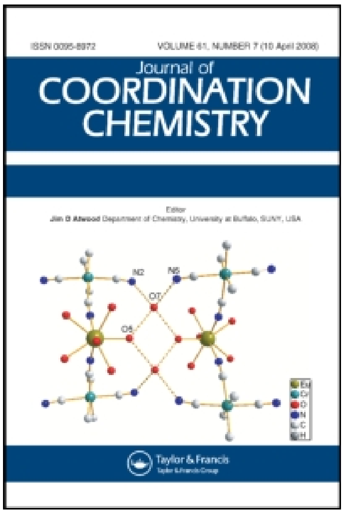

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A mixed carboxylate polymer as an intermediate during synthesis of mononuclear <i>bis</i>-3, 5-dimethylpyrazole copper(II) benzoates

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A mixed carboxylate polymer as an intermediate during synthesis of mononuclear *bis*-3, 5-dimethylpyrazole copper(II) benzoates

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The crystal structures of *bis*-3,5-dimethylpyrazole copper(II) 4-methylbenzoate, *bis*-3,5-dimethylpyrazole copper(II) 3-methylbenzoate, *bis*-3,5-dimethylpyrazole copper(II) 4-nitrobenzoate show that 3,5-dimethylpyrazole in the *cis* or *trans* positions is related to axial distortion of Cu-O bond in carboxylate groups. A metastable mixed carboxylate co-ordination polymer presumably intermediate to the one described above which has alternate paddlewheel and mononuclear units is structurally characterized.

Keywords: Co-ordination polymer; Copper carboxylates; 3,5-Dimethylpyrazole; Metastable complex

1. Introduction

Copper carboxylate complexes are important in biology [1] and also in material science [2]. Different binding modes of carboxylate can contribute to different nuclearity copper complexes [3]. Polymeric structures with alternating dinuclear carboxylate-bridged structures (scheme 1) involving benzoate are rare [4], but could be formed from different combinations as illustrated in scheme 1. Polymeric complex of type A was shown recently but all combinations are important as they may be considered as metastable complexes, whose decomposition can either lead to mononuclear or dinuclear complexes. However, there are other possibilities such as combination of a mononuclear carboxylate and dinuclear carboxylate-bridged structures with another carboxylate [4, 5]. In this study we report the structure of a metastable carboxylate complex which is alternate mono- and dinuclear complexes of two different carboxylic acids (type B, scheme 1).

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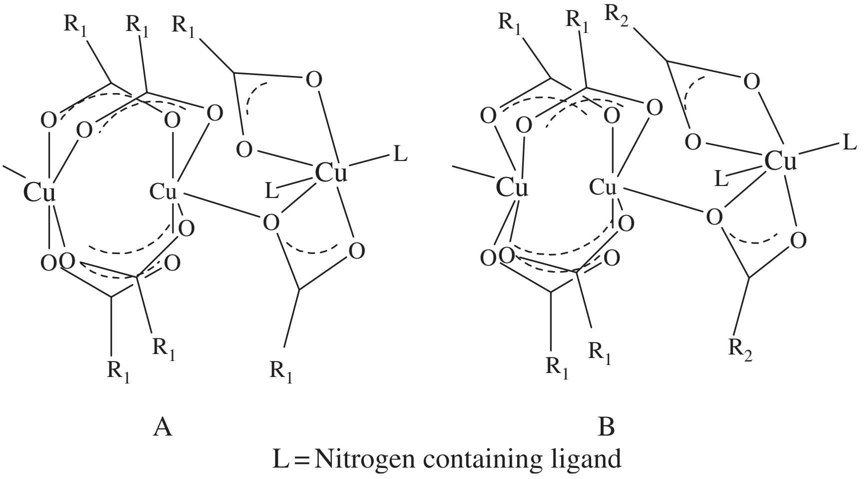


