

# Allosteric pitch length tuning of a dinuclear double helicate

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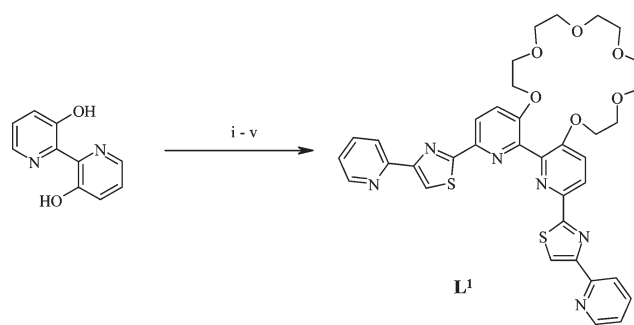
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Self assembly of the ditopic ligand **L**<sup>1</sup> with Cu<sup>2+</sup> gives the dinuclear double helicate [Cu<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>]<sup>4+</sup>, which can further coordinate s-block cations. This coordination alters the helicate pitch to a variety of different lengths depending on the size and charge of the guest cation.

The defining characteristic of a transition metal helicate is that one or more organic ligands wrap about and coordinate to a series of metal ions producing a helical axis. The distance between turns of the helicate is referred to as the pitch length and is usually measured by the distance between the two metal ions.<sup>1</sup> This distance can vary considerably for different helicate systems and is usually programmed within the ligand chain or is a consequence of the preferred metal coordination geometry. The helicates derived from 3,3'-polymethylene-2,2'-bi-1,10-phenanthroline and Cu<sup>+</sup> provide an example of how pitch lengths vary. When the ligand contains a short dimethylene group linking the two phenanthroline units a dicopper(i) double helicate is formed, with a pitch length of 2.92 Å, whereas the more flexible tetramethylene linker gives a helicate with a pitch of 3.59 Å.<sup>2</sup> Thus a relatively subtle change in the composition of the ligand can have a dramatic effect on the metal–metal distance. Although the pitch lengths of different helicates vary considerably, each ligand is programmed at the synthetic stage to give, upon reaction with a metal ion, a helicate with a preprogrammed pitch length. Herein, we describe a new ditopic ligand **L**<sup>1</sup> which forms, upon reaction with Cu<sup>2+</sup>, a dinuclear double helicate. The pitch length of this helicate can be modulated by coordination of different s-block metal cations to the crown ether moiety.

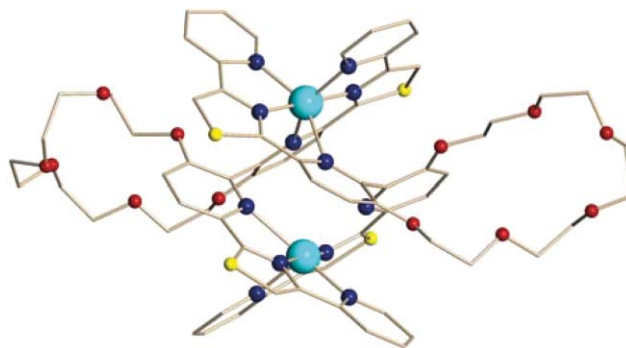
The ditopic ligand **L**<sup>1</sup> was prepared from 2,2'-bipyridine-3,3'-diol as outlined in Scheme 1.<sup>†</sup> This ligand contains a potentially hexadentate pyridyl–thiazole ligand chain with an additional “external” crown ether binding site connecting the two halves of the central bipyridine moiety. Upon reaction of **L**<sup>1</sup> with Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O in MeCN a green solution was produced and ESI-MS was consistent with the formation of a dinuclear double helicate, with an ion at *m/z* 1846 corresponding to [Cu<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>](ClO<sub>4</sub>)<sub>3</sub><sup>+</sup>. Slow diffusion of CH<sub>3</sub>CO<sub>2</sub>Et produced green crystals from which single-crystal diffraction studies established the formation of a dinuclear double helical structure [Cu<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub> **1**. In the crystal, the ligand splits into two bis-tridentate binding domains, with two Cu<sup>2+</sup> ions coordinated by two bridging ligands in a double-helical arrangement (Fig. 1). Each of the Cu<sup>2+</sup> centres



