Synthesis, structural characterization and dioxygen reactivity of imidazole-ligated Cu(I) complexes

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(Received July 28, 1993; revised December 2, 1993)

Abstract

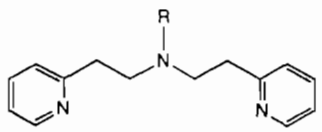
{Bis[(heterocycle)ethyl]amine}copper(I) complexes with a least one imidazole ligand react with 0.5 equiv. of dioxygen at −78 °C to give purple peroxo species. The dioxygen adduct of {*N*-2-[(2-pyridyl)ethyl]-*N*-2-[1-butyl-2-imidazolyl]ethyl}amine}copper(I) tetrafluoroborate having one imidazole and one pyridine donor has absorption maxima at 332, 435 and 538 nm and is unreactive toward acid and triphenylphosphine at low temperature, characteristics that have been ascribed to μ-η^2,η^2 coordination. {Bis[2-(1-methyl-2-imidazolyl)ethyl]amine}copper(I) tetrafluoroborate (**11**) has been structurally characterized by X-ray crystallography and has the expected T-shape. Crystal data for **11**: monoclinic, $a = 9.2181(21)$, $b = 11.638(3)$, $c = 14.914(4)$ Å; $\beta = 92.059(19)°$; $Z = 4$; space group = $P2_1/c$; 1748 independent non-zero ($I > 2.5\sigma(I)$) reflections with 2θ between 2 and 50°; $R = 6.5\%$; $R_w = 8.5\%$.

Key words: Crystal structures; Copper complexes; Dioxygen complexes; Imidazole complexes

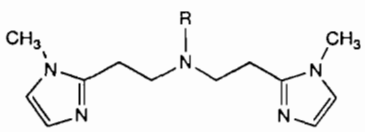
Introduction

A diverse group of copper-containing proteins carries out the transport and activation of the O_2 molecule in biological systems [1–5]. Biomimetic analogs for two of those, hemocyanin and tyrosinase, have been extensively characterized over the past several years with the result that we are beginning to understand the inorganic chemistry of peroxocopper complexes at the molecular level [6–20]. Especially important to this field was the characterization in 1989 by Kitajima *et al.* of the first μ-η^2,η^2-peroxocopper(II) complex [12], a discovery that dramatically changed the way we viewed the probable structures of the oxygenated form of hemocyanin. Theoretical [21], experimental [22] and structural [23] work since that time has focused on understanding the detailed structural and reactivity properties of this unusual coordination mode.

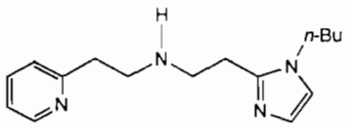
Because of the ubiquity of histidine as a ligand of copper ions in proteins, copper(I) complexes having coordinated imidazoles have become increasingly studied as model compounds for protein active sites [7, 10]. We report here copper(I) complexes of some imidazole-containing ligands and their dioxygen reactivity which differs slightly from related imidazole-ligated species described previously [7].



1 R = CH_3 { **9** = $Cu(1)^+$ }
2 CH_2Ph { **10** = $Cu(2)^+$ }



3 R = H { **11** = $Cu(3)^+$ }
4 CH_2Ph { **12** = $Cu(4)^+$ }



5 { **13** = $Cu(5)^+$ }

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SSDI 0020-1693(93)03792-9

Experimental

General

All solvents and reagents are commercially available and were used without further purification. All procedures involving air sensitive compounds were performed under nitrogen in a Vacuum Atmospheres drybox at less than 0.2 ppm O_2. ^1H NMR spectra (200 MHz) were recorded on a Bruker AC-200 spectrometer, and chemical shifts (δ) are reported in ppm downfield from TMS. Low-temperature UV–Vis spectra were recorded as previously described [24] using a Shimadzu 165 spectrophotometer. Elemental analyses were performed by Atlantic Microlabs, Norcross, GA. Ligands **2–4** and compound **6** were prepared by the literature methods [7, 11]. Oxygen uptake was measured by the previously reported method [24].

