

Copper complexes of two isomeric NS₂-macrocycles

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Abstract Two isomeric NS₂-macrocycles incorporating a xylyl group at *ortho* (*o*-L) and *meta* (*m*-L) positions were employed and their copper complexes (**1**–**5**) were prepared and structurally characterized. The copper(II) nitrate complexes [Cu(L)(NO₃)₂] (**1**: L = *o*-L, **2**: L = *m*-L) for both ligands were isolated. In each case, the copper center is five-coordinated with a distorted square pyramidal geometry. Despite the overall geometrical similarity, **1** and **2** show the different ligand conformation due to the discriminated packing pattern. Reaction of *o*-L with copper(II) perchlorate afforded complex **3** containing two independent complex cations [Cu(*o*-L)(H₂O)(DMF)(ClO₄)]⁺ and [Cu(*o*-L)(H₂O)(DMF)]²⁺; the coordination geometry of the former is a distorted octahedron while the latter shows a distorted square pyramidal arrangement. In the reactions of copper(I) halides (I or Br), *o*-L gave a mononuclear complex [Cu(*o*-L)I] (**4**) with a distorted tetrahedral geometry, while *m*-L afforded a unique exodentate 2:1 (ligand-to-metal) complex [*trans*-Br₂Cu(*m*-L)₂] (**5**) adopting a *trans*-type square-planar arrangement.

Keywords NS₂-Macrocycle · Isomer · Copper complex · Crystal structure · Anion effect · Coordination geometry

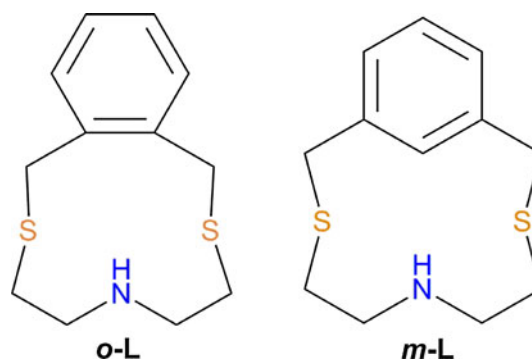
Introduction

The versatility of sulfur-containing macrocyclic ligands make them useful for a range of complexation products because the sulfur donor atom tends to bind toward soft

metal ions such as Ag(I), Hg(II), Pd(II), and Pt(II) in either an *exo*- or *endo*cyclic mode [1–4]. Indeed, a range of homo- and heteronuclear complexes of the thiamacrocycles based on the *exo*-coordination have been reported by us [5–8] and other groups [9–12].

Recently, we reported the synthesis of NS₂-macrocyclic isomers (*o*-L, *m*-L, and *p*-L) with a rigid xylyl subunit at *ortho*-, *meta*-, and *para*-positions and their silver(I) and mercury(II) complexes adopting a unique cyclic oligomer and leaf-like 1D chain conformations [13]. More recently, we employed the semi-rigid *m*-L and presented its thiaphilic metal ion complexes with different types of coordination modes (*endo*- and *exo*-) and topologies (discrete, 1D and 2D networks) including silver(I)/palladium(II) heterobinuclear complex with a 2D network by using [*cis*-Cl₂Pd(*m*-L)] as a metalloligand [14].

The continuing interest in assemblies incorporating the isomeric NS₂-donor macrocycles and the limited research in the area so far has prompted us to investigate the synthesis of copper complexes by employing *o*-L and *m*-L. And the effects of anions and oxidation state of the copper ion are also our interest. Herein, we present the synthesis and structural characterization of the five copper complexes for *o*-L and *m*-L.



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Experimental

Materials and instrumentation

All chemicals and solvents used in the syntheses were of reagent grade and were used without further purification. The NS₂-donor macrocycles were prepared as described previously by us [13]. Mass spectra were obtained on a Thermo Scientific LCQ Fleet spectrometer. The FT-IR spectra were measured with a Shimadzu FT-IR 8100 spectrometer.