**Scheme 1** Reagents and conditions: i, penta(ethylene glycol) di-*p*-toluenesulfonate, DMF, NaH, 67%; ii, *m*CPBA, CH<sub>2</sub>Cl<sub>2</sub>, 66%; iii, TMSCN, PhCOCl, CH<sub>2</sub>Cl<sub>2</sub>, 80%; iv, H<sub>2</sub>S, Et<sub>3</sub>N, EtOH, 88%; v, 2-( $\alpha$ -bromoacetyl)pyridine, EtOH, 70%.

has a distorted octahedral geometry formed by coordination of two thiazole–pyridyl tridentate N-donor units [1.927(4)–2.192(5) Å]. The longest Cu–N bonds arise from coordination to the central bipyridine unit [2.397(4)–2.517(5) Å], presumably as a consequence of the poor ligating ability of the pyridyl–thiazole–pyridyl unit.<sup>3</sup> Each ligand is twisted about the bond between the two central pyridyl rings (NCCN torsion angles = 64.0 and 59.9°).

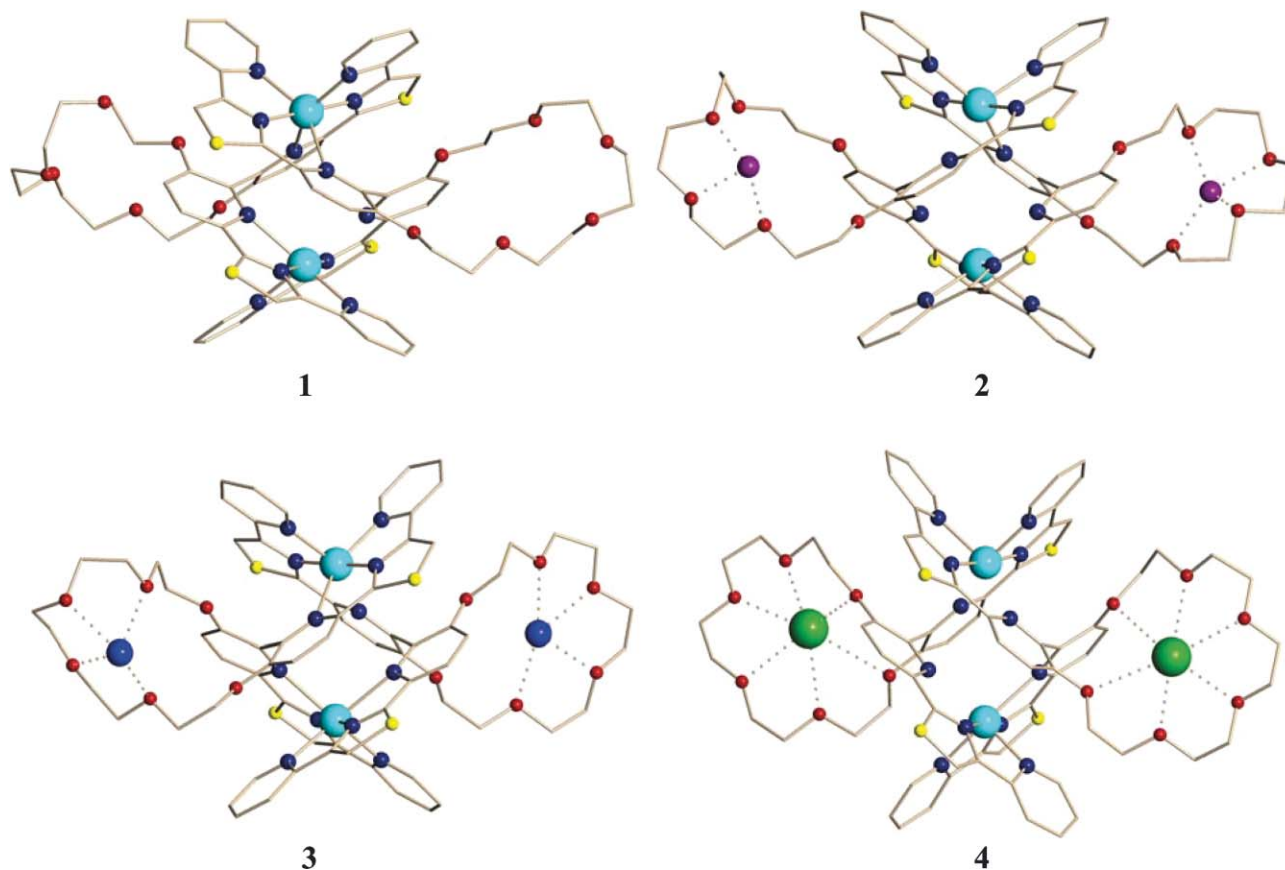
Reaction of **1** with either Li<sup>+</sup>, Na<sup>+</sup> or Ba<sup>2+</sup> gives ions in the ESI-MS corresponding to [Cu<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>Li<sub>2</sub>](ClO<sub>4</sub>)<sub>5</sub><sup>+</sup>, [Cu<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>Na<sub>2</sub>](ClO<sub>4</sub>)<sub>5</sub><sup>+</sup> and [Cu<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>Ba<sub>2</sub>](ClO<sub>4</sub>)<sub>7</sub><sup>+</sup> (*m/z* = 2059, 2091 and 2518 respectively), indicating the crown ether moiety in **1** can further coordinate s-block metal cations. In each case crystals were obtained in a similar manner to **1** and single-crystal diffraction studies established the formation of the species [Cu<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>Li<sub>2</sub>]<sup>6+</sup> **2**, [Cu<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>Na<sub>2</sub>]<sup>6+</sup> **3** and [Cu<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>Ba<sub>2</sub>]<sup>8+</sup> **4** (Fig. 2). All the complexes are structurally very similar to the parent complex **1**, as in each case the ligand splits into two tridentate domains, with two



