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# Construction of 1D and 2D Copper(I) Coordination Polymers Assembled by $PhS(CH_2)_nSPh$ ($n$ = 1, 2) Dithioether Ligands: Surprising Effect of the Spacer Length on the Dimensionality, Cluster Nuclearity and the Fluorescence Properties of the Metal–Organic Framework

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*Dedicated to the memory of Prof. Liliane G. Hubert-Pfalzgraf*

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Treatment of CuI with $PhSCH_2SPh$ in MeCN solution affords, by a self-assembly reaction, the monodimensional metal–organic coordination polymer $[Cu_4I_4\{\mu\text{-}PhS_2CH_2SPh\}_2]_n$ (**1**), in which $Cu_4(\mu^3\text{-}I)_4$ cluster units are linked by the dithioether ligand in a 1D necklace structure. In contrast, the reaction of $PhSCH_2CH_2SPh$ with CuI results in the formation of the metallopolymer $[(CuI)_2\{\mu\text{-}PhS(CH_2)_2SPh\}_2]_n$ (**2**). The 2D network of **2** is built from dimeric $Cu_2I_2$ units which are connected by 1,2-bis(phenylthio)ethane bridging ligands. The solid-state luminescence spectrum of **1** exhibits a strong emission around 532 nm, whereas a weak emission centred at 413 nm is observed in the case of **2**.


## Introduction

It is well established that interaction of various nucleophiles (L) such as phosphanes, aniline and pyridyl type ligands with copper(I) halides often affords tetranuclear cubane-like $Cu_4X_4L_4$ clusters by a self-assembly process.[1] The interest in these polymetallic systems, in particular those incorporating the $Cu_4I_4$ unit, stems from their remarkable photophysical properties,.[2] Therefore these compounds have also been the object of theoretical studies.[3] Less common is the incorporation of the tetranuclear $Cu_4I_4$ core in a metal–organic network. The known examples of 1D to 3D coordination polymers including $Cu_4I_4$ cores were assembled by using an alkanedinitrile ligand,[4] difunctional pyridyl ligands,[5] dimethylsufide and diethylsulfide,[6a,6b] a functionalized dithioether ligand,[6c] polydentate thioether macrocycles,[7] and a triselenoether macrocycle.[8] The topology of extended networks based on flexible bidentate thioether ligands has been shown in the case of silver(I) to be very dependent on the spacer between the coordinated functions.[9] Our interest in the coordination chemistry of bi- and polydentate thioether ligands[10] has led us to investigate the reactivity of the flexible dithioether ligands $PhS–(CH_2)_n–SPh$ ($n$ = 1–2) towards CuI in order to evaluate the influence of the spacer on the resulting framework.

## Results and Discussion

The reaction of CuI with an equimolar amount of bis(phenylthio)methane in acetonitrile gave colourless crystals of the general formula $[Cu_4I_4\{\mu\text{-}PhSCH_2SPh\}_2]_n$ (**1**) (Scheme 1). Modification of the molar ratio, for example from 1:1 to 1:2, had no influence on the composition of the resulting material, and only compound **1** was formed. This observation is in contrast to the results reported by Sheldrick et al., who used an alkanedinitrile ligand (L) to obtain the 1:1 and 2:1 coordination polymers, $[(CuI)_2L_2]$ and $[(CuI)_4L_2]$, respectively, from the appropriate molar ratio of reactants.[4]

The crystal structure of **1**, viewed along the $c$ axis in Figure 1, consists of cubane-like $Cu_4I_4$ clusters linked by bridging dithioether ligands to form an infinite chain with Cu–S distances of 2.292(2) and 2.301(2) Å. The Cu–I bond lengths range from 2.6077(11) to 2.7704(11) Å. The Cu···Cu distances [2.6173(18)–2.7864(14) Å], comparable to the sum of the van der Waals radii (2.8 Å), lie in the range of distances reported for this interaction in other structurally

