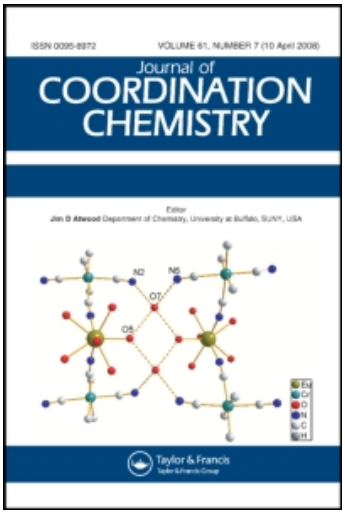

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Synthesis and structural characterization of copper(II) complexes of pincer ligands derived from benzimidazole

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Synthesis and structural characterization of copper(II) complexes of pincer ligands derived from benzimidazole

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A few pincer-type ligands, 1,3-*bis*(2′-benzimidazolyl)benzene (**L_1**), 2,6-*bis*(2′-benzimidazolyl)-pyridine (**L_2**), and their *N*-alkylated derivatives were prepared and characterized by IR and ^{1}H NMR spectroscopy. The *N*-alkylated benzimidazolyl ligands, 2,6-*bis*(*N*-benzylbenzimidazolyl)pyridine (**L_3**), 2,6-*bis*(*N*-allylbenzimidazolyl)pyridine (**L_4**), and 1,3-*bis*(*N*-allylbenzimidazolyl)benzene (**L_5**) form 1 : 1 complexes with copper nitrate. X-ray diffraction showed that $[Cu(NO_3)(MeOH)(L_4)](NO_3)$ (**7**) and $[Cu(NO_3)_2(L_3)]$ (**8**) are mononuclear complexes, whereas $[Cu(NO_3)_2(L_5)]\cdot 2DMF$ (**9**) exhibits one-dimensional zigzag motif. The chain consists of mutually bridged $Cu(NO_3)_2$ and L_5 ligand. Crystal data: **7**, triclinic, $P\bar{1}$, $a = 9.035(3)$ Å, $b = 11.149(4)$ Å, $c = 14.664(5)$ Å, $\alpha = 104.856(5)^\circ$, $\beta = 99.635(5)^\circ$, $\gamma = 99.409(5)^\circ$, $V = 1374.2(8)$ Å^3, $Z = 2$, and $R_1 = 0.0666$, $wR_2 = 0.1753$; **8**, monoclinic, Cc, $a = 12.979(5)$ Å, $b = 14.343(5)$ Å, $c = 16.966(6)$ Å, $\beta = 109.958(6)^\circ$, $V = 2968.9(18)$ Å^3, $Z = 4$, and $R_1 = 0.0582$, $wR_2 = 0.1352$; **9**, monoclinic, $P2_1/c$, $a = 17.278(6)$ Å, $b = 15.234(5)$ Å, $c = 16.161(5)$ Å, $\beta = 111.221(5)^\circ$, $V = 3965(2)$ Å^3, $Z = 4$, and $R_1 = 0.0658$, $wR_2 = 0.1612$.

Keywords: Pincer complex; Copper; Benzimidazole; Coordination polymer; Structure

1. Introduction

Pincer ligands are a type of terdentate ligands, which wrap around the metal center to create bonds on opposite sides of the metal as well as a bond in between (Chart 1). The effect of pincer ligands having nitrogen and phosphorous donating atoms on the metal is similar to amines, phosphines, and mixed donor ligands. This creates a situation where the activity of the metal can be tailored. For example, since pincer ligands place high demand on the stereochemistry of the complex, reactions of the metal ions are limited and selective [1].

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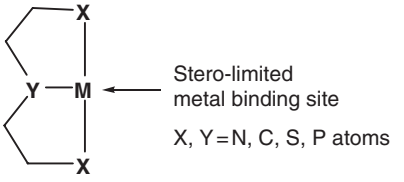


Chart 1. Schemetic illustration of the pincer ligands.

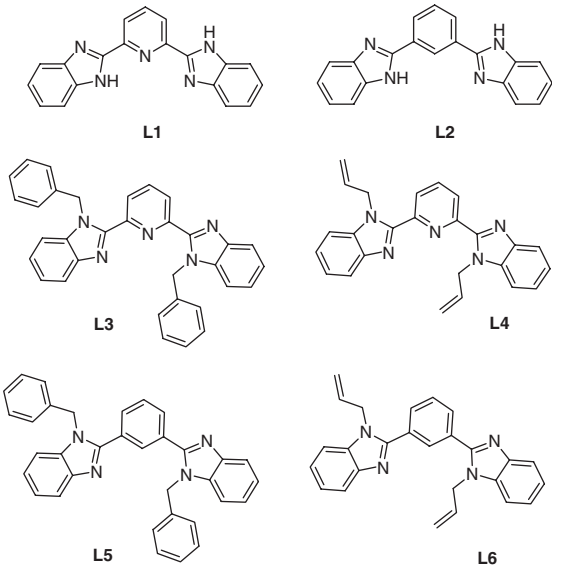


Chart 2. The pincer ligands employed in this paper.