CAUTION! Perchlorate salts of metal complexes are potentially explosive and should be handled with great care.

Preparation of [Cu(o-L)(NO₃)₂] (1). Complex **1** as a green crystalline solid was obtained after adding a small amount of toluene to the top layer of a dichloromethane (2 mL) solution of **o-L** (15.0 mg, 0.063 mmol) then layering this with a methanol (2 mL) solution of Cu(NO₃)₂·3H₂O (12.9 mg, 0.069 mmol), allowing the three phase system to stand. Isolated yield was approximately 30%. Mp: 165–166 °C. IR (KBr, cm⁻¹): 3226, 2346, 1450, 1384, 1326, 1283, 1038, 1021, 961, 927, 771, 696. ESI-MS: *m/z* 364.07 [Cu(**o-L**)NO₃]⁺.

Preparation of [Cu(m-L)(NO₃)₂] (2). Complex **2** as a green crystalline solid was obtained after adding a small amount of toluene to the top layer of a dichloromethane (2 mL) solution of **m-L** (15.0 mg, 0.063 mmol) then layering this with a methanol (2 mL) solution of Cu(NO₃)₂·3H₂O (12.9 mg, 0.069 mmol), allowing the three phase system to stand. Isolated yield was approximately 40%. Mp: 150–151 °C. IR (KBr, cm⁻¹): 3017, 2800, 1596, 1486, 1385, 1332, 1041, 804, 703. ESI-MS: *m/z* 363.85 [Cu(**m-L**)NO₃]⁺.

Preparation of {[Cu(o-L)(H₂O)(DMF)(ClO₄)] [Cu(o-L)(H₂O)(DMF)](ClO₄)₃·H₂O} (3). Cu(ClO₄)₂·6H₂O (18.1 mg, 0.069 mmol) was dissolved in methanol and was added to the solution of **o-L** (15.0 mg, 0.063 mmol) in dichloromethane. Turquoise blue precipitate formed immediately. The precipitate was filtered off. A green crystalline product **3** suitable for X-ray analysis was obtained by vapor diffusion of diethyl ether into a DMF solution of the precipitate. Isolated yield was approximately 30%. IR (KBr, cm⁻¹): 3211, 2361, 1648, 1369, 1097, 701, 626. ESI-MS: *m/z* 400.80 [Cu(**o-L**)ClO₄]⁺.

Preparation of [Cu(o-L)I] (4). Complex **4** as a colorless crystalline solid was obtained after adding a small amount of toluene to the top layer of a dichloromethane (2 mL) solution of **m-L** (15.0 mg, 0.063 mmol) then layering this with a methanol (2 mL) solution of CuI (13.1 mg, 0.069 mmol), allowing the three phase system to stand. Isolated yield was approximately 30%. Mp: 198–199 °C. IR (KBr, cm⁻¹): 3285, 2921, 1440, 1417, 1096, 910, 894, 712, 669. ESI-MS: *m/z* 302.17 [Cu(**o-L**)]⁺.

Preparation of [Cu(m-L)₂Br₂] (5). Complex **5** as a green crystalline solid was obtained after adding a small amount of toluene to the top layer of a dichloromethane (2 mL) solution of **m-L** (15.0 mg, 0.063 mmol) then layering this with an acetonitrile (2 mL) solution of CuBr (9.9 mg, 0.069 mmol), allowing the three phase system to stand. Isolated yield was approximately 20%. Mp: 203–205 °C (decomp.). IR (KBr, cm⁻¹): 3011, 2918, 1648, 1421, 1210, 1059, 994, 646, 535. ESI-MS: *m/z* 302.08 [Cu(**o-L**)]⁺.