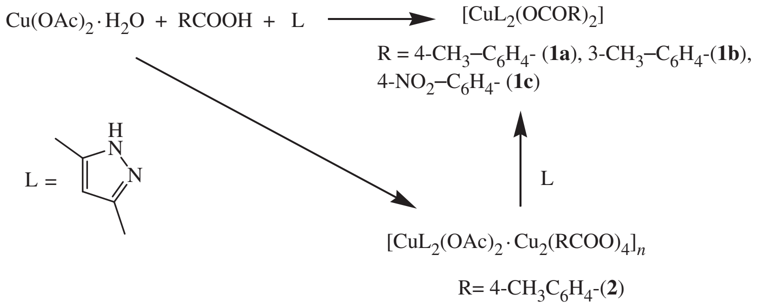
Scheme 1. Two types polymeric chains from mononuclear and binuclear copper(II) carboxylates.

2. Results and discussion

Reaction of copper(II) acetate monohydrate with 3,5-dimethylpyrazole and aromatic carboxylic acids such as 4-methylbenzoic, 3-methylbenzoic or 4-nitrobenzoic acid in methanol gives mononuclear complexes [6] as shown in scheme 2.

Crystal structures of each of these complexes are determined and are shown in figure 1 and the crystal parameters are listed in table 1. These compounds show N–H stretches around 3435 cm^{-1} and methyl group stretching at 2924–2928 cm^{-1}. The N–N stretching of the pyrazole ring appears at 1181–1185 cm^{-1}. The stretching frequencies for the chelating carboxylate for **1a**, **1b** and **1c** are at 1586, 1549 and 1584 cm^{-1}, respectively. The three compounds show d–d transitions at 703–706 nm due to the $E \rightarrow T_2$ transition. The *bis*-3,5-dimethylpyrazole copper(II) 4-methylbenzoate has 3,5-dimethylpyrazole *trans*, whereas the *bis*-3,5-dimethylpyrazole copper(II) 3-methylbenzoate has the two 3,5-dimethylpyrazole ligands *cis*. Selected bond distances are listed in table 2. In these complexes one Cu–O bond is short, 1.96–1.98 Å; another pair of Cu–O bond distances in the case of **1a** and **1b** are 2.64 and 2.56 Å, respectively, and for **1c**, Cu–O2 is 2.91 Å. Thus, in **1c** the complex is square planar. This difference in bond distances reflects the geometry of the benzoate groups, whether the 3,5-dimethylpyrazoles are *cis* or *trans*. There is a large number of copper complexes of 3,5-dimethylpyrazole [6] with different focus; here we prepare specific compounds for understanding the structures as well as their nucleation and geometrical consequences from stoichiometry and reaction conditions. Projections of the non-co-ordinating N–H of pyrazole are different in each compound, for example in **1a** and in **1c** they are *trans* to each other, whereas in **1b** they lie in two planes far apart. The methyl groups of the 3-methylbenzoates in **1b** are *trans* to reduce steric congestion allowing the complex to have a *cis* structure. Complexes **1a**–**1c** self assemble through intermolecular hydrogen bonds, as illustrated in figures 1d–1f. The hydrogen bond parameters are listed in table 3.

From reaction of 4-methylbenzoic acid with copper(II) acetate in the presence of 3,5-dimethylpyrazole, we obtain a polymeric compound which has repeated



Scheme 2. Reactions of 3,5-dimethylpyrazole with copper(II) acetate and aromatic acids.