**Fig. 1** Structure of the complex cation in [Cu<sub>2</sub>(L<sup>1</sup>)<sub>2</sub>](ClO<sub>4</sub>)<sub>4</sub> (**1**).

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**Fig. 2** Structures of the complex cations in  $[\text{Cu}_2(\text{L}^1)_2](\text{ClO}_4)_4$  (**1**),  $[\text{Cu}_2(\text{L}^1)_2\text{Li}_2](\text{ClO}_4)_6$  (**2**),  $[\text{Cu}_2(\text{L}^1)_2\text{Na}_2](\text{ClO}_4)_6$  (**3**) and  $[\text{Cu}_2(\text{L}^1)_2\text{Ba}_2](\text{ClO}_4)_8$  (**4**).

**Table 1** Selected bond lengths and angles for structures 1–4

	Cu–Cu distance (Å)	Inter-domain torsion angles <sup>a</sup> (°)	Cu–N bond length <sup>b</sup> (Å)
$[\text{Cu}_2\text{L}_2]^{4+}$ <b>1</b>	4.871(1)	62.0	2.452
$[\text{Cu}_2\text{L}_2\text{Li}_2]^{6+}$ <b>2</b>	5.034(1)	66.1	2.500
$[\text{Cu}_2\text{L}_2\text{Na}_2]^{6+}$ <b>3</b>	5.043(1)	70.3	2.479
$[\text{Cu}_2\text{L}_2\text{Ba}_2]^{8+}$ <b>4</b>	5.261(1)	80.2	2.523

<sup>a</sup> Average of the two NCCN torsion angles. <sup>b</sup> Average of the central bipyridyl Cu–N bond lengths.

octahedral  $\text{Cu}^{2+}$  ions coordinated by two bridging ligands in a double-helical arrangement. The only major differences are the inter-domain torsion angles, the pitch length and, to a much lesser degree, the Cu–N bond lengths between the metal ions and the central bipyridine groups (Table 1).

