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X-ray structure and density functional theory studies of an unexpected product: *trans*-bis{2-[(2-cyanoethyl)-iminomethyl]phenolato}copper(II)

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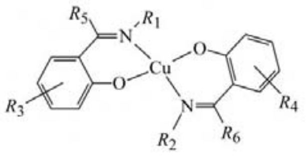
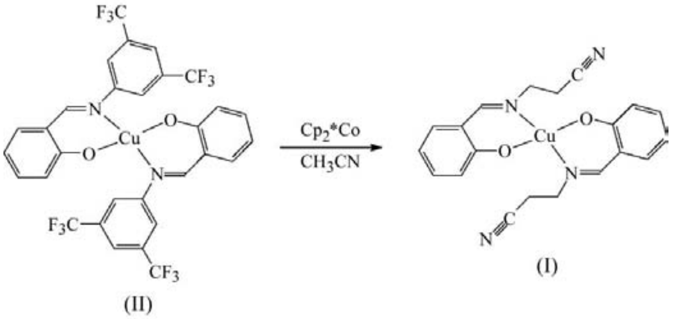
The title compound, $[Cu(C_{10}H_9N_2O)_2]$ or $[Cu^{II}(CYMB)_2]$, (I), was obtained in an attempt to reduce *trans*-bis(2-{[3,5-bis(trifluoromethyl)phenyl]iminomethyl}phenolato)copper(II), $[Cu(TIMB)_2]$, (II), with bis(pentamethylcyclopentadienyl)cobalt(II) [decamethylcobaltocene, $Cp^*{}_2Co$, (III)]. The molecular structure of (I) has the Cu^{II} centre located on an inversion centre of the *C*2/*c* space group. A density functional theory (DFT) analysis at the B3LYP/Lanl2dz(CuF);6-31G**(CHNO) level performed in order to optimize the structures of the free ligands $CYMB^-$ and $TIMB^-$, and the metal complexes $[Cu^{I/II}(CYMB)_2]^{-/0}$ and $[Cu^{I/II}(TIMB)_2]^{-/0}$, reproduced well the X-ray diffraction structure and allowed us to infer the insertion of the cyanomethide anion on the 3,5-bis(trifluoromethyl)phenyl system from an evaluation of the Mulliken atomic charges and the electronic energies.

Comment

The interest in Schiff base salicylaldehyde copper(II) complexes of the type shown in the scheme stems in large part from their redox properties. In fact, chemical and electrochemical reactions have been shown to produce the corresponding Cu^I and Cu^{III} species. In recent years, several studies have been reported in the literature on the bioinorganic behaviour of these complexes as models for biological systems (Abdel-Latif *et al.*, 2007, and references therein; Toyota *et al.*, 2001; Filomeni *et al.*, 2007) and their photochromic, thermochromic (Chatziefthimiou *et al.*, 2006) and magnetic properties (Bian *et al.*, 2003). The molecular structures of such complexes have been accurately investigated *via* spectroscopic and X-ray diffraction (XRD) methods. The Cambridge Structural Database (CSD, Version of January 2008; Allen, 2002) shows hundreds of hits for this type of complex. The original papers combine the structural data with redox, electron paramagnetic resonance (EPR) and UV–Vis properties. Recently, some of us reported the properties of a series of derivatives with R_3–R_6 = H and $R_1 = R_2$ = 3,4,5-trisubstituted phenyl (where the substituents consist of a variety of atoms or groups). The derivative with $R_1 = R_2$ = 3,5-bis(trifluoromethyl)phenyl has been investigated for its redox and spectroscopic properties but not through X-ray diffraction (XRD), while the analogous 3,5-dimethylphenyl derivative has been investigated *via* XRD (see Corsini *et al.*, 2003, and references therein). Against this background, the study of the reactivity of *trans*-bis(2-{[3,5-bis(trifluoromethyl)phenyl]iminomethyl}phenolato)copper(II), $[Cu(TIMB)_2]$, (II), with reducing agents could be worthwhile. We report here the results of a study performed first by reacting (II) with decamethylcobaltocene ($Cp^*{}_2Co$), (III), in acetonitrile under reflux and under a nitrogen atmosphere. The reaction produced crystalline (I), the title compound, which surprisingly contains the unreduced Cu^{II}–CYMB chelate. This, to the best of our knowledge, constitutes a new ligand, with the $-CH_2-CH_2-CN$ function linked to the imine N atom in place of the 3,5-bis(trifluoromethyl)phenyl group, and its structure has not previously been deposited in the CSD or elsewhere.





