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CRYSTTAL STRUCTURES OF 3-METHYLPYRROLO[2,3-*b*]TROPONE AND ITS COPPER(II) COMPLEX[†]

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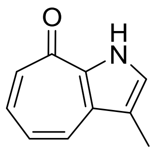
Abstract – The crystal structures of 3-methylpyrrolo[2,3-*b*]tropone (**1**) and its Cu(II) complex ($\mathbf{1}_2$·Cu) were analyzed by X-ray crystallography. The structure of **1** exists in the crystal in its keto form rathar than in the enol form (**1'**). Pyrrolotropone (**1**) formed a 2:1 complex with Cu(II). The Cu(II) ion has a tetragonal environment formed by two tropone O atoms and two pyrrole N atoms.

Pyrroles represent an important class of heterocycles in organic chemistry. They are structural units in many natural products such as porphyrin, which form the complexes with Fe(II) and Cu(II) ions.[1] Troponoids, being a remarkable class of non-benzenoid π conjugated systems, form complexes with metal salts such as $CuCl_2$, $ZnCl_2$, $CdCl_2$, $CoCl_2$, $MnCl_2$, and $HgCl_2$.[2] Pyrrolo[2,3-*b*]tropones (cyclohepta[*b*]pyrrol-8(1*H*)-one), being isoelectronic with 8-quinolinols, are interesting compounds biochemically.[3] They give coloration when treated with metal ion such as Fe(III) and Cu(II). The color fades upon addition of mineral acid.[3,4] This suggests that pyrrolo[2,3-*b*]tropones can be used as an analytical reagent for metal cations. However the crystal structures of the metal complex of pyrrolo[2,3-*b*]tropone have not been elucidated. We now report the structures of 3-methylpyrrolo[2,3-*b*]tropone (**1**) and its Cu(II) complex ($\mathbf{1}_2$·Cu).



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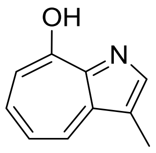
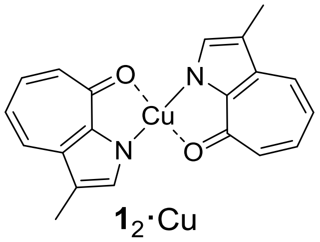


1'



$\mathbf{1}_2$·Cu

[†] Dedicated to Professor Dr. Isao Kuwajima on the occasion of his 77th birthday

Compound (**1**)[5] was prepared by condensation of 2-hydrazinotropone with 1-propanal accompanied by cyclization as reported in a previous paper.[3] Single crystals of **1** were grown in a mixture of chloroform-methanol (1:1 *v/v*) at room temperature. An ORTEP drawing[6] of molecule of **1** is shown in Figure 1a. The structure of **1** contains two crystallographically independent molecules (**1a**) and (**1b**). The pyrrolotropone moiety of **1** is approximately planar; the deviations from the least-squares plane defined by C1-C9/O1/N1 do not exceed 0.1 Å. The C-C bond lengths of seven-membered ring show bond alternation typical of tropone; the C1-O1 bond length (1.248(3) Å) is similar to that observed in the structure of unsubstituted tropone (1.259 Å).[7] The C-C and C-N bond lengths in the pyrrole ring are close to those found in unsubstituted pyrrole.[8] The objective location of the H1 atom bond to N1, rather than O1, as well as the tropone-like bond-length distribution, makes assignment of the keto form (**1**) rather than the enol form (**1'**), unambiguous.

