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Speciation of Copper(II)

The Species of Fehling's Solution

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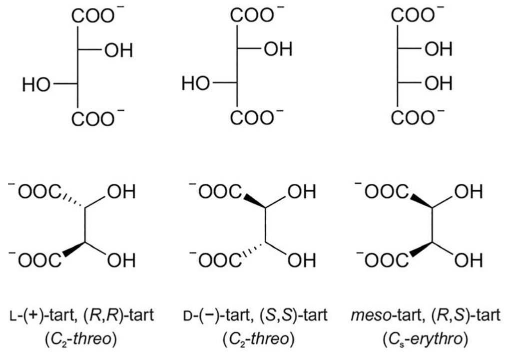
Abstract: A species model for the copper(II)/L-(+)-tartaric acid (LH_2, tartH_2) aqueous system between pH 1.9 and 12.3 has been established by potentiometric, UV/Vis spectroscopic, solubility and crystallographic studies. Eight species were detected, including the oligonuclear major species $Cu_8L_6H_{-10}$ in the neutral region and the mononuclear major species CuL_2H_{-4} in the alkaline region, the latter being associated with Fehling's solution. The octanuclear complex was isolated as its lithium salt $Li_7[Cu_8(\text{L-tartH}_{-2})_4(\text{L-tartH}_{-1})_2(H_2O)_6]NO_3\cdot 19H_2O$ (**1**). The "Fehling species" CuL_2H_{-4} was crystallized as its sodium, potassium and caesium salts, namely $K_2Na_4[Cu(\text{L-tartH}_{-2})_2]\cdot 12H_2O$ (**2**), $Na_6[Cu(\text{L-tartH}_{-2})_2]\cdot 9H_2O$ (**3**), $Na_6[Cu(\text{L-tartH}_{-2})_2]\cdot 14H_2O$ (**4**), and $Cs_6[Cu(\text{L-tartH}_{-2})_2]\cdot 8H_2O$ (**5**). Each of them shows a distorted square-planar environment of copper(II), similar to the related non-chiral cuprate $[Cu(\textit{rac}\text{-tartH}_{-2}\text{-}\kappa^2O^2,O^3)_2]^{6-}$ (S. Albrecht, P. Klüfers, *Z. Anorg. Allg. Chem.* **2013**, *639*, 280–284). By comparing the components of the UV/Vis spectra of Fehling's solution and the solids, we confirmed the identity of the major solution species.

Introduction

Fehling's solution, an alkaline solution containing copper(II) and L-(+)-tartaric acid (LH_2 = tartH_2; the different isomeric forms of tartrate are illustrated in Scheme 1), is a well-known standard probe for detecting reducing substances. Originally invented by Hermann Christian von Fehling in 1848 to determine the amount of glucose in urine samples,[1] it is nowadays used to distinguish between reducing and non-reducing sugars.[2] Moreover, it is one of the first detection probes students are faced with in undergraduate courses. Although the usage of the deep-blue solution reaches back almost 170 years, the structure of the obvious tartratocuprate(II) species that prevents precipitation of cupric hydroxide in solution has remained unknown. Strangely enough, textbooks such as that of Cotton et al. assume that *meso*-tartaric acid is a component of Fehling's solution,[3] although recipes from both the European and the U.S. Pharmacopeia require L-(+)-tartaric acid because of the higher stability of the cuprates formed. According to these procedures, copper sulfate, potassium sodium L-(+)-tartrate (Seignette salt) and sodium hydroxide are mixed in a molar ratio of 1:3.8:5.8 in water (c_{Cu} = 0.217 mol L^{-1}) to obtain deep-blue solutions (pH 13.5–14).[4,5] Samples are checked for reducing properties by adding a few drops of this solution; after heating gently, the formation of a red precipitate of Cu_2O indicates the presence of reducing species.



Scheme 1. Various isomers of tartarate. Top: Fischer projections; bottom: stereochemical drawings. The atomic numbering is used in the κ^2O^2,O^3-style specification of the copper-chelating ligand atoms .

At the beginning of the 20th century, several research groups started to reveal the composition of the active species. The first studies concerning alkalized solutions of copper(II) and enantiopure tartaric acid were reported by Bullnheimer and Seitz in 1899 and 1900, and by Traube in 1921. Both groups concluded that the anion $[Cu(\text{L-tartH}_{-2})_2]^{6-}$ was the species in Fehling's solution.[6–8] Owing to the methodological limitations at that time, the formulae of some alkali salts of the cuprate were resolved by elemental analysis, but the structure of the species remained unclear. Since then only a few synthetic studies on compounds obtained in the alkaline region have been published, most of them, such as the work of Pfeiffer et al. in 1948, confirmed earlier results.[9] In fact, until now, no compound with copper and L-(+)-tartaric acid has been isolated from solutions above pH 9 and characterized by single-crystal X-ray analysis, unlike the case of racemic tartaric acid. With the racemate, three compounds were isolated and fully characterized: $Na_4[Cu_2(\textit{rac}\text{-tartH}_{-2}\text{-}\kappa^2O^1,O^2{:}\kappa^2O^3O^4)_2]\cdot 10H_2O$,[10–12] $Li_4[Cu_2(\textit{rac}\text{-tartH}_{-2}\text{-}\kappa^2O^1,O^2{:}\kappa^2O^3O^4)_2]\cdot 11.75H_2O$ and $Na_6[Cu(\textit{rac}\text{-tartH}_{-2}\text{-}\kappa^2O^2,O^3)_2]\cdot 14H_2O$,[2] the last being considered a Fehling-analogous complex. In terms of stoichiometry, these species resemble the formulae $Cu_2L_2H_{-4}$ and CuL_2H_{-4}.

To reveal the species in solution, potentiometric,[13–18] polarographic,[19–22] electrophoretic,[23] UV/Vis and CD spectro-

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scopic[24–28] as well as extraction studies[29] of the copper(II) and L-(+)-tartaric system have been reported. However, only a few of them focused on the alkaline regime (pH > 9) or presented a model for a wide pH region. Upon a closer look, most of them showed a similar model for the acidic and neutral regions. Whereas mono- and dinuclear species such as CuL, CuLH and Cu_2L_2 were formed at low pH values, oligonuclear species such as $Cu_8L_6H_{-10}$ or $Cu_6L_4H_{-7}$ predominated in solution at neutral pH. One of the first comprehensive studies of this system was performed by Lefebvre in 1957. By using potentiometric titration and UV/Vis spectroscopy, he suggested a model including CuL in the acidic region and the octanuclear $Cu_8L_6H_{-10}$ at pH 6 and higher, with the Cu_8 species being favoured over the tetranuclear $Cu_4L_3H_{-5}$ species with the same overall stoichiometry. He also drew conclusions about the alkaline region and postulated species such as $[Cu_3L_3(OH)_6]^{6-}$, $[CuL_2(OH)_2]^{2-}$ and $[CuL_2(OH)_4]^{6-}$. The last was assigned as Fehling's complex.[13] Later research groups confirmed the existence of mono- and dinuclear complexes in the acidic region, especially the species CuL, which is in equilibrium with its dimer Cu_2L_2. Still later, Johansson also examined the neutral region and confirmed the presence of oligonuclear species $Cu_8L_6H_{-10}$.[16] However, the alkaline environment was investigated through potentiometric titration by just one group after Lefebvre's studies: Blomqvist and Still found the additional species $Cu_2L_2H_{-3}$ and $Cu_2L_2H_{-4}$ above pH 9, which are formed by stepwise deprotonation of the $Cu_2L_2H_{-2}$ species.[15] The most recent potentiometric study of the copper(II)/L-(+)-tartaric acid aqueous system was performed by Piispanen and Lajunen in 1995. By considering all the species formulated in the past, the authors reported a model with seven species in the pH region between 2.4 and 7.5: CuL, Cu_2L_2, CuHL and $Cu_2L_2H_{-1}$ for pH < 4.5, and $Cu_2L_2H_{-2}$, $Cu_6L_4H_{-7}$ and $Cu_8L_6H_{-10}$ in the neutral region. It was also shown that, despite a three-fold molar excess of ligand over copper, the last two oligonuclear species were the predominating complexes for pH > 5. Nevertheless, as with several other studies, the alkaline region was missing from this work.[17] Most recently, progress has been made regarding the structures of copper–tartrate species in the crystalline state. In their 2013 work, Liu et al. prepared the cupric L-(+)-tartrates $[\{Cu_2(\text{L-tart})_2(H_2O)_2\}_{n/n}]\cdot{\approx}3.5H_2O$ and $[\{Cu_2(\text{L-tart})_2\}_n]$ as two- and three-dimensional coordination polymers in a hydrothermal approach.[30] The structure of the hydrated polymer has been described by other groups previously.[18,31–33] To the best of our knowledge, these structural analyses have provided the only available crystallographic data on copper complexes of enantiopure tartrate.