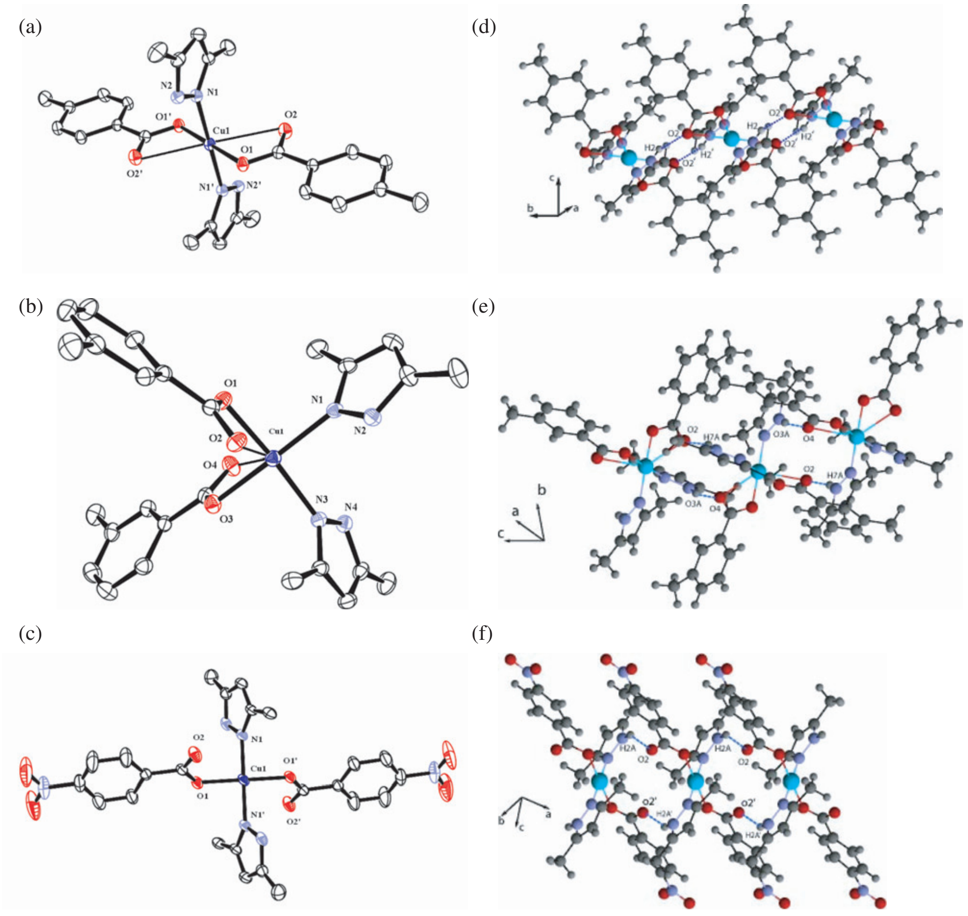


Figure 1. The crystal structures of complex (a) *bis*-3,5-dimethylpyrazole copper(II) 4-methylbenzoate (**1a**). (b) *bis*-3,5-dimethylpyrazole copper(II) 3-methylbenzoate (**1b**), (c) *bis*-3,5-dimethylpyrazole copper(II) 4-nitrobenzoate (**1c**) (hydrogen atoms are omitted for clarity drawn with 20% thermal ellipsoids). Hydrogen bond interactions and packing in (d) **1a**, (e) **1b** (f) **1c**.

Table 1. Crystallographic parameters of **1a**–**1c** and **2**.