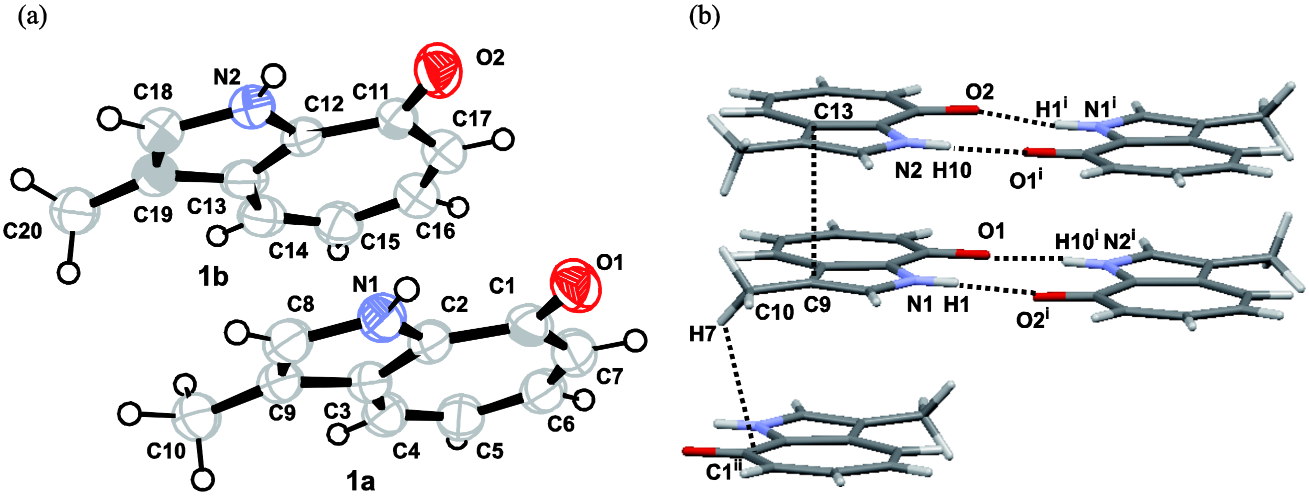


Figure 1. (a) ORTEP structure of **1**, showing 50% probability ellipsoids and (b) intermolecular N-H···O, π···π, and CH···π interactions in **1**. Symmetry codes: (i) 1-x, -y, 2-z; (ii) 1-x, 1-y, 2-z, (iii) 3-x, 2-y, 3-z.

Table 1. Selected bond lengths (Å) of **1** and $\mathbf{1}_2$·Cu

Bond Lengths	**1a**	**1b**	$\mathbf{1}_2$·Cu
C1-O1 (C11-O2)	1.248(3)	1.243(3)	1.285(4)
C2-N1 (C12-N2)	1.347(3)	1.369(3)	1.355(4)
C1-C2 (C11-C12)	1.459(4)	1.427(4)	1.423(4)
C2-C3 (C12-C13)	1.409(4)	1.415(4)	1.420(4)
C3-C4 (C13-C14)	1.402(4)	1.393(4)	1.405(4)
C4-C5 (C14-C15)	1.354(4)	1.377(4)	1.379(4)
C5-C6 (C15-C16)	1.410(4)	1.403(4)	1.410(5)
C6-C7 (C16-C17)	1.364(4)	1.369(4)	1.369(5)
C7-C1 (C17-C11)	1.435(4)	1.432(4)	1.425(4)
C8-C9 (C18-C19)	1.376(4)	1.355(4)	1.428(4)
C9-C3 (C19-C13)	1.442(4)	1.449(4)	1.387(5)
N1-C8 (N2-C18)	1.362(3)	1.367(3)	1.360(4)
C9-C10 (C19-C20)	1.481(4)	1.492(4)	1.489(5)
Cu1-O1	-	-	1.9860(19)
Cu1-N1	-	-	1.912(3)

The pyrrole NH group participates in an intermolecular hydrogen bond of the N-H···O type as shown in Figure 1b and Table 2. An intermolecular π···π interaction is observed. The distance between intermolecular pyrrolotropone planes is 3.424(4) Å for C9···C13, which is within the range associated with π···π interactions.[4,9] There is an intermolecular C-H···π interaction with distance for this type of interaction (2.8–3.1 Å).[4,10] The combination of intermolecular N-H···O, π···π, and C-H···π interactions in **1** builds up a three-dimensional network.

Table 2. Hydroge-bond geometry (Å, °) of **1**

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O2^{i}	0.860	1.985	2.815(3)	162
N2—H10···O1^{i}	0.860	1.941	2.768(3)	161
C10—H7···C1^{ii}	0.989	2.839	3.475(4)	123

Symmetry codes: (i) 1-x, -y, 2-z; (ii) 1-x, 1-y, 2-z.

Single crystals of Cu(II) complex of **1** (**1**$_2$·Cu) were grown in a mixture of chloroform-methanol (1:1 *v/v*) containing of **1** (2 eq.) and copper(II) acetate (1eq.) at room temperature. An ORTEP drawing[11] of molecule of **1**$_2$·Cu is shown in Figure 2a. The pyrrolotropone (**1**) forms 2:1 complex with Cu(II) ion. The complex has a tetragonal planar Cu(II). The Cu atom is positioned at the center of symmetry, coordinated with two N atoms of the pyrrole ring and two O atoms of the tropone ring. The Cu-O bond distance (1.9860(19) Å) is shorter than that (2.036 Å)[12] of bis(2-acetylpyrrolate)copper(II) and longer than that (1.913, 1.915 Å)[13] of bis(tropolonato)copper(II). The Cu-N bond distance is similar to that (1.912 Å)[13] of bis(2-acetylpyrrolate)copper(II). The C-O bond length is longer than that of **1** and agree with those (1.27-1.31 Å)[13,14] in other metal tropolonates.