The reaction of (II) with (III) under reflux for 1.5 h under nitrogen and in the absence of light afforded a dark-green solution from which dark-green crystals of (I) formed (see scheme). The complex molecule is shown in Fig. 1, and selected bond distances and angles are reported in Table 1. The Cu^{II} centre lies on a crystallographic inversion centre and is chelated by two ligand molecules through the enolate O atom and the imino N atom, the two ligands being arranged *trans* to each other. As a consequence, the coordination environment is square planar. The nitrile group is not involved in any interactions with the metal centre. It should be noted that the structure of (I) is reminiscent of that of $[Cu(DIMB)_2]$, where DIMB is 2-[(3,5-dimethylphenyl)iminomethyl]phenolate, which is an analogue of (II) having methyl groups in place of the trifluoromethyl substituents (Corsini *et al.*, 2003). In the case of $[Cu(DIMB)_2]$, two different coordination molecules

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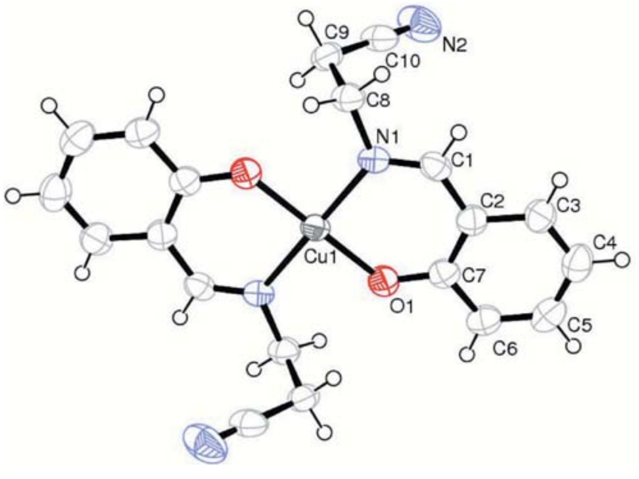

Figure 1
The X-ray structure of complex (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. The Cu^{II} atom lies on an inversion centre.

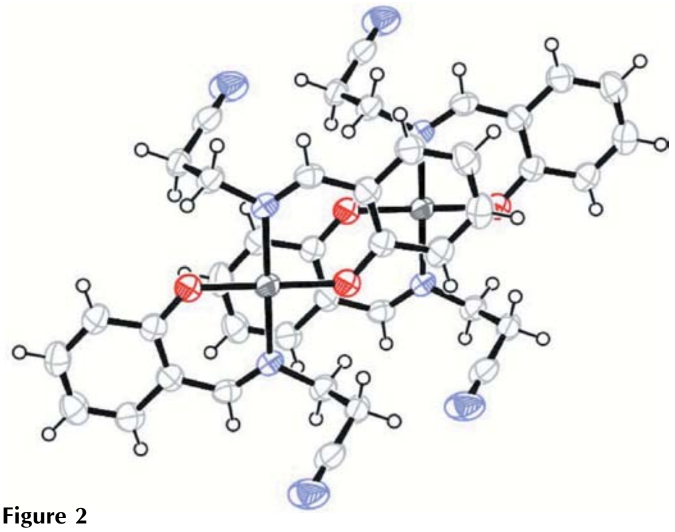

Figure 2
A diagram showing the π–π stacking interactions between the benzene ring of one molecule of (I) and the imino and enolate systems of an adjacent molecule at symmetry position (x, y + 1, z).

