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Preparation and Characterization of Chiral Copper 12-Metallacrown-4 Complexes, Inorganic Analogues of Tetraphenylporphyrinatocopper(II)

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Transition metal complexes of chiral ligands have been applied with great success to the enantioselective synthesis of organic compounds, and also show promise for chiral recognition of organic compounds in solution.¹ While discrete mononuclear complexes of chiral ligands are often readily prepared, the controlled synthesis of chiral, polynuclear clusters poses considerable challenges.² Metallacrowns, inorganic analogues of organic crown ethers,³ offer one solution to this problem, as we recently reported the facile preparation of chiral, face-differentiated 15-metallacrown-5 complexes derived from optically pure α -aminohydroxamic acids.⁴ We have now extended this strategy to the preparation of chiral 12-metallacrown-4 complexes through the use of enantiomerically pure β -aminohydroxamic acids. Herein, we describe structural and spectroscopic properties of these compounds, which confirm the solution stability of the chiral clusters and reveal that these 12-metallacrown-4 complexes adopt structures reminiscent of complexes of the versatile *meso*-tetraphenylporphyrinato ligand.

Achiral 3-aminopropionohydroxamic acid (β -alaninehydroxamic acid) generates the copper 12-metallacrown-4 complex $\text{Cu}^{\text{II}}[12\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\beta\text{-aha})\text{-4}](\text{ClO}_4)_2$ in aqueous solution.⁵ We have now demonstrated that chiral β -aminohydroxamic acids may also be used to prepare metallacrowns under similar conditions. The synthesis of such ligands relies on the isolation of multigram quantities of optically pure β -amino acids or their esters. Our approach to the synthesis of *S*-3-amino-3-phenylpropionohydroxamic acid (*S*- β -phenylalaninehydroxamic acid) is shown in Supporting Information as Scheme S1, and relies on precedented methods for the synthesis, esterification, and resolution of β -amino acids.^{6,7} This strategy allows access to both antipodes of β -phenylalaninehydroxamic acid (*R*- and *S*- H_2 - β -pheha) in multigram quantities (in about 10% overall yield) using readily available, inexpensive starting materials, and also allows for the introduction of functional groups into the ligands through the use of appropriately substituted benzaldehydes.⁸

Chiral pentacopper 12-metallacrown-4 complexes were obtained by the reaction of one antipode of the chiral hydroxamic acids with an appropriate copper(II) source in the presence of a weak base (Figure 1).⁶ Thus, $\text{Cu}^{\text{II}}\text{SO}_4[12\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{S}-\beta\text{-pheha})\text{-4}](\text{S,S,S,S-1})$ was prepared by admixture of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, *S*- H_2 - β -pheha, and NaOAc in water, and was isolated as a green crystalline solid by filtration in 89% yield. Similarly, stirring $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, *S*- H_2 - β -pheha, and NaOAc in methanol yielded $\text{Cu}^{\text{II}}(\text{OAc})_2[12\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{S}-\beta\text{-pheha})\text{-4}](\text{S,S,S,S-2})$ and $\text{Cu}^{\text{II}}\text{Cl}[12\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{S}-\beta\text{-pheha})\text{-4}]\text{Cu}^{\text{II}}(\text{OAc})_3(\text{S,S,S,S-2'})$, which cocrystallized in 79% overall yield [based on Cu^{II}]. The source of the chloride anion in *S,S,S,S-2'* is ascribed to substoichiometric amounts of HCl present in bulk samples of *S*- H_2 - β -pheha.⁶ These metallacrowns are soluble and stable in polar protic media, and were subjected to comprehensive physicochemical characterization. The FAB-MS of crystalline *S,S,S,S-1* is dominated by a molecular ion (M^+) envelope corresponding to $\{\text{Cu}^{\text{II}}\text{SO}_4[12\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{S}-\beta\text{-pheha})\text{-4}] + \text{H}\}^+$, whereas that of *S,S,S,S-2* contains an M^+ peak corresponding to $\{\text{Cu}^{\text{II}}\text{OAc}[12\text{-MC}_{\text{Cu}^{\text{II}}\text{N}(\text{S}-\beta\text{-pheha})\text{-4}]\}^+$. Examination of methanol solutions of *S,S,S,S-1* and *S,S,S,S-2/S,S,S,S-2'* by electrospray ionization mass spectrometry (ESI-MS) revealed intact M^+ envelopes which are entirely consistent with those obtained for solid samples. The visible spectra of methanol solutions of *S,S,S,S-2/S,S,S,S-2'* and *R,R,R,R-2/R,R,R,R-2'* (prepared identically, substituting *R*- H_2 - β -pheha)⁹ exhibited a d–d band at 602 nm ($\epsilon = 435 \text{ M}^{-1} \text{ cm}^{-1}$), and the CD spectra over the same range revealed equal but opposite extinction of polarized visible light by the two enantiomeric complexes (Figure S1), behavior which has been observed previously in chiral, face-differentiated 15-metallacrown-5 complexes prepared from α -aminohydroxamic acids.⁴ Thus, these copper(II) metallacrowns retain their structure and their chirality in polar, protic media.

Single crystals of cocrystallized *S,S,S,S-2/S,S,S,S-2'* proved amenable to X-ray structural analysis, which revealed the presence of two crystallographically independent metallacrowns in the asymmetric unit of the triclinic (*P1*) unit cell.¹⁰ The 12-metallacrown-4 motif is present in both complexes, with square planar or square pyramidal $\text{Cu}(\text{II})$ in both the ring and central

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