pnma (No. 62), Z = 4	
Lattice constants	single crystal data	powder data [19]
	a = 607.4(1) pm	a = 607.2(1) pm
	b = 891.2(1) pm	b = 891.4(2) pm
	c = 1201.0(2) pm	c = 1201.3(3) pm
Diffractometer	IPDS (Stoe & Cie)	STADI P (Stoe & Cie)
Radiation	Mo(K_a), λ = 71.073 pm	Cu(K_a), λ = 154.0598 pm
F(000)	471.8	
Absorption coefficient	μ = 3.48 mm^{-1}	
Measured reflections	5035	
Unique reflections	806	
Measured range	$-8 \le h \le 8$, $-10 \le k \le 11$, $-13 \le l \le 15$, $2\,\Theta_{max}$ = 56.15°	
R(int)	0.0307	
Absorption correction	X-RED, X-SHAPE [20]	
Structure solution and refinement	SHELXL-97 [21]	
Number of refined parameters	60	
R_1	0.0223 for 675 $F_o > 4\sigma(F_o)$, 0.0298 for all data	
wR2	0.0641	
GooF	0.961	

Table 2 Atomic positions, coefficients of the “anisotropic” and equivalent temperature factors in pm^2 for $Na_5[CuO_2](OH)_2$

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Cu	4 c	0.00356(5)	0.75	0.52402(3)	100(2)	116(2)	119(2)	0	11(1)	0	111(1)
Na1	4 c	0.9138(2)	0.75	0.2706(1)	149(6)	226(8)	176(6)	0	–13(5)	0	184(3)
Na2	8 d	0.7580(1)	0.49435(9)	0.63883(7)	236(5)	93(5)	224(4)	14(3)	3(3)	4(3)	184(2)
Na3	4 c	0.0517(2)	0.75	0.0406(1)	137(5)	294(8)	138(5)	0	27(4)	0	190(3)
Na4	4 c	0.4363(2)	0.75	0.7069(1)	210(6)	483(11)	209(6)	0	98(5)	0	301(4)
O1	4 c	0.7741(3)	0.75	0.6211(1)	132(9)	93(12)	110(9)	0	22(7)	0	112(4)
O2	4 c	0.1936(3)	0.75	0.4104(2)	123(9)	120(11)	158(9)	0	40(8)	0	134(4)
O3	8 d	0.8691(3)	0.4536(2)	0.8283(1)	161(7)	239(9)	174(7)	30(6)	7(6)	18(7)	191(3)
H	8 d	0.786(5)	0.490(2)	0.871(2)							62(59)

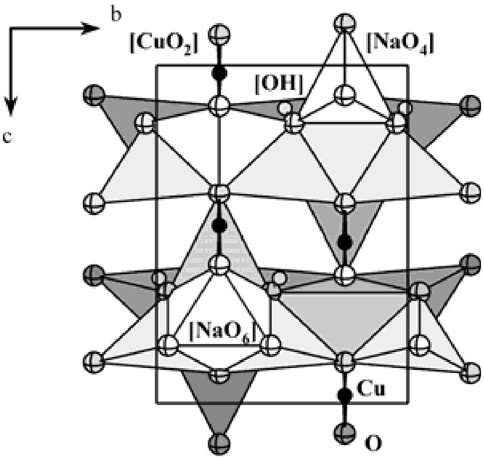

Fig. 3 Projection of the crystal structure of $Na_5[CuO_2](OH)_2$.

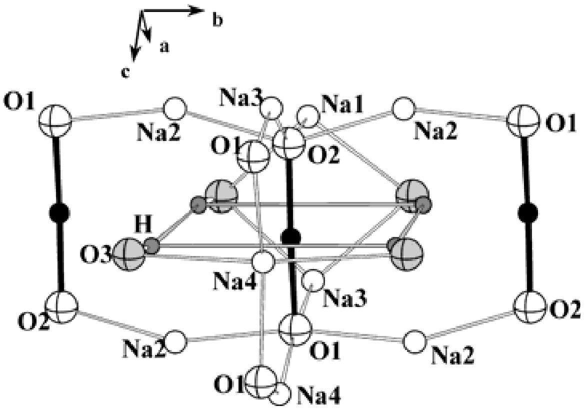

Fig. 4 View along the channels containing $[CuO_2]^{3-}$ and OH^- ions in $Na_5[CuO_2](OH)_2$. The grey-shaded bonds between the hydrogen atoms illustrate only the plane perpendicular to the dumb-bell like oxocuprate.