Stoichiometric and catalytic applications of transition metal complexes of pincer ligands have been widely studied and a large number of NNN [2], NCN [3], PCP [4], PNP [5], SCS [6], and CCC [7] type ligands have been prepared. Pincer ligands can be anionic or neutral. Complexes have shown to be catalytically active in a number of organic transformations; for example, rhodium(III) complexes of the NCN *bis*(oxazoline) ligands are robust catalysts for Heck reactions [8]. A pincer PCP–Pd complex can catalyze allylation of aldehydes and imines via nucleophilic allyl palladium intermediates [9]. Imine pincer complexes of palladium displayed high catalytic activity in the Heck reaction of aryl iodides and butyl acrylate [10]. Mesogenic nickel and palladium complexes with pincer ligands derived from pyridine-2,6-*bis*(thiocarboxylic) acid show an important lowering in their melting point temperatures and give rise to chiral smectic C and chiral nematic phases [11].

Pincer complexes have also recently been studied for their use as molecular sensors and switches [12, 13]. Arylplatinum(II) complexes of the N,C,N′-terdentate-coordinating monoanionic pincer ligand can spontaneously absorb SO_2 to form pentacoordinated adducts, making these compounds useful for repetitive qualitative and quantitative diagnostic gas sensor applications. In this report we describe the preparation and characterization of a few pincer-type imidazolyl ligands (Chart 2) and their copper complexes.

2. Experimental

2.1. *Materials and general methods*

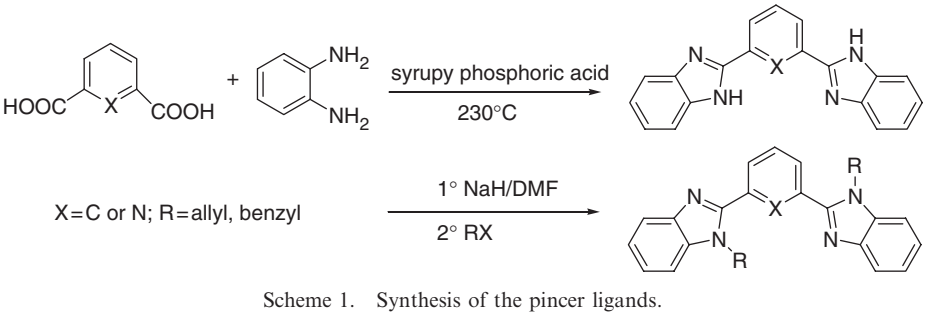
All commercially available reagents for synthesis and analyses were of analytical grade and used as received. $\mathbf{L_1}$ and $\mathbf{L_2}$ are prepared according to the published procedure [14]. DMF was distilled over CaH_2 prior to use. IR spectra (KBr pellets) were taken on a Bruker Zactor-22 spectrometer. C, H, and N microanalyses were performed with a Perkin Elmer 2400II CHNO/S instrument. ^{1}H NMR spectra were measured on a Bruker Avance-400 spectrometer (400 MHz) at 25°C with tetramethylsilane as the internal reference.

2.2. *Synthesis of benzimidazole derivatives*

The ligands were obtained from condensation of the dicarboxylic acids and phenylenediamine and subsequent alkylation (scheme 1).

2.2.1. Preparation of 2,6-*bis*(2′-benzimidazolyl)pyridine ($\mathbf{L_1}$). A mixture of pyridine-2,6-dicarboxylic acid (3.35 g, 20 mmol) and 1,2-phenylenediamine (4.7 g, 44 mmol) in 40 mL of 85% phosphoric acid was stirred at ca 230°C for 4 h. The dark green melt was poured into 1 L of vigorously stirred cold water. After it was cooled to room temperature, the bulky blue-green precipitate was collected by filtration, then slurried into 300 mL of hot aqueous sodium carbonate solution (10%). The resulting solid was filtered off and recrystallized from methanol to give colorless prisms. Yield: 3.3 g, 53%. Anal. Calcd for $C_{19}H_{13}N_5$(%): C, 73.30; H, 4.21; N, 22.49. Found: C, 73.12; H, 4.36; N, 22.03. ^{1}H NMR (DMSO-d_6): δ 13.0 (s, 2H), 8.36–8.38 (d, 2H), 8.19–8.23 (t, 1H), 7.76–7.80 (q, 4H), 7.34–7.37 (m, 4H).

2.2.2. Preparation of 1,3-*bis*(2′-benzimidazolyl)benzene ($\mathbf{L_2}$). The compound was prepared similarly as for $\mathbf{L_1}$ by using isophthalic acid (3.32 g, 20 mmol) and *o*-phenylenediamine (4.7 g, 44 mmol). Yield: 3.5 g, 57%. Anal. Calcd for $C_{20}H_{14}N_4$(%): C, 77.40; H, 4.55; N, 18.05. Found: C, 77.49; H, 4.22; N, 18.36. ^{1}H NMR (DMSO-d_6): δ 13.23 (s, 2H), 9.07 (d, 1H), 8.26–8.28 (d, 2H), 7.56–7.75 (m, 4H), 7.23–7.24 (s, 4H).