Crystallographic structure determinations

The data for **1**, **2**, **4**, and **5** were collected on a Bruker Smart diffractometer equipped with a graphite monochromated Mo K α ($\lambda = 0.71073$ Å) radiation source and a CCD detector. The 45 frames of two dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The first 50 frames were retaken after complete data collection. The crystal showed no significant decay. The frame data were processed to give structure factors using the SAINT [15]. The structure was solved by direct methods and refined by full matrix least squares methods on F^2 for all data using SHELXTL software [16]. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were placed in calculated positions and refined with a riding model with U_{iso} constrained to be 1.2 times U_{eq} of the parent atom. The data for **3** were collected on a Bruker SMART APEX II ULTRA diffractometer equipped with graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å) generated by a rotating anode. The cell parameters for the compounds were obtained from a least-squares refinement of the spot (from 36 collected frames). Data collection, data reduction, and semi-empirical absorption correction were carried out using the software package of APEX2 [17]. All of the calculations for the structure determination were carried out using the SHELXTL package [18]. In all cases, all nonhydrogen atoms were refined anisotropically and all hydrogen atoms except coordinated water molecules were placed in idealized positions and refined isotropically in a riding manner along with the their respective parent atoms. In the cases of coordinated water molecules, the initial positions of the hydrogen atoms were obtained from difference electron density maps and refined with riding constraints. Relevant crystal data collection and refinement data for the crystal structures were listed in Table 1.

Results and discussion

Preparation and structural description of copper(II) nitrate complexes (1 and 2). Reactions of **o-L** and **m-L** with one equivalent of Cu(NO₃)₂·3H₂O afforded the green

Table 1 Crystal and experimental data for **1–5**

	1	2	3	4	5
Formula	C ₁₂ H ₁₇ CuN ₃ O ₆ S ₂	C ₁₂ H ₁₇ CuN ₃ O ₆ S ₂	C ₃₀ H ₅₄ Cl ₄ Cu ₂ N ₄ O ₂₁ S ₄	C ₁₂ H ₁₇ CuINS ₂	C ₂₄ H ₃₄ Br ₂ CuN ₂ S ₄
Formula weight	426.95	426.95	1203.89	429.83	702.13
Temperature	173(2)	173(2)	173(2)	173(2)	173(2)
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>Pna</i> 2 ₁	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>Z</i>	4	4	4	4	2
<i>a</i> (Å)	15.5973(7)	16.6843(12)	17.7752(6)	14.1987(7)	11.177(2)
<i>b</i> (Å)	7.6252(4)	10.9480(8)	14.6051(5)	8.2280(4)	6.9312(14)
<i>c</i> (Å)	13.7438(6)	8.7412(6)	18.6360(6)	13.0913(6)	18.337(4)
α (°)	90	90	90	90	90
β (°)	98.6890(10)	90	105.633(2)	103.4450(10)	97.821(4)
γ (°)	90	90	90	90	90
<i>V</i> (Å ³)	1615.82(13)	1596.7(2)	4659.1(3)	1487.50(12)	1407.4(5)
<i>D</i> _{calc} (g/cm ³)	1.755	1.776	1.716	1.919	1.657
2 θ _{max} (°)	53.98	52.98	51.76	52.00	55.00
<i>R</i>	0.0292	0.0269	0.0381	0.0274	0.0471
<i>wR</i>	0.0838	0.0603	0.0898	0.0714	0.1119
No. of reflection used [>2 σ (<i>I</i>)]	3499 <i>R</i> _{int} = 0.0541	3004 <i>R</i> _{int} = 0.0339	8978 <i>R</i> _{int} = 0.0547	2884 <i>R</i> _{int} = 0.0233	2894 <i>R</i> _{int} = 0.1247
Diffractometer	Bruker SMART CCD	Bruker SMART CCD	Bruker APEX II ULTRA	Bruker SMART CCD	Bruker SMART CCD
Structure determination	SHELXTL	SHELXTL	SHELXTL	SHELXTL	SHELXTL
Refinement	Full-matrix	Full-matrix	Full-matrix	Full-matrix	Full-matrix

crystalline complexes **1** and **2**, respectively, that proved suitable for crystallography. The crystal structures of **1** and **2** are shown in Figs. 1 and 2, and selected geometric parameters are presented in Table 2.