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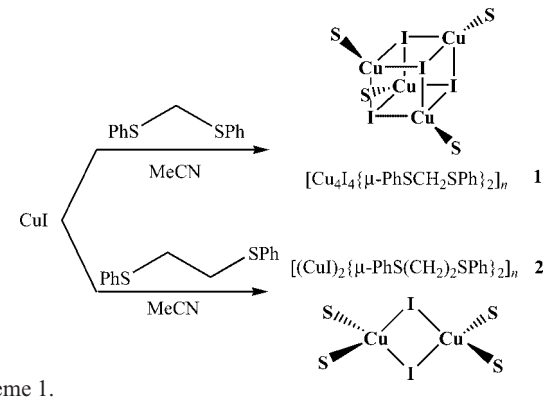


Scheme 1.

characterized $Cu_4I_4$ units. Two adjacent $Cu_4I_4$ cores are linked by two flexible dithioether ligands leading thus to the formation of a 1D necklace structure. Note also that the phenyl substituents adopt a parallel orientation with a short $C_{ipso}$–$C_{ipso}$ distance of 3.502 Å.

Despite the fact that the phenyl groups of neighbouring ribbons are somewhat interpenetrated, there are no close inter-ribbon interactions between the 1D chains of coordination polymer **1**, the separation between the midpoints of two adjacent $Cu_4I_4$ units being 11.64 Å (Figure 2).

The colourless crystals obtained from the reaction between equimolar amounts of CuI and 1,2 bis(phenylthio)-ethane in acetonitrile were identified by an X-ray study as the coordination polymer $[(CuI)_2\{\mu\text{-}PhS(CH_2)_2SPh\}_2]_n$ (**2**). This framework consists of centrosymmetric $Cu_2(\mu^2\text{-}I)_2$ rhomboid dimers, each connected to an adjacent unit via one $\mu^2$-bridging dithioether ligand (Figure 3). Each Cu atom is in a distorted tetrahedral environment, coordinated to the bridging iodido ligand and thioether group of two different ligands.

The 2D network resulting from this coordination mode includes centrosymmetric 24-membered metallomacrocycles constituted from four dithioether ligands, six Cu atoms and two iodido ligands (Figure 4). The average length of the two Cu–S bonds [2.3000(11) and 2.3855(10) Å] is somewhat greater than that in **1**. The Cu···Cu separation of 2.8058(11) Å is much greater than those observed in the above-mentioned $Cu_4I_4$ unit of **1**. A survey of the literature indicates that Cu···Cu separations vary in $[Cu(\mu^2\text{-}I)_2Cu]$ compounds. A dithioether-functionalized tetrathiafulvalene Cu complex was reported to have a relatively small Cu···Cu separation of 2.65 Å.[11a] Distances close to the value in **2** have been reported for $[Cu_2I_2[16]aneS_4]_n$ ([16]aneS$_4$ = 1,5,9,13-tetrathiacyclohexadecane) [2.8079(12) Å][7] and $[\{MeSi(CH_2SMe)_3\}CuI]_2$ [2.862(2) Å].[11b] A far longer

