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Hierarchy of Supramolecular Arrangements and Building Blocks: Inverted Paradigm of Crystal Engineering in the Unprecedented Metal Coordination of Methylene Blue

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# **Inorganic Chemistry**

# <sup>1</sup> Hierarchy of Supramolecular Arrangements and Building Blocks: <sup>2</sup> Inverted Paradigm of Crystal Engineering in the Unprecedented <sup>3</sup> Metal Coordination of Methylene Blue

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9 **Supporting Information** 

ABSTRACT: The aromatic methylene blue cation (MB<sup>+</sup>) shows unprecedented ligand 10 11 behavior in the X-ray structures of the trigonal-planar (TP) complexes  $MBMCl_2$  (M = Cu<sup>1</sup>, 12 Ag<sup>1</sup>). The two isostructural compounds were exclusively synthesized by grinding together 13 methylene blue chloride and MCl solids. Only in the case of AuCl did the technique lead to a different, yet isoformular, Au<sup>I</sup> derivative with separated MB<sup>+</sup> and AuCl<sub>2</sub><sup>-</sup> counterions and no 14 direct N-Au linkage. While the density functional theory (DFT) molecular modeling failed 15 in reproducing the isolated Cu and Ag complexes, the solid-state program CRYSTAL 16 satisfactorily provided for Cu the correct TP building block associated with a highly compact 17  $\pi$  stacking of the MB<sup>+</sup> ligands. In this respect, the dispersion interactions, evaluated with the 18 DFT functional, provide to the system an extra energy, which likely supports the 19 unprecedented metal coordination of the MB<sup>+</sup> cation. The feature seems governed by subtle 20 chemical factors, such as, for instance, the selected metal ion of the coinage triad. Thus, the 21 2.2 electronically consistent Au<sup>1</sup> ion does not form the analogous TP building block because of a looser supramolecular arrangement. In conclusion, while a given crystalline design is 23



24 generally fixed by the nature of the building block, a peculiarly efficient supramolecular packing may stabilize an otherwise

25 unattainable metal complex.

# 26 INTRODUCTION

27 Methylene blue (MB) is a salt of the formula 28  $[(C_{16}H_{18}SN_3)^+Cl^-]$  [IUPAC name: 3,7-bis(dimethylamino)-29 phenothiazin-5-ium chloride]. The MB<sup>+</sup> cation consists of three 30 condensed six-membered rings and two coplanar NMe<sub>2</sub> 31 substituents. The aromaticity is suggested by the total 18 p<sub> $\pi$ </sub> 32 electron count, as indicated from the resonant structures in 33 Scheme 1.

A qualitative molecular orbital (MO) picture<sup>1</sup> corroborates the donor weakness of the phenothiazine N atom, given that its in-plane  $\sigma$  lone pair lies well below the frontier MO region. The region weakness of MO is instead an accessible  $\pi^*$  level, favoring the N-atom reduction to an amide, with the system's puckering due to the lost aromaticity. The acquired N





<sup>*a*</sup>Electron pairs at the heteroatoms are distinguished for their  $p_{\pi}$  or  $\sigma$  character.

basicity  $^{2,3}$  is also consistent with the known N–H/N–R  $_{\rm 40}$ derivatives,<sup>4</sup> also stable in the monoxidized form.<sup>5,6</sup> For the 41 redox reversibility, promoted by the alternative glucose and  $O_2$  42 reactants and the associated color change, MB is often used as 43 an indicator.<sup>7</sup> Other applications are in photocatalysis<sup>8,9</sup> and 44 enzyme-catalyzed redox reactions. As a drug, MB is employed 45 for treating diseases such as methemoglobinemia,  $^{10}$  cya-  $_{46}$  nide,  $^{11,12}$  carbon monoxide poisoning,  $^{13}$  malaria,  $^{14-16}$  and  $_{47}$ Alzheimer's.<sup>17</sup> In these fields, the combination of MB with a 48 metal center could be, in principle, advantageous, but its 49 coordination capabilities remain elusive in the literature. 50 Perhaps, the closest example of bonding to a metal is in the 51 crystal structure of MB<sup>+</sup>[HgCl<sub>3</sub>]<sup>-,18</sup> although the N–Hg 52 distance of 2.779 Å exceeds the sum of the covalent radii as 53 well as the average value, evaluated from the Cambridge 54 database.<sup>19</sup> Other invoked cases of MB<sup>+</sup> coordination to a metal 55 are even more speculative in the lack of structural character- 56 ization.<sup>20,21</sup>

