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Green, purple, blue – $[Cu(N\text{-}Methylimidazole)_n(OOCCH_3)_2]_m$, what is in a colour

Research Article

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Abstract: Starting from the paddlewheel complex copper(II)acetate, the green N-methylimidazole adduct of copper(II)acetate is formed and transformed into the monomeric and dimeric N-methylimidazole adducts of copper(II)acetate $[Cu(C_4H_6N_2)_2(CH_3COO)_2]_n \cdot xH_2O$ (n = 1 ,2; x = 0, 6). The formation of the blue dimer or the purple monomer depends on the solvent and the presence or absence of water.

Keywords: *Copper • Imidazole • Polymorphism • Paddlewheel complex*

1. Introduction

Back in 1832, Wöhler and Liebig for the first time observed that an organic compound, benzamide as it was, apparently existed in two different crystal structures [1] that were distinguished by different π-stacking interactions. Some 175 years later, three different structures had been found and were solved [2]. The phenomenon is called polymorphism and is very important in the field of material science and pharmacy. Huge efforts are made to understand the implications and find meaningful applications.

In most instances, polymorphism in organic materials, including active pharmaceutical ingredients, is caused by different π-stacking interactions like the ones observed in benzamide. Changing hydrogen bonding patterns is far less common. Since organic materials are usually colourless with an occasional foray into the region of yellow, polymorphism goes unnoticed by the naked eye. In coordination compounds involving transition metals this might be different, since here the colour is caused by the interplay between ligand and central metal atom. If differences in π-stacking interactions involve coordinated heterocycles, the colour of the complex might well be affected.

By definition, polymorphs have the same composition but different structures. That seems sensible, but what about solvent content? In the case of copper(II)sulphate, the dry compound is white and the pentahydrate blue, because now four water molecules coordinate to the copper(II) ion. Clearly, the solvent (ligand) has actively changed the structure of the compound. There is clearly no polymorphism involved. But what, if the solvent does not take an active part? If the solvent does not coordinate, not even participates in hydrogen bonding with the actual compound? Would it be justified to call it analogous to polymorphism or even pseudo-polymorphism, with the solvent an innocent bystander?

In the present case, we report on a reaction whose course can be followed by the analysis of three products that can be isolated from the same Schlenk tube. They include two pseudo-polymorphs (of above definition) with differing solvent content and the reaction intermediate. They are distinguished by their own distinct colours: green, purple and blue.

2. Experimental Procedure

NMR spectra were recorded on a multinuclear FT NMR spectrometer ARX300 (Bruker) at 300.1 (^{1}H) and 75.5 (^{13}C) MHz. The chemical shift of the solvent DMSO was used as shift reference for ^{1}H and ^{13}C. Elemental analysis was performed with a CHNS-932 analyser from LECO using standard conditions. Solvents were dried over KOH and products stored in Schlenk tubes.

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2.1. Synthesis of [Cu(N- Methylimidazole)$_2$(OOCCH$_3$)$_2$] 1

A mixture of 998 mg (5 mmol) copper(II)acetate monohydrate and 0.80 mL (10 mmol) N-methylimidazole were stirred in 20 mL THF for 15 h after which time a purple solution had formed. Concentration of the solution in vacuo yields purple crystals. Addition of n-hexane to the mother liquor results in a purple precipitate. Combined yield: 1.61 g (93%).

Elemental analysis for $C_{12}H_{18}CuN_4O_4$ (346.0898): calc. C 41.65 H 5.24 N 16.26; found C 41.43 H 5.35 N 15.98

2.2. Synthesis of [Cu$_2$(κ^2-CH$_3$COO)$_4$(C$_4$H$_6$N$_2$)$_2$]3

A mixture of 998 mg (5 mmol) copper(II)acetate monohydrate and 0.80 mL (10 mmol) N-methylimidazole were stirred in 20 mL dry ethanol for 15 h after which time a purple solution had formed. Concentration of the solution *in vacuo* yields purple crystals of **1** at the wall of the Schlenk tube and green crystals of **3** at the bottom. Yield of **3**: 952 mg (41%).