Scheme 1. Synthesis of the pincer ligands.

2.2.3. Preparation of 2,6-*bis*(*N*-benzylbenzimidazolyl)pyridine (L_3). L_1 (0.432 g, 1.39 mmol) was treated with sodium hydride (0.139 g, 3.47 mmol, 60% oil dispersion) in 10 mL of dry DMF at 0°C. After stirring 1 h at room temperature, benzyl chloride (0.44 g, 3.47 mmol) was added, and the resulting solution was stirred for 18 h. The mixture was then poured into water (150 mL), and the precipitate was filtered, dissolved in dichloromethane (50 mL), dried over sodium sulfate, and evaporated to dryness. The crude product was purified by column chromatography (Al_2O_3, CH_2Cl_2/MeOH 99 : 1), and then crystallized from CH_2Cl_2/hexane to give L_3 as yellow solid. Yield: 0.57 g, 85%. Anal. Calcd for $C_{33}H_{25}N_5$ (%): C, 80.63; H, 5.13; N, 14.25. Found: C, 80.74; H, 5.27; N, 13.89. ^{1}H NMR ($CDCl_3$): δ 8.38–8.40 (d, 2H), 8.01–8.02 (t, 1H), 7.87–7.89 (d, 2H), 7.30–7.33 (t, 2H), 7.15–7.27 (m, 10H), 6.80–6.82 (d, 4H), 5.55 (s, 4H). IR (KBr pellet, cm^{-1}): 3037w, 2981w, 1674w, 1570m, 1496m, 1450s, 1408m, 1352m, 1252m, 992m, 922m, 870m, 822m, 737s, 565w.

2.2.4. Preparation of 2,6-*bis*(*N*-allylbenzimidazolyl)pyridine (L_4). The compound was prepared from 2,6-*bis*(2′-benzimidazolyl)pyridine (0.43 g, 1.39 mmol) and allyl chloride (0.27 g, 3.47 mmol) using the same procedure as for L_3. The compound was obtained as a yellow solid. Yield: 0.45 g, 83%. Anal. Calcd for $C_{25}H_{21}N_5$ (%): C, 76.70; H, 5.41; N, 17.89. Found: C, 76.46; H, 5.21; N, 17.58. ^{1}H NMR ($CDCl_3$): δ 8.36–8.38 (d, 2H), 8.00–8.04 (t, 1H), 7.87–7.89 (m, 2H), 7.42–7.45 (m, 2H), 7.33–7.37 (m, 4H), 5.88–5.94 (m, 2H), 5.40–5.41 (d, 4H), 5.10–5.13 (d, 2H), 4.96–4.96 (d, 2H). IR (KBr pellet, cm^{-1}): 3059w, 1642m, 1572s, 1484m, 1443s, 1412s, 1330s, 1291m, 1249s, 1175m, 1090m, 1006m, 924m, 860m, 824m, 744s, 581w.

2.2.5. Preparation of 1,3-*bis*(*N*-benzylbenzimidazolyl)benzene (L_5). The compound was prepared similarly as for L_3 by using 1,3-*bis*(2′-benzimidazolyl)benzene (0.431 g, 1.39 mmol), sodium hydride (0.14 g, 3.47 mmol, 60% oil dispersion), and benzyl chloride (0.44 g, 3.47 ml); it is isolated as yellow pellets. Yield: 0.58 g, 85%. Anal. Calcd for $C_{34}H_{26}N_4$ (%): C, 83.24; H, 5.34; N, 11.42. Found: C, 83.11; H, 5.02; N, 11.37. ^{1}H NMR ($CDCl_3$): δ 8.09 (s, 1H), 7.85–7.87 (d, 2H), 7.79–7.80 (d, 2H), 7.55–7.56 (t, 1H), 7.32–7.37 (m, 2H), 7.21–7.30 (m, 10H), 7.03–7.05 (m, 4H), 5.41 (s, 4H). IR (KBr pellet, cm^{-1}): 3058w, 1607w, 1451s, 1388m, 1351m, 1329m, 1158m, 1002w, 809m, 743s, 697s.