This paper provides the first evidence of the MB<sup>+</sup> ligand <sup>58</sup> behavior based on the structures of the three-coordinated <sup>59</sup> complexes [(MBMCl<sub>2</sub>) with  $M = Cu^{I}$  or Ag<sup>I</sup>. Support from <sup>60</sup>

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61 suitable density functional theory (DFT) calculations is also 62 provided when taking into account crystalline supramolecular 63 interactions. Among the latter, the London dispersion forces 64 play a decisive role in some sterically encumbered organic 65 compounds, as emphasized by a recent review article.<sup>22</sup> The 66 role is instead much less considered for transition-metal 67 complexes, concerning, in particular, possible effects on metal 68 coordination. A conclusion reached by this study is that the 69 supramolecular interactions, among which is the  $\pi$  stacking of 70 aromatic units, can end up conferring unknown coordination 71 capabilities to an unsuited species such as MB<sup>+</sup>.

## 72 RESULTS AND DISCUSSION

73 Only by using a mechanochemical strategy was the synthesis of 74 complexes [(MBCuCl<sub>2</sub>] and [(MBAguCl<sub>2</sub>] (simplified as 75 MBCu and MBAg) successfully achieved. This implied the 76 grinding together of the solid methylene blue chloride 77 pentahydrate and CuCl or AgCl. Conversely, the equivalent 78 combination of reactants in solution failed. The progress of the 79 reactions was monitored by powder X-ray diffraction (PXRD) 80 analysis. In the case of Cu, the traces of the starting reagents 81 disappeared completely after 30 min of grinding without the 82 addition of a solvent's drop. In the case of Ag, a few drops of 83 acetone had to be added to complete the reaction within 20 84 min. In both cases, the color changed from dark green to 85 reddish brown, while some PXRD traces of the final powders 86 indicated the attainment of new crystalline phases (Figure 1).

t1



**Figure 1.** Experimental and calculated PXRD patterns of MBCu and MBAg products. Distinct positions of the experimental and calculated signals likely depend on the temperature of the data collection (298 and 100 K for PXRD and single-crystal diffraction, respectively).

Suitable crystals for X-ray analyses were isolated upon slow 87 88 evaporation of the dimethylformamide (MBCu) and acetoni-89 trile (MBAg) solutions of the ground solids. As shown in 90 Figure 1, the recorded PXRD patterns coincide with those 91 calculated from the determined single-crystal X-ray structures.<sup>23</sup> 92 Select geometric parameters of the isostructural MBCu and 93 MBAg compounds are shown in Table 1, where the values in brackets are those of the MBCu optimization with CRYSTAL.<sup>24</sup> 94 Approximate trigonal-planar (TP) metal complexes are 95 96 formed by the two Cl<sup>-</sup> and the MB<sup>+</sup> ligands. This result is 97 surprising because, in general, a cationic ligand hardly forms an uncharged metal complex.<sup>25-28</sup> The behavior of MB<sup>+</sup> as a 2e<sup>-</sup> 98 donor is corroborated by the relatively short N-M linkages of 99 1.987(4) and 2.329(5) Å in the Cu and Ag compounds, 100 101 respectively. The Ag coordination is comparatively less effective 102 because the N-Ag bond is larger than the sum of the covalent 103 radii and the average value from all of the corresponding 104 CCDC structures.<sup>19</sup> The point is also supported by the 105 somewhat more open Cl-Ag-Cl angle (119.48° vs 113.73°). 106 In no case is the Cl<sub>2</sub>M fragment either coplanar or orthogonal 107 to the MB<sup>+</sup> plane, thus excluding any higher symmetry of the Table 1. Experimental Geometric Parameters (Å and deg) of the Isostructural Complexes (MB)MCl<sub>2</sub> (M = Cu, Ag)<sup>*a*</sup>



<sup>*a*</sup>The values in square brackets are for the Cu model, optimized with CRYSTAL.<sup>24</sup>

complexes. The corresponding  $\tau$  rotation of Cl<sub>2</sub>M about the 108 N–M linkage has intermediate values of 75.2 and 66.8° for 109 MBCu and MBAg, respectively. Another important parameter, 110 defined in Table 1, concerns the out-of-plane shift of the metal 111 from the MB<sup>+</sup> plane, which is almost equivalent in the two 112 complexes (angles 11.8° and 9.5°). However,  $\tau$  rotation has 113 consequences on the extended heap, formed by the parallel 114 MB<sup>+</sup> units in an alternating head-to-tail arrangement (Figure 115 f2 2).