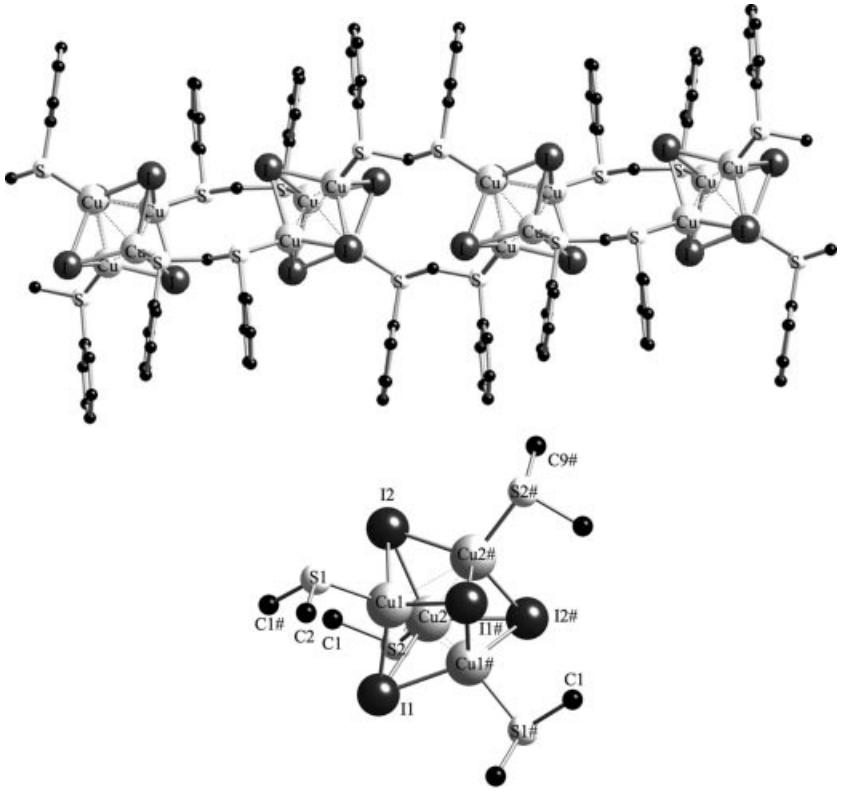


Figure 1. (top) View on the 1D chain of **1** along the *c* axis. H atoms are omitted for clarity. Selected bond lengths [Å]: Cu(1)–S(1) 2.292(2), Cu(2)–S(2) 2.301(2), Cu(1)–Cu(2) 2.7864(14), Cu(1)–Cu(1)#2 2.6173(18), Cu(1)–Cu(2)#2 2.6464(13), Cu(2)–Cu(2)#2 2.663(2), Cu(1)–I(1) 2.6486(15), Cu(1)–I(2) 2.7621(11), Cu(2)–I(2)#2 2.6077(10), Cu(2)–I(2) 2.6825(12), Cu(2)–I(1) 2.7704(11), I(1)–Cu(1)#2 2.6228(12), I(2)–Cu(2)#2 2.6077(11), C(1)–S(2) 1.804(7), C(1)–S(1)#1 1.818(7). (bottom) View of the tetranuclear $Cu_4(\mu^3\text{-}I)_4$ core of **1**. Only the *ipso* carbon atoms C2 and C9 of the phenyl groups are shown for clarity. Symmetry operations used to generate equivalent atoms: #1: $-x + 2, -y + 1, -z$; #2: $-x + 2, y, -z + 1/2$.

  

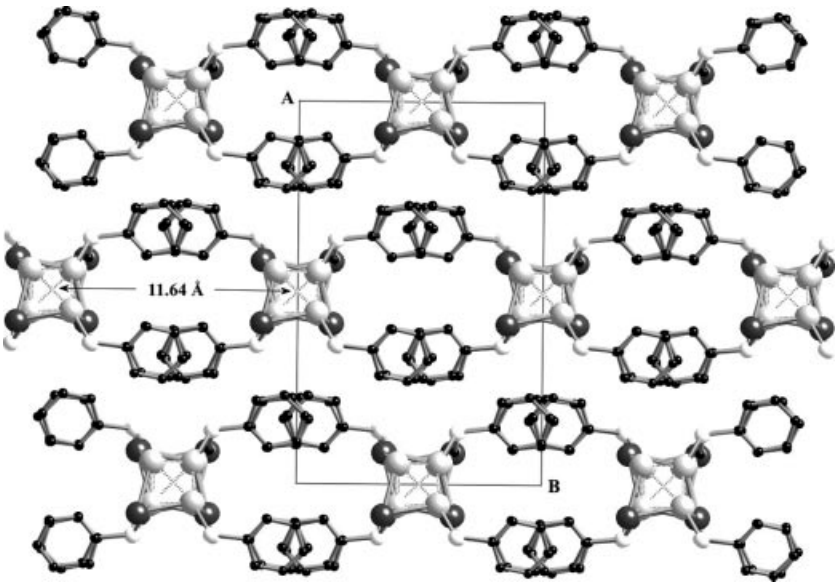


Figure 2. View of packing of **1** on the *ab* plane.