N-[2-(1-Butyl-2-imidazolyl)ethyl]phthalimide (7)

Under a dinitrogen atmosphere, a slurry of compound **6** (5.0 g, 18 mmol) in 25 ml of anhydrous DMF was cooled to 0 °C in an ice bath. To this was added NaH (1.3 g, 54 mmol), and the mixture was stirred at 0 °C. After 1 h, 1-iodobutane (13.2 g, 72 mmol) was added and the mixture was stirred at room temperature for 15 h. The reaction mixture was poured into 250 ml of ethyl acetate and washed with three 150 ml portions of water and 100 ml of saturated sodium chloride solution. The resultant yellow solution was dried over Na_2SO_4, filtered and evaporated to afford a viscous, yellow oil. The crude oil was purified by flash chromatography [25] with ethyl acetate as the eluent ($R_f = 0.45$) to yield 3.1 g (59%) of the desired product as a white crystalline solid. ^1H NMR ($CDCl_3$): δ 1.13–1.36 (m, 2H, C–CH_2–C), 1.56–1.72 (m, 2H, C–CH_2–C), 2.96 (t, $J = 7.7$ Hz, 2H, Im–CH_2), 3.81 (t, $J = 7.3$ Hz, 2H, imidazolyl N–CH_2–), 4.01 (t, $J = 7.7$ Hz, 2H, phthalimido N–CH_2–), 6.77 (d, $J = 1.3$ Hz, 1H, imidazolyl C–H), 6.83 (d, $J = 1.3$ Hz, 1H, imidazolyl C–H), 7.60–7.77 (m, 4H, Ar–H).

[2-(1-Butyl-2-imidazolyl)ethyl]amine (8)

A mixture of **7** (2.2 g, 7.4 mmol) and hydrazine monohydrate (1.0 g, 20 mmol) in 100 ml of absolute ethanol was heated at reflux for 5 h. The reaction mixture was cooled, and the resultant precipitate was filtered and washed with 15 ml of chloroform. The combined filtrates were evaporated to dryness under reduced pressure. The residue was dissolved in 50 ml of chloroform and dried over $MgSO_4$. The solution was filtered and evaporated under reduced pressure to yield a pale yellow oil. The product was purified by flash chromatography with methanol as the eluent ($R_f = 0.4$) to yield 1.0 g (83%) of the desired product as a yellow oil. ^1H NMR ($CDCl_3$): δ 1.16–1.36 (m, 2H, C–CH_2–C), 1.52–1.69 (m, 2H, C–CH_2–C), 2.14 (s(br), 2H, NH_2), 2.69 (t, $J = 7$ Hz, 2H, N–CH_2–), 3.06 (t, $J = 7$ Hz, 2H, Im–CH_2–), 3.75 (t, $J = 7$ Hz, 2H, imidazolyl N–CH_2–), 6.74 (d, $J = 1$ Hz, 1H, imidazolyl C–H), 6.84 (d, $J = 1$ Hz, 1H, imidazolyl C–H).

{N-2-[(2-Pyridyl)ethyl]-N-2-[1-butyl-2-imidazolyl]ethyl}amine (5)

A solution of **8** (1.0 g, 6.0 mmol), 2-vinylpyridine (1.25 g, 12 mmol) and glacial acetic acid (1 ml) in 100 ml of methanol was heated at reflux for 5 days. The solvent was then evaporated under reduced pressure, and the orange residue was dissolved in 100 ml of chloroform. The chloroform solution was washed with saturated aqueous $NaHCO_3$, saturated aqueous sodium chloride, and dried over Na_2SO_4. Filtration and evaporation of the solvent yielded an orange oil that we purified by chromatography with 0.5% NH_4OH in methanol as the eluent ($R_f = 0.5$) to yield 0.6 g (38%) of **5** as a yellow oil. ^1H NMR ($CDCl_3$): δ 1.18–1.38 (m, 2H, C–CH_2–C), 1.57–1.72 (m, 2H, C–CH_2–C), 2.48 (s, 1H, N–H), 2.80 (t, $J = 6.9$ Hz, 2H, N–CH_2–), 2.90–3.10 (m, 6H, Im–CH_2–, Py–CH_2–CH_2–), 3.78 (t, $J = 7.3$ Hz, 2H, imidazolyl N–CH_2–), 6.76 (d, $J = 1.1$ Hz, 1H, imidazolyl C–H), 6.87 (d, $J = 1.1$ Hz, 1H, imidazolyl C–H), 7.03–7.15 (m, 2H, pyridyl C–H), 7.54 (m, 1H, pyridyl C–H), 8.47 (m, 1H, pyridyl C–H).