The crystal structures show that **1** and **2** are 1:1:2 (ligand-to-metal-to-anion) complexes of formula [Cu(L)(NO₃)₂] with similar coordination atmosphere. In each case, for example, the copper(II) center facially coordinated to the NS₂ donors in the macrocycle together with two monodentate nitrate ligands to yield an overall metal coordination of five. Both coordinated anions are located on the one side of the bound macrocycle.

In case of the five-coordinated complex system, many compounds cannot be classified readily into trigonal bipyramid (TBP) or square pyramid (SP) geometries because of their intermediate natures due to the orbital hybridization. According to the Addison's approach [19], the Cu atoms in **1** and **2** have distortion parameter τ values 0.34 and 0.32: $\tau = (\theta_1 - \theta_2)/60$, where θ_1 and θ_2 are the largest angles in the coordination sphere, then $\tau = 0$ means perfect SP and $\tau = 1$ means perfect TBP.

Thus, both of the copper(II) coordination in **1** and **2** can be best described as a distorted SP. In **1**, N1, S1, O1 and O4 atoms form the square plane and S1 atom occupies the apex

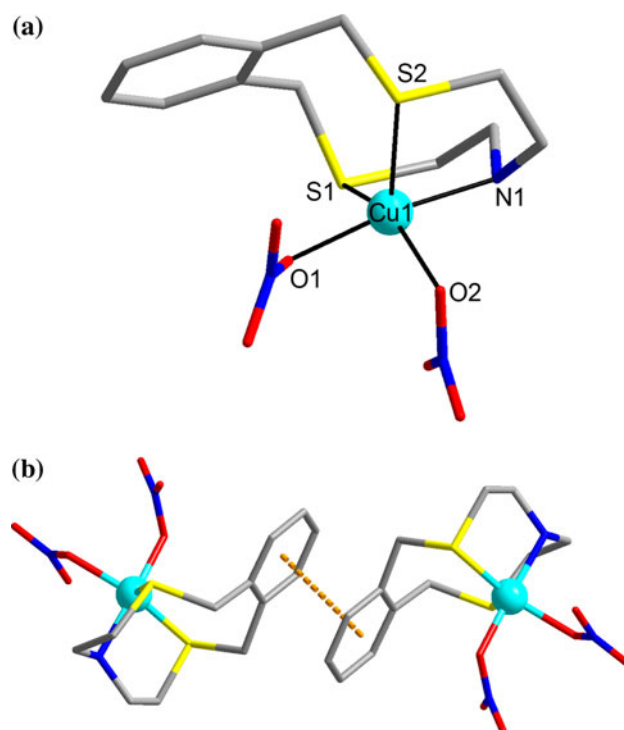


Fig. 1 **a** Crystal structure of **1**, [Cu(*o*-L)(NO₃)₂] and **b** its intermolecular π - π stacking (dashed line 3.647 Å)

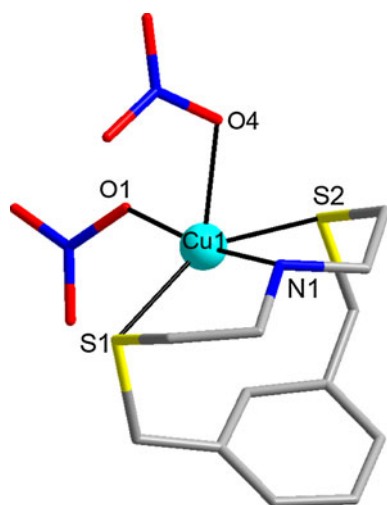


Fig. 2 Crystal structure of **2**, [Cu(*m*-L)(NO₃)₂]