In this work, which was focused on the alkaline regime and includes Fehling's solution, we present a species distribution model that is complemented by crystallographic evidence of the identified species. In particular, we provide structural data on the major species in this part of the pH range, $Cu_8L_6H_{-10}$ and the Fehling species CuL_2H_{-4}.

Results and Discussion

The strongly alkaline region is difficult to investigate by potentiometric methods due to a marked increase in the so-called alkali ion error.[34] Thus, a reliable analysis was hampered in the pH regime that is typical of Fehling's solution. We therefore supplemented potentiometric data with a UV/Vis spectroscopic analysis and solubility studies.

Combined Potentiometric Titration and UV/Vis Spectroscopy

By recording both the pH value and the UV/Vis spectrum of the titration solution (Cu/L-tart = 1:3, c_{cu} = 0.01 mol L^{-1}) at each added volume increment of sodium hydroxide we obtained a titration curve as well as a series of absorption spectra without isosbestic points between pH 1.9 and 12.3. With increasing pH, the spectra show a shift of λ_{max} for the crystal-field transition to lower wavelengths, from 816 (pH 1.9) to 676 nm (pH 12.3; see Figure S4 in the Supporting Information). According to Martell's definition of critical stability constants, the most reliable published species, specifically, the species from refs.[15–17], were chosen and their stability constants were considered for modelling.[35] Furthermore, the CuL_2H_{-4} species, which is supposed to be the predominating species in Fehling's solution, was taken into account. The protonation constants of L-(+)-tartaric acid used in the refinement were determined by a separate potentiometric titration (pK_{a1} = 2.58, pK_{a2} = 3.69; ionic strength I = 0.5 M, $NaClO_4$). Under these premises, a satisfying model containing eight species resulted (Figure 1). Fewer species led to a markedly worse fit, whereas more species did not improve the goodness of fit (see the Exp. Sect.) but caused noisy molar extinction curves or refinement errors. Moreover, factor analysis (see the Exp. Sect.) showed at least six species that contributed significantly to the UV/Vis spectra, further compounds were therefore not considered. The mixed stability constants (see Table 1) are in good agreement with the species of the latest published data, which have now been completed by the previously unconsidered CuL_2H_{-4} species.[15–17] In addition to stability constants, the spectral molar absorption for each absorbing

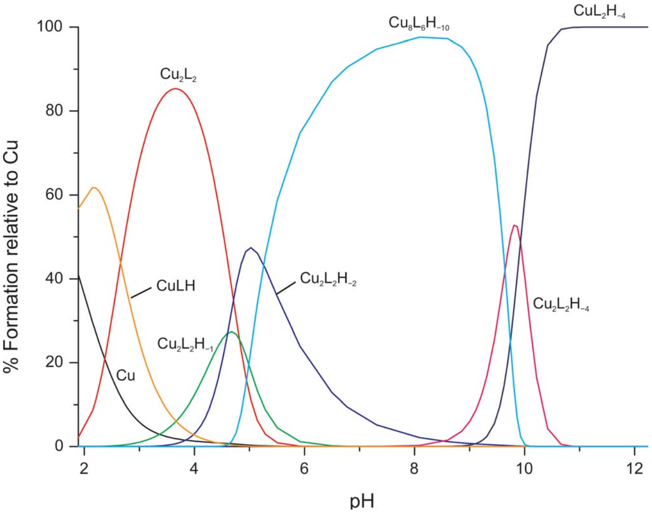

Figure 1. Distribution of species in the copper(II)/L-(+)-tartaric acid system [Cu/LH_2 = 1:3, c_{Cu} = 0.01 M in 0.5 M $NaClO_4$, LH_2 = L-(+)-tartaric acid]. Charges have been omitted.[36,37]

species was calculated (Figure 2).[36,37] As a result of these analyses, the dominating species of three pH regions are discussed. In the sense of a consensus model, the species of our solution study are common to most of the published analyses with some more rarely considered species skipped, namely $Cu_2L_2H_{-3}$ and $Cu_6L_4H_{-7}$. Moreover, the frequently addressed CuL species was also omitted for the reasons discussed in the next paragraph.

Table 1. Log β, λ_{max} and ε_{max} values of the different species observed in HypSpec2014. Charges have been omitted.[36,37]

Species	log β	$\lambda_{max}(H_2O)$ [nm]	ε_{max} [L mol^{-1} cm^{-1}]
Cu	–	817	6.13
Cu_2L_2	9.22	839	27.22 ± 0.16
$Cu_2L_2H_{-1}$	4.38	744	32.66 ± 0.89
$Cu_2L_2H_{-2}$	–0.22	756	36.93 ± 0.48
$Cu_2L_2H_{-4}$	–17.32	694	36.17 ± 0.18
CuL_2H_{-4}	–27.68	680	28.79 ± 0.02
CuLH	6.22	813	20.62 ± 0.12
$Cu_8L_6H_{-10}$	–7.36	697	(38.76 ± 0.32

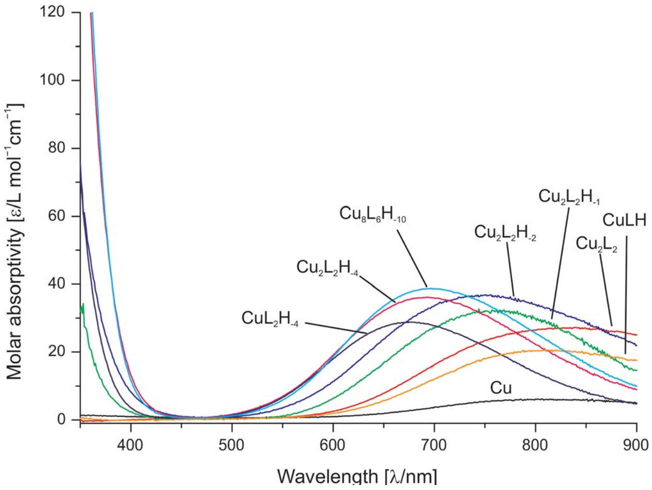

Figure 2. Molar absorptivity spectra of the different species observed in HypSpec2014. Charges have been omitted.[36,37]

The Acidic Region

As concluded by past researchers, mono- and dinuclear species are formed between pH 1.9 and 5.0, that is, aquated copper(II) ions Cu, CuLH, Cu_2L_2, $Cu_2L_2H_{-1}$ and $Cu_2L_2H_{-2}$. In contrast to most of the preceding studies, the inclusion of the species CuL in the model did not result in a stable refinement. It should be noted that both CuL and Cu_2L_2 are cupric tartrate. The presence of a Cu_2L_2 species in the refinement points to the fact that in the solid dinuclear building blocks of the respective polymers are recognised. Thus, a non-polymeric Cu_2L_2 solution species maybe derived from a dinuclear cutout of the polymer by saturating the vacant bonding sites by additional aqua ligands. CuLH and $Cu_2L_2H_{-1}$ seem to play a minor role in solution in contrast to Cu_2L_2; $Cu_2L_2H_{-2}$ reaches its maximum (46 %) at pH 4.9. None of these species has been isolated and characterized, which may be explained by the tendency of the Cu_2L_2 species to form polymeric precipitates.