Elemental analysis for $C_{20}H_{24}Cu_2N_4O_8$ (575.7728): calc. C 41.72 H 4.20 N 9.77; found C 41.38 H 4.05 N 9.86. MS (MALDI-tof): 542 [M+ - 2 Me], 441 [M+ - 2 $C_3H_3N_2$]; 434 [M+ - imidaole – acetate].

2.3. Crystal Structure Determination

Crystals were cryocooled in a nitrogen stream at 100 K (Cryostream, Oxford Cryosystems, Oxford, UK) or used at room temperature for X-ray diffraction data collection. With Cu Kα X-rays from a Micromax007 rotating anode generator and a Saturn92 CCD detector (Micromax007, Osmic multilayer mirrors, Rigaku MSC, Kemsing, UK) data were collected at 0.85 Å resolution. The data were integrated with CRYSTALCLEAR [3] scaled with SCALA [4] and the structures were solved and refined with SHELX. [5] Refinement involved anisotropic least squares refinement with riding hydrogens.

The purple crystals were obtained from THF. A single crystal (0.27 × 0.17 × 0.17 mm^3) was used for data collection at 100 K. The green crystals were obtained from dry ethanol and measured at 293 K (Table 1).

Measurements were performed on a diffractometer optimised for macromolecules, which determines cell parameters less accurately and does not allow the collection of a data set at high resolution as complete as that for the known structure of the blue dimer [6]. However, a significant decrease in the quality of the final structure was not observed when we compared our setup against a known structure in a previous investigation [7].

Hydrogen atoms were not refined. In consequence, discussion of hydrogen bonding can only be taken as an approximation. Nonetheless, the apparent weakness of most observed hydrogen bonds is beyond doubt.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 794040 (**1**) and No. 794041 **(3)**. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.htmL, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

3. Results and Discussion

When we reacted a bis-imidazolium dibromide that contained adventitious N-methylimidazole with copper(II) acetate monohydrate in THF as the solvent, we obtained purple crystals in low yield (see Fig. 1). An x-ray crystal structure determination of these crystals revealed their identity as [Cu(N-Methylimidazole)$_2$(OOCCH$_3$)$_2$]. A search of this compound in scifinder yielded a structurally determined compound of the same molecular formula, but with three major differences. The known compound had a dimeric structure, contained three molecules of water per formula unit and was described as blue [6].

Our purple compound crystallises in the orthorhombic space group P 2$_1$ c a with four formula units in the unit cell. It has a near perfect square planar geometry with the two imidazole rings in trans position towards each other (see Fig. 1). The square planar geometry is fairly common for the d^9-copper(II) system [8,9] due to the Jahn-Teller-effect [10].

The bond lengths and angles present no surprises with Cu-N bond lengths of 198.54(31) and 197.04(31) pm, respectively. The Cu-O bond lengths are 197.22(33) and 195.86(31) pm. The bond length to oxygen ought to be slightly smaller than that to nitrogen as the atomic radius would be slightly smaller owing to the respective positions in the periodic table. The donor bond (Cu-N) is apparently of the same length as the covalent bond (Cu-O), again as expected [9]. The bond angles testify to the near perfect square planar geometry: N-Cu-N 178.94(19)°, O-Cu-O 178.15(17)° are almost linear and O-Cu-N with 89.06(13) to 91.38(14)° are all close to a right angle.

The crystal packing is dominated by a π-stacking interaction of one of the imidazole rings of the molecule (see Fig. 2). The two imidazole rings are perfectly aligned with a distance of between 367.6 and 374.1 pm. They cause the rest of the molecule to protrude from the stack

alternatingly and at an angle that reflects the pentagonal structure of imidazole. This stacking interaction causes two parallel, zickzack bands to occur within the plane of the crystal.