are present in the asymmetric unit, the coordination environments of which are significantly tetrahedrally distorted, the distortion being due to the steric hindrance arising from the 3,5-dimethylphenyl substituent on the imino N atom. In (I), the Cu—O and Cu—N bond distances (Table 1) are in perfect agreement with the values previously reported for similar compounds: $[Cu(DIMB)_2]$ [1.899 (1) and 1.962 (1) Å; Corsini *et al.*, 2003]; *trans*-bis{2-[3-(dimethylamino)propyliminomethyl]phenolato}copper(II) diperchlorate [1.891 (2) and 1.895 (2), and 1.992 (2) and 1.994 (2) Å; Saha *et al.*, 2003]; *trans*-bis{1-[3-(cyclohexylamino)propyliminomethyl]-2-naphtholato}copper(II) dichloride dihydrate [1.832 (2) and 1.913 (2) Å; Zhang, 2004]; bis{2-[3-(diethylamino)propyliminomethyl]phenolato}copper(II) diperchlorate [1.888 (4) and 2.002 (4) Å; You *et al.*, 2004]. The *cis* angles at the metal atoms are within 1.80 (12)° of the ideal value of 90° (Table 1). In fact, O1—Cu1—N1 [91.8 (1)°] and O1—Cu1—N1($-x + \frac{1}{2}$, $-y + \frac{1}{2}$, $-z + \frac{1}{2}$) [88.2 (1)°] deviate by just 1.8 (1)° (absolute value). The Cu^{II} centre deviates slightly [0.0692 (1) Å] from the plane defined by the five-atom chelating O1/C5–C7/N1 ring and the deviation is on the opposite side to the nitrile group. The metal centre is also almost coplanar with the C1–C6 aromatic ring [deviation = 0.0282 (1) Å] and the coordination plane deviates by *ca* 3° from both the chelating plane and the aromatic plane.

The bond distances and angles within the ligand have normal values on the basis of comparative analysis with literature data. For example, the C—O and C═N bond distances are 1.308 (5) and 1.285 (5) Å in the structure of (I), and average 1.301 (4) and 1.291 (4) Å for $[Cu(DIMB)_2]$. The iminomethylphenolate moiety is planar, the dihedral angle between the benzene ring and the chelating ring being 2.9 (1)°. The cyanoethyl branch protrudes out of the plane of the rest of the ligand and the two arms are opposite each other. The Cu1—N1—C8—C9 and N1—C8—C9—C10 torsion angles are −76.1 (4) and −65.7 (4)°, respectively, whereas the angle between the line defined by atoms N2 and C10 and the normal to the coordination plane is 47.6 (4)°. The N2—C10 bond distance is in agreement with uncoordinated nitrile groups (Britton *et al.*, 2004), and the C9—C10—N2 bond angle is almost linear. It should be noted that nitrile/isonitrile isomerism is badly distinguished by the C—N bond distance (Britton *et al.*, 2004). As a consequence, the nitrile model for the present structure was checked through a comparative analysis with the corresponding isonitrile group. The nitrile model was accepted as being correct on the basis of the conventional agreement factors ($R1$ and $wR2$) being lower than those obtained for the isonitrile derivative (0.051 and 0.141, respectively).

The complex molecules are stacked almost parallel to the b crystallographic cell edge when the line that connects the metal centres is taken into account. However, the molecular planes and the b edge are tilted by 45°. Adjacent columns of molecules are set in a V-type arrangement (see supplementary material, Fig. S1). The shortest contact distance between metal centres is 5.400 (2) Å, so that any direct Cu⋯Cu interaction can be excluded in the solid state. It should be noted that the stacking mode is stabilized by π–π stacking interactions that mainly involve the benzene ring of one molecule and the imino and enolate system of an adjacent molecule (Fig. 2). For example, the C1⋯C4 contact distance between two adjacent molecules is 3.400 (7) Å, whereas the contact distance between atoms O1 and C7 is 3.428 (6) Å. Noticeably, this stacking mode has infinite chains of $C6^{i}\cdots Cu1\cdots C6^{ii}$ atoms [symmetry codes: (i) $-x + \frac{1}{2}$, $-y - \frac{1}{2}$, $-z$; (ii) x, $y + 1$, z], with an interatomic Cu1⋯C6 distance of 3.345 (4) Å and an angle at the metal of 180.0 (1)°. On the basis of the values of the van der Waals radii for a Cu atom (1.4 Å) and a C atom (1.7 Å) (Bondi, 1964), a linking interaction between C4 and Cu1 seems to be absent in (I). Thus, the linking force between adjacent molecules should stem only from the π–π van der Waals-type bond between delocalized electron systems. Interestingly, intermolecular C1—H1⋯N2 hydrogen-bond interactions involve the imino and nitrile functions, with