{N,N-Bis[2-(1-methyl-2-imidazolyl)ethyl]amine}copper(I) tetrafluoroborate (11)

Ligand **3** (320 mg, 1.4 mmol) was dissolved in methanol (4 ml) in an inert atmosphere box. A solution of tetrakis(acetonitrile)copper(I) tetrafluoroborate (0.43 g, 1.4 mmol) in methanol (10 ml) was added, and the mixture allowed to stir for 10 min. A white precipitate was collected and recrystallized by cooling a warm acetonitrile solution of the powder. ^1H NMR (DMSO-d_6): δ 2.92 (m, 8H, N–CH_2–CH_2–Im), 3.63 (s, 7H, N–Me, N–H), 7.02 (d, $J = 1.5$ Hz, 2H, imidazolyl C–H), 7.27 (d, $J = 1.5$ Hz, 2H, imidazolyl C–H). *Anal.* Calc. for $C_{12}H_{15}N_5CuBF_4$: C, 37.57; H, 4.99; N, 18.2. Found: C, 37.10; H, 4.97; N, 18.0%.

{N-2-[(2-Pyridyl)ethyl]-N-2-[1-butyl-2-imidazolyl]ethyl}amine}copper(I) tetrafluoroborate (13)

To a solution of **5** (0.41 g, 1.5 mmol) in 6 ml of anhydrous THF was added tetrakis(acetonitrile)-copper(I) tetrafluoroborate (0.47 g, 1.5 mmol). The resultant mixture was stirred at ambient temperature for 6–7 h. The precipitate that formed during this time was collected and washed with a small amount of THF to yield 0.5 g of **13** (80%) as a bright yellow solid. *Anal.* Calc. for $C_{16}H_{24}BCu_4N_4$: C, 45.56; H, 5.72; N, 13.25. Found: C, 45.54; H, 5.68; N, 13.31%. ^1H NMR ($CDCl_3$): δ 1.22 (m, 2H, C–CH_2–C), 1.60 (m, 2H,

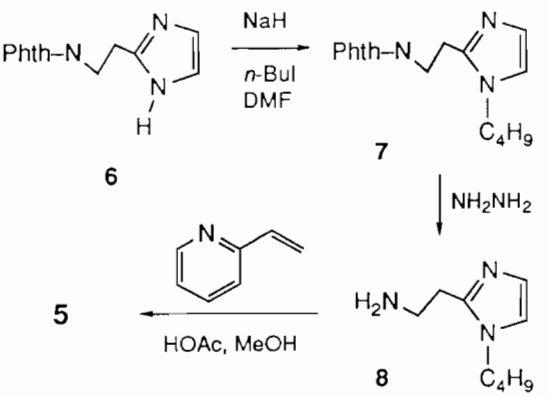
C–CH_2–C), 2.84 (m, 4H, N–CH_2–), 2.91 (br s, 4H, Im–CH_2–, Py–CH_2–), 3.94 (t, J=7.2 Hz, imidazolyl N–CH_2–), 4.55 (br s, 1H, N–H), 7.15 (d, J=1.4 Hz, Im–H), 7.29 (d, J=1.4 Hz, Im–H), 7.39–7.49 (m, 2H, Py–H), 7.90 (t of d, J^1=7.9 Hz, J^2=1.8 Hz, 1H, Py–H), 8.67 (d of d, J^1=4.3 Hz, J^2<1.0 Hz, 1H, Py–H).