2.2.6. Preparation of 1,3-*bis*(*N*-allylbenzimidazolyl)benzene (L_6). The same procedure as for L_3 was adopted for the preparation of L_6 from 1,3-*bis*(2′-benzimidazolyl)benzene (0.431 g, 1.39 mmol), sodium hydride (0.14 g, 3.47 mmol, 60% oil dispersion), allyl chloride (0.27 g, 3.47 mmol). It is isolated as yellow pellets. Single crystals of 1,3-*bis* (*N*-allylbenzimidazolyl)benzene suitable for X-ray diffraction were grown by slow diffusion of hexane into its CH_2Cl_2 solution. Yield: 0.48 g, 89%. Anal. Calcd for $C_{26}H_{22}N_4$ (%): C, 79.97; H, 5.68; N, 14.35. Found: C, 80.12; H, 5.59; N, 14.10. ^{1}H NMR ($CDCl_3$): δ 8.27(s, 1H), 8.12–8.14 (d, 2H), 7.79–7.80 (d, 2H), 7.55–7.56 (t, 1H), 7.38–7.40 (m, 2H), 7.32–7.35 (m, 4H), 6.08–6.10 (m, 2H), 5.30–5.33 (t, 2H), 5.11–5.12 (q, 2H), 4.86–4.87 (m, 4H). IR (KBr pellet, cm^{-1}): 3056w, 2924w, 1657w, 1454s, 1383m, 1362m, 1323, 1285m, 1158w, 921m, 738s, 704m.

2.3. *Synthesis of the copper(II) complex*

2.3.1. [Cu(NO$_3$)(MeOH)(L$_4$)](NO$_3$) (7). A solution of **L$_4$** (0.098 g, 0.2 mmol) in 10 mL methanol was added to a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.048 g, 0.2 mmol) in 10 mL of methanol. The solution was stirred for 1 day, and the precipitate was filtered, giving green solid. Crystals suitable for X-ray diffraction were prepared by diffusing ether into DMF solution. Yield: 0.12 g, 88%. Anal. Calcd for $C_{26}H_{25}CuN_7O_7$(%): C, 51.10; H, 4.12; N, 16.05. Found: C, 51.10; H, 4.12; N, 16.05.

2.3.2. [Cu(L$_3$)(NO$_3$)$_2$] (8). **L$_3$** (0.098 g, 0.2 mmol) in methanol (10 mL) was added to a solution of $Cu(NO_3)_2 \cdot 3H_2O$(0.048 g, 0.2 mmol) in methanol (10 mL). The solution was stirred for 1 day, and the precipitate was filtered, giving green solid. Yield: 0.12 g, 88%. Crystals suitable for X-ray diffraction were prepared by diffusing ether into DMF solution. Anal. Calcd for $C_{33}H_{25}CuN_7O_6$ (%): C, 58.36; H, 3.71; N, 14.44. Found: C, 58.66; H, 3.92; N, 14.17.

2.3.3. [Cu(L$_5$)(NO$_3$)$_2$] · 2DMF (9). **L$_3$** (0.078 g, 0.2 mmol) in methanol (10 mL) was added to a solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.048 g, 0.2 mmol) in methanol (10 mL). The solution was stirred for 1 day, and the precipitate was filtered, giving green solid. Yield: 0.14 g, 87%. Crystals suitable for X-ray diffraction were prepared by diffusing ether into its DMF solution. Anal. Calcd for $C_{39}H_{39}CuN_9O_8$(%): C, 56.76; H, 4.76; N, 15.27. Found: C, 56.57; H, 4.69; N, 15.43.

2.4. *Crystallographic data collection and structure determination*

Suitable crystals were mounted on a glass fiber on a Bruker SMART 1000 CCD diffractometer operating at 50 kV and 40 mA using Mo-Kα radiation (0.71073 Å). Unit-cell dimensions were obtained with least-squares refinement. Data collection and reduction were performed using the SMART and SAINT software [15]. The structures were solved by direct methods, and the non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using SHELXTL [16]. The hydrogen atoms were generated geometrically and included in structure factor calculations. Crystal data and refinement details are given table 1.

3. Results and discussion

3.1. *X-ray structural description of L$_6$*

The structure is shown in figure 1, and selected bond distances and angles are summarized in table 2. The compound crystallizes in a monoclinic space group $P2_1/c$. The structure displays a butterfly conformation, and the dihedral angles between the two imidazolyl rings and the phenyl ring are ca 30°. The two C=C bond distances are 1.230(6), 1.343(5) Å, whereas the two C–C of the allyl groups are 1.337(5) and 1.420(5) Å, respectively, reflecting some electronic delocalization of the allyl groups. The single and double bond distances of the two allyl groups are quite different from each other due to the disorder of the allyl groups.

Table 1. Crystal data and structure refinement summary for $\mathbf{L_6}$ and **7**–**9**.