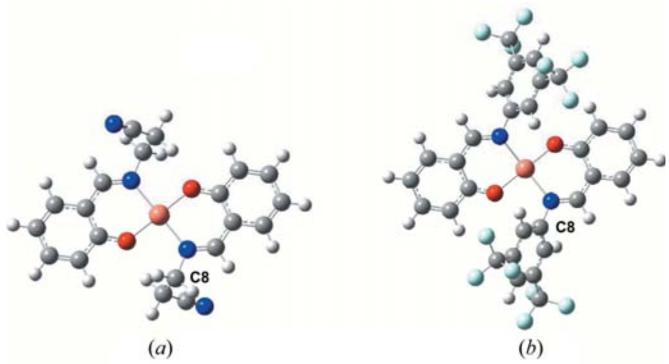

Figure 3
Drawings of (*a*) the [Cu(CYMB)$_2$] complex, (I), and (*b*) the [Cu(TIMB)$_2$] complex, (II), as optimized at the BS5 level of theory (see supplementary material for details).

C1$\cdots$N2 = 3.549 (7) Å and C1—H1$\cdots$N2 = 177 (1)°. Chains of complex molecules are built up through these interactions (see supplementary material, Fig. S1).

A density functional theory study was carried out on the CYMB– and TIMB–Cu$^{I/II}$ derivatives. The optimized structures for [Cu$^{I/II}$(CYMB)$_2$]$^{-/0}$ and [Cu$^{I/II}$(TIMB)$_2$]$^{-/0}$ are represented in Fig. 3 (selected computed geometric parameters are reported in the supplementary material). The agreement between computed and experimental bond distances for (I) is good, with the computed distances (coordinate bond) being larger by less than 0.048 Å, whereas those for the ligand have an even better accuracy. It should be noted that computed bond distances in the gas phase are usually larger than the corresponding values found in the solid state (Cini *et al.*, 2007; Tamasi *et al.*, 2009). The BS5 basis set (see *Experimental* and supplementary material) is more accurate than BS4, as expected, and has roughly the same accuracy as the more expensive (in terms of computational time) BS6 basis set in terms of geometric parameters. Therefore, the following analysis is mostly based on computations performed at the BS5 level for all the molecules. Even bond angles and torsion angles computed at the BS5 level are very accurate, suggesting that intermolecular forces in the solid state do not have a large effect on ligand conformation.

