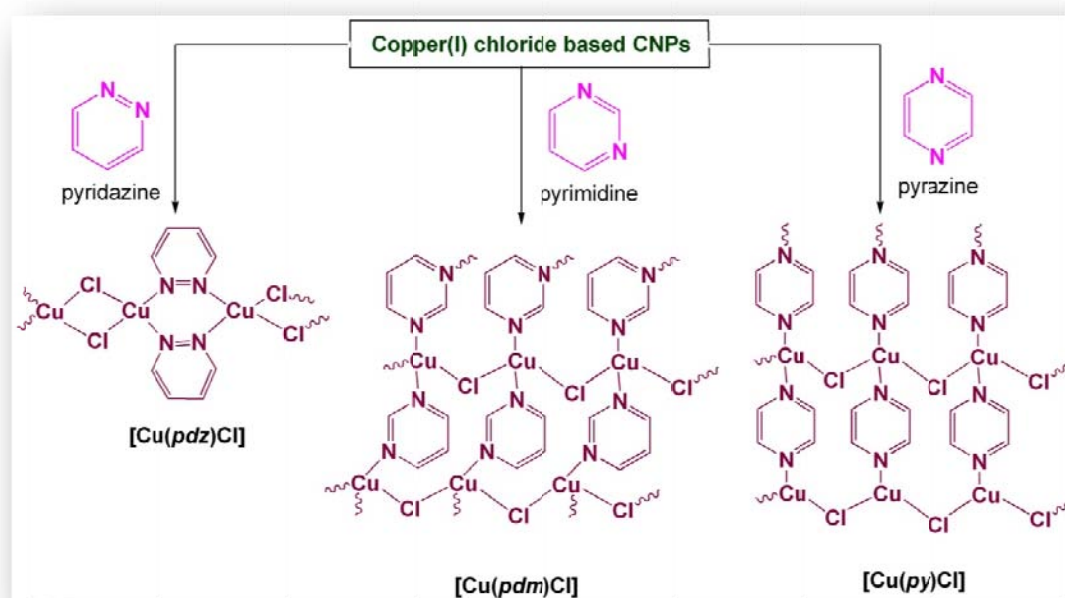


Designing Materials of Contemporary Interest: A perspective

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In the early 1900s, zeolites and synthetic microporous analogues such as aluminophosphates and silicoaluminophosphates were of major commercial implication, due to their potential applications in sorption and separation. However, their applications were limited to a certain extent owing to the tetrahedral geometry and stable oxidation state of the silicon center. The search for new materials having greater flexibility, with the ability to tolerate variation in oxidation state led to the emerging field of coordination polymers based on transition and rare earth metals. The solids in which the metal ions and organic ligands, self-assemble infinitely leading to one-, two- and three-dimensional networks, having direct metal ligand coordination at least along any one of the dimensions are commonly known as coordination polymers (CNPs) or metal organic frameworks (MOFs). [1] By careful selection of organic ligands with appropriate functional groups and metal ions with specific directionality and functionality, it is possible to design materials of technological importance. While the ability of metals to exist in multiple oxidation states exhibiting different coordination geometries and the multidentate nature of organic ligands dictate the dimensionality and directionality of the metal-ligand coordinate covalent bonds; flexibility, functionality and chirality in the MOFs is imposed by the nature of the ligand. For example, consider the formation of CNPs based on copper (I) chloride using isomeric pyridazine (*pdz*), pyrimidine (*pym*) and pyrazine (*py*). While *pym* and *py* can

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Scheme 1. Scheme showing the CNPs based on isomers *pzd*, *pym* and *py*

form 2D sheets; *py* can form only 1D chains (Scheme 1). [2-4] It is evident from the geometry of ligands that unlike *pym* and *py*, *pdz* has nitrogens at ortho position which limits its ability to form 2D sheets or 3D network with tetrahedral copper (I) centre. On the other hand, a multidentate ligand along with metal center having octahedral coordination can form a 3D framework. $[\{Cu_2(4,4'-bpy)_5(H_2O)_4\} \cdot x(\text{anion}) \cdot 2H_2O \cdot 4EtOH]$, $x(\text{anions}) = 4PF_6^-$ and $2ClO_4^-$, *bpy* = bipyridine, wherein the Cu^{II} center has an octahedral coordination environment with four nitrogen atoms of 4,4'-*bpy* ligands in the equatorial plane and two oxygen atoms of H_2O molecules at the axial sites [5] is a classical example of the 3D CNP. Besides dimensionality, chirality is also manifested by appropriate choice of ligands. Recently, a chiral 3-D inorganic-organic hybrid coordination polymer, $[\{Cu_6I_5(L)_3\}(BF_4) \cdot H_2O]$, $L = 1, 4$ -bis(2pyrimidinesulfanyl)methyl)benzene, containing a 2-D inorganic $\{Cu_6I_5\}^+$ layer composed of three interwoven 1D $\{CuI\}$ helices in different directions and connected by ligand *L* through its nitrogen and sulfur atoms, was reported.[6]