plane perpendicular to the dumb-bell like oxocuprate anions, Fig. 4. Obviously OH^- is nonbonding to Cu^+ and only coordinated by Na^+. Within the channels along [010] interatomic distances of d(Cu–Cu) = 448 pm occur, which are similar to those in $KNa_2[NiO_2]$ and $Na_5[NiO_2][CO_3]$ [11, 12]. $K_5[AuO_2]I_2$ [13] contains a similar structural segment with channels of $[AuO_2]^{3-}$ complexes with d(Au–Au) = 551 pm and d(Au–I) = 425 pm for the four I^-, defining the perpendicular plane to the dumb-bell like linear oxoaurate

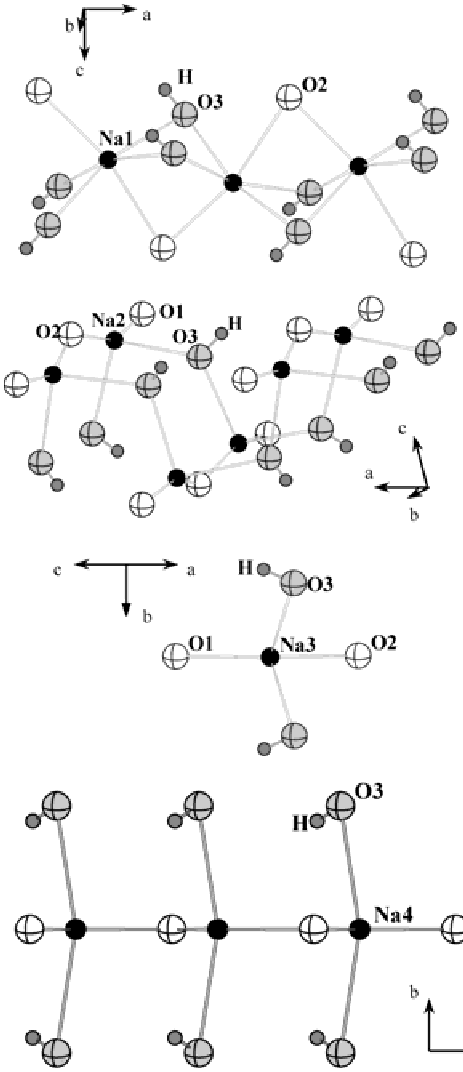

Fig. 5 Connection of crystallographically independent $[NaO_x]$ polyhedra with its equivalents present in $Na_5[CuO_2](OH)_2$.

units. The difference to $Na_5[CuO_2](OH)_2$ is that in $K_5[AuO_2]I_2$ all K^+ are coordinated by four I^- and two O^{2-}.

Four crystallographically independent sites are occupied by sodium. Na1 forms chains along [100] with its crystallographically equivalent ones. These are connected via triangular trans faces of the distorted octahedra, built of four OH^- and two trans O^{2-}, Fig. 5.

Table 3 Motifs of coordination relationships [22] $Na_5[CuO_2](OH)_2$ with distances in pm

	O1	O2	O3 (OH)	C.N.	ECoN	MEFIR
Na1		2/2 238.8(2) 255.3(2)	4/2 253.8(2) 259.3(2)	6	5.8	108.9
Na2	1/2 290.0(1)	1/2 227.5(1)	2/2 240.1(2) 242.2(2)	4	3.9	96.5
Na3	1/1 236.6(2)	1/1 225.3(2)	2/1 244.9(2)	4	3.8	98.2
Na4	2/2 228.8(2) 229.6(2)		2/1 270.5(2)	4	3.0	99.1
Cu	1/1 181.7(2)	1/1 178.8(2)		2	2.0	50.2
C.N.	6	6	6			
ECoN	5.9	5.7	5.7			
MEFIR	134.1	133.6	144.7			

Initial values in pm: r(Na1) = 106.33, r(Na2) = 98.50, r(Na3) = 99.56, r(Na4) = 100.13, r(Cu) = 54.07, r(O) = 140

The distorted tetrahedra, $[Na4O_2(OH)_2]$, are connected only via O^{2-} to zigzag chains along [100]. For Na2 a similar motif along [010] is observed, but further bridging to crystallographically equivalent sodium atoms occurs via both OH^- to layers. In contrast to all other sodium atoms, Na3 is in this respect isolated with a C. N. of 2 + 2. For a detailed list of interatomic distances and motifs of coordination see Tab. 3.