Table 2 Comparison of bond lengths (Å) and bond angles (°) for **1** and **2**

	1	2
Bond lengths (Å)		
Cu1–S1	2.325(1)	2.362(1)
Cu1–S2	2.464(1)	2.475(1)
Cu1–N1	2.008(2)	2.001(2)
Cu1–O1	1.965(2)	1.973(2)
Cu1–O4	2.067(2)	2.194(2)
Bond angles (°)		
S1–Cu1–N1	88.2(1)	88.5(1)
N1–Cu1–S2	85.6(1)	87.6(1)
S1–Cu1–S2	115.1(1)	149.7(1)
S1–Cu1–O1	88.2(1)	95.6(1)
S2–Cu1–O4	95.4(1)	81.6(1)
O1–Cu1–O4	87.4(1)	84.2(1)
O1–Cu1–N1	169.9(1)	168.9(1)
N1–Cu1–O4	91.0(1)	85.2(1)
O4–Cu1–S1	149.4(1)	128.0(1)
O1–Cu1–S2	104.5(1)	93.9(1)

position. In this case, the bond length of Cu1–S2 [2.464(1) Å] is longer than that of Cu1–S1 [2.325(1) Å] due to the Jahn–Teller distortion. In **2**, the N₂S donors from one *m*-L and O1 atom from one nitrate ligand define the square plane and the apex position is occupied by O4 atom from another nitrate ligand. The bond length of Cu1–O4 [2.194(2) Å] is longer than that of Cu1–O1 [1.973(2) Å] due to the Jahn–Teller distortion. The Cu–N bond length [2.008(2) Å] in **1** is typical and similar to that in **2** [2.001(2) Å]. The bite angles of S–Cu–N for both complexes are very similar [85.6(1)–88.6(1)°], but those of S–Cu–S [115.1(1)° for **1** and 149.7(1)° for **2**] are different, in particular, **2**

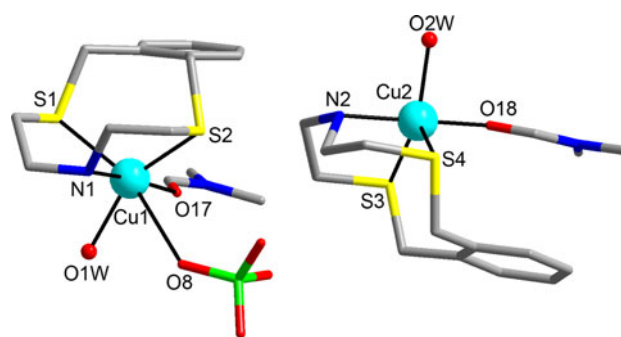


Fig. 3 Crystal structure of **3**, {[Cu(*o*-L)(H₂O)(DMF)(ClO₄)][Cu(*o*-L)(H₂O)(DMF)](ClO₄)₃·H₂O}. Non-coordinating anions and solvent molecule are omitted

shows much larger value because of its *meta*-substitution isomer effect.

Despite the overall geometrical similarity with the [M(tridentate)X₂] pattern, **1** and **2** show a difference in the packing structure. For example, interligand π – π stacking interaction between two aromatic rings (dashed line, centroid-to-centroid distance 3.647 Å) is found for **1** but no significant interaction exists for **2**. Probably because of this reason, the ligand itself is slightly bent in **1**, however, that in **2** is severely folded due to the arrangement of its donors in the basal plane.

Preparation and structural description of copper(II) perchlorate complex (3). Reaction of *o*-L with one equivalent of Cu(ClO₄)₂·6H₂O afforded the green crystalline complex **3** that proved suitable for crystallography. The crystal structure of **3** is shown in Fig. 3 and selected geometric parameters are presented in Table 3. The preparation of the corresponding copper(II) perchlorate complex with *m*-L was not possible.