The Neutral Region

The predominant species between pH 5.3 and pH 9.6 is $Cu_8L_6H_{-10}$, which represents almost 100 % of the Cu species present at pH 8.1. $Cu_2L_2H_{-4}$ plays a minor rule in this pH region. Notably, all past solution models include such an octanuclear species in preference to the formula $Cu_4L_3H_{-5}$. In fact, the tetranuclear formula is used in work based on elemental analysis, such as that of Masson and Steele in 1899 and of Packer and Wark in 1921, who may have had the octanuclear entity in their hands.[38,39] Specifically, both research groups isolated a copper(II) complex with L-(+)-tartaric acid in the neutral region and assigned to it the formula $M_3[Cu_4(\text{L-tartH}_{-2})_2(\text{L-tartH}_{-1})]\cdot 4H_2O$ (M = Na, K, Ag). Masson and Steele obtained the potassium salt as a blue powder by mixing copper tartrate with an excess of aqueous KOH and adding ethanol. (They falsely claimed this compound as Fehling's complex, although it reacted neutrally with litmus.[38]) In 1954, Ablov and Popovich reported the isolation of the salts $M^{III}[Cu_4(\text{L-tartH}_{-2})_2(\text{L-tartH}_{-1})]$ with large cations {M = $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_5(H_2O)]^{3+}$, $[Co(en)_3]^{3+}$ and $[Cr(urea)_6]^{3+}$} at pH 7.[40] In an attempt to use their procedure for the preparation of crystals, we obtained the $[Co(NH_3)_6]^{3+}$ salt as small, dark-green crystals, which were reasonably suitable for X-ray diffraction analysis. However, although the anion structure was fairly well resolved and showed the expected octanuclear structure, which results from doubling the net formula, the entire analysis did not meet the quality criteria for publication due to cation disorder (see Figure S24 in the Supporting Information).

Crystals of improved quality were eventually obtained from $Cu(NO_3)_2\cdot 3H_2O$, L-(+)-tartaric acid and $LiOH\cdot H_2O$ in a molar ratio of 4:3:11 in water (pH ≈ 9). From these solutions, blue blocks of $Li_7[Cu_8(\text{L-tartH}_{-2})_4(\text{L-tartH}_{-1})_2(H_2O)_6]NO_3\cdot 19H_2O$ (**1**) were grown by slow evaporation over the course of several months. The structure of the cuprate ion resembles the octanuclear anion of the $[Co(NH_3)_6]^{3+}$ salt and confirms the existence of an oligonuclear $Cu_8L_6H_{-10}$ species in the addressed pH region. The assignment by past research groups of the major species in the neutral regime was, thus, correct.

The Alkaline Region

Owing to the fundamental problems of analysing strongly alkaline solutions by a potentiometric approach, establishing a model needed care. We found two species above pH 9.6, the minor $Cu_2L_2H_{-4}$ and major CuL_2H_{-4} species, the latter predominating above pH 9.9 and being the only one above pH 11.7. Attempts to crystallize the minor dinuclear species, the crystallization of which is straightforward in the analogous copper(II)/*rac*-tart system,[2] were unsuccessful. As a starting point, we had chosen the work of Bullnheimer and Seitz;[7] we interpreted their $Na_2[Cu(\text{L-tartH}_{-2})]\cdot 4H_2O$ as $Na_4[Cu_2(\text{L-tartH}_{-2})_2]\cdot 8H_2O$, in close resemblance to its racemic variant.[2,10–12] We agree with the statement of the former authors that the mother liquors of this compound were unstable (the lithium analogue showed still increased instability). However, we were not able to isolate the solid sodium salt.

To clarify the marked difference between *rac*- and L-tart-based dicuprates, we modelled both anions by a DFT approach. For steric reasons, the centrosymmetric $[Cu_2(rac\text{-}tartH_{-2})_2]^{4-}$ tetraanion with its five-membered chelate ring cannot be assembled with a single enantiomer. Instead, a reasonable dinuclear analogue needed six-membered chelate rings with $[Cu_2(\text{L-}tartH_{-2}\text{-}\kappa^2O^1,O^3\text{-}\kappa^2O^2,O^4)_2]^{4-}$ bonding. Based on five different functionals, Ahlrich's def2-tzvp basis set and the COSMO solvent model, the racemic compound is 22 (TPSS) to 33 kJ mol^{-1} (B3LYP) more stable than the enantiopure compound, clearly due to lower ring strain (see Figure 3 and Table 2). Because of this instability, we assume that $Cu_2L_2H_{-2}$ is not a species truly competing with CuL_2H_{-4} in Fehling's solution. Moreover, taking into consideration the conditions of the standard recipe for the preparation of Fehling's solution with respect to the species-distribution curve obtained here,[4,5] and, extrapolating from pH 12.3, we see that CuL_2H_{-4} is the dominating species between pH 13.5 and pH 14 (Figure 4).

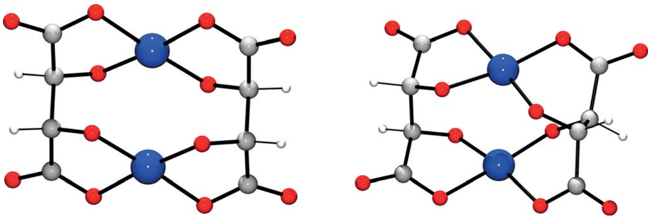

Figure 3. Optimized structures (def2-tzvp, B3LYP, cosmo, d3) of $[Cu_2(rac\text{-}L)_2H_{-4}]$ (left, *rac* = racemic) and $[Cu_2L_2H_{-4}]$ (right).

Table 2. Energy differences (ΔE) between $Cu_2L_2H_{-4}$ (racemic, E_{rac}) and $Cu_2L_2H_{-4}$ (enantiopure, E_{ena}).