The inter-domain torsion angle for **1** is substantially less than  $90^\circ$  producing a helicate with a shallow twist between the two coordination domains. One possible reason for this is the poor ability of a pyridyl–thiazole–pyridyl unit to act as a tridentate coordination domain arising from the divergent nature of the central five-membered thiazole ring.<sup>3</sup> Upon reaction of this helicate with  $\text{Li}^+$ , complex **2** is formed where the lithium ions are coordinated to the oxygen atoms of the crown ether unit. However, due to the small size of the lithium ion, the crown ether only partially coordinates *via* the “outer” oxygen atoms of the crown ether, with one of the lithium ions coordinated to four oxygen atoms [2.00(2)–2.12(2) Å] and the other forming only three Li–O bonds [1.97(2)–2.32(2) Å]. Even though only the “outer” oxygen atoms of the crown ether moiety are coordinated, an

increase in the inter-domain torsion angle and pitch length is observed. In the  $\text{Na}^+$  complex **3** both sodium ions are again coordinated by the “outer” oxygen atoms of the crown ether [2.372(6)–2.574(5) Å] but in this case, due to the larger size of the metal ions, both ions are coordinated by four oxygen atoms. This coordination of the larger sodium ion again increases the inter-domain torsion angle and pitch length compared to the lithium analogue. In the case of  $\text{Ba}^{2+}$ , which is a much better match to the [20]crown-6 fragment, all *six* of the crown ether oxygen atoms coordinate the metal ions [2.669(4)–3.265(6) Å] with the longest bonds arising from the aryl oxygen atoms [3.027(4)–3.265(6) Å]. Coordination of  $\text{Ba}^{2+}$  to the crown ether moiety increases the inter-domain torsion angles to  $79.46^\circ$  and  $80.87^\circ$ , values much closer to  $90^\circ$  which is the ideal inter-domain torsion angle for a dinuclear double helicate formed by a bis-tridentate ligand and an octahedral metal ion. As a result of coordination by barium ions the pitch length is increased to 5.261(1) Å.

Thus, the pitch length (and the torsion angle) of the helicate can be altered by addition of metal ions to a remote site present within

the helicate assembly. Indeed, the helicate can adopt a number of possible states as the pitch length can be varied by reaction with different s-block metal ions.

This control over the structure, as with other examples of similar ligands, can be attributed to two factors,<sup>4</sup> firstly, an allosteric effect; upon coordination of the crown ether unit the inter-domain torsion angle increases. This is most clearly observed in the barium analogue **4** where the torsion angle must increase to facilitate better overlap between the aryl oxygen atoms and the barium ions. However, the change in structure could also be due to an electrostatic effect. Thus, upon coordination of the crown ether rings with either mono- or divalent metal ions the overall charge of the complex will rise. An increase in the Cu–Cu distance would reduce the electrostatic repulsion, again increasing the pitch length and torsion angle. However, careful comparison of the structures indicates that both effects are important. The lithium and sodium complexes **2** and **3** both have an overall charge of 6+, with the only difference being the size of the s-block metal ions. This difference in size does have a small, but measurable effect on the pitch length (*ca.*  $\Delta 0.01$  Å) and torsion angle ( $\Delta 4.2^\circ$ ). In contrast, comparison of the sodium **3** and barium **4** analogues, where the size difference of the cations is comparable to the difference in **2** and **3** but where barium is dicationic, shows a much greater increase in both the pitch length ( $\Delta 0.22$  Å) and torsion angle ( $\Delta 10.0^\circ$ ). Given these results, it is clear that no one factor is dominant in control of the pitch length and that both electrostatic and allosteric effects could play important roles.

This system is the first example of a metallo-helical array in which the pitch length can be varied according to the size and charge of an s-block ion present in a remote crown ether site. Furthermore, preliminary experiments indicate a dramatic change in the EPR spectrum upon addition of barium ions to a solution of **1**, presumably due to a change in the pitch-dependent metal–metal communication.