	$\mathbf{L_6}$	**7**	**8**	**9**
Empirical formula	$C_{26}H_{22}N_4$	$C_{26}H_{25}CuN_7O_7$	$C_{33}H_{25}CuN_7O_6$	$C_{39}H_{39}CuN_9O_8$
Formula weight	390.48	611.07	679.14	825.33
Space group	$P2_1/c$	$P\bar{1}$	Cc	$P2_1/c$
a (Å)	11.776(3)	9.035(3)	12.979(5)	17.278(6)
b (Å)	16.143(4)	11.149(4)	14.343(5)	15.234(5)
c (Å)	12.074(3)	14.664(5)	16.966(6)	16.161(5)
		104.856(5)		
β (°)	117.023(4)	99.635(5)	109.958(6)	111.221(5)
		99.409(5)		
V (Å^3)	2044.8(8)	1374.2(8)	2968.9(18)	3965(2)
Z	4	2	4	4
D_{Calcd} (g cm^{-3})	1.268	1.477	1.519	1.382
μ(mm^{-1})	0.077	0.853	0.796	0.614
F(000)	824	630	1396	1716
Range of h, k, l	−14/13, −19/19, −8/14	−10/10, −12/13, −17/17	−7/15, 6/17, 20/17	−15/20, −8/8, −19/19
Reflections collected	10571	7174	7669	20620
Reflections unique (R_{int})	3588 (0.0795)	4762 (0.0279)	3615 (0.0510)	6999 (0.0709)
Max. and min. transmission	0.9924/0.9796	0.951/0.7212	0.7681/0.7413	0.7912/0.7570
Data/restraints/parameters	3588/80/271	4762/254/427	3615/86/424	6999/145/517
Goodness-of-fit on F^2	0.999	1.025	1.006	1.014
Final R indices [$I > (2\sigma)I$]	0.0601	0.0666	0.0582, 0.1352	0.0658, 0.1612
	0.1076	0.1753		
R indices (all data)	0.1883	0.1092	0.0957, 0.1570	0.1592, 0.2389
	0.1345	0.2066		
Largest diff. peak and hole (e Å^{-3})	0.330/−0.261	0.692h/−0.323	0.519/−0.330	0.632/−0.453
		3	0	3

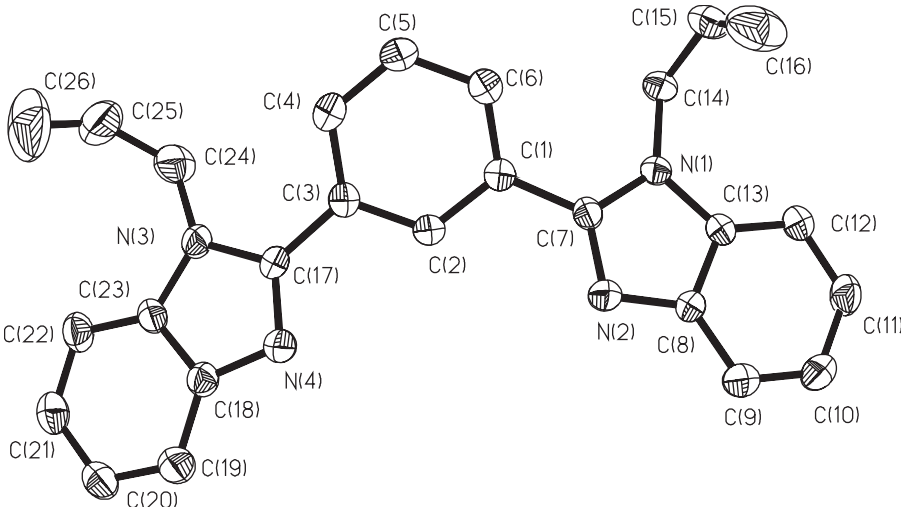


Figure 1. Molecular structure of 1,3-*bis*(*N*-allylbenzimidazolyl)benzene. All H atoms were omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°) for (**L_6**).

N1–C13	1.377(4)	N3–C23	1.381(4)
N1–C7	1.379(4)	N3–C17	1.389(4)
N1–C14	1.450(4)	N3–C24	1.434(5)
N2–C7	1.306(4)	N4–C17	1.311(4)
N2–C8	1.394(4)	N4–C18	1.384(4)
C13–N1–C7	105.9(3)	C9–C8–N2	130.1(4)
C13–N1–C14	123.4(3)	C13–C8–N2	109.9(4)
C7–N1–C14	130.4(4)	N1–C13–C12	131.2(4)
C7–N2–C8	104.8(3)	N1–C13–C8	106.1(3)
C23–N3–C17	106.7(3)	C15–C14–N1	116.2(4)
C23–N3–C24	124.5(3)	N4–C17–N3	112.0(4)
C17–N3–C24	127.8(4)	N4–C17–C3	123.5(4)
C17–N4–C18	105.0(3)	N3–C17–C3	124.5(4)
N2–C7–N1	113.2(4)	C23–C18–N4	111.2(4)
N2–C7–C1	122.9(4)	N4–C18–C19	129.0(4)
N1–C7–C1	123.8(4)	C22–C23–N3	131.8(4)
C25–C24–N3	123.2(5)	C18–C23–N3	105.1(4)

3.2. *Structure of [Cu(NO$_3$)(MeOH)(L$_4$)](NO$_3$) (7)*

The structure of **7** consists of a discrete cation $[Cu(NO_3)(\mathbf{L_4})(MeOH)]^+$ and a disordered nitrate. The structure of the cation is shown in figure 2, and selected bond distances and angles are listed in table 3. The copper atom in the cation is coordinated by two imidazole nitrogen atoms, one pyridine nitrogen atom, two nitrate oxygen atoms and one methanol molecule forming an elongated octahedron about copper. The three nitrogen atoms of 2,6-*bis*(2′-benzimidazolyl)pyridine and one nitrate oxygen constitute the equatorial plane with MeOH and a nitrate oxygen atom located at the axial positions. MeOH is disordered with the carbon atom occupying two sites. One of the allyl groups is also disordered as shown in figure 2. Both the Cu–O and Cu–N distances at the equatorial positions are normal, but one Cu–$O_{nitrate}$ and Cu–O_{MeOH} distances