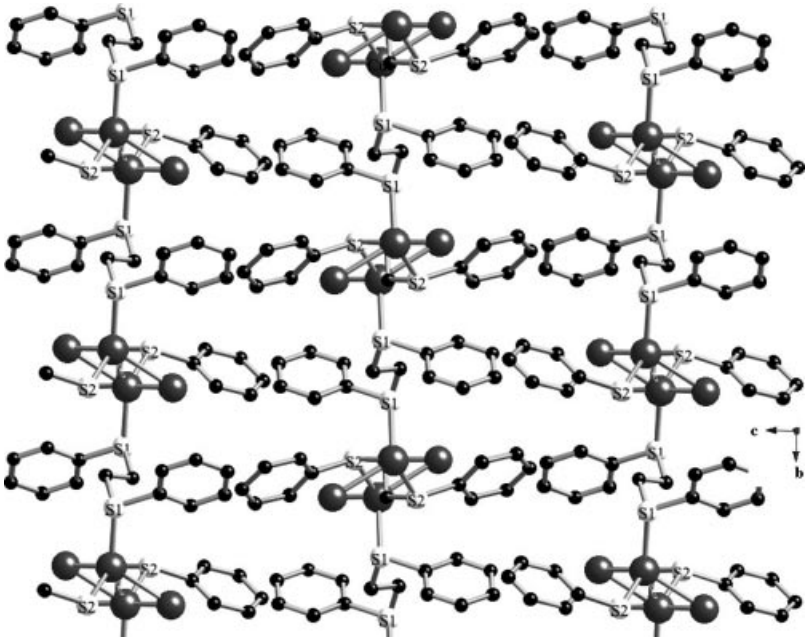


Figure 3. View of the packing of **2** on the *bc* plane.

Cu···Cu interaction of 3.18 Å has been found in the two-dimensional sheet structure of polymeric $[Cu_2I_2(dtpcp)_2]$·thf (dtpcp = 2,11-dithia[3.3]paracyclophane).[11c–11d] Our discovery that a subtle steric modification of the dithioether has a major impact on the cluster nuclearity suggests that a small energetic difference exists between the centrosymmetric rhomboid $Cu_2I_2$ motif and the cubane-like $Cu_4I_4$ cluster. Note that treatment of $[Cu(MeCN)_4][BF_4]$ with 1,2-bis(phenylthio)ethane affords the mononuclear chelate complex $[Cu\{PhS(CH_2)_2SPh\}_2][BF_4]$, which has been reported to undergo facile ligand dissociation in solution.[12]

The solid-state emission spectra of **1** and **2** are shown in Figure 5. Upon excitation at 360 nm, a strong emission band was observed for the tetranuclear adduct, **1**, with a maximum at 532 nm. Emissions in a similar spectral range have been observed for nitrogen-substituted $Cu_4I_4L_4$ clusters and were attributed to an emission from a triplet cluster centred excited state ($^3$CC).[3b,13] In fact, this broad CC excited state emission is mixed in character with equal contributions of iodine to copper charge transfer (XMCT) and copper orbital centred (d→s) transitions.[3b] In contrast, the emission spectrum recorded for polymeric **2** containing the

  