In recent times, porous CNPs have been attracting attention as a result of their ordered internal surface areas, which may be exploited for applications such as gas storage, catalysis, etc. Unfortunately, the open spaces in these materials are, more often than not, filled by solvent molecules or counter ions. In many instances, interpenetration precludes the observation of porosity. It, therefore, remains a challenge to design and construct stable porous coordination polymers. [7]

The choice of the metal centers is equally crucial. Most of the coordination polymers exhibit interesting luminescence properties as a result of the ability of the metal cations to affect, upon coordination, the emission properties of organic ligands leading to a new class of electroluminescent materials with potential for application as light-emitting diodes. The versatile coordination behavior of f-block metal ions provides further depth in this area. Crystal engineering of non-centrosymmetric coordination polymers paves way for materials with second and third order non-linear

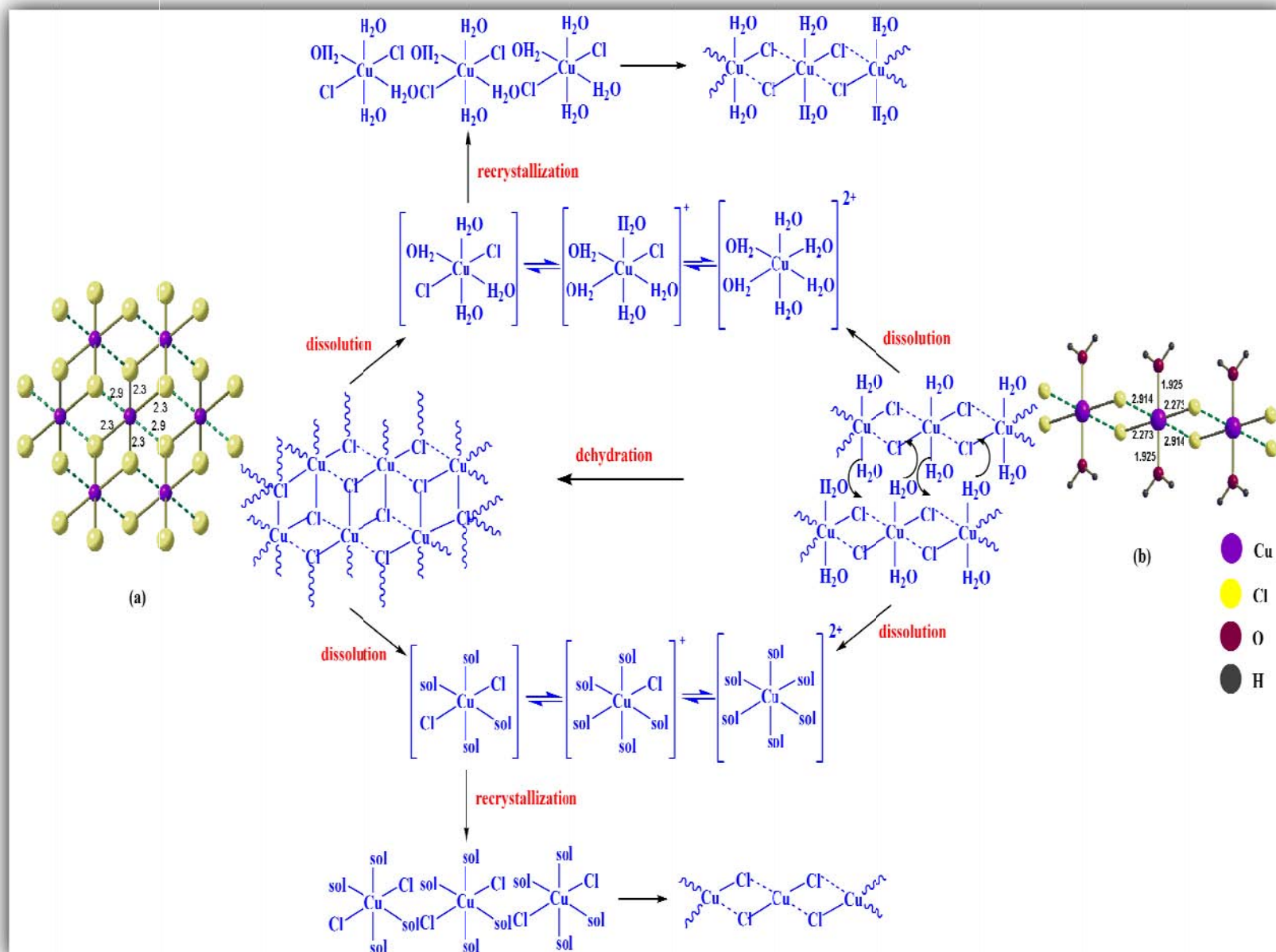
optical properties. For instance, while in $[\text{Cd}(1,4\text{-bdc})(\text{py})]$, bdc = benzene dicarboxylate, py = pyridine, where complex formation significantly (about 100 times) enhances the fluorescent intensity of the free 1,4-bdc ligand, probably due to the symmetry

fluorescence, due to the presence of molecular metal-ligand species.