Functional	$\Delta E = E_{rac} - E_{ena}$ [kJ mol^{-1}]
B3LYP	33.0
PBE0	31.9
TPSSh	25.8
BP86	25.3
TPSS	22.2

The Dilemma of the Alkaline Regime: CuL_2H_{-4} versus $CuLH_{-4}$ versus CuH_{-4}

Owing to the known problems of potentiometric analyses in the high-pH region, both the species CuH_{-4} and the hypothetical $CuLH_{-4}$ instead of CuL_2H_{-4} gave a similar fit with similar stability constants, that is, measuring pH and UV/Vis spectra did not suffice to establish a reliable model. Thus, solubility studies were performed in addition, which proved the solubility of $Cu(OH)_2$ in 1 M NaOH (note: the final hydroxide concentration of a titration solution was approximately 0.1 mol L^{-1}). By mixing $Cu(OH)_2$ and NaOH in a molar ratio of 1:2 at c_{NaOH} = 1 mol L^{-1}, practically all the $Cu(OH)_2$ was recovered and the resulting solution was clear and colourless. A mixture of $Cu(OH)_2$, L-(+)-tartaric acid and NaOH in a molar ratio of 1:1:2, which resembles the stoichiometry of a $CuLH_{-4}$ species, in water yielded 26.8 % of dissolved $Cu(OH)_2$, whereas a mixture of $Cu(OH)_2$, L-(+)-tartaric acid and NaOH in a molar ratio of 1:2:6, the stoichiometry of the CuL_2H_{-4} species, resulted in a clear deep-blue solution with no remaining solid (both experiments: c_{NaOH} = 1 mol L^{-1}). This indicates that $[Cu(OH)_4]^{2-}$ ($\equiv CuH_{-4}$) did not play a role in the titration solution. In fact, $Cu(OH)_2$ is soluble in >5 M NaOH (λ_{max} = 641 nm, ε = 31.3 dm^3 mol^{-1} cm^{-1}; in 10 M NaOH) only. Typical synthetic procedures for $Na_2[Cu(OH)_4]$ require 45–50 % aqueous NaOH.[41,42] The situation is less clear for a $CuLH_{-4}$ species, which may be present as a minor species. Thus, attempts were made to isolate crystals from high-pH solutions.

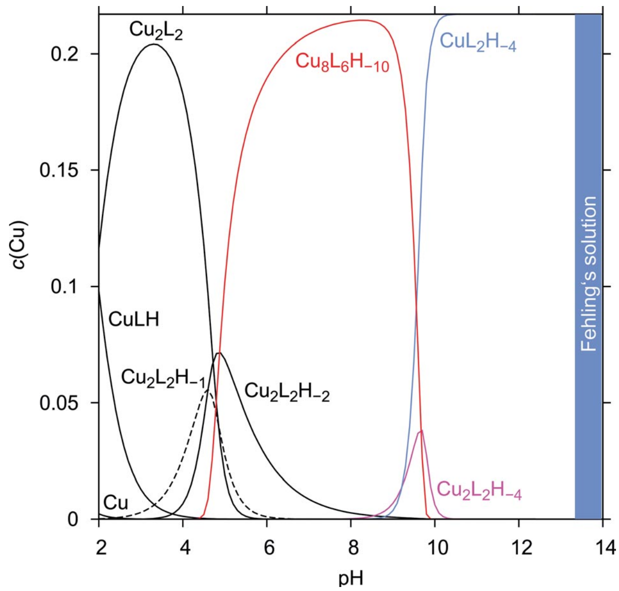

Figure 4. Species distribution diagram *c*(Cu) vs. pH. Here, the conditions of the standard recipe for the preparation of Fehling's solution were considered ($c_{Cu,tot}$ = 0.217 mol L^{-1}). Values at pH > 12.3 were extrapolated by using a local variant of Motekaitis's SPE.[35]

CuL_2H_{-4} Salts

To confirm the CuL_2H_{-4} species and analyse its structure, we reproduced the synthetic procedure of Bullnheimer and Seitz for $Na_6[Cu(\text{L-}tartH_{-2})_2]\cdot 13H_2O$ and $K_2Na_4[Cu(\text{L-}tartH_{-2})_2]\cdot 11H_2O$; the latter is reported to co-crystallize with $K_3Na_3[Cu(\text{L-}tartH_{-2})_2]\cdot 11H_2O$, which, however, did not precipitate in any of our crystallization batches. Moreover, powder X-ray diffraction patterns of the batches always resembled the calculated patterns of the K_2Na_4 salt.[6] By mixing $Cu(OH)_2$, potassium sodium L-(+)-tartrate tetrahydrate (Seignette salt), KOH and NaOH according to their recipe, we obtained blue rods in 36 % yield by concentrating the dark-blue solutions. Crystal-structure analysis revealed $K_2Na_4[Cu(\text{L-}tartH_{-2})_2]\cdot 12H_2O$ (**2**), quite close to the reported composition of Fehling's complex. Similarly, $Na_6[Cu(\text{L-}tartH_{-2})_2]\cdot 9H_2O$ (**3**) and $Na_6[Cu(\text{L-}tartH_{-2})_2]\cdot 14H_2O$ (**4**) were isolated as blue crystals. In addition to the work of Bullnheimer and Seitz, we also prepared the caesium salt $Cs_6[Cu(\text{L-}tartH_{-2})_2]\cdot 8H_2O$ (**5**), which is a hygroscopic solid that is stable for a few hours only. In general, crystals were isolated only from relatively concentrated solutions ($c_{Cu} \approx$ 1.1 mol L^{-1}). The instability of the complexes, which was evidenced by red or black discoloration due to the formation of copper oxides, increased in the series **3** < **4** ≈ **2** << **5**.

Solid-State versus Solution UV/Vis Spectra

As additional proof to demonstrate that the crystals' anion $[Cu(L\text{-}tartH_{-2})_2]^{6-}$ resembles the high-pH solution species, the compounds were studied by UV/Vis spectroscopy in aqueous solution and in the solid state (see the Supporting Information). The observed λ_{max} values for the d–d transitions of **2**, **3** and **5** are presented in Table 3. For comparison, $\lambda_{max,tit}$ = 680 nm. In the case of compound **4**, only a few crystals were obtained and therefore it was not possible to record its UV/Vis spectrum. The absorption spectra of each compound both in aqueous solution and in the solid state give good agreement with the absorption spectra of the species CuL_2H_{-4} obtained from the analysis of the potentiometric data. Thus, the major species, practically the only one, in Fehling's solution is CuL_2H_{-4} {≡ $[Cu(L\text{-}tartH_{-2})_2]^{6-}$}.

Table 3. λ_{max} of the d–d transitions of compounds **2**, **3** and **5**.

Compound	$\lambda_{max}(H_2O)$ [nm]	λ_{max}(solid) [nm]
2	673	656
3	671	661
5	671	669

Structures

$Li_7[Cu_8(L\text{-}tartH_{-2}\text{-}\kappa^4O^1,O^2,O^3,O^4)_4(L\text{-}tartH_{-1}\text{-}\kappa^3O^1,O^2,O^4)_2(H_2O)_6]NO_3\cdot 19H_2O$

Following common rules, species of low nuclearity dominated the acidic as well as the alkaline region, but an oligonuclear aggregate makes up the neutral solution. In fact, the repeatedly formulated $Cu_8L_6H_{-10}$ species was precisely confirmed by an X-ray study of crystals of **1**. The octanuclear cuprate exhibits a saddle-shaped $[Cu_8(L\text{-}tartH_{-2}\text{-}\kappa^4O^1,O^2,O^3,O^4)_4(L\text{-}tartH_{-1}\text{-}\kappa^3O^1,O^2,O^4)_2(H_2O)_6]^{6-}$ ion. Figure 5 shows the Cu–tart framework of the structure (ORTEP plot is provided in Figure S16 in the Supporting Information). The whole anion lies in the asymmetric unit, the apparent C_2 symmetry is non-crystallographic. The cupric centres show typical strongly Jahn–Teller-elongated octahedra with tartrate O atoms forming the equatorial planes of four closer ligand atoms.