The computed structure for [Cu^{I}(CYMB)$_2$]$^-$ has a pseudo-linear N—Cu—N coordination arrangement. In fact, the computed Cu—N and Cu—O bond distances are 2.029 and 2.303 Å, respectively. This arrangement could not be confirmed from XRD structures for mononuclear copper(I) complexes with salicylideneimine ligands. In fact, no structure for this latter type of complex was deposited in the 2008 release of the CSD and no other structural assignment was found in the literature from spectroscopic data. The electronic energies for complex formation in the gas phase for [Cu$^{I/II}$(CYMB)$_2$]$^{-/0}$ from the free metal cation and free anionic ligands are −426.63 (Cu^{I}) and −856.35 kcal mol^{-1} (Cu^{II}) (1 kcal = 4.184 kJ), showing that the Cu^{II} species is intrinsically much more stable than the Cu^{I} species. Once computed at BS4, a similar gap between formation energy was found (438.03 instead of 429.72 kcal mol^{-1}). The computed structure for [Cu^{II}(TIMB)$_2$] (BS5) has Cu—N and Cu—O bond lengths of 2.040 and 1.918 Å, respectively. The corresponding values computed at BS4 are close (2.021 and 1.922 Å) and good agreement was also found with the values determined in the solid state for the related [Cu^{II}(DIMB)$_2$] complex [1.962 (2) and 1.899 (2) Å, respectively; Corsini *et al.*, 2003]. The computed structure for [Cu^{I}(TIMB)$_2$]$^-$ (BS4) has a pseudo-tetrahedral coordination arrangement and the Cu—N and Cu—O bond distances are 2.051 and 2.076 Å, respectively. Interestingly, the formation energy for [Cu^{I}(TIMB)$_2$]$^-$ is less favourable by 25 kcal mol^{-1} than that for [Cu^{I}(CYMB)$_2$]$^-$, in agreement with the large steric hindrance generated by the 3,5-bis(trifluoromethyl)phenyl substituents at the imine N atom in the TIMB$^-$ derivative compared with the cyanoethyl groups for the CYMB$^-$ derivative. These effects play a part in directing the reaction of [Cu^{II}(TIMB)$_2$] with Cp$_2$*Co^{II} (in anhydrous acetonitrile) towards a pathway that ends in [Cu^{II}(CYMB)$_2$], instead of causing a reduction at the metal centre {and formation of [Cu^{I}(TIMB)$_2$]$^-$}.

In order to confirm better the accuracy of the computations, the calculated vibration frequencies were compared with the experimental ones for [Cu^{II}(CYMB)$_2$] and [Cu^{II}(TIMB)$_2$] (obtained by FT–IR spectroscopy). The absorption band (weak, *w*) at 2241 cm^{-1} for (I) is attributable to the nitrile C—N stretching vibration (computed at BS4: 2276 cm^{-1}, 19.946 km mol^{-1}). Thus, the experimental-to-computed frequency ratio (0.985) is good when compared with literature values (Foresman & Frisch, 1996). Other relevant absorption bands for (I) are located at 1623 (strong, *s*), 1352 (medium, *m*) and 760 (*m*) cm^{-1}. They are assignable to, respectively, imine C—N stretching vibrations coupled with aromatic ring motions (1657 cm^{-1}, 922.457 km mol^{-1}), and H—C—C bending in (1339 cm^{-1}, 381.224 km mol^{-1}) and out of the plane (790 cm^{-1}, 179.070 km mol^{-1}). As expected, the experimental and computed spectra for [Cu^{II}(TIMB)$_2$] do not have any appreciable absorption band in the region 1800–3000 cm $^{-1}$, whereas selected strong effects were found at 1603, 1370 and 768 cm^{-1} that correspond to imine C—N stretching vibrations coupled with salicyl ring motions (1622 cm^{-1}, 664.317 km mol^{-1}) and H—C—C bending in (1413 cm^{-1}, 282.760 km mol^{-1}) and out of the plane (791 cm^{-1}, 153.433 km mol^{-1}). Computed absorption effects (very weak) due to Cu—N and Cu—O stretching vibrations for (I) occur at 578 and 476, and 615 and 594 cm^{-1}, respectively.

Another noteworthy result from the computations is the trend in atomic charges. In fact, the values from the Mulliken population analysis for [Cu^{II}(TIMB)$_2$] show that atom C8 (Fig. 3*b*) has the highest positive charge compared with all the other phenyl ring C atoms. The charges computed at BS4 and BS5 for atom C8 are 0.472 and 0.455 e {single-point calculations for a non-optimized structure built up from the XRD structure of [Cu^{II}(DIMB)$_2$]}, whereas those for the other five C atoms are equal to or lower than 0.303 e (see supplementary material). A similar trend was found for the optimized structure. The trend in atomic charges in the free TIMB$^-$ ligand is significantly different. In fact, the positive charge on C8 is smaller than that of the other phenyl ring C atoms. This means that the metal ligation to TIMB$^-$ favours nucleophilic attack on C8. One can expect that, if the reaction media provide suitable nucleophilic agents, the reaction could occur on that site. This could happen when Cp$_2$*Co^{II} is refluxed in anhydrous acetonitrile. In fact, the formation of a cyanomethanide anion and a Cp$_2$*Co^{III} hydride species is reasonable when it is considered that several such compounds have been reported previously in the CSD and other literature databases (*e.g.* Heeres *et al.*, 1990). Of course, the hypothesis must be studied *via* deeper theoretical and experimental effort. Nevertheless, the computational part of this work has given sound preliminary explanations for the unexpected result of the attempted chemical reduction of a copper(II) complex.