In contrast, the blue, dimeric compound of the same general composition [Cu(N-Methylimidazole)$_2$(OOCCH$_3$)$_2$]$_2$•6H$_2$O published by Boukari *et al*. [6] has a square pyramidal geometry at copper and the coordination number five. The bond angles of O-Cu-O 174.25° and N-Cu-N 172.82° suggest that the structure contains the square planar subunit of our purple monomer that dimerises by forming Cu-O-Cu bridges, whereby the bridging oxygen atom occupies the apical position in the other monomeric unit (see Fig. 1). The oxygen bridges are not symmetrical with 198.6 pm and 242.4 pm, respectively. The shorter of the two Cu-O bond lengths is only marginally longer than the bond length in our purple monomer. The longer Cu-O bond however is significantly elongated by some 45 pm and represents a rather weak donor interaction compared to the Cu-N donor bonds present in both the blue and the purple crystals (199.5 pm in the blue and 197.8 pm in the purple, respectively). Since the six molecules of crystal water in the blue dimer do not participate as donor ligands for the copper(II) centre, but merely seem to complete the lattice, one should inspect the role of the C=O carbonyl oxygen atom more closely.

We have already noted that copper(II) d^9-systems are subject to the Jahn-Teller-Effect [10] and frequently display elongated donor bonds in axial positions, effectively forming distorted octahedra [8]. In the blue dimer **2**, we have already identified one of these axial coordination sites in the bridging oxygen atom occupying an apical position (Cu-O 242.4 pm). In the purple monomer **1**, the situation is even more straight forward. Here the two C=O carbonyl oxygen atoms occupy the axial positions forming elongated donor bonds (Cu-O 273.7 and 288.2 pm).

The three-dimensional arrangement in the crystal lattice represents an energetic minimum for the entire structure including all weak interactions between parts of the molecule. Incorporation of a weakly donating oxygen atom by the central copper atom (dimerisation) apparently minimises this energy. Especially since the Cu-O distance of this donor bond in **2** is much shorter (some 30-45 pm) than in **1**. Another energy optimisation is effected by the π-stacking interaction between the imidazole rings in the purple monomer. Both are local minima and thus can exist independently.

The purple monomer **1** has a significant kinetic advantage over the blue dimer **2** in as much as it carries the C=O groups in axial positions with it. There is no need for two moieties to find each other, orientate correctly and then dimerise. All that is required is that the monomer rotates into the correct position and then packs into the crystal. It is therefore not surprising that we obtained the monomer **1** rather than the dimer **2** when we rapidly removed the solvent (either THF or ethanol).

Table 1. Crystal data and structure refinement for the purple compound **1** and the green **3**

	1	**3**
Formula	$C_{12}H_{16}CuN_4O_4$	$C_{16}H_{24}Cu_2N_4O_8$
M_r	345.8	527.47
Temperature (K)	100(2)	293(2)
λ (Å)	1.54178 (Cu Kα)	1.54178 (Cu Kα)
Crystal system	orthorhombic	orthorhombic
Space group	P c a 21	P b c a
a (Å)	22.177(6)	12.944(9)
b (Å)	9.112(5)	8.718(11)
c (Å)	7.393(2)	19.039(15)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
V (Å ^{3})	1494.0(10)	2148(4)
Z	4	4
ρ_{calc}. (Mg m^{-3})	1.538	1.613
F (000)	716	1080
Crystal size (μm)	270 × 170 × 170	150 × 150 × 50
Abs. coef. (mm^{-1})	2.267	2.889
2 Θ_{max} (°)	70.26	50.53
Reflections (coll.)	1491	977
Reflections (ind.)	1315	639
Parameters	190	139
R (I > 2 σ (I))	0.0394	0.0909
wR_2 (all data)	0.1037	0.1354
$(\Delta/\rho)_{min}$ (e Å^{-3})	-0.834	- 1.002
$(\Delta/\rho)_{max}$ (e Å^{-3})	0.507	0.134

Unfortunately, the system is not quite so simple. When we tried to repeat the experiment of Boukari et al. using THF to form the purple momer and ethanol to form Boukari's blue dimer, we obtained our monomer in near quantitative yield from THF as expected. But from the blue ethanolic solution (predried ethanol, argon athmosphere), the purple monomer and a light green compound precipitated that was similar in colour to the common basic copper(II) salts. The elemental analysis of this green compound is compatible with the general formula [Cu(N-Methylimidazole)(OOCCH$_3$)$_2$] containing no solvent molecules. There is one N-methylimidazole ligand missing from each copper atom. This is compatible with the general paddlewheel structure of copper(II) acetate dihydrate [11-13]. A crystal structure determination confirmed this (see Fig. 3). The product is isostructural to the starting material with the coordinated water being replaced by N-methylimidazole.