Compound No.	**1a**	**1b**	**1c**	**2**
Identification name	CuPtaDmp	CuMtaDmp	CuPnbaDmp	CuPt_Dmp(poly)
Formula	$C_{26}H_{30}CuN_4O_4$	$C_{26}H_{30}CuN_4O_4$	$C_{24}H_{24}CuN_6O_8$	$C_{46}H_{50}Cu_3N_4O_{12}$
Mol. wt.	526.08	526.08	588.03	1041.52
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	$P2_1/n$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Temperature (K)	296	296	296	296
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Unit cell dimensions (Å, °)				
a	13.7701(7)	10.4330(2)	5.2839(8)	10.1608(9)
b	6.0277(3)	11.5034(2)	9.4720(14)	11.0929(9)
c	16.7092(8)	11.6865(2)	13.312(2)	12.1839(11)
α	90.00	85.2260(10)	96.811(11)	80.391(6)
β	111.709(3)	71.0580(10)	96.293(12)	67.355(6)
γ	90.00	76.9740(10)	91.593(10)	75.732(6)
V (Å^3)	1288.53(11)	1292.39(4)	657.00(17)	1224.33(18)
Z	2	2	1	1
Density (Mgm^{-3})	1.356	1.352	1.486	1.413
Abs. coeff. (mm^{-1})	0.886	0.883	0.890	1.353
Abs. correction	None	None	None	None
$F(000)$	550	550	303	537
Total no. of reflections	15786	13389	6342	14171
Reflections, [$I > 2\sigma(I)$]	3123	5989	2437	4603
Max.2θ(°)	28.30	28.28	26.11	26.00
Ranges (h, k, l)	$-18 \le h \le 17$ $-7 \le k \le 7$ $-22 \le l \le 20$	$-13 \le h \le 13$ $-15 \le k \le 15$ $-15 \le l \le 14$	$-6 \le h \le 6$ $-11 \le k \le 11$ $-16 \le l \le 16$	$-12 \le h \le 12$ $-13 \le k \le 13$ $-14 \le l \le 15$
Complete to 2θ (%)	97.6	93.4	93.1	95.7
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/ parameters	3123/0/163	5989/0/316	2437/0/178	4603/0/300
Goodness of fit F^2	1.070	1.018	1.047	1.121
R indices [$I > 2\sigma(I)$]	0.0357	0.0460	0.0479	0.1316
R indices (all data)	0.0555	0.0735	0.0606	0.1491

Table 2. Selected bond distances (Å) and angles (°) of **1a**, **1b** and **1c**.

1a		**1b**		**1c**	
Cu1–N1	1.9699(17)	Cu1–O1	1.9778(18)	Cu1–O1	1.960(2)
Cu1–O1	1.9846(14)	Cu1–O3	1.9814(18)	Cu1–N1	1.972(3)
Cu1–O2	2.640	Cu1–N1	1.990(2)		
		Cu1–N3	1.992(2)		
		Cu1–O4	2.560		
N1–Cu1–N1′	180.00(7)	O1–Cu1–O3	88.17(8)	O1–Cu1–O1′	180.00(6)
N1–Cu1–O1	89.58(7)	O1–Cu1–N1	88.42(8)	O1–Cu1–N1	91.32(10)
N1–Cu1–O1	90.42(7)	O3–Cu1–N1	174.00(8)	O1–Cu1–N1	88.68(10)
O1–Cu1–O1′	180.00(7)	O1–Cu1–N3	177.89(8)	N1–Cu1–N1′	179.99(2)
		O3–Cu1–N3	91.30(8)		
		N1–Cu1–N3	92.28(9)		

Table 3. Hydrogen bond parameters in **1a**–**1c**.

	$d_{\text{D–H}}$ (Å)	$d_{\text{H}\cdots\text{A}}$ (Å)	$d_{\text{D}\cdots\text{A}}$ (Å)	∠D-H···A (°)
Complex **1a**				
N2–H2A···O2	1.999	0.860	2.747	144.94
Complex **1b**				
N2–H7A···O2	1.896	0.859	2.731	163.68
N4–H3A···O4	1.911	0.860	2.738	161.17
Complex **1c**				
N2–H2···O2	0.860	1.941	2.747	155.62