Intermolecular π···π interactions in the crystal structure of **1**$_2$·Cu are observed in Figure 2b. The distance between intermolecular pyrrolotropone planes is 3.454(4) Å for C1···C8^{iv} (symmetry codes: (iv) x, y-1, z), which is within the range associated with π···π interactions.[4,9] Intermolecular C-H···π and C-H···O interactions (Figure 2b and Table 3) are observed with distances typical for these type of interactions:

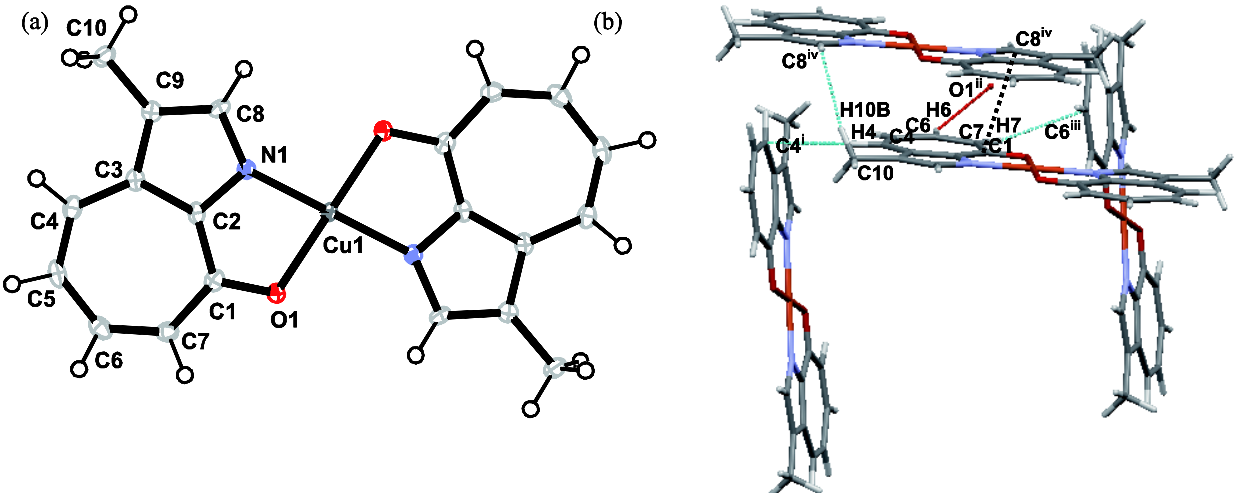


Figure 2. (a) ORTEP structure of **1**$_2$·Cu, showing 50% probability ellipsoids and (b) intermolecular π···π, CH···π, and C-H···O interactions in **1**$_2$·Cu. Symmetry codes: (i) 3/2-x, y-1/2, 1/2-z; (ii) 1/2-x, y-1/2, 1/2-z; (iii) 1/2-x, 1/2+y,1/2- z; (iv) x, y-1, z.

C-H···π=2.8–3.1 Å and C-H···O=2.5–2.7 Å.[4,10] The combination of intermolecular C-H···π and C-H···O interactions and π···π stacking interactions in $\mathbf{1}_2\cdot$Cu build up a three-dimensional network.

Table 3. Hydroge-bond geometry (Å, °) of $\mathbf{1}_2\cdot$Cu

D—H···A	D—H	H···A	D···A	D—H···A
C4—H4···C4^{i}	0.950	2.847	3.701(4)	160
C6—H6···O1^{ii}	0.950	2.696	3.412(4)	133
C7—H7···C6^{iii}	0.950	2.847	3.641(4)	142
C10—H10B···C8^{iv}	0.980	2.719	3.687(4)	170

Symmetry codes: (i) 3/2-x, y-1/2, 1/2-z; (ii) 1/2-x, y-1/2, 1/2-z; (iii) 1/2-x, 1/2+y,1/2- z; (iv) x, y-1, z.

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5. ^{1}H NMR (600 MHz, $CDCl_3$) $\delta = 2.36$ (3H, s), 6.89 (1H, dd, $J = 10.6$, 8.6 Hz), 7.19 (1H, d, $J = 12.0$ Hz), 7.24 (1H, s), 7.37 (1H, dd, $J = 12.0$, 8.6 Hz), 7.66 (1H, d, $J = 10.6$ Hz), and 10.60 (1H, brs). ^{13}C NMR (125 MHz, $CDCl_3$) $\delta = 9.8$, 119.7, 123.0, 124.3, 128.0, 131.3, 134.0, 136.3, 138.4, and 176.3.
6. Crystal data of **1**, $C_{10}H_9NO$, $M_r = 159.19$, Monoclinic, $P2_1/n$, $a = 11.307(6)$ Å, $b = 9.990(5)$ Å, $c = 14.040(8)$ Å, $\beta = 101.64(3)$°, $V = 101.64(3)$ Å^3, $Z = 8$, $D_x = 1.361$ Mg m^{-3}, $T = 293$ K, $\mu = 7.127$ cm^{-1}, $wR(F^2) = 0.2280$, $R = 0.0753$.
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