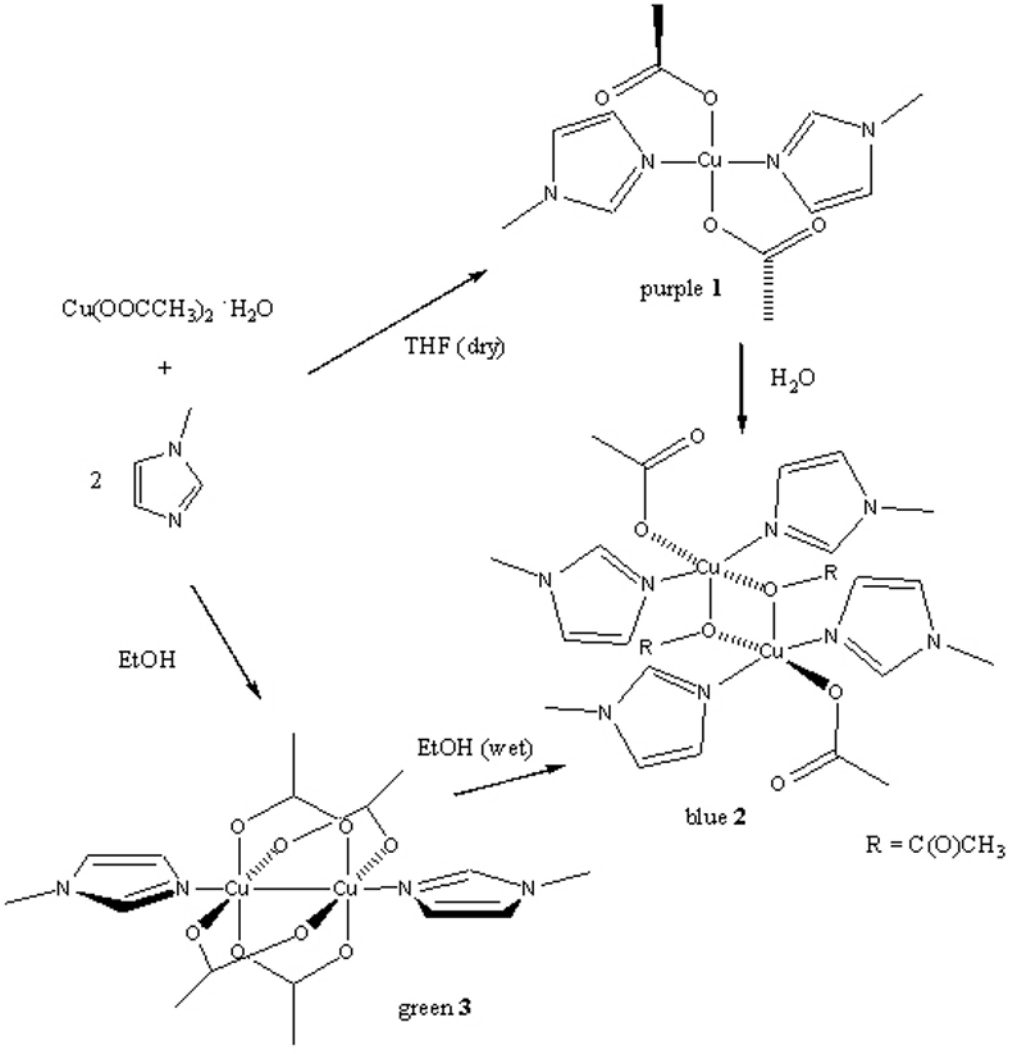

Figure 1. Synthesis of [Cu(N-Methylimidazole)$_2$(OOCCH$_3$)$_2$]