X-ray crystallographic structure determination of ***11***

Crystals suitable for X-ray analysis were grown by diffusing THF into a methanol solution of **11**. Crystallographic measurements were carried out using a Nonius diffractometer and graphite-monochromatized Mo Kα radiation (λ(Kα)=0.71073 Å). Unit cell constants were derived from a least-squares refinement of 20 reflections in the range $30<2\theta<35°$ (the θ–2θ scan technique was used to record intensities). A stationary count for 0.1 of the scan time at each end of the peak was used to correct for background counts. Peaks were subjected to profile analysis and any portions of the scan not included in the peak were used to improve background estimates. The structure was refined using full-matrix least-squares techniques. The function minimized was $[\Sigma w(F_o-F_c)^2]^{0.5}$ with weights based on counter statistics. Calculations were performed using the NRCVAX system [26]. In the final cycles of refinement, all non-hydrogen atoms were given anisotropic thermal parameters. Hydrogen atoms were placed in calculated positions 0.96 Å from the atom to which they are bonded and assigned isotropic thermal parameters based on the thermal parameters of that atom. The BF_4 counterion was disordered and was modeled by two superimposed groups with 60 and 40% occupancies. Crystal data are given in Table 1.

TABLE 1. Crystallographic data for Cu^I(bimea)(BF_4)

Formula	$C_{12}H_{19}CuBF_4N_5$
Temperature (°C)	25
Crystal size (mm)	0.40×0.40×0 10
Crystal system	monoclinic
Space group	$P2_1/c$
a (Å)	9.2181(21)
b (Å)	11.638(3)
c (Å)	14.914(4)
β (°)	92.059(19)
Volume (Å^3)	1598.9(6)
Z	4
Formula weight	383.66
ρ_{calc} (Mg/cm^3)	1.594
μ (mm^{-1})	1.41
Transmission factors	0.636–0.995
Reflections collected	2987
Unique reflections	2803
Reflections of $I>2.5\sigma(I)$	1748
R (all reflections)	0.102
R_w (all reflections)	0.093
R (obs. reflections)	0.065
R_w (obs. reflections)	0.085
No. parameters	245
Maximum shift/sigma	2 362
Maximum residual electron density (e/Å^3)	0.92
Minimum residual electron density (e/Å^3)	−0.62



Scheme 1.

Results and discussion

Synthesis

Recently we reported a general synthesis of imidazole-containing chelates from aminonitriles [7]. A previous comparison of the initial dioxygen reactivity of the copper(I) complexes **10** and **12** (CuL^+, L=**2** and **4**, respectively) demonstrated essentially no spectroscopic differences [7]. A more detailed study of *N*-alkylated bis(pyridylethyl)amine copper(I) complexes explored both the initial reactivity of the complexes toward dioxygen, as well as subsequent reactions upon warming [11]. Not only does irreversible oxidation of the copper centers occur, but ligand oxidation can also be seen in some cases.

Ligand **5** was prepared by the route illustrated in Scheme 1; and ligands **1–5** are converted to complexes **9–13** by reaction with $[Cu(CH_3CN)_4]BF_4$ in methanol or tetrahydrofuran under an inert atmosphere. The recognized low solubility of imidazole-ligated complexes **11** and **12** in methylene chloride [7] prompted us to prepare the *n*-butyl derivative of the mixed pyridine–imidazole ligand **5** to circumvent that potential problem.

To ensure that the imidazole-ligated Cu(I) complexes had structures analogous to previously characterized pyridine, pyrazole and benzimidazole species [6], we carried out a crystal structure determination of {*N*,*N*-bis[2-(2-imidazolyl)ethyl]amine}copper(I) tetrafluoroborate (**11**) (Fig. 1).

Solid state structure of [Cu(bimea)][BF$_4$] (11)

The X-ray crystal structure of the cation portion of **11** is shown in Fig. 1. The geometry of the cationic species has the expected T-shape, which is common

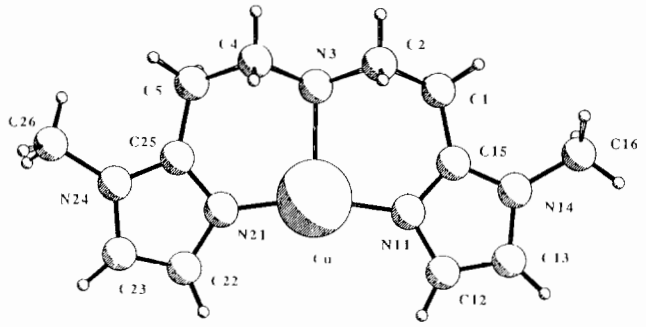


Fig. 1 Structure of the cation portion of complex **11**. Bond lengths (Å) and angles (°): Cu1–N11 = 1.898(7), Cu–N21 = 1 899(7), Cu–N3 = 2 213(7), N11–Cu–N21 = 164.9(3), N11–Cu–N3 = 97.7(3), N21–Cu–N3 = 96.9(3).