Experimental

A clear yellow–brown solution was prepared by dissolving (II) (14 mg, 0.02 mmol) in deaerated CH$_3$CN (7 ml). A second clear yellow solution was prepared by dissolving (III) (7 mg, 0.037 mmol) in deaerated CH$_3$CN (25 ml). The two solutions were mixed and the final clear brown mixture was heated under reflux with stirring under an anaerobic atmosphere (N$_2$, 1 atm; 1 atm = 101325 Pa). The colour turned to dark green after *ca* 30 min reflux; heating was continued for 60 min. The resulting solution was left to stand for 24 h, kept under nitrogen and in the dark. Needle-shaped dark-green crystals of (I) deposited on slow cooling and storing. These were filtered off, washed with small portions of cold acetonitrile and then stored in air (yield 6 mg, 76%). The IR spectra were recorded in the solid state from KBr matrixes at 298 K using a Perkin–Elmer 1600 FT–IR spectrometer.

Crystal data

[Cu(C$_{10}$H$_9$N$_2$O)$_2$]
M_r = 409.93
Monoclinic, $C2/c$
a = 20.655 (6) Å
b = 5.400 (1) Å
c = 17.653 (3) Å
β = 108.29 (1)°
V = 1869.5 (7) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.19 mm^{-1}
T = 293 K
0.40 × 0.15 × 0.15 mm

Data collection

Siemens *P*4 diffractometer
Absorption correction: ψ scan (*XEMP*; Siemens, 1994)
$T_{\rm min}$ = 0.810, $T_{\rm max}$ = 0.835
2211 measured reflections
1652 independent reflections
1269 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.047
3 standard reflections
every 97 reflections
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.140
S = 1.03
1652 reflections
124 parameters
H-atom parameters constrained
$\Delta\rho_{\rm max}$ = 0.68 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.76 e Å^{-3}

All H atoms were placed in geometric positions and allowed to ride on their parent C atoms, with C—H = 0.93–0.97 Å and $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). All density functional theory calculations were performed using *GAUSSIAN03* (Frisch *et al.*, 2004), implemented on an IBM SP5 machine at CINECA (Inter-University Computing Centre, Casalecchio di Reno, Bologna, Italy). All structures were fully optimized (unless otherwise specified, see *Comment* and supplementary material) using B3LYP methods and different levels of theory (Frisch & Frisch, 1998) for comparative purposes (see supplementary material for details). All calculations were performed in the gas phase without any constraint. A Hessian analysis was also performed. Molecular drawings were obtained using *GAUSSVIEW03* software (Dennington *et al.*, 2003) implemented on a Pentium IV machine.

Table 1
Selected geometric parameters (Å, °).

Cu1—O1	1.893 (3)	N1—C1	1.285 (5)
Cu1—N1	2.007 (3)	N1—C8	1.472 (5)
O1—C7	1.308 (5)	N2—C10	1.129 (5)
O1—Cu1—N1	91.80 (12)	C8—N1—Cu1	120.5 (2)
C7—O1—Cu1	130.3 (3)	N1—C8—C9	111.9 (3)
C1—N1—C8	115.3 (3)	C10—C9—C8	112.6 (4)
C1—N1—Cu1	124.1 (3)	N2—C10—C9	178.7 (5)

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS* and *XEMP* (Siemens, 1994); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008) and *WinGX* (Farrugia, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008) and *WinGX*; molecular graphics: *ORTEPIII* (Johnson & Burnett, 1996) and *GAUSSVIEW03* (Dennington *et al.*, 2003); software used to prepare material for publication: *CIFTAB* (Sheldrick, 2008) and *PARST97* (Nardelli, 1997).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3303). Services for accessing these data are described at the back of the journal.

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