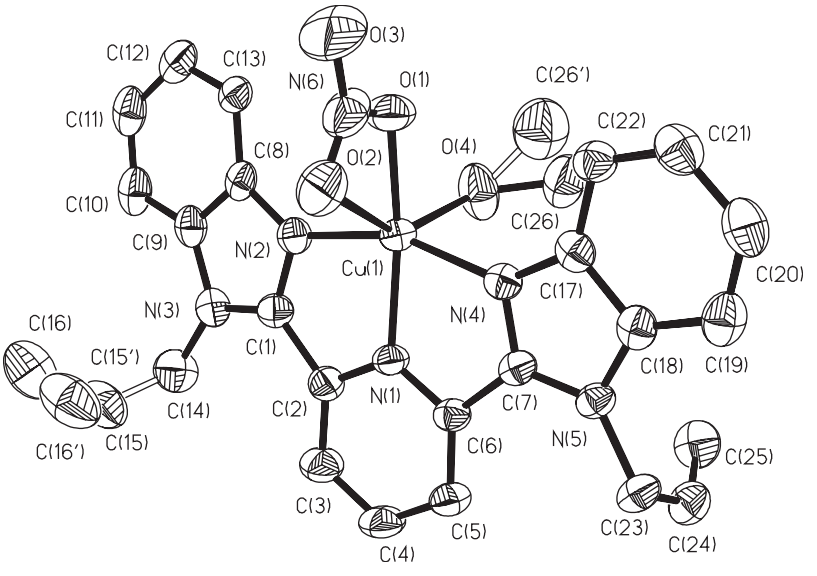


Figure 2. Molecular structure of **7**. All hydrogen atoms were omitted for clarity.

Table 3. Selected bond lengths (Å) and bond angles (°) for [Cu(NO_3)(MeOH)(**L_4**)](NO_3).

Cu1–O1	1.959(5)	Cu1–N4	1.988(5)
Cu1–N1	1.983(4)	Cu1–N2	2.003(5)
Cu1–O4	2.278(5)	Cu–O2	2.618(6)
O1–Cu1–N1	168.0(2)	N4–Cu1–N2	159.2(19)
O1–Cu1–N4	99.66(19)	O1–Cu1–O4	92.40(3)
N1–Cu1–N4	79.32(18)	N1–Cu1–O4	99.60(2)
O1–Cu1–N2	100.3(2)	N4–Cu1–O4	93.20(18)
N1–Cu1–N2	79.92(19)	N2–Cu1–O4	91.91(18)

are quite long. The Cu–O2 bond [2.618(6) Å] is so long that the Cu–O interaction can be neglected. Thus the structure of the compound may also be viewed as a square pyramid. The noncoordinated NO_3^- ion is nearly parallel to the equatorial plane of copper, and the anion forms hydrogen bond with the coordinated methanol molecule with O4 $\cdots$ O5 and O4 $\cdots$ O6 distances of 2.51(2) and 2.61(2), respectively.

3.3. *X-ray structural description of [Cu(L_3)(NO_3)$_2$] (8)*

The ligand 2,6-*bis*(*N*-benzylbenzimidazolyl)pyridine and copper nitrate also form mononuclear complex **8** and its structure was determined by X-ray diffraction. The compound crystallizes in a monoclinic space group $P2_1/c$. The central copper atom is pentacoordinate by two nitrate anions and three nitrogen atoms of a 2,6-*bis* (*N*-benzylbenzimidazolyl)pyridine molecule. The structure can be viewed as a distorted pyramid with a nitrate and 2,6-*bis*(*N*-benzylbenzimidazolyl)pyridine located at the equatorial plane, and another nitrate at the axial position. The Cu–O_{eq} distance is much shorter than that of Cu–O_{ax} bond. The imidazolyl ligand is roughly planar because of the coordination constraint. The two benzyl groups are below and above

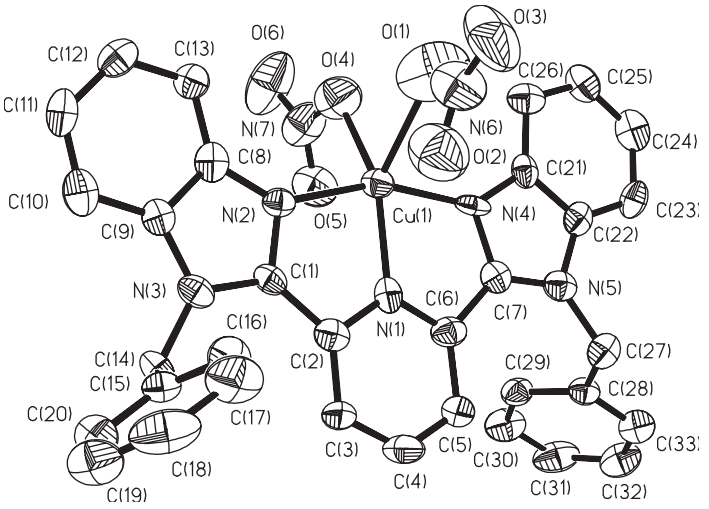


Figure 3. Molecular structure of **8**. All hydrogen atoms were omitted for clarity.