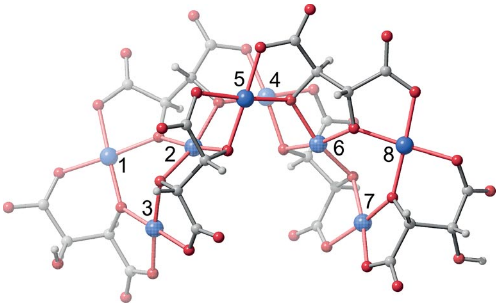

Figure 5. Octanuclear, almost C_2-symmetrical copper(II)–tartrate assembly in crystals of **1**. Carbon atoms are shown in gray, copper in blue, oxygen in red and hydrogen in white. Lithium ions, the nitrate ion and water molecules have been omitted for clarity.

Below, the mononuclear bis(diolato) structure of the CuL_2H_{-4} core is described in detail. This core is also a suitable starting point to construct the Cu_8 cluster. It is based around the Cu2 and Cu6 centres. To build the entire cluster, one should add two more copper atoms to each of the two $tartH_{-2}$ ligands of the two bis(diolato) cores. The bonding sites for each of these two copper atoms are the deprotonated hydroxy-carboxy functions, which form five-membered chelate rings on κ^2O^1,O^2 and κ^2O^3,O^4 coordination in addition to the κ^2O^2,O^3 diolato mode. One should now double this motif by the application of a two-fold axis close to Cu4 and Cu5. Finally, two terminating $tartH_{-1}$ ligands are added to the Cu1/Cu3 and Cu7/Cu8 couples. As a result, the six copper atoms that are not bonded in a bis(diolato) core share a common bonding pattern: a *cis*-bis(alkoxido) and *cis*-bis(carboxylato) pattern. It should be noted that the octanuclear cluster is not formed from two Cu_4 parts by Jahn–Teller-elongated, weaker contacts and is thus not prone to cleavage in solution. Accordingly, the Cu_8 species is a stable and persistent solution species.

The $Cu_8(tart)_6$ assembly in Figure 5 is complemented in the actual crystal structure by aqua ligands and bridging carboxylate O atoms, which bind along the Jahn–Teller-elongated axes. The coordination number of the cupric centres thus is either five (Cu2, Cu4, Cu6, Cu7) or six (Cu1, Cu3, Cu5, Cu8). In the case of Cu3, a disordered nitrate ion completes the coordination sphere. (There is some uncertainty whether or not the nitrate-assigned electron density is caused by a hydrogen carbonate ion because the reaction solution was left in air for crystallization.)

The octanuclear anions are linked by Cu8 and Cu1 bonding to neighbouring carboxylate ligands and build up a two-dimensional network. We assumed that these links are replaced by aqua ligands in aqueous solution, so that isolated $[Cu_8(L\text{-}tartH_{-2})_4(L\text{-}tartH_{-1})_2(H_2O)_x]^{6-}$ ($x \geq 8$) exist in aqueous media. The coordination sphere of the copper atoms can be interpreted in greater depth by using continuous shape measures (CShM), as established by Alvarez et al.[43] Details are presented in the Supporting Information.

The formation of crystals of non-chiral copper–tartrate assemblies seems to be less critical. By using aiding ligands, supramolecular networks and ordered functional crystalline solids have been reported. Thus, the decanuclear compound $[Cu_{10}(rac\text{-}tart)_4(rac\text{-}tartH_{-1})_4]\cdot(apy)_8\cdot 13H_2O$ (apy = 2-aminopyridine) and the pentadecanuclear cluster $[Cu_{15}(rac\text{-}tartH_{-2})_6(OH)_6(H_2O)_{10}]\cdot 20H_2O$ were synthesized to examine the role of hydrogen bonds and antiferromagnetic or ferromagnetic interactions.[44,45] Moreover, we recently described the isolation and molecular structure of $K_8[Cu_{10}(rac\text{-}tartH_{-2})_4(rac\text{-}tartH_{-1})_4(H_2O)_4]\cdot 18H_2O$.[2] The structure of the decanuclear anion in this cuprate devoid of aiding nitrogen ligands is ruled by the same principles as derived for **1**. As for L-(+)-tartrate, further cupric ions become attached to two bis(diolato) nuclei resulting in carboxylate-terminated $Cu_3(\mu\text{-}O)_3$ cores. In the racemic compound, the Cu_3O_3 hexagons are the only structural motif, in **1**, they are connected by a Cu_4O_4 octagon.

An analysis of the magnetic properties is pending. However, antiferromagnetic spin-coupling paths are clearly recognisable in terms of the Cu–μ-O–Cu angles. Considering the $d_{x^2-y^2}$ orbital in each plane made up of the four short Cu–O contacts as the magnetic orbital, two antiferromagnetic paths with obtuse Cu–O–Cu angles become evident (Figure 6). We will report on the results of the magnetic investigation in a separate work.

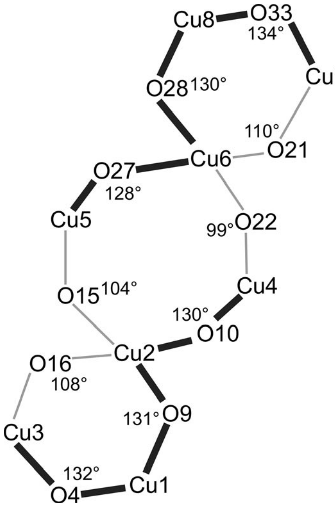

Figure 6. Antiferromagnetic spin-coupling pathways in terms of Cu–μ-O–Cu angles in **1**. Note the two clearly resolved fields of angles: more obtuse angles of about 130° that impart strong super-exchange in terms of the Goodenough–Kanamori rules,[46] and angles of less than 110° that impart weaker spin coupling. Note that an overall $S = 0$ ground state of the Cu_8 cluster results.

The Bis(diolato) Anions in $M_6[Cu(\text{L-tartH}_{-2}\text{-}\kappa^2O^2,O^3)_2]\cdot xH_2O$ 2–5

The central copper(II) ions of **2**–**5** are part of two diolato chelates in a distorted square-planar environment. The bond lengths between the copper(II) and alkoxo oxygen atoms are similar, ranging from 1.890 (Cu3–O33 in **3**) to 1.996 Å (Cu1–O4 in **2**). The distance between the next oxygen atoms of a carboxylato group and the central copper atom in **3** and **5** is rather large ($d_{Cu-O} > 2.96$ Å). The coordination in **2** and **4**, however, can be regarded as a 4+2 environment due to Cu–O contacts of about 2.5 Å along the Jahn–Teller-elongated axis. A continuous shape measures analysis of the coordination environment is given in the Supporting Information.[43,47] In summary, the tartratocuprate(II) ions show a slight distortion in the square-planar base, caused by the incompatibility of the chiral ligands and the intrinsic centrosymmetry of a square-planar motif. As an illustration, the dihedral angle between the two CuO_2 triangles of the spiro motif around copper ranges from 3.7(7)° for the Cu1 atom in **3** to 18.2(2)° in the caesium salt.

The molecular structure of $K_2Na_4[Cu(\text{L-tartH}_{-2}\text{-}\kappa^2O^2,O^3)_2]\cdot 12H_2O$ (**2**), which is also representative of **3**–**5**, is depicted in Figure 7. Like **4** and **5**, the crystals of **2** are stabilized by an extensive three-dimensional hydrogen-bonding system. A section of the crystal structure is shown in Figure 8. (Owing to the poor crystallinity of **3**, hydrogen atoms bonded to the solvent oxygen atoms could not be located properly and therefore have been omitted.)