First of all, the view down the N-M vector (Figure 2a) 117 highlights the "leaning tower" shape of the heap, consistent 118 with the continuous lateral sliding of each complex unit by a 119 half condensed hexagon. In this manner, the atoms of two 120 adjacent MB<sup>+</sup> cations do not eclipse each other. Conversely, 121 Figure 2b clarifies the role of the  $\tau$  and  $\theta$  angles for the whole 122 system. The Cl<sub>2</sub>M rotation shortens the contact between any 123 Cl atom and one H-C group of one adjacent MB<sup>+</sup> cation. This 124 allows single but continuous hydrogen-bonding interactions 125 with an apparent stabilization of the heap. On the other hand, 126 the latter cannot be pairwise equivalent because of the  $\theta$  127 deviation, which favors one Cl···H-C interaction with respect 128 to the subsequent one. In fact, the Cl...H distances are as 129 different as 2.614 and 2.89 Å and 2.622 and 2.816 Å in MBCu 130 and MBAg, respectively. As a major consequence, the heap's 131 building block cannot be a single complex but one of two 132 alternative dimers. The first one features two N-M vectors, 133 which simultaneously point toward the associated MB<sup>+</sup> unit 134 (green box in Figure 2b), while the vectors diverge in the dimer 135 formed by the two central complexes (red box). The two 136 possible building blocks have different interplanar distances of 137 3.506 vs 3.403 Å and 3.485 vs 3.307 Å in MBCu and MBAg, 138 respectively. Remarkably, the dimer with the closer contacts 139 between the cations is the one with larger Cl···H-C contacts. 140 This suggests an inverse correlation between the main 141 supramolecular forces ( $\pi$ - $\pi$  and hydrogen bonding), as further 142 discussed in the computational part. 143

The compound MBAu, formed by the third coinage metal 144 (gold), was similarly synthesized by grinding together with the 145 solid reactants MB and Au(tht)Cl (tht = tetrahydrothiophene). 146 Five cycles of solvent-assisted grinding were necessary to 147



**Figure 2.** Layered MBCu and MBAg complexes. (a) View down the N–M linkages, highlighting the "leaning tower" shape of the heap. (b) Orthogonal view down the largest  $MB^+$  dimension, showing the two possible dimeric building blocks in the boxes.

148 completely convert the starting materials into a new crystalline 149 phase, as evidenced by the PXRD monitoring of the reaction 150 (see the Supporting Information, PXRD3-5). In this manner, 151 the concomitant formation of a crystalline gold metal phase 152 also emerged, as shown by new signals in place of those 153 attributed to the target phase. Crystals suitable for X-ray 154 analysis were obtained upon the slow evaporation of a filtered 155 dichloromethane solution of the powder.

The X-ray structure **Of** MBAu in Figure 3 is indicative of a 157 salt of formula  $[(MB^+)(AuCl_2^-)]$ . In fact, the N–Au separation 158 of 4.201 Å excludes MB<sup>+</sup> coordination because it is 159 corroborated by the quasi-linearity of the AuCl\_2<sup>-</sup> anion 160 (angle of 177.57°). Discrete ion pairs may also be excluded 161 because the metal fragments form hydrogen bonds with distinct



**Figure 3.** Packing features of the MBAu crystalline phase,<sup>23</sup> showing Cl···H contacts between linear AuCl<sub>2</sub><sup>-</sup> fragments and MB<sup>+</sup> molecules.

counterions and  $\pi$  stacking holds the parallel MB<sup>+</sup> units 162 together in a head-to-tail arrangement. 163