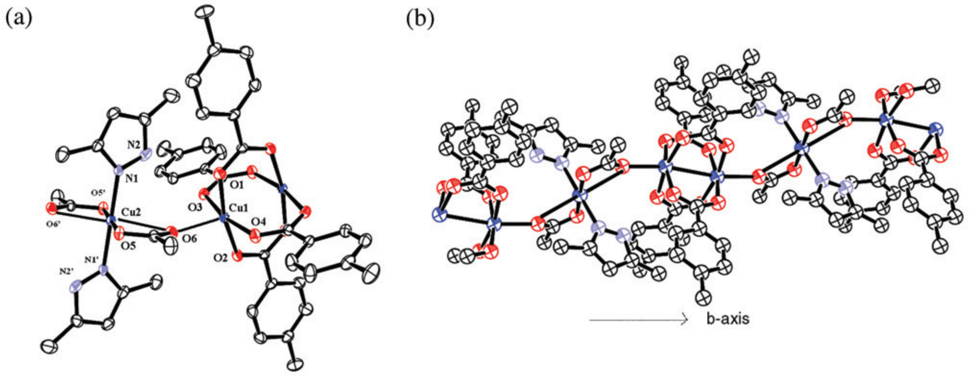


Figure 2. (a) The repeated units of the co-ordination polymer **2** and (b) the polymer chain along *b*-axis (drawn with 20% thermal ellipsoid, hydrogen atoms are omitted for clarity).

mononuclear and dinuclear copper centers as shown in figure 2. In our earlier study, we have shown polymeric structures of mononuclear and binuclear species of type A in scheme 1. In this study we have obtained an unstable polymeric compound of type B (scheme 1). The dinuclear repeated units have the structures resembling regular paddle wheel structures observed in dinuclear copper(II) complexes. The axial positions are occupied by the oxo-bridges of acetate from the mononuclear part. The one-dimensional polymeric structure grows along the *b*-crystallographic axis (figure 2b). Some of the bond distances and bond angles are listed in table 4. It is clear that the co-ordination geometry around the two copper centers is different. The mononuclear copper has a distorted octahedral geometry, whereas the binuclear complex has a distorted square pyramidal geometry. Copper(II) acetate from which complex **2** is prepared has a paddle wheel structure, but in **2** the copper(II) acetate is mononuclear and the acetate groups are chelating. In the carboxylate-bridged, dinuclear part the Cu1–Cu1 distance is 2.67 Å, whereas in the chain structure the Cu1–Cu2 distance is 4.37 Å. In copper(II) acetate the Cu–Cu distance [7] is 2.61 Å. This suggests that there may be an equilibrium between mono and binuclear carboxylates when an external carboxylic acid is added to the system and the nitrogen donor ligand/s stabilizes either form. This would also explain our earlier observation on formation of type A structure (scheme 1). Polymeric complex **2** has IR absorptions at 1627 (ν_{asym} CH_3COO^-)cm^{-1}, 1546 (ν_{asym} $CH_3C_6H_4COO^-$)cm^{-1} and 1407 (ν_{sym} CH_3COO^-)cm^{-1}. The polymeric chain along crystallographic b-axis

Table 4. Selected bond distance (Å) and angles (°) of **2**.

Cu1–O3	1.948(11)	O3–Cu1–O4	168.1(5)
Cu1–O4	1.968(10)	O3–Cu1–O1	89.7(5)
Cu1–O1	1.985(10)	O4–Cu1–O1	89.1
Cu1–O2	1.992(10)	O3–Cu1–O2	87.2(5)
Cu1–O6	2.150	O4–Cu1–O2	91.4(5)
Cu2–N1	1.979(12)	O1–Cu1–O2	167.3(4)
Cu2–O5	1.992(10)	O3–Cu1–O6	90.5(4)
		O4–Cu1–O6	101.4(4)
		O1–Cu1–O6	88.1(4)
		O2–Cu1–O6	104.2(4)
		N1–Cu2–N1′	179.998(1)
		N1–Cu2–O5	88.8(5)
		O5–Cu2–O5′	179.9

is stabilized by N2–H2···O1 interactions between the pyrazole ring NH and an oxygen of carboxylato group ($d_{\text{D-H}}$(Å) 0.852, $d_{\text{H}\cdots\text{A}}$(Å) 2.122, $d_{\text{D}\cdots\text{A}}$(Å) 2.942, ∠D–H···A(°) 161.21). From these observations it is apparent that addition of an aromatic acid to copper(II) acetate causes equilibration between dinuclear and mononuclear species and the nitrogen donor ligand can trap different structures.