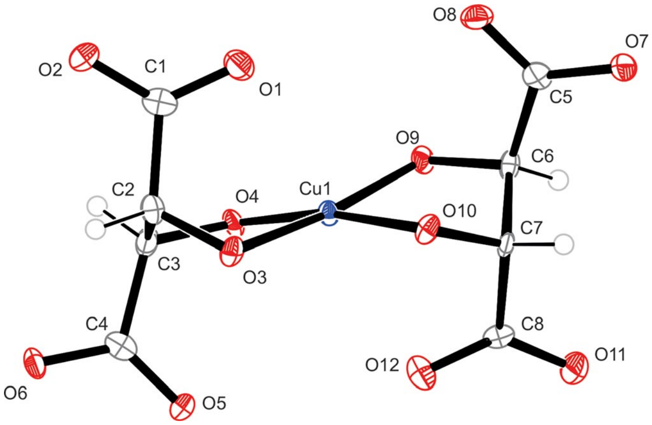

Figure 7. Molecular structure of the anion in **2**. Carbon atoms are shown in grey, copper in blue, oxygen in red and hydrogen in white. Sodium ions, potassium ions and water molecules have been omitted for clarity. Ellipsoids are plotted at the 75 % probability level.

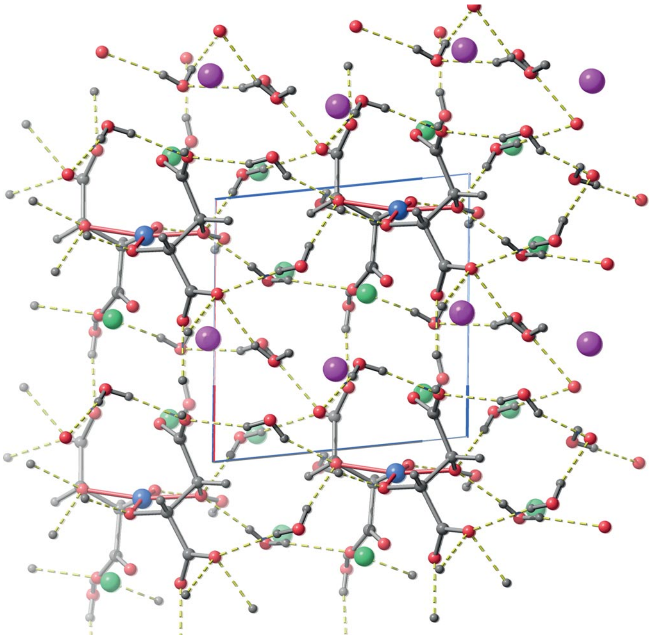

Figure 8. Hydrogen bonding in **2** viewed along [001]. Carbon atoms are shown in grey, copper in blue, oxygen in red, hydrogen in white, sodium in green and potassium in magenta.

Conclusions

A species model for the copper(II)/L-(+)-tartaric acid (LH_2, $tartH_2$) system in aqueous solution in the pH range from 1.9 to 12.3 has been established by potentiometric, UV/Vis spectroscopic and solubility studies. Herein, seven tartrato–copper(II) species were identified and refined: CuLH, Cu_2L_2, $Cu_2L_2H_{-1}$, $Cu_2L_2H_{-2}$, $Cu_8L_6H_{-10}$, $Cu_2L_2H_{-4}$ and the major species in Fehling's solution, CuL_2H_{-4}. As the focus of this work, structural information is provided for the major species of the neutral and alkaline regimes. From almost neutral solutions, the $Cu_8L_6H_{-10}$ species, which was frequently formulated in previous solution studies, crystallized as its lithium salt, $Li_7[Cu_8(\text{L-tartH}_{-2}\text{-}\kappa^4O^1,O^2,O^3,O^4)_4(\text{L-tartH}_{-1}\text{-}\kappa^3O^1,O^2,O^4)(H_2O)_6]NO_3\cdot 19H_2O$.

The main aim of this work was to reveal the structure of Fehling's complex, the tartratocuprate complex of the strongly alkaline region, the tentative CuL_2H_{-4} species. Unfortunately, potentiometry is hampered in the strongly alkaline media that are obtained when Fehling's solution is prepared following the typical recipes of the various pharmacopeias. Thus, UV/Vis spectroscopic as well as solubility studies on $Cu(OH)_2$ in various media were conducted to overcome the limited reliability of the potentiometric results. As the most powerful support, four salts of the anion in question were structurally resolved, namely $K_2Na_4[Cu(\text{L-tartH}_{-2}\text{-}\kappa^2O^2,O^3)_2]\cdot 12H_2O$ (**2**), $Na_6[Cu(\text{L-tartH}_{-2}\text{-}\kappa^2O^2,O^3)_2]\cdot 9H_2O$ (**3**), $Na_6[Cu(\text{L-tartH}_{-2}\text{-}\kappa^2O^2,O^3)_2]\cdot 14H_2O$ (**4**) and $Cs_6[Cu(\text{L-tartH}_{-2}\text{-}\kappa^2O^2,O^3)_2]\cdot 8H_2O$ (**5**). Each copper(II) centre shows a distorted square-planar coordination environment of the tartrate's alkoxido groups. The absorption maxima of the d–d bands of these solids are in good agreement with the spectra calculated from the solution analysis.[36,37]

Thus, the active species in Fehling's solution, which is responsible for the characteristic deep-blue colour, is the $[Cu(\text{L-tartH}_{-2}\text{-}\kappa^2O^2,O^3)_2]^{6-}$ anion.

Experimental Section

Combined Potentiometric and UV/Vis Titration of the Copper(II) and L-(+)-Tartaric Acid System in General: The combined potentiometric and UV/Vis titration to determine the protonation constants of the ligand and the stability constants of the formed copper(II) complexes were carried out at $T = (25.00 \pm 0.02)$ °C under nitrogen in aqueous solution (four-necked Schlenk flask). The reagents $Cu(ClO_4)_2\cdot 6H_2O$ (Fluka, >98 %), L-(+)-tartaric acid (Fluka, ≥99.5 %) and $NaClO_4$ (Riedel-de-Haën, pure, >97.5 %) were used without further purification. A 1.0 M NaOH solution (Fischer Chemical, factor limits 0.999–1.001), which was standardized against potassium hydrogen phthalate (Aldrich, ≥99.95 %) as a primary standard, functioned as titre. To keep carbonate impurity in the basic solution as low as possible, nitrogen was bubbled through it before the titration was started. The NaOH solution was added in known volume increments (see Table S1 in the Supporting Information) to the sample solution by an automatic titrator system, Titrando 809, whereas the pH was measured after each added volume with a combined glass electrode with a fixed ground-joint diaphragm (unitrode). The electrode was calibrated with standard buffers at pH 4.01, 7.00 and 9.00 (Merck). When the pH was constant for a longer time, a UV/Vis spectrum was recorded by using a Cary50 conc UV/Vis spectrometer with an optical probe (Hellma Analytics 661.702-UV, stainless steel, optical path length 10 mm). This procedure was performed in the wavelength region of 350–900 nm and in the pH region of 1.890–12.235. Deionized, oxygen-free and carbonate-free water served as a baseline.

Preparation of the Initial Solution: $Cu(ClO_4)_2\cdot 6H_2O$ (667.3 mg, 1.801 mmol, 1.000 equiv.) and L-(+)-tartaric acid (810.5 mg, 5.400 mmol, 2.999 equiv.) were mixed together in freshly prepared 0.5 M $NaClO_4$ solution (180 mL) prepared in distilled water. After stirring for 0.5 h under a constant stream of nitrogen, the first UV/Vis spectrum of the sample solution was recorded.