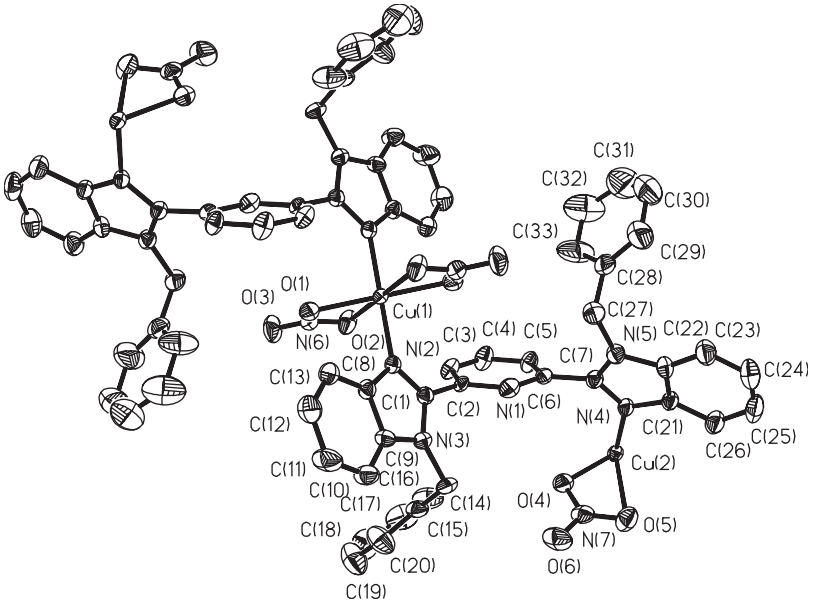


Figure 4. Asymmetric unit of the coordination polymer **9** with numbering scheme.

the equatorial plane. The Cu1–O2 and Cu1–O5 bond distances are 2.469(12) and 2.642(9) Å, respectively, which are remarkably longer than those of usual Cu–O bonds, and thus the two nitrate anions are viewed as monodentate ligands.

3.4. *X-ray structural description of* $[Cu(L_5)(NO_3)_2] \cdot 2DMF$ *(9)*

Compound **9** was obtained as green crystals by reacting copper nitrate and one equivalent of 2,6-*bis*(*N*-benzylbenzimidazolyl)pyridine in methanol. The structure of **9**

Table 4. Selected bond lengths (Å) and bond angles (°) for [Cu($\mathbf{L_3}$)$(NO_3)_2$].

Cu1–N1	1.981(9)	Cu1–N2	1.990(8)
Cu1–N4	1.984(8)	Cu1–O1	2.326(17)
Cu1–O4	1.984(10)		
N2–Cu1–O1	105.6(4)	N1–Cu1–O2	89.80(4)
N1–Cu1–N4	79.20(3)	N4–Cu1–O2	96.10(4)
N1–Cu1–O4	152.5(4)	O4–Cu1–O2	116.9(5)
N4–Cu1–O4	102.6(3)	N2–Cu1–O2	85.80(4)
N1–Cu1–N2	79.90(3)	O1–Cu1–O2	45.50(5)
N4–Cu1–N2	159.0(3)	N1–Cu1–O5	100.9(3)
O4–Cu1–N2	95.10(3)		
N1–Cu1–O1	132.9(4)	N4–Cu1–O5	87.60(3)
N4–Cu1–O1	90.30(4)	O4–Cu1–O5	52.20(3)
O4–Cu1–O1	74.50(5)	N2–Cu1–O5	94.40(3)
O2–Cu1–O5	169.1(5)	O1–Cu1–O5	124.6(4)

Table 5. Selected bond lengths (Å) and bond angles (°) for [Cu($\mathbf{L_5}$)$(NO_3)_2$]·2DMF.