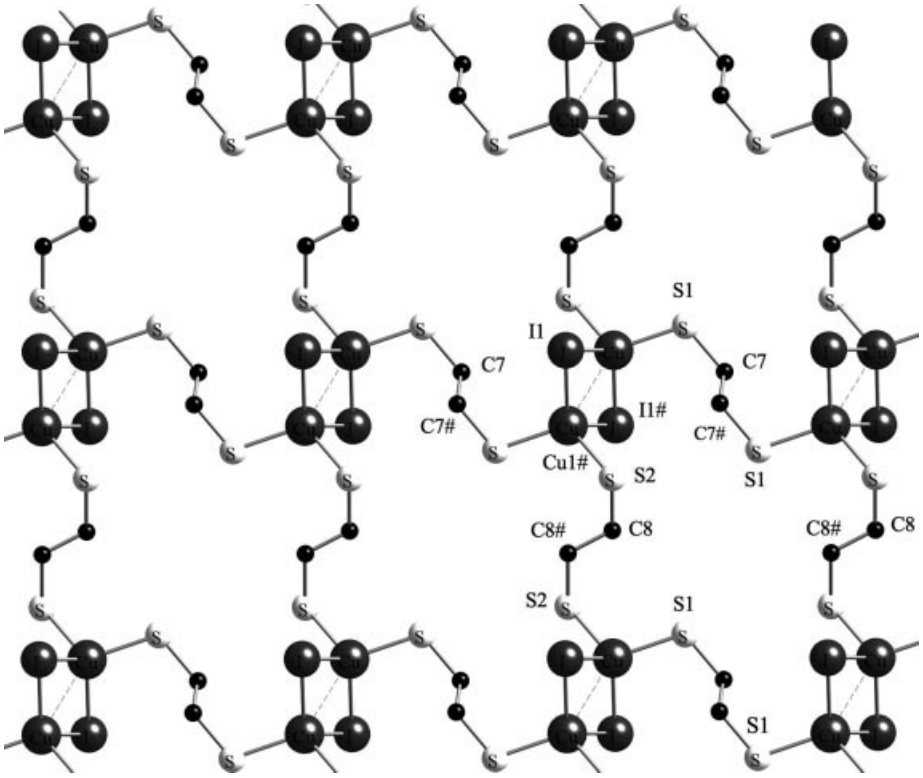


Figure 4. View of the core structure of **2** on the *ab* plane. H atoms and phenyl groups are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu(1)–S(1) 2.3000(11), Cu(1)–S(2) 2.3855(10), Cu(1)–I(1) 2.6108(7), Cu(1)–I(1)#3 2.6169(8), Cu(1)–Cu(1)#3 2.8058(10), C(7)–S(1) 1.820(3), C(8)–S(2) 1.816(4); S(1)–Cu(1)–S(2) 109.24(4), S(1)–Cu(1)–I(1) 120.26(3), S(1)–Cu(1)–I(1)#3 105.57(3), S(2)–Cu(1)–I(1)#3 110.00(3), S(2)–Cu(1)–I(1) 96.12(3), I(1)#3–Cu(1)–I(1) 115.08(2), Cu(1)#3–I(1)–Cu(1) 64.92(2), C(7)–S(1)–Cu(1) 110.61(11). Symmetry operations used to generate equivalent atoms: #1: $-x + 2, -y + 2, -z$; #2: $-x + 1, -y + 1, -z$; #3: $-x + 2, -y + 1, -z$.

dinuclear $Cu_2I_2$ unit exhibits, under similar experimental conditions, only a very weak emission centred at 413 nm with a shoulder at 438 nm. Although less studied than the tetranuclear systems, photophysical properties of some dinuclear $Cu_2X_2$ compounds have been reported in the literature, but are currently limited to those of *N*-heterocyclic ligands.[3c,14] The observation of a shoulder suggests a mixed emission with different contributions from the XMCT and Cu (d→s) transitions. To confirm this hypothesis, advanced photophysical studies and ab initio calculations are in progress. Solution measurements carried out in acetonitrile at room temperature show no luminescence for either **1** or **2**. This is probably due to a disassembly of the cluster units by this strongly coordinating solvent.

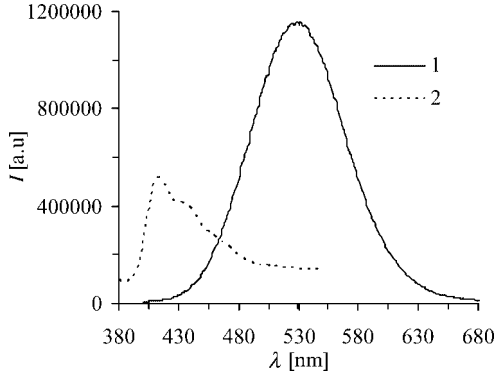


Figure 5. Corrected solid-state luminescence spectra recorded at room temperature for compounds **1** (solid) and **2** (dotted).[15]

## Conclusions

In summary, this work has shown that the dithioether ligand spacer length has a significant impact on the dimensionality of the resulting coordination polymer and the cluster nuclearity. It therefore determines, indirectly, the luminescence properties of the resulting metal–organic framework. We are currently varying the spacer length and nature of the copper salt systematically in order to establish a correlation between $PhS(CH_2)_nSPh$ and the motif of the framework. In addition, detailed photophysical studies and theoretical computations on these coordination polymers are underway.