The now larger interplanar separation of 3.599 Å is indicative 164 of weaker interactions between the planes, also because the 165 adjacent cations are now shifted by one entire six-membered 166 ring. The reduced lattice energy is therefore likely insufficient to 167 compensate for the difficult formation of the N-Au<sup>I</sup> 168 coordination bond.<sup>29</sup> Examples of the latter are rare and not 169 well-defined, with one example being a T-shaped species with a 170 P-Au-S linear moiety associated with an orthogonal pyridine 171 ligand, which remains 2.56 Å far from the metal.<sup>30</sup> On the other 172 hand, the propensity of the d<sup>10</sup> coinage metals to add a third 173 coplanar ligand diminishes down the triad, as found for a 174 P<sub>2</sub>MCl series (P<sub>2</sub> = chelate diphosphine) with the progressively 175 larger Cl separation.<sup>31</sup>

Some authors attributed the different behavior of Au to 177 relativistic effects,<sup>32</sup> which remained elusive when included in 178 some of our DFT calculations. The latter were initially based on 179 the molecular modeling of the single  $MBMCl_2$  complexes (M = 180 Cu, Ag) carried out with the B3LYP-DFT<sup>33</sup> method both in the 181 gas phase and in a CHCl<sub>3</sub> solvent.<sup>34,35</sup> Unfortunately, these 182 optimizations were not consistent with the X-ray structural 183 data. Only Cu apparently formed a three-coordinated complex 184 with the MB<sup>+</sup> ligand, but its geometry was clearly incorrect. Not 185 only were the N-Cu distance and the Cl-Cu-Cl angle 186 overestimated by about +0.15 Å and +32°, respectively, but the 187 metal was far from lying on the MB<sup>+</sup> plane ( $\hat{\theta} = 49^{\circ}$ ). MBAg 188 optimization was even less performing because a N…Ag 189 separation of >6.0 Å excluded the existence of the coordination 190 bond, consistently with a quasi-linear  $Cl_2Ag^-$  fragment (170°). 191 In this respect, MBAg seemed more similar to MBAu than the 192 MBCu compound, which was similarly optimized. At this point, 193 it became evident that the neglected intermolecular forces 194 could have a role in the  $\mathrm{MB}^{\scriptscriptstyle +}$  coordination, as was already  ${}^{195}$ implicit in the spectroscopic analysis of the MBCu and MBAg 196 compounds in an acetonitrile solution. In fact, no NMR or MS 197 signal was attributable to the possible N–Cu or N–Ag 198 coordination. 199

Evidence for supramolecular forces at work in the extended 200 heap of MBCuCl<sub>2</sub> units emerged from the solid-state 201 calculations with the program CRYSTAL.<sup>24</sup> Before going into 202 the details, it is worth mentioning that the stacking had been 203 explored at the molecular level for the single dimeric building 204 block of Figure 2b. Remarkably, the standard B3LYP<sup>33</sup> 205 calculations indicated immediate scission of the single 206 complexes, which attain the mentioned incorrect geometry. 207 Conversely, the dispersion correction in the B97D functional<sup>36</sup> 208 afforded an acceptable optimization of the  $(MBCuCl_2)_2$  209 assembly with two in-pointing N-Cu vectors, although with 210 a  $\theta$  angle of 23.8° (Figure S4), which shortens the Cl. H–C 211 interactions (ave. 2.48 Å). Interestingly, a third stacked complex 212 (Figure 4) restores the experimental  $\theta$  value of 11° at the 213 f4 central unit but not at the terminal ones (16° and 29°). This  $_{214}$ problem of boundary conditions disappears in the solid-state 215 approach. 216

The *CRYSTAL* optimization with the B97D functional shows 217 an acceptable geometry of the stacked complex units (see the 218 values in brackets in Table 1). Also, the "leaning tower" aspect 219 of the heap is well reproduced (Figure S5a) with distinct and 220 alternating dimeric building blocks, although with smaller and 221 similar interplanar separations (3.10 and 3.06 Å). To evaluate 222 the effect, likely attributable to the dispersion forces, a new 223 *CRYSTAL* optimization was attempted at the **BLYP** level. At 224



Figure 4. DFT-optimized assembly of three MBCuCl<sub>2</sub> complexes.