In the crystal structure of **3**, two independent complex cations [Cu(*o*-L)(H₂O)(DMF)(ClO₄)]⁺ and [Cu(*o*-L)(H₂O)(DMF)]²⁺ were found, adopting slightly different conformation. The Cu1 atom is six-coordinated, being bound to the NS₂ donors of the ligand and three oxygen atoms from one DMF, one water molecule and one perchlorate ion in monodentate manner. The Cu1–O8 (perchlorate) distance [2.857(1) Å] is longer than those of Cu1–O17 (DMF) [1.965(2) Å] and Cu1–O1W [2.078(3) Å], suggesting that the DMF and water molecules are bonded more strongly to the Cu1 center. Thus, the coordination geometry of Cu1 can best be described as a distorted octahedron with the N1 and S2 from the ligand and two oxygen atoms from water and DMF molecules defining the square plane and the axial positions occupied by S1 from the ligand and O8 from perchlorate ion. The S1–Cu1–O8 angle is 160.8(1)°.

Unlike Cu1 atom, the Cu2 atom in **3** is five-coordinated, being bound to one nitrogen and two sulfur donors from *o*-L. Two remaining sites are occupied by two oxygen atoms from one water and one DMF molecules. The

Table 3 Selected bond lengths (Å) and bond angles (°) for **3**

Bond lengths (Å)	
Cu1–N1	1.991(2)
Cu1–S2	2.327(1)
Cu1–O17	1.965(2)
Cu2–S3	2.321(1)
Cu2–O2W	2.032(3)
Cu2–O18	1.947(3)
Cu1–S1	2.498(1)
Cu1–O1W	2.078(3)
Cu1–O8	2.857(1)
Cu2–N2	1.991(3)
Cu2–S4	2.484(1)
Bond angles (°)	
S1–Cu1–O8	130.2 (1)
N1–Cu1–O1W	88.0(1)
N1–Cu1–S2	87.7(1)
O17–Cu1–S1	102.7(1)
O1W–Cu1–S1	95.3(1)
S3–Cu2–S4	116.2(1)
N2–Cu2–O2W	91.2(1)
N2–Cu2–S3	86.6(1)
O18–Cu2–S4	101.7(1)
O2W–Cu2–S4	99.1(1)
O17–Cu1–O1W	90.2(1)
O17–Cu1–S2	90.1(1)
O1W–Cu1–S2	149.5(1)
N1–Cu1–S1	85.0(1)
S2–Cu1–S1	114.3(1)
O18–Cu2–O2W	90.3(1)
O18–Cu2–S3	87.2(1)
O2W–Cu2–S3	144.4(1)
N2–Cu2–S4	86.5(1)

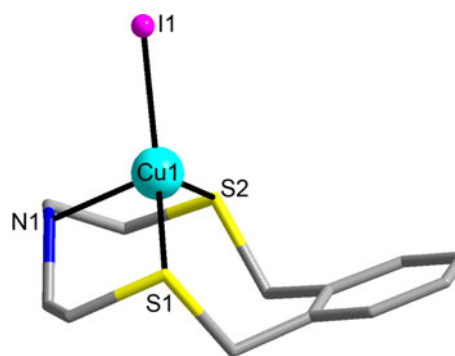
coordination geometry can best be described as a distorted square pyramid (τ value 0.45) with N2 and S3 donors from **L** and two oxygens from water and DMF defining the square plane and the apex position occupied by S4 atom from **o-L**.

Preparation and structural description of copper halide complexes (4 and 5). Having obtained three copper(II) complexes **1–3** for the two isomeric macrocycles, copper(I) halides were used to prepare the related complexes.