Long-range ordering of paramagnetic metal ions in coordination polymers causes them to be suitable candidates for molecule-based magnets. Multitopic, closed shell

unpaired electrons, short oxo, cyano or azido bridges are needed. Therefore, polymeric metal cyanide compounds are frequently encountered in magnetic investigations. [9]

However, design or crystal engineering of CNPs with



Scheme 2. The scheme gives the sequence of dissolution of the solid, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and CuCl_2 and reassembling back into the dihydrate or anhydrous copper chloride. (a) Crystal structure of anhydrous copper chloride. The structure resembles 'rutile' if we consider 2.9\AA as bonding distance (shown in dashed lines). (b) Crystal structure of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$

decrease by serious ligand twisting [8]; the solution, from which the terbium compounds $[\text{Tb}(\text{O}_2\text{CPh})_3(\text{MeOH})_2(\text{H}_2\text{O})]$ and $[\text{Tb}_2(\text{O}_2\text{CPh})_6(4,4\text{-bipy})]$ are grown, emits bright green

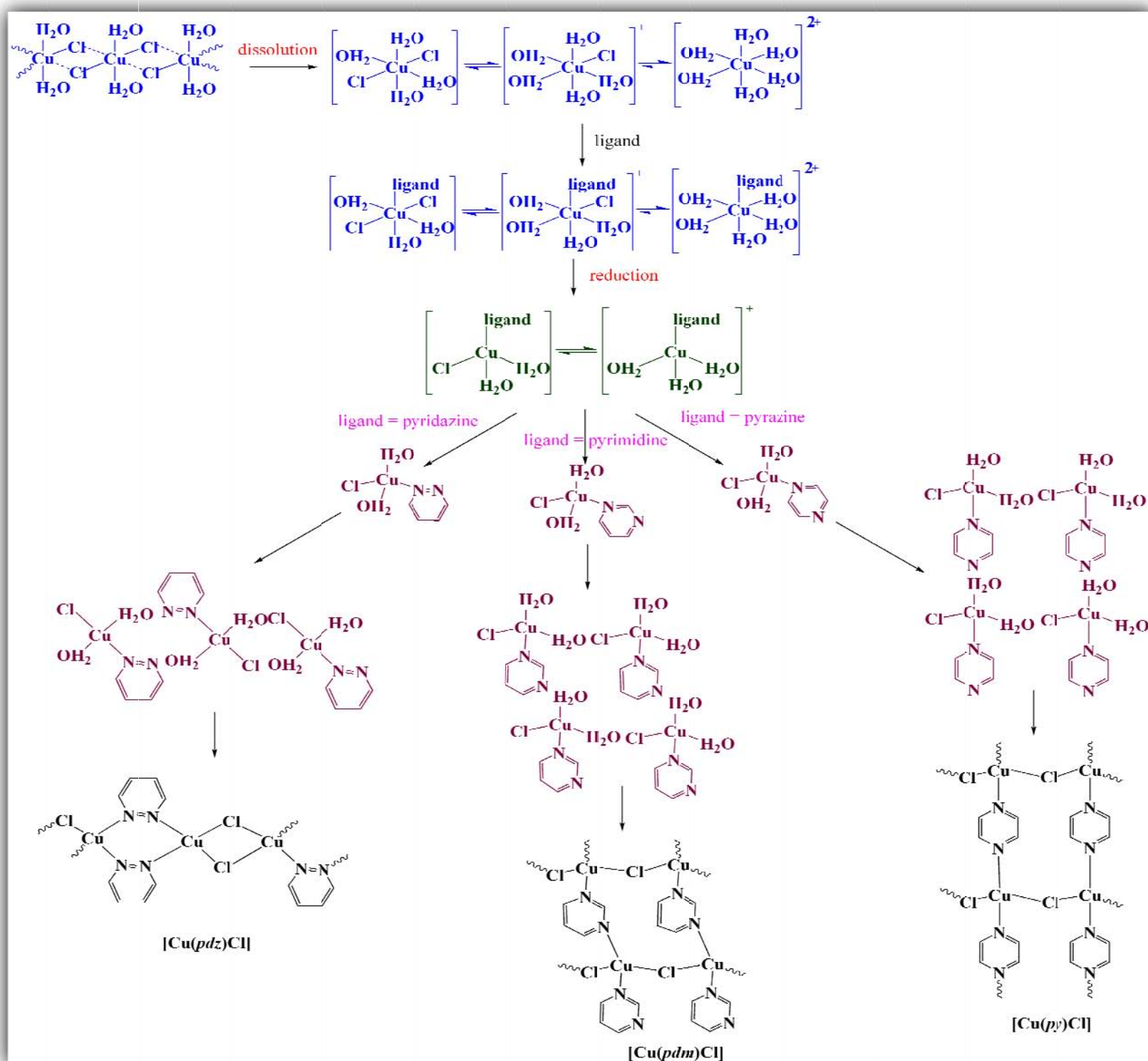
organic ligands which are typically used in coordination polymers usually give rise to only weak magnetic interactions. In order to achieve a strong coupling between the metal centers with their