4 IR Spectrum of $Na_5[CuO_2](OH)_2$

Selected single crystals of $Na_5[CuO_2](OH)_2$ were investigated by infrared spectroscopy. The two typical hydoxide modes for a bridging OH^- [14] are observed at 3437 cm^{-1} and 1085cm^{-1} for $\nu(OH)$ and $\delta(NaOH)$, respectively. It is interesting to note that the infrared spectrum confirms that no further hydrogen bonding is present here. The shortest interatomic distances are d(Na–**O**H) = 224–270 pm, d(Cu–**H**O) = 320 pm and d(**O–H**O) = 350–390 pm. Furthermore, the asymmetric stretching mode of the $[O\text{–}Cu\text{–}O]^{3-}$ complex is observed at 796 cm^{-1}. Since this complex is not exactly linear, the symmetric stretching vibration should be allowed for observation in the infrared spectrum for C_{2v} symmetry. In fact, we observe a band located at 617 cm^{-1}. This is about 50 cm^{-1} lower than in $K_3[NiO_2]$ and $KNa_2[NiO_2]$ with d(Ni–O) = 177 pm [11]. But it is approximately the value derived from the vibrational progression in the first excited state of a linear $[NiO_2]^{3-}$ complex with two electrons in the d_z^2 orbital and an interatomic distance of 180 pm, which is the case for the $[CuO_2]^{3-}$ assembling d^{10} configuration. This sequence also holds, if one compares with Cu_2O: d(Cu–O) = 184 pm, ν_{as} = 615 cm^{-1} [15] and the second exited state progression observed for $K_3[NiO_2]$ with d(Ni–O) = 184 pm, ν_s = 535 cm^{-1} [11]. The derived force constants for the stretching modes ($D_{\infty h}$) [16] are 4.2 mdyn/Å, 3.4–3.7 mdyn/Å and 2.4–2.7 mdyn/Å for 177 pm, 180 pm and 184 pm, respectively. The (NaO) vibrations are commencing from 550 cm^{-1} towards smaller wavenumbers. In the FIR region of the spectrum a broad band at 250 cm^{-1} is observed with a shoulder at 130 cm^{-1} which might indicate the very weak bending mode for the $[O\text{–}Cu\text{–}O]^{3-}$ complex, see also [2].

5 MAPLE calculations [17]

The difference between the MAPLE value of the binary and the pseudo-ternary compounds is less than –1%, see Tab. 4.

Since the $[CuO_2]^{3-}$ complex is bent (170.14(8)°), we have investigated the influence of the interatomic distance and angle by modifying the Cu_2O structure [18] in the range of d(Cu–O) = 175–185 pm and ∠(O–Cu–O) = 160–180°. As expected, there is only a small dependence of the MAPLE value for Cu^+ upon a distortion from 180°. We find that this value is reduced by 3 kcal/mol towards a bent bridging angle of 160° and just ≈ +1 kcal/mol for 170°. Therefore, the bending should occur as a result of the lattice effects caused by the difference in the anionic part of the structure, in this case O^{2-} and OH^-. The MAPLE contribution for Cu^+ increases by 10 to 12 kcal/mol when the interatomic distance is reduced to 175 pm. This explains very nicely the already observed fact that MAPLE(M^+) for ternary oxometalates (d(M–O) = 177 pm) is approximately 10 to 15 kcal/mol larger than the estimated value from the binary components [11]. For Cu_2O the interatomic distance d(Cu–O) equals 184 pm [18].

Table 4 **Ma**delung **P**art of the **L**attice **E**nergy (MAPLE) in kcal/mol for $Na_5[CuO_2](OH)_2$

		binary	quaternary	Δ (binary-quaternary)
Na1	1×	117.1[a)]	114.1	3.0
Na2	2×	117.1[a)]	125.0	–15.8
Na3	1×	117.1[a)]	120.1	–3.0
Na4	1×	117.1[a)]	115.9	1.2
Cu	1×	147.7[b)]	162.5	–14.8
O1	1×	465.1[c)]	465.2	–0.1
O2	1×	465.1[c)]	453.9	11.2
O3 (OH)	2×	118.3[d)]	118.2	0.2
Σ		1900.0	1918.1	–18.1 = –0.95%

[a)] average value from 2 MAPLE($Na^+(NaOH)$) + 3 MAPLE($Na^+(Na_2O)$)
[b)] MAPLE($Cu^+(Cu_2O)$)
[c)] average value from 0.5 MAPLE($O^{2-}(Cu_2O)$) + 1.5 MAPLE($O^{2-}(Na_2O)$)
[d)] MAPLE($OH^-(NaOH)$)

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Supplementary Material Available: Details of the structure refinement, coefficients of anisotropic displacement factors, interatomic distances and angles have been deposited at the Fachinformationszentrum, Karlsruhe, Germany
(e-mail: crysdata@fiz-karlsruhe.de). ICSD 411865.

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