Evaluation of Data: The potentiometric data (95 points) were analysed by using the HypSpec program[36] (Protonic software, 2014), which uses non-linear least-squares methods. The stability constants were refined by minimizing the objective function, the sum of squares U. U is defined by Equation (1):

$$U = \Sigma_{i=1,np} W_i r_i \qquad (1)$$

in which W_i is a (diagonal) weight and r_i is a residual (i.e., the difference between observed and calculated pH).[36,37] To estimate the standard deviations of the absorbances, an absorbance-error function was determined by scanning a slightly acidic solution of $K_2Cr_2O_7$ (Grüssing, 99 %) about 20 times in the region 235–310 nm. HypSpec was then able to calculate the weights and yielded a single scale, σ, through which the quality of fit could be estimated. Moreover, HypSpec adjusted the molar absorptivities and defined the minimum number of absorbing main species by performing a factor analysis (= in HypSpec a singular value decomposition of the absorption matrix. The singular values should be positive or zero in the absence of experimental errors. The number of positive values is the same as the number of absorbing species, that is, the number of independent columns in the data).[36] To reduce the number of refining parameters, a 0.01 M $Cu(ClO_4)_2\cdot 6H_2O$ solution was scanned and the corresponding species "Cu" was set as "known".

Synthesis and Characterization of Compounds in General: All reactions were carried out in aqueous solution under ambient conditions. Solid compounds formed during the reaction or that did not dissolve after a certain time were separated from the reaction solution by filtration through a glass filter frit (G3 or G4) and/or by centrifuging for 12 min at 3000 rpm. All chemicals purchased for the synthesis of the compounds were used without further purification. Table S2 in the Supporting Information shows all the chemicals, their purity and their manufacturers.

Copper(II) Hydroxide: Copper(II) sulfate pentahydrate (99.9 g, 0.400 mmol) was dissolved in boiling water. The blue solution was cooled to 50 °C and, within 10 min, a 25 % NH_4OH solution (69.6 mL, 0.930 mol) was added dropwise with stirring, until the reaction mixture became blue-violet. The greenish-blue precipitate was allowed to settle and the slightly alkaline solution was separated from the solid component by decantation. The precipitate was washed with water (2 × 800 mL), suspended in water (600 mL) and cooled to 10 °C. Sodium hydroxide (83.00 g, 2.075 mol) was dissolved in water (337 mL) and added to the blue suspension under continuous stirring at 10 °C. The light-blue precipitate was decanted and washed with water (600 mL), until the wash solution had a neutral pH and was free of sulfate. Washing with acetone, decanting (3 × 100 mL) and drying for 1 d at 45 °C gave copper(II) hydroxide (27.1 g, yield: 69 %) as a homogeneous light-blue powder, which was stored in a brown flask to protect from light.

Characterization of the Synthesized Compounds: To determine the amount of carbon and hydrogen in the bulk sample, elemental analyses were performed with Vario Micro cube and Vario El instruments. UV/Vis spectra were recorded with Cary50 conc UV/Vis (solution) and Cary500 Scan UV/Vis/NR spectrometers (solid samples). Because only the diffuse reflectance spectra could be determined on the latter spectrometer, the measured data was converted into absorption data by using the Kubelka–Munk Equation (2):[48]

$$f(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{K}{S} \qquad (2)$$

in which R_∞ is the relative reflectivity of an infinitely thick layer of a sample, K is the absorption coefficient of the sample and S is the scattering coefficient of the sample.

For measurement, the samples were mixed with barium sulfate to minimize the intensity of the colour so that absorption follows the Kubelka–Munk function. Owing to an automatic detector change at 800 nm by the Cary500 Scan UV/Vis-NR spectrometer, small absorption jumps at this wavelength could not be prevented.

X-ray Crystallography: Crystals suitable for single-crystal X-ray diffraction were selected by using a microscope (Leica MZ6 with polarization filters), covered with paraffin oil and mounted either on a micro mount or a loop. The measurements were performed at 100, 173 or 300 K with Oxford XCalibur 3 and d8Venture diffractometers with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods (ShelxS2014) and refined by full-matrix, least-squares calculations on F^2 (ShelxL2014).[49] All non-hydrogen atoms were initially located and later refined anisotropically; hydrogen atoms were refined isotropically. Suitable intra- and intermolecular hydrogen bonds to locate hydrogen atoms on the difference Fourier map in compounds **1**, **2**, **4** and **5** were estimated by using Ortep-3 2.02.[50] Owing to the poor crystallinity of **3**, hydrogen atoms bonded to solvent oxygen atoms could not be located properly and therefore were omitted. In the case of **1**, some oxygen atoms are disordered and therefore the corresponding hydrogen atoms were omitted. C–H bonds and the corresponding angles were idealized (a C–H bond length of 1.000 Å and angles of approximately 108.9° were assumed). Shelxle (version 7.25)[51] was used as a graphical user interface for . Powder X-ray diffraction was performed with a Huber G670 diffractometer with Co-$K_{\alpha1}$ radiation (λ = 1.788965 pm) and a Ge-111 monochromator at room temperature. The measurement range was 5.0–99.98°. The STOE WinX$^{\mathrm{Pow}}$ software package (version 2.21)[52] was used to visualize the powder diffraction data (GRAPHIC) and to calculate the theoretical pattern from single crystal data (THEO).

CCDC 1423088 (for **1**), 1423089 (for **2**), 1423090 (for **3**), 1423091 (for **4**) and 1423092 (for **5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Synthesis of $\mathrm{Li_7[Cu_8(L\text{-}tartH_{-2}\text{-}\kappa^4\mathit{O}^1,\mathit{O}^2,\mathit{O}^3,\mathit{O}^4)_4(L\text{-}tartH_{-1}\text{-}\kappa^3\mathit{O}^1,\mathit{O}^2,\mathit{O}^4)_2\ (H_2O)_6]NO_3\cdot 19H_2O}$ (1): A copper nitrate solution (7 mL, 0.772 mol L^{-1}, 5.40 mmol, 4.00 equiv.) was added dropwise to a solution of L-(+)-tartaric acid (4.05 mmol, 608 mg, 3.00 equiv.) and lithium hydroxide monohydrate (14.8 mmol, 624 mg, 11.0 equiv.) in distilled water (5 mL). The resulting deep-blue reaction solution was stirred for 60 min at room temperature and filtered. Methanol (1 mL) was added to the filtrate (1 mL). After some months of slow evaporation at 4 °C, a few blue blocks of **1** among an amorphous blue powder were collected. The product is very soluble in water, and loss of crystallinity occurs after a few days at room temperature.

Synthesis of $\mathrm{K_2Na_4[Cu(L\text{-}tartH_{-2}\text{-}\kappa^2\mathit{O}^2,\mathit{O}^3)_2]\cdot 12H_2O}$ (2): Potassium sodium L-(+)-tartrate tetrahydrate (7.80 mmol, 2.20 g, 1.00 equiv.) was dissolved in distilled water (5 mL) at 65 °C. Then sodium hydroxide (12.5 mmol, 0.500 g, 1.60 equiv.), potassium hydroxide (12.1 mmol, 0.800 g, 1.55 equiv.) and copper hydroxide (10.3 mmol, 1.00 g, 1.32 equiv.) were added stepwise to the clear solution. The resulting deep-blue reaction mixture was stirred at 65 °C for another 20 min, filtered and centrifuged. Concentration of the viscous deep-blue solution with KOH yielded **2** as blue rods after several weeks (1.044 g, yield: 36.0 %). The product was very soluble in water (pH 12.5) and a small amount seemed to decompose to insoluble black CuO; drying in vacuo resulted in the loss of crystallinity. UV/Vis: $\lambda_{\max}$(H_2O) = 673 nm; $\lambda_{\max}$(crystal) = 656 nm. The powder X-ray diffraction pattern gave good agreement with that calculated on the basis of the single-crystal diffraction studies and indicated the product was homogeneous (see Figure S26 in the Supporting Information).