In conclusion, an aromatic carboxylic acid added to copper(II) acetate establishes an equilibrium between the mononuclear and dinuclear carboxylate complexes and mononuclear, binuclear, or polynuclear complexes can be prepared by treating this equilibrating mixture with 3,5-dimethylpyrazole. The substituent attached on an aromatic carboxylate provides twist to carboxylato group to four or six co-ordinate copper(II) in *cis* or *trans* isomers.

3. Experimental

Synthesis of **1a** and **2**: To a solution of 4-methylbenzoic acid (2 mmol, 0.272 g) in methanol (20 ml), copper(II) acetate monohydrate (1 mmol, 0.199 g) was added and stirred for 10 min and a solution of 3,5-dimethylpyrazole (2 mmol, 0.192 g) was added. The solution became blue and small amount of THF (10 ml) was added and allowed to stir for another 15 min to ensure complete dissolution of the precipitate. Some green unstable crystals were obtained after 3 days, subsequently converted to blue the next day. The yield of the crystalline product was 78% (**1a**). UV–vis ($\lambda_{\max}$ methanol) 703 nm ($\varepsilon = 69\,\text{L mol}^{-1}\text{cm}^{-1}$). IR (KBr, cm^{-1}) 3186(m), 3088(s), 2928(s), 2869(s), 1586(s), 1546(s), 1309(m), 1183(w), 1058(w), 861(s), 765(s). Molar conductance, 10.5 $\text{S cm}^2\text{mol}^{-1}$. Magnetic moment μ_{eff} 1.89 BM (RT).

The unstable crystals can be immediately taken to the diffractometer and structure solved, giving polymeric complex **2**. IR (KBr, cm^{-1}) 3437(s), 2924(s), 2851(m), 1744(w), 1628(s), 1546(s), 1408(s), 762(m).

Complexes **1b** and **1c** are prepared by using 3-methylbenzoic acid or 4-nitrobenzoic acid in a similar manner to **1a** with 62% and 72% yields, respectively. For **1b**: UV–Vis ($\lambda_{\max}$ methanol) 706 nm ($\varepsilon = 66\,\text{L mol}^{-1}\text{cm}^{-1}$). IR (KBr, cm^{-1}) 3095(m), 3033(m), 2873(m), 1549(s), 1429(s), 1389(s), 1304(s), 1183(w), 1053(w), 803(s), 751(s). Molar conductance, 14.8 S $\text{cm}^2\,\text{mol}^{-1}$. Magnetic moment μ_{eff} 2.0 BM (RT). **1c**.

UV–Vis (λ_{max}, THF) 703 nm ($\varepsilon = 196\,\mathrm{L\,mol^{-1}\,cm^{-1}}$). IR (KBr, $\mathrm{cm^{-1}}$) 3191(s), 3045(s), 1615(s), 1584(s), 1518(s), 1374(s), 1344(s), 1056(w), 833(s), 792(s), 723(s). Magnetic moment μ_{eff} 1.80 BM (RT).

3.1. *Structure determination*

The X-ray diffraction data were collected at 296 K with Mo Kα radiation ($\lambda = 0.71073$ Å) using a Bruker Nonius SMART CCD diffractometer equipped with graphite monochromator. SMART software was used for data collection and also for indexing the reflections and determining the unit cell parameters; the collected data were integrated using SAINT software. The structures were solved by direct methods and refined by full-matrix least-squares calculations using SHELXTL software. All non-H atoms were refined in anisotropic approximation. The crystallographic parameters of the compounds studied are given in table 1.

Supplementary materials

The crystallographic information files are deposited to the Cambridge Crystallographic Database and has CCDC numbers 666774-666776 and 666825.

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