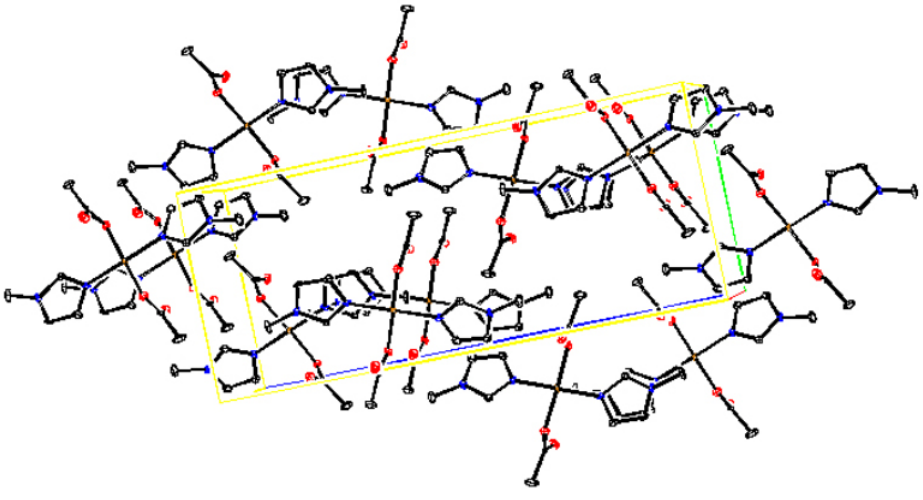

Figure 2. ORTEP plot (50% probability) of the crystal packing of purple [Cu(N-Methylimidazole)$_2$(OOCCH$_3$)$_2$]; hydrogen atoms omitted for clarity.

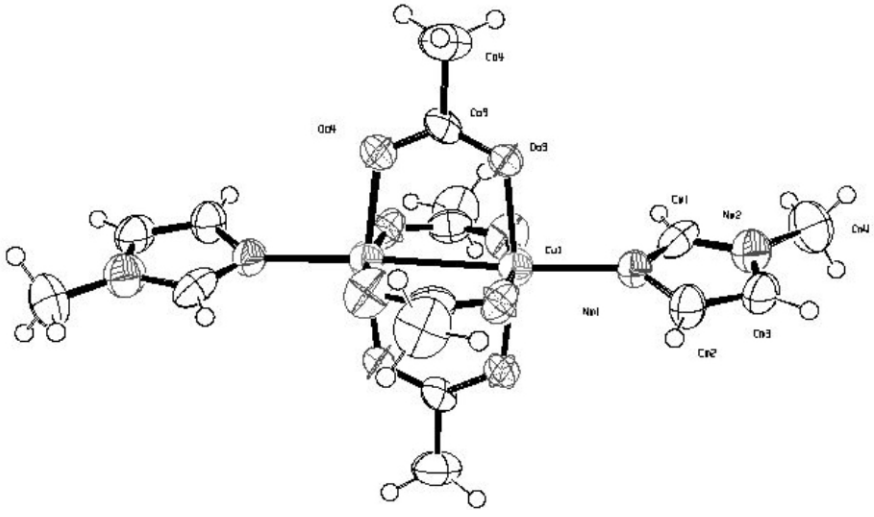

Figure 3. ORTEP plot of the crystal structure of 3 [Cu(N-Methylimidazole)(OOCCH$_3$)$_2$]$_2$. Spheres show 50% probability.

The cores of the two structures, the paddlewheels, are remarkably similar, even identical within the margin of error. Compound **3** contains six coordinate, octahedrally coordinated copper atoms. Four oxygen atoms from the bridging four acetate ligands in the equator, the nitrogen atom from N-methylimidazole and the second copper atom occupying the axial positions. The N-methylimidazole ligands lie in one plane, but are askew to the two perpendicular axes formed by the acetate ligands. The methyl groups are located such as to form a centre of inversion in the middle of the Cu-Cu bond. The Cu-O and Cu-Cu bonds are virtually identical to those in copper(II)acetate dihydrate. With a 210.0 (8) pm bond distance between copper and nitrogen, the Cu-N bond is some 10 pm shorter than the Cu-O bond (Cu-OH$_2$) in the dihydrate. That is rather remarkable as it is oxygen that has an atomic radius smaller than nitrogen. We can safely assume that the N-methylimidazole ligand is much more strongly bonded than the water molecules.

