Supporting Information

Silver Complexation by Metallacryptates

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Crystals of **1a**.

Refinement Details

The structures were solved by Patterson method and refined on F^2 as implemented in SHELXL13. In the well ordered main residue, non-H atoms were refined with anisotropic displacement parameters and hydrogen atoms were placed in idealized positions as riding with $U_{iso}(H) = 1.2 U_{eq}(non-H)$. Each proline molecule and the ordered perchlorate was treated with rigid bond restraints (RIGU) as implemented in SHELXL13. Disorder models were applied for the terminal coordination of the axial copper atoms:

The remaining electron density of **1a** around the fourfold axis was modeled with a perchlorate coordinated to Cu1 and disordered solvent coordinated to Cu3. The tetrahedral perchlorate's geometry was restrained by using distance restraints on all Cl---O distances (1.4 Å) and similarity restraints on all O---O distances. The Cl atom was refined anisotropically; the four oxygen atoms were given one joint isotropic displacement parameter (0.048(5)). The electron density in axial position of Cu3 was modelled with a substitution disorder of one methanol molecule and two water molecules. Three symmetry independent electron density maxima were identified in difference Fourier maps. The highest is the coordinating O13, that is either one of two water molecules or the methanol oxygen. In covalent bonding distance to O13 electron density was assigned to a lower occupancy methyl-C (C11) that was restrained

to an O---C distance of 1.4 Å (s.u. 0.001). In hydrogen bond distance to O13 the third electron density maximum was assigned as second water molecule O14. The three atoms were refined with a joint isotropic displacement parameter (0.029(6)). The occupancy of O14 and C13 was refined adding up to 1×0.25 (0.58(5) $\times 0.25$ for C11).

The remaining electron density of **1b** around the fourfold axis could not be refined by using the same model as in **1a**. Difference Fourier maps show that both structures are different, most notable above Cu3 (Fig. S1). Careful investigation revealed an end-to-end disorder as most suitable model for **1b** where alternatively to the model in **1a** the terminal coordinating molecules occur disordered with switched positions. However, a refinement of the MeOH/2(H₂O) positions was not possible and the model was left at describing the two perchlorate positions and the coordinating oxygen of the solvent disorder.



Figure S1. Difference Fourier map of 1a (left) and 1b (right) without disorder models of axial Cu-coordination.

The perchlorate connected to Cu1 was treated with distance restraints (Cl---O = 1.43; O---O: 2.34); the alternative position (connected to Cu3) was initially treated similarly but then allowed for unrestrained geometry refinement. Both Cl-positions were assigned with a joint isotropic displacement parameter (0.028(3)). Oxygen atoms were refined with $U_{iso}(O) = 1.2$ $U_{iso}(Cl)$. The occupancy of the perchlorate positions was refined adding up to 1×0.25 (0.568(12)×0.25 for the molecule coordinated to Cu1). However, the coordinated oxygen atoms O9A/O9B were set to an occupancy of 1×0.25 to address the alternative solvent molecule coordination. As the model of **1a** indicates, the positions above Cu1 and Cu3 differ with respect to the size of the coordinating group. This is reflected in **2**, as the perchlorate position near Cu3 is tightly wrapped around the fourfold axis, whereas the perchlorate position near Cu1 is located next to the axis (Fig. S2).



Figure S2. Model of the two independent perchlorate anions disordered around the fourfold axis in 1b.

The ratio of Ag1 to Na1 inside the cryptate **1b** was refined by constraining both atoms to the same position and anisotropic displacement parameters. Their occupancy was then refined to sum up to 1×0.25 (0.563(6) $\times 0.25$ for Ag1). A representation of the asymmetric units as displacement ellipsoid plot of **1a** and **1b** including the naming scheme is given in Fig. S3.



Figure S3. Displacement ellipsoid plot (drawn at 80% probablility) of 1 (left) and 2 (right).



Figure S4. ESI mass spectra of 0.1 mM solution of 1(Na) (above) or 1a (below) in methanol.





Figure S5. ESI mass spectra of 0.1 mM solution of 1(Na) (above) or 1a (below) in water.



Figure S6. ESI mass spectrum of a 0.1 mM solution of 1(Na) in methanol/water 9:1 (v/v) mixture. Below is reported the spectrum in the 1000-2000 m/z range.

100



Figure S7. ESI mass spectrum of a 0.1 mM solution of **1a** in methanol/water 9:1 (v/v) mixture. Below is reported the spectrum in the 1000-2000 m/z range.

MC6 CONE 50 11 (0.189) Cm (7:21)

100



Figure S8. Calculated molar absorbances of $[Cu(Pro)_2]$ (black), $Cu(ClO_4)_2 \cdot 6H_2O$ (red), **1**(Na) (dashed blue) and **1a** (dashed magenta) in methanolic solution. The molar spectra of **1**(Na) and **1a** were divided by a factor of 6 (*i.e.* normalized for the Cu²⁺concentration).



Figure S9. Calculated molar absorbances of $[Cu(Pro)_2]$ (black), $Cu(ClO_4)_2 \cdot 6H_2O$ (red), **1**(Na) (dashed blue) and **1a** (dashed magenta) in aqueous solution. The molar spectra of **1**(Na) and **1a** were divided by a factor of 6 (*i.e.* normalized for the Cu²⁺concentration).



Figure S10. Spectra of the dilution titration of **1a** in methanol (4.18 mM diluted to 32.6 μ M, no background salt added).



Figure S11. Spectra of the dilutiontitration of **1a** in water (4.95 mMdiluted to 38.7 μ M, no background salt added).



Figure S12. Spectra of the dilution titration of $\mathbf{1}$ (Na) in methanol with a 0.1 M NaClO₄ solution in methanol (5.02 mMdiluted to 39.2 μ M).



Figure S13. Spectra of the dilution titration of 1(Na) in water with a 0.1 M NaClO₄ solution in water (5.14 mM diluted to 40.2 μ M).