## Notes and references

† Ligand **L**<sup>1</sup> was synthesised in 5 steps from 2,2'-bipyridine-3,3'-diol and was fully characterised by <sup>1</sup>H NMR, elemental analysis and mass spectroscopy. <sup>1</sup>H NMR [400 MHz, CDCl<sub>3</sub>]:  $\delta$  8.67 (2H, d,  $J = 4.5$ , py), 8.37 (2H, d,  $J = 8.1$ , py), 8.26 (2H, d,  $J = 8.0$ , py), 8.13 (2H, s, th), 7.81 (2H, ddd,  $J = 7.7, 7.6, 3.1$ , py), 7.49 (2H, d,  $J = 8.5$  Hz, py), 7.25 (2H, m, py), 4.25 (4H, m, –CH<sub>2</sub>–), 3.79 (4H, m, –CH<sub>2</sub>–), 3.70–3.55 (12H, m). ESI-MS:  $m/z$  711 (M + H<sup>+</sup>). Found: C, 61.1; H, 5.0; N, 11.4%; C<sub>36</sub>H<sub>34</sub>N<sub>6</sub>O<sub>6</sub>S<sub>2</sub> requires: C, 60.8; H, 4.8; N, 11.8%.

**1**: The complex was synthesised by reaction of **L**<sup>1</sup> and Cu(ClO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O in MeCN, isolated by slow diffusion of CH<sub>3</sub>CO<sub>2</sub>Et. Complexes **2–4** were all prepared by addition of an excess of the appropriate cation to the MeCN solution and slow diffusion of CH<sub>3</sub>CO<sub>2</sub>Et (CH<sub>2</sub>Cl<sub>2</sub> in the case of **4**). Elemental analysis and ESI-MS were as expected.

X-Ray single-crystal diffraction data for structures **1–4** were collected on a Bruker Proteum-CCD area detector diffractometer (Cu rotating anode with Osmic beam focussing) under a stream of cold nitrogen. Crystal data **1**(ClO<sub>4</sub>)<sub>2</sub>·2.5 MeCN·0.5H<sub>2</sub>O;  $M = 2058.15$ , triclinic,  $P\bar{1}$ ,  $a = 13.5921(3)$ ,  $b = 17.9777(5)$ ,  $c = 18.9909(5)$  Å,  $\alpha = 72.997(2)$ ,  $\beta = 82.980(2)$ ,  $\gamma = 85.769(2)^\circ$ ,  $V = 4400.9(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_c = 1.553$  Mg m<sup>-3</sup>,  $F(000) = 2116$ ,  $\mu(\text{Cu}_{K\alpha}) = 3.360$  mm<sup>-1</sup>,  $T = 100$  K. A total of 31372