Synthesis of $\mathrm{Na_6[Cu(L\text{-}tartH_{-2}\text{-}\kappa^2\mathit{O}^2,\mathit{O}^3)_2]\cdot 9H_2O}$ (3): NaOH (99.00 mmol, 3.960 g, 11.00 equiv.) and L-(+)-tartaric acid (16.00 mmol, 2.402 g, 1.778 equiv.) were carefully mixed together in distilled water (7 mL) at 4 °C. The reaction mixture was heated at 60 °C, until all components dissolved. Then copper(II) hydroxide (9.00 mmol, 878 mg, 1.00 equiv.) in water (1 mL) was added dropwise and the resulting deep-blue suspension was stirred at 62 °C for 1 h. To separate the blue solution from remaining copper(II) hydroxide, the mixture was filtered and centrifuged. The concentration of the viscous deep-blue solution with KOH yielded **3** as blue crystals after several weeks (2.85 g, yield: 48.3 %). The product was very soluble in water (pH 12.5) and drying in vacuo resulted in the loss of crystallinity. UV/Vis: $\lambda_{\max}$ (H_2O) = 671 nm (ε = 22.28 dm^3 mol^{-1} cm^{-1}); $\lambda_{\max}$(crystal) = 661 nm. $C_8H_4CuNa_6O_{12}\cdot 9H_2O$ (655.73): calcd. C 14.65, H 3.38; found C 14.46, H 3.33. The powder X-ray diffraction pattern gave good agreement with that calculated on the basis of the single-crystal diffraction studies and indicated the product was homogeneous (see Figure S25).

Synthesis of $\mathrm{Na_6[Cu(L\text{-}tartH_{-2}\text{-}\kappa^2\mathit{O}^2,\mathit{O}^3)_2]\cdot 14H_2O}$ (4): NaOH (99.00 mmol, 3.960 g, 11.00 equiv.) and L-(+)-tartaric acid (16.00 mmol, 2.402 g, 1.778 equiv.) were carefully mixed together in distilled water (7 mL) at 4 °C. The reaction mixture was heated at 60 °C, until all components dissolved. Then copper(II) hydroxide (9.00 mmol, 878 mg, 1.00 equiv.) in water (1 mL) was added dropwise and the resulting deep-blue suspension was stirred at 62 °C for 2.5 h. To separate the blue solution from the remaining copper(II) hydroxide, the mixture was filtered and centrifuged. Large blue crystals of **4** were isolated after 1 h following the addition of ethanol (15 mL) to the reaction solution (5 mL) and diluting with water (5 mL).

Synthesis of $\mathrm{Cs_6[Cu(L\text{-}tartH_{-2}\text{-}\kappa^2\mathit{O}^2,\mathit{O}^3)_2]\cdot 8H_2O}$ (5): Caesium hydroxide monohydrate (50.0 mmol, 8.40 g, 8.33 equiv.) and L-(+)-tartaric acid (8.00 mmol, 1.20 g, 1.33 equiv.) were mixed together in distilled water (4 mL) at 4 °C. The reaction mixture was warmed to room temperature and copper(II) hydroxide (6.00 mmol, 585 mg, 1.00 equiv.) in water (1 mL) was added dropwise. The deep-blue reaction mixture was stirred for 2 h at room temperature and centrifuged. The concentration of the deep-blue solution with KOH yielded **5** as blue crystals after several weeks and, as side-products, black CuO and red Cu_2O (2.60 g). The product was very soluble in water (pH 12.5), and a small amount seemed to decompose to insoluble CuO; dried crystals of **4** are very hygroscopic and decompose within a few hours. UV/Vis: $\lambda_{\max}$(H_2O) = 671 nm; $\lambda_{\max}$(crystal) = 591sh, 669 nm.

Solubility Studies in General: Solubility studies were performed in aqueous solution under ambient conditions. Copper hydroxide was prepared as described above; L-(+)-tartaric acid (Fluka, ≥99.5 %) was used without any further purification. The 1.0 M NaOH solution (Fischer Chemical, factor limits 0.999–1.001) was standardized against potassium hydrogen phthalate (Aldrich, ≥99.95 %) as a primary standard. Solid compounds were separated from the reaction solution by using a glass filter crucible and a Büchner flask.

Study Considering $\mathrm{CuH_{-4}}$: $Cu(OH)_2$ (292.7 mg, 3.000 mmol) was suspended in 1 M NaOH (6 mL, 6.000 mmol) and stirred for 1 h. The blue reaction mixture was filtered and the light-blue solid washed with acetone and dried at 50 °C overnight. The filtrate was clear and colourless, yield 291.7 mg.

Study Considering $\mathrm{CuLH_{-4}}$: $Cu(OH)_2$ (292.7 mg, 3.000 mmol) and L-(+)-tartaric acid (450.2 mg, 3.000 mmol) were suspended in 1 M

NaOH (6 mL, 6.000 mmol) and stirred for 1 h. The blue reaction mixture was filtered and the light-blue solid washed with acetone and dried at 50 °C overnight. A clear deep-blue solution and a light-blue solid compound were isolated, yield 79.9 mg.

Study Considering CuL_2H_{-4}: $Cu(OH)_2$ (292.7 mg, 3.000 mmol) and L-(+)-tartaric acid (900.4 mg, 6.000 mmol) were dissolved in 1 M NaOH (6 mL, 6.000 mmol) and stirred for 1 h. The deep-blue solution was filtered and no remaining solid compounds were observed.

Quantum Chemical Calculations and Continuous Shape Measures: All calculations were performed by using the Orca (version 3.0.3)[53] software package. Structures were optimized with Ahlrich's latest version of the tzvp base set (in Orca: Def2/tzvp)[54] and with five different functionals (Becke ′88 exchange and Perdew ′86 correlation BP, the TPSS meta-GGA functional, the hybrid version of TPSS named TPSSh, the one-parameter hybrid version of the Perdew–Burke–Ernzerhof GGA functional named PBE0 and the popular B3LYP functional)[55]. COSMO[56] was used to simulate aqueous conditions. Atom-pairwise dispersion correction of the DFT energy was performed with Becke–Johnson damping.[57] Found stationary points were confirmed by subsequent frequency analyses at the corresponding level of theory. Coordinates for Cu_2*rac*-L_2H_{-4} were obtained from the molecular structure of $Li_4[Cu_2(\textit{rac}\text{-tartH}_{-2}\text{-}\kappa^2O^1,O^2{:}\kappa^2O^3,O^4)_2]\cdot 11.75H_2O$ previously described,[2] whereas the initial structure for $Cu_2L_2H_{-4}$ was prepared by using GaussView v. 5.0.8.[58] Continuous shape measures were calculated by using the SHAPE program established by Alvarez et al.[59]

Supporting Information (see footnote on the first page of this article): Details of the combined potentiometric UV/Vis titration, ORTEP plots, structural data including bonds and angles, conformational analysis, hydrogen bonds and continuous shape measures, UV/Vis spectra and powder diffraction data.

Keywords: Copper · Fehling's solution · Stability constants · UV/Vis spectroscopy

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