Colorless single crystals of complex **4** was obtained after adding a small amount of toluene to the top layer of dichloromethane solution of **o-L** then layering this with an acetonitrile solution of CuI, allowing the three phase system to stand. The crystal structure of **4** is shown in Fig. 4 and selected geometric parameters are presented in Table 4. The X-ray analysis reveals that **4** is a mononuclear complex of formula [Cu(**o-L**)I]. The Cu(I) center is facially coordinated by two S and one N donors from **o-L**, with the

Table 4 Selected bond lengths (Å) and bond angles (°) for **4**

Bond lengths (Å)	
Cu1–N1	2.135(3)
Cu1–S2	2.307(1)
Cu1–S1	2.280(1)
Cu1–I1	2.534(1)
Bond angles (°)	
I1–Cu1–S1	90.3(1)
S1–Cu1–S2	115.5(1)
S1–Cu1–I1	127.5(1)
N1–Cu1–S2	88.0(1)
N1–Cu1–I1	110.6(1)
S2–Cu1–I1	112.9(1)

**Fig. 4** Crystal structure of **4**, [Cu(**o-L**)I]

fourth coordination site occupied by an iodo ligand. The coordination sphere of the metal center is distorted tetrahedral; the “tetrahedral” angles range from 88.0(1)° for N1–Cu1–S2 to 127.5(1)° for S1–Cu1–I1.

Since the copper(I) iodide complex of **m-L** obtained was very unstable in air, copper(I) bromide complex **5** was prepared in the same condition. In this case, unlike **4**, green single crystals of **5** were obtained after adding a small amount of toluene to the top layer of dichloromethane solution of **m-L** then layering this with an acetonitrile solution of copper(I) bromide, allowing the three phase system to stand. The crystal color of this product initially suggested that it was a copper(II) species and this was subsequently confirmed by a crystal structure determination.

The crystal structure of **5** is shown in Fig. 5 and selected geometric parameters are presented in Table 5. The X-ray analysis reveals that **5** is a unique exodentate 2:1:2 (ligand-to-metal-to-anion) complex of formula [*trans*-Br₂Cu(**m-L**)₂]. The Cu atom outside the cavity is four-coordinated, being bound by two monodentate ligands via N–Cu bonds and two Br atoms, adopting a *trans*-type square-planar arrangement. In each macrocycle, two sulfur donors remain uncoordinated. The Cu1–N1 bond length [2.040(4) Å] is not remarkable [20]. In the present study, a simple change of substitution position from *ortho*- (**o-L**) to *meta*-type

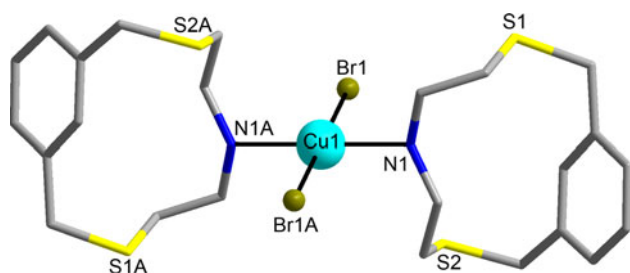


Fig. 5 Crystal structure of **5**, [*trans*-Br₂Cu(*m*-L)₂]

Table 5 Selected bond lengths (Å), bond angles (°) for **5**

Bond lengths (Å)	
Cu1–N1	2.040(4)
Cu1–Br1	2.398(1)
Bond angles (°)	
N1–Cu1–N1A	180.0(1)
Br1–Cu1–N1A	87.6(1)
N1–Cu1–Br1	92.4(1)
Br1–Cu1–Br1A	180.0(1)

[Symmetry operation: (A) $-x + 1, -y, -z$]

(*m*-L) thus results in the complex of the latter ligand adopting both a new oxidation state and a different geometry relative to the corresponding complex of *o*-L. The observed behavior can be explained that more rigid conformation of *m*-L as well as the high affinity of nitrogen donor for copper(II) aid the attainment of the square planar geometry upon oxidation of the metal center.

Conclusions

The present article describes the synthesis and structural characterization of five copper complexes with the two isomeric NS₂-macrocycles. The assembly reactions of the proposed macrocyclic isomers with the respective copper salts (different anions and oxidation states of the metal ions) provide a facile means of generating different complexes, including endocyclic 1:1 (ligand-to-metal) and exocyclic 2:1 species.

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