predetermined structure and functionality still remains a challenge. The underlying chemistry issue such as solubility, reactivity of starting precursors etc. play a critical role in

determining the formation of a particular CNP. In this context, the recent paper by Ramanan and Whittingham is significant [10] wherein they have demonstrated the

the nucleation of a particular crystal. As soon as a metal salt is dissolved in water or a nonaqueous solvent, a soluble metal complex is initially formed. The most important driving

spontaneous ordered aggregation of their soluble molecular precursors. The aggregation and there after condensation of the molecular species to form a particular solid is dictated by



Scheme 3. Copper chloride forms soluble molecular species (*pzc* as well as ionic) in solution that are in equilibrium with each other. The *pzc*, i.e., $[\text{CuCl}_2(\text{H}_2\text{O})_4]$ complexes with ligand through the nitrogen atom to form $[\text{CuCl}_2(\text{H}_2\text{O})_3\text{ligand}]$. The reduction of the latter results in tetrahedral species $[\text{CuCl}(\text{H}_2\text{O})_2\text{ligand}]$ which is responsible for the self-assembled MOFs based on copper chloride

occurrence of several neutral MOFs in terms of chemical events that precede

force involved in the self-assembly of metal ions and ligands involves

supramolecular interactions such as hydrogen bonding, $\text{CH}\cdots\pi$ and $\pi\cdots\pi$

interactions. For example, consider the formation of CNPs based on copper (I) chloride using *pdz*, *pym* and *py* as discussed earlier in Scheme 1. When $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ or CuCl_2 is dissolved in water/solvent, soluble molecular species are formed (refer Scheme 2). In nonaqueous solvent, it is convenient to consider the metal complex coordinated by the solvent. However, in predominantly water containing medium (mixed solvent like methanol/water) it is appropriate to consider the metal aqua complex. As long as the two Cl atoms are linked to the metal, the charge on the complex is zero (*pzc*). If one or both the Cl atoms replaced by water (or solvent), then the complex thus formed will be ionic specie like $[\text{CuCl}(\text{H}_2\text{O})_5]^+$ or $[\text{Cu}(\text{H}_2\text{O})_6]^{+2}$. In the presence of suitable mono-dentate ligands, the following molecular species viz. $[\text{CuCl}_2(\text{H}_2\text{O})_3(\text{organic})]^+$, $[\text{CuCl}(\text{H}_2\text{O})_4(\text{organic})]^+$ or $[\text{Cu}(\text{H}_2\text{O})_5(\text{organic})]^{+2}$ would be present predominantly in the reaction medium. However, reduction of Cu(II) to Cu(I) would result in change in coordination and form $[\text{CuCl}(\text{H}_2\text{O})_2(\text{organic})]$ or $[\text{Cu}(\text{H}_2\text{O})_3(\text{organic})]^+$. Since it is expected that the overall charge of all the species present in the supramolecular reaction (i.e., supra-molecular assembly that eventually result in the nucleation of a particular crystal) will be neutral, the self assembly of $[\text{CuCl}(\text{H}_2\text{O})_2(\text{organic})]$ species would ultimately lead to 1D chains and 2D sheets using *pdz* and *pym* and *py* respectively (refer Scheme 3). Recently, the formation of copper coordination polymers based on molybdates, transition metal complex templated octamolybdates and water clusters has also been discussed in terms of supramolecular aggregation of their molecular precursors [11-13]. The arguments for the formation of copper chloride based complexes and MOFs reported lately also explain explicitly the role of non-bonding interactions in nucleation of a solid. [14] Yet rational

design of MOFs with predetermined structure and function is still elusive although an array of opportunities that these materials offer over a wide range of disciplines makes them an attractive area of research. It is indeed needless to emphasize that the coordination polymers promise to exhibit a variety of properties that are otherwise impossible to attain. ■

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