reflections were measured in the range  $2.45 \leq \theta \leq 70.35^\circ$  ( $hkl$  range indices  $-15 \leq h \leq 16$ ,  $-21 \leq k \leq 21$ ,  $-22 \leq l \leq 23$ ), 14656 independent reflections ( $R_{\text{int}} = 0.0545$ ). The structure was refined on  $F^2$  to  $R_w = 0.2307$ ,  $R = 0.0830$  [11800 reflections with  $I > 2\sigma(I)$ ] and GOF = 1.046 on  $F^2$  for 1282 refined parameters, largest difference peak and hole 2.743 and  $-0.572$  eÅ<sup>-3</sup>. CCDC reference number 270151. Crystal data **2**(ClO<sub>4</sub>)<sub>6</sub>·5 MeCN;  $M = 2364.55$ , monoclinic,  $P2(1)/c$ ,  $a = 18.949(2)$ ,  $b = 25.450(2)$ ,  $c = 22.770(2)$  Å,  $\beta = 112.518(5)^\circ$ ,  $V = 10144(1)$  Å<sup>3</sup>,  $Z = 4$ ,  $\rho_c = 1.548$  Mg m<sup>-3</sup>,  $F(000) = 4848$ ,  $\mu(\text{Cu}_{K\alpha}) = 3.532$  mm<sup>-1</sup>,  $T = 100$  K. A total of 65632 reflections were measured in the range  $2.52 \leq \theta \leq 70.25^\circ$  ( $hkl$  range indices  $-22 \leq h \leq 23$ ,  $-30 \leq k \leq 30$ ,  $-25 \leq l \leq 23$ ), 18563 independent reflections ( $R_{\text{int}} = 0.0360$ ). The structure was refined on  $F^2$  to  $R_w = 0.2228$ ,  $R = 0.0782$  [15741 reflections with  $I > 2\sigma(I)$ ] and GOF = 1.221 on  $F^2$  for 1314 refined parameters, largest difference peak and hole 1.693 and  $-1.679$  eÅ<sup>-3</sup>. CCDC reference number 270154. Crystal data **3**(ClO<sub>4</sub>)<sub>6</sub>·3 MeCN;  $M = 2314.55$ , triclinic,  $P\bar{1}$ ,  $a = 13.5033(3)$ ,  $b = 17.4605(4)$ ,  $c = 21.8269(5)$  Å,  $\alpha = 93.053(2)$ ,  $\beta = 94.952(2)$ ,  $\gamma = 106.653(1)^\circ$ ,  $V = 4895.5(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_c = 1.570$  Mg m<sup>-3</sup>,  $F(000) = 2368$ ,  $\mu(\text{Cu}_{K\alpha}) = 3.723$  mm<sup>-1</sup>,  $T = 100$  K. A total of 37678 reflections were measured in the range  $2.04 \leq \theta \leq 70.02^\circ$  ( $hkl$  range indices  $-16 \leq h \leq 16$ ,  $-20 \leq k \leq 20$ ,  $-26 \leq l \leq 25$ ), 16519 independent reflections ( $R_{\text{int}} = 0.0678$ ). The structure was refined on  $F^2$  to  $R_w = 0.2105$ ,  $R = 0.0809$  [9589 reflections with  $I > 2\sigma(I)$ ] and GOF = 0.944 on  $F^2$  for 1263 refined parameters, largest difference peak and hole 1.742 and  $-0.908$  eÅ<sup>-3</sup>. CCDC reference number 270152. Crystal data **4**(ClO<sub>4</sub>)<sub>8</sub>(H<sub>2</sub>O)<sub>2</sub>;  $M = 2655.02$ , triclinic,  $P\bar{1}$ ,  $a = 14.1100(3)$ ,  $b = 19.0281(5)$ ,  $c = 19.2925(5)$  Å,  $\alpha = 73.495(1)$ ,  $\beta = 80.584(1)$ ,  $\gamma = 75.378(1)^\circ$ ,  $V = 4781.9(2)$  Å<sup>3</sup>,  $Z = 2$ ,  $\rho_c = 1.844$  Mg m<sup>-3</sup>,  $F(000) = 2652$ ,  $\mu(\text{Cu}_{K\alpha}) = 10.595$  mm<sup>-1</sup>,  $T = 100$  K. A total of 37734 reflections were measured in the range  $2.40 \leq \theta \leq 70.21^\circ$  ( $hkl$  range indices  $-17 \leq h \leq 16$ ,  $-23 \leq k \leq 23$ ,  $-23 \leq l \leq 23$ ), 16319 independent reflections ( $R_{\text{int}} = 0.0534$ ). The structure was refined on  $F^2$  to  $R_w = 0.1724$ ,  $R = 0.0545$  [13719 reflections with  $I > 2\sigma(I)$ ] and GOF = 0.797 on  $F^2$  for 1368 refined parameters, largest difference peak and hole 1.603 and  $-0.816$  eÅ<sup>-3</sup>. CCDC reference number 270153. See <http://dx.doi.org/10.1039/b506199g> for crystallographic data in CIF or other electronic format.

As with many supramolecular crystal structures, all of those described herein contain regions of disorder associated with diffuse lattice solvent species (water/acetonitrile/non-coordinating perchlorate counter-ions) and the conformationally flexible crown ether fragments. Accordingly, high angle data were generally weak, necessitating the use of geometric restraints and constraints (in many cases throughout all stages of refinement) in attempt to model the disorder. Where such attempts failed to account for persistent peaks in the electron density map, a diffuse solvent correction was applied using the SQUEEZE routine in PLATON.<sup>5</sup> A full description of the refinement details is given in the electronic supplementary information (CIF). Notwithstanding the obvious problems associated with these structures, we are confident that the gross solutions are correct.

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