for Cu(I) complexes of this type of ligand [6, 11]. Moreover, the bond distances and angles vary little from those observed in related systems. In particular, the Cu–N_{Im} distances of 1.90 Å are quite similar to those for a bis(pyridylethyl)amine-ligated complex in which the Cu–N_{py} distances are 1.91 and 1.92 Å [11]. The Cu–N(amine) bond length of 2.21 Å in **11** is much longer than the Cu–imidazole bonds, as expected; and this also differs little from the 2.23 Å observed in the pyridine-ligated analog [11]. The angle formed by the nitrogen atoms of the heterocycle, through the copper ion, are also comparable for the two structures: 164.9° for **11**, 159.6° for the pyridine complex. In this case, the larger angle for **11** probably results from the fact that the imidazole rings have only five atoms, compared with the six-membered ring in the pyridine chelates.

Reactions with dioxygen

The reaction of dioxygen with the complexes dissolved in methylene chloride at −78 °C is slow. As noted already, the bis(pyridine) complexes **9** and **10** [11] and the bis(imidazole) complex **12** [7] react with dioxygen to give brown species characterized previously. We were therefore greatly surprised to find complex **11** reacts rapidly under the same conditions to give a purple species. Unfortunately, its lifetime was less than a minute at −78 °C. We were able to increase the stability of the adduct by preparing the mixed imidazole–pyridine complex **13**. That compound gives what appears to be the same purple species upon treatment with O_2, but the adduct is stable for up to two hours at low temperature (Fig. 2). Manometry on the soluble complex at −78 °C in methylene chloride reveals a stoichiometry of 2 Cu per 1 O_2: three measurements were performed, and the individual samples absorbed 0.85, 1.0 and 1.05 equiv. of dioxygen per 2 equiv. of copper.

Karlin and co-workers have proposed that the dioxygen adducts formed from copper(I) complexes of *N*-alkyl(bispyridylethylamine) ligands have the μ-η^2,η^2 structure **B** [11]. This conclusion is based on EXAFS

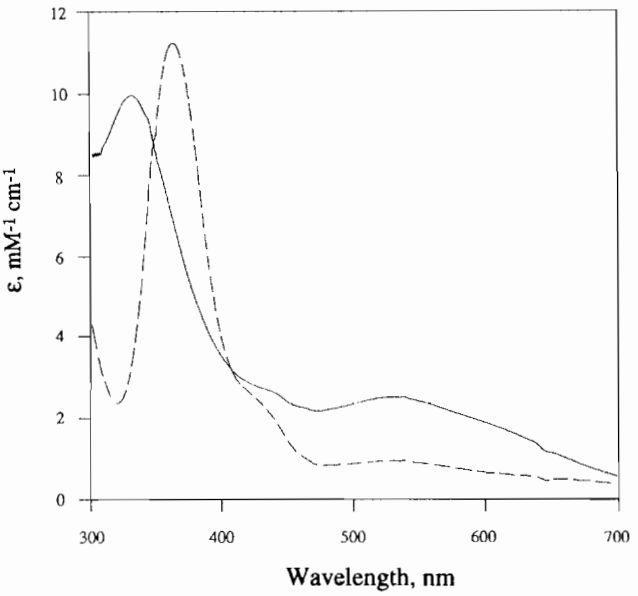
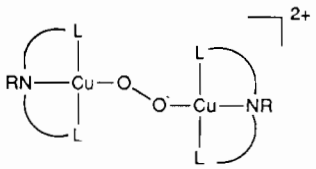
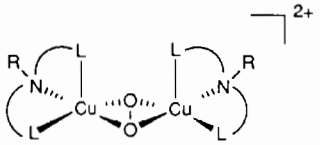


Fig. 2 Absorption spectra for complexes **10a** (– – –) and **13** (——) after reaction with dioxygen in dichloromethane at −78 °C

spectra and on differences in reactivity, versus other types of dioxygen adducts, toward a variety of reagents including protons and triphenylphosphine [27].