## Experimental Section

$PhSCH_2SPh$ and $PhS(CH_2)_2SPh$ were prepared according to ref.[16] and ref.,[17] respectively. The solid-state emission spectra were recorded at room temperature with a Jobin–Yvon Fluorolog-3 spectrometer using a cylindrical 0.5 cm diameter quartz capillary with a scan speed of 1 nm/s. Intensity scales are presented in arbitrary units.

  

**Preparation of 1 and 2**: To a suspension of CuI (191 mg, 1.0 mmol) in acetonitrile (10 mL) was added $PhSCH_2SPh$ (232 mg, 1.0 mmol). The mixture was heated at reflux for 15 min, then the solution was allowed to reach room temperature. After one day, colourless crystals of **1** formed. Yield 0.22 g, 72%. $C_{13}H_{12}Cu_2I_2S_2$ (613.23): calcd. C 25.46, H 1.97; found C 25.89, H 2.05. The reaction of CuI with $PhS(CH_2)_2SPh$ under similar conditions afforded compound **2**. Yield 0.33 g, 75%. $C_{14}H_{14}CuIS_2$ (436.81): calcd. C 38.49, H 3.23; found C 38.77, H 3.30.

**X-ray Crystallography:** Crystal data and experimental details are given in Table 1. Data were collected with a Stoe IPDS diffractometer at 173(2) K. The intensities were determined and corrected with the program INTEGRATE in IPDS.[18] An empirical absorption correction was employed using the FACEIT program in IPDS.[19] All structures were solved by applying direct and Fourier methods. For each structure, the non-hydrogen atoms were refined anisotropically. All hydrogen atoms were placed in geometrically calculated positions, and each was assigned a fixed isotropic displacement parameter based on a riding model. Refinement of the structures was carried out by full-matrix least-squares methods based on $F_o^2$. All calculations were performed with the WinGX crystallographic software package, using the programs SHELXS-90[20] and SHELXL-97.[21] CCDC-623106 and -623107 contain the supplementary data for **1** and **2**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table 1. Crystal data and structure refinement details for **1** and **2**.

| Compound | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{13}H_{12}Cu_2I_2S_2$ | $C_{14}H_{14}CuIS_2$ |
| Formula weight | 613.13 | 436.81 |
| $T$ [K] | 173(2) | 173(2) |
| Crystal system | monoclinic | monoclinic |
| Space group | $C2/c$ | $P2_1/n$ |
| $a$ [Å] | 20.857(4) | 9.4711(18) |
| $b$ [Å] | 11.656(2) | 7.928(2) |
| $c$ [Å] | 15.530(3) | 19.632(4) |
| $\beta$ [°] | 119.42(3) | 97.78(2) |
| $V$ [Å$^3$] | 3288.5(11) | 1460.5(6) |
| $Z$ | 8 | 4 |
| $\rho_{calcd.}$ [g/cm$^3$] | 2.477 | 1.987 |
| $\mu$ [mm$^{-1}$] | 6.578 | 3.874 |
| $F$(000) | 2288 | 848 |
| Crystal size [mm] | 0.40 × 0.20 × 0.20 | 0.30 × 0.30 × 0.10 |
| $\theta$ range [°] | 2.22 to 25.00 | 2.28 to 26 |
| Index ranges | $-24 \le h \le 24$ | $-11 \le h \le 11$ |
| | $-12 \le k \le 13$ | $-9 \le k \le 9$ |
| | $-18 \le l \le 18$ | $-24 \le l \le 24$ |
| Reflections collected | 9932 | 13463 |
| Independent reflections | 2871 | 2782 |
| Refinement method | | full-matrix least squares on $F^2$ |
| Data/restraints/parameters | 2871/0/172 | 2782/0/164 |
| Goodness-of-fit on $F^2$ | 1.033 | 1.066 |
| $R_1$, $wR_2$ [$I > 2\sigma(I)$] | 0.0463, 0.1404 | 0.0353, 0.0874 |
| $R_1$, $wR_2$ [all data] | 0.0480, 0.1421 | 0.0395, 0.0898 |
| $\Delta\rho$(min), $\Delta\rho$(max) [e·Å$^3$] | 1.119, –1.104 | 1.060, –0.759 |

**Supporting Information** (see footnote on the first page of this article): View of the structure and packing of **2** along the *b* axis and of **1** on the *bc* plane.

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