This trend is continued with the purple (**1**) and the blue (**2**) compounds, where the Cu-N bond lengths are 197.8 and 199.5 pm, respectively. As the apparent coordination number drops from six over five to four, the Cu-N bond length decreases indicating that the N-methylimidazole is more and more tightly bound. In contrast, the Cu-O bond length seems hardly to be affected ranging from 195.2 pm to 198.7 pm, respectively. The only exceptions are the long Cu-O bond lengths to the oxygen atoms in apical positions. Here, the blue compound has a clear advantage over the purple one, as it has the shorter carbonyl donor bond (242 pm in **2** and 273.7 and 288.2 in **1**). This is reflected by the apical nitrogen atom (210 pm) in **3**.

The reaction clearly proceeds in the first step by ligand substitution (N-methylimidazole for water), but the paddlewheel framework stays intact. The paddlewheel structure then disintegrates leaving a dimeric structure that breaks further down to the monomer. Compounds **1** and **2** are not formed sequentially, though, as only **1** is formed in THF and **2** is formed in ethanol. It seems that the solvent determines the structure and the progress of the paddlewheel disintegration. In THF none of the initial paddlewheel structure could be retrieved, whereas in ethanol **2** and **3** coexist. It is interesting to note that **1** is transformed into **2**, if water enters the system. Purple crystals of **1** slowly turn into blue **2** upon exposure to humidity.

It needs to be remembered that our initial gateway to this chemistry was adventitious N-methylimidazole present in an otherwise completely different ligand. Despite the very low concentration of the ligand, the purple product **1** was formed in THF, whereas in dry ethanol a substantial amount of the intermediate **3** remains. Therefore, the outcome of the reaction seems to depend on the solvent rather than on the ligand ratio. Another interesting observation is the colour change of purple crystals of **1** to blue upon exposure to moisture.

4. Conclusion

We have synthesised a new pseudo-polymorph of [Cu(N-Methylimidazole)$_2$(OOCCH$_3$)$_2$] besides the blue dimer published by Boukari *et al*. [6]. In addition, we could isolate an intermediate in the reaction from copper(II)acetate dihydrate to our product. This intermediate turned out to be the N-methylimidazole

adduct of copper(II)acetate. The product preference **1** or **2** as opposed to **3** is dependent on the choice of solvent with THF yielding exclusively the intended product and ethanol yielding substantial amounts of the intermediate **3**. The question of whether the dimer **2** or the monomer **1** is formed seems to be dependent upon the amount of water present. Wet ethanol yields **2** [6] whereas dry THF or dry ethanol yield **1**. Crystals of **1** turn blue upon exposure to moisture. Moisture (or the absence of it) is a common storage parameter and thus it is of great import that it changes the structure of **1** to **2** without direct involvement of water (solvent). Water acts as an external parameter that causes a structural change in the compound.

References

[1] F. Wöhler, J. Liebig, Ann. Pharm. 3, 249 (1832)
[2] J. Thun, L. Seyfarth, J. Senker, R.E. Dinnebier, J. Breu, Angew. Chem. Int. Ed. 46, 6729 (2007)
[3] J.W. Pflugrath, Acta Cryst. 55D, 1718 (1999)
[4] P.R. Evans, Acta Cryst. 62D, 72 (2005)
[5] G.M. Sheldrick, Acta Cryst. 64A, 112 (2008)
[6] P.Y. Boukari, A. Busnot, F. Busnot, A. Leclaire, M.A. Bernard, Acta Cryst. B38, 2458 (1982)
[7] O. Kühl, G. Palm, Tetrahedron: Asymmetry 21, 393 (2010)
[8] N.N. Greenwood, A. Earnshaw, Chemistry of the Elements (Pergamon Press, Oxford 1989)
[9] N. Wiberg, Hollemann-Wiberg, Lehrbuch der Anorganischen Chemie, 91st -100th editions (Walter der Gruyter, Berlin, 1985) (In German)
[10] I.B. Bersuker, Coord. Chem. Rev. 14, 357 (1975)
[11] J.N. Van Niekerk, F.P.L. Schoening, Nature 171, 36 (1953)
[12] A. Werner, Ann. Chem. 375, 1 (1910)
[13] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry (John Wiley & Sons, Chichester, 1988)