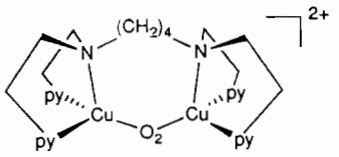


A



B

The dioxygen adduct of **13** is like that formed from **10**, as well as the dicopper complexes previously described by Tyeklar and Karlin (e.g. **14**) [9], in that it is unreactive at −78 °C toward protons (up to 10 equiv.) and toward Ph_3P. In contrast, the only structurally characterized *trans*-μ-1,2-peroxo copper(II) complex, **15** [28], reacts immediately with 2 equiv. of acid, generating hydrogen peroxide, or with triphenylphosphine, liberating dioxygen and forming a copper(I) phosphine adduct. Thus for the dioxygen adduct of **13**, the observed reactivity patterns favor assigning the structure as **B**.



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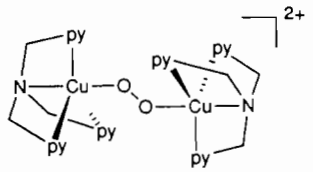

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It is difficult to compare the structure of the dioxygen adduct of **13** with the structurally characterized μ-η^2,η^2 peroxo(dicopper) complex reported by Kitajima *et al.* [12], because the ligands that are used in each case are so different. The absorption spectrum shown in Fig. 2 is qualitatively similar to that reported by Kitajima *et al.* in that each dioxygen adduct displays a strong absorption in each of the regions 330–350 and 540–550 nm. However, the extinction coefficients are quite different – in particular, the ratio of intensities for the two bands (350 versus 550 nm) is about 4 for the dioxygen adduct of **13** (Table 2), and 20 for Kitajima's complex. Furthermore, the species reported here has an additional band at approximately 435 nm. That feature may reflect distortion of the $Cu(O_2)Cu$ unit from the planar structure found by Kitajima, a concept that has been discussed previously by Karlin and co-workers [27].

It is interesting to note that removal of the alkyl group from the amine group of the previously reported tridentate ligands [7, 11] causes subtle changes in the absorption spectra of the resulting dioxygen adduct. In particular, the highest energy absorption shifts to even higher energy, while the 540 nm band increases in intensity (Fig. 2). Both of those effects lead to a change in color from brown to purple for the dioxygen adduct, and the spectrum more closely mimics that observed for oxyhemocyanin from arthropods (Table 2). We are currently attempting to understand these results by investigating other analogs of these ligands. Clearly, more data are needed to explain the structure/reactivity relationships among the different types of copper–dioxygen complexes.

TABLE 2 Spectroscopic properties of copper dioxygen complexes, $\{[CuL]_2O_2^{2+}\}[BF_4]_2$

CuL^+	λ_{max} (nm) (ϵ (mM^{-1} cm^{-1}))		
9[a]	355 (14 7)	405 (2.50)	530 (0 400)
10[b,c]	362 (11.4)	427 (2.50)	534 (0 875)
11	[d]		
12[b,e]	360	430	540
13	332 (10.0)	435 (2.75)	538 (2.50)
Hemocyanin[f]	335 (20 0)	434 (0.83)	579 (0.780)

[a]Ref. 11, PF_6^- salt [b]Ref 7. [c]Karlin and co-workers [11] report 362 (11.4), 415 (2.60) and 533 (0 650) for the PF_6 salt of this complex. [d]Lifetime <1 min [e]Reacts with solvent, so accurate extinction coefficients could not be obtained. [f]From *Cancer borealis*, ref. 29.

Conclusions

Imidazole ligation of Cu(I) is used to create complexes having a higher reactivity, but lower stability, toward dioxygen than analogs with pyridine ligands. The inclusion of a secondary amine, instead of a tertiary amine, as the third donor in the coordination sphere of the Cu(I) ion alters the appearance of the absorption spectrum to one that is more like that observed for hemocyanin. The reactivity of this violet dioxygen adduct with protons and with triphenylphosphine is consistent with μ-η^2,η^2 coordination of the peroxide ligand.

Supplementary material

A full listing of all bond distances and angles as well as final atomic coordinates for **11** is available upon request.

Acknowledgements

The authors acknowledge the National Science Foundation (CHE #9100280) and the University Research Council of the University of North Carolina for support of this work.

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