Cu1–N2	1.971(5)	Cu2–N4	1.964(6)
Cu1–O1	2.041(5)	Cu2–O4	2.020(5)
Cu1–O2	2.462(6)	Cu2–O5	2.546(6)
N2–Cu1–N2	180.0(2)	N4–Cu2–N4	180.0(13)
N2–Cu1–O1	89.40(2)	N4–Cu2–O4	90.10(2)
N2–Cu1–O1	90.60(2)	N4–Cu2–O4	89.90(2)
O1–Cu1–O1	180.0(1)	O4–Cu2–O4	180.0(1)
N2–Cu1–O2	91.60(2)	N4–Cu2–O5	87.60(2)
O1–Cu1–O2	56.10(2)	O4–Cu2–O5	54.40(2)
C1–N2–Cu1	129.7(5)	N6–O2–Cu1	83.10(4)
C8–N2–Cu1	123.2(4)	N7–O4–Cu2	105.9(5)
C7–N4–Cu2	130.0(5)	N7–O5–Cu2	82.00(5)
N6–O1–Cu1	102.6(4)		

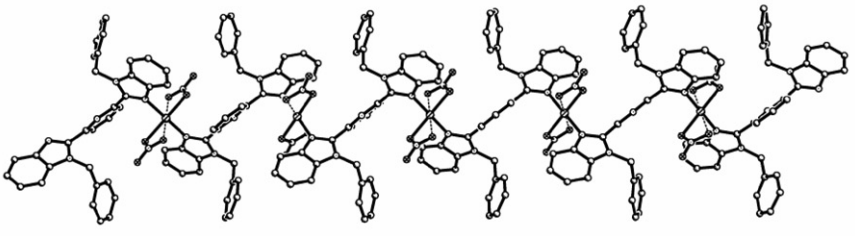


Figure 5. One-dimensional zigzag chain structure of [Cu($\mathbf{L_5}$)$(NO_3)_2$]·2DMF. The longer Cu–O bonds are illustrated in dashed lines.

is shown in figure 4, and some important bond distances and angles are given in table 5. The structure is an infinite one-dimensional zigzag chain consisting of alternate 2,6-*bis*(*N*-benzylbenzimidazolyl)pyridine and $Cu(NO_3)_2$, which are mutually bridged. An asymmetric unit contains two independent copper atoms, one 2,6-*bis* (*N*-benzylbenzimidazolyl)pyridine, and two DMF molecules. Each copper atom has octahedral geometry and is surrounded by two nitrate anions and two imidazolyl groups which are mutually *trans*. Nitrate anions are bonded in an unsymmetrical chelating mode. One of the two Cu–O bonds is significantly longer than the other one. The chain structure is shown in figure 5.

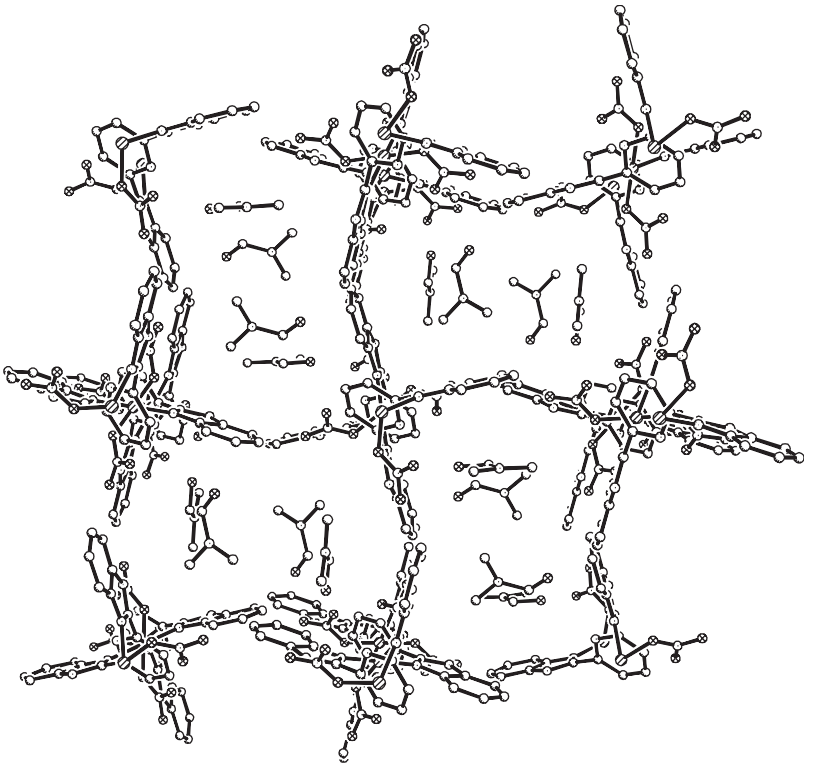


Figure 6. Crystal packing of **9** viewed along the crystallographic *a* axis showing the tetragonal arrangement of 1D chains. DMF molecules occupy the voids of the channels.

One-dimensional chains run along the crystallographic *a* axis, arranged parallel and forming a tetragonal array with tetragonal channels. As shown in figure 6, DMF molecules fill in the tetragonal channels generated by four chains.

In summary, a number of pincer ligands and their copper complexes have been prepared and structurally characterized. The results show that the pincer ligands described above form copper complexes with different structures. The influence of the N-substituents on the structures and the properties of these compounds merit further study.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 606751 and 606754 for compound **L6**, and **7**–**9**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK. [Fax. (int code) +44(1223)336-033 or Email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk].

Acknowledgements

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