225 first sight, the structure (Figure S5b) was better behaving, 226 especially for the larger and more asymmetric interplanar 227 separations of 3.41 and 3.30 Å. However, this result is 228 associated with a questionable stereochemistry, given that the 229 rotation of each Cl<sub>2</sub>Cu fragment about the N–Cu linkage is in 230 the opposite sense (negative  $\tau$  angle). Consequently, the Cl–S 231 contacts are preferentially shortened with respect to the Cl··· 232 H–C ones. This suggests a residually positive S atom in MB<sup>+</sup>, 233 possibly consistent with resonance structures rather than those 234 in Scheme 1. In any case, the stereochemical conflict between 235 the optimized and experimental structures kept us from further 236 exploring the problem.

The combined strategy of molecular and solid-state modeling 237 offered the possibility of deriving useful energy data on the 238 239 interaction between adjacent complexes.<sup>37</sup> On average, the 240 enthalphy of the attraction is about -40 kcal mol<sup>-1</sup>, mostly 241 because of the dispersion forces. In fact, the dismissal of the 242 latter in the **BLYP** approach transforms the interaction into a 243 minor repulsion (~+2 kcal mol<sup>-1</sup>). Therefore,  $\pi$  stacking has a 244 governing role and overwhelms other contributions such as 245 hydrogen-bonding or residual electrostatic attraction between 246 differently charged counterions at different complexes. 247 Consider in this respect that the components of the latter 248 type are equally included in the two adopted functionals, 249 without any major evidence of their specific contribution in 250 favoring the assembly of the planar and formally closed-shell 251 complexes.

To support the still scarcely documented role of the packing 252 253 forces in assisting metal coordination, we mention a previous study reported by some of us (C.M. and A.I.)  $^{38,39}$  on  $Mn^{\rm II}$ 254 dimers with four carboxylate bridges and a terminal bipyridine 255 256 (bipy) chelate per metal. In these species, the local metal coordination was trigonal-prismatic, while in the crystal, the 257 unsubstitued bipy ligands were involved in extended and 258 compact  $\pi$  stacking. However, the introduction of some methyl 2.59 substituent at bipy induces a major structural effect, such as the 260 261 forcing of an octahedral Mn<sup>II</sup>, also because the CH<sub>3</sub> 262 substituents do not allow the same effective  $\pi$  stacking of the 263 planar chelates. In fact, the loss of lattice energy (although 264 unvalued by calculations) cannot support the trigonal-prismatic 265 coordination anymore. With respect to the latter case, the 266 present MB<sup>+</sup> behavior seems even more remarkable because  $\pi$ 267 stacking controls not only the coordination geometry but also Werner's coordination number<sup>40</sup> (from 2 to 3). 268

### 269 CONCLUSION

 $^{270}$  In conclusion, the coordination capabilities of the aromatic  $^{271}$  MB<sup>+</sup> cation have been assessed for the first time. Analyses have  $^{272}$  shown that the supramolecular forces govern the overall  $^{273}$  stereochemistry to the point of affording in some cases

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otherwise disfavored and still unknown complexes of MB. 274 Because the latter compound already has a relevant number of 275 applications in different areas of chemistry, it cannot be 276 excluded that some new fruitful usage may be derived in 277 combination with a transition-metal center. For this reason, the 278 synthetic procedures, stereochemistry, and electronic underpinnings of our solid-state systems may represent a useful 280 guideline in the search for new supramolecular systems, where 281 MB (or a similar synthon) is associated with various metal 282 centers. In this respect, an added value of this paper is the 283 mechanochemical technique used, in place of other standard 284 synthetic strategies in solution. Hopefully, the formation of 285 other highly energetic supramolecular patterns may offer 286 important perspectives for chemistry. 287

# ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the 290 ACS Publications website at DOI: 10.1021/acs.inorg- 291 chem.6b02980. 292

X-ray crystallographic data in CIF format (CIF) 293 Experimental details on the syntheses of the compounds 294 at issue, IR and PXRD characterization data, the CCDC 295 search outcome on the N–Cu and N–Ag coordination 296 length bonds, and drawings and coordinates of computed 297 structures (PDF) 298

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Author Contributions	307
This paper received contributions of all the authors. These	<mark>308</mark>
authors contributed with the DFT calculations and the further	309
interpretation of the computed results.	310

 Notes
 311

 The authors declare no competing financial interest.
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#### DEDICATION

319

Dedicated to Antonio Tiripicchio on the occasion of his 80th 320 birthday. 321

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paper. These data are provided free of charge by The Cambridge
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