cis- and *trans*-Bis(benzoylacetonato)pyridinecopper(II): co-crystallisation of isomers and reversible pyridine loss with retention of crystallinity

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The pyridine adduct of bis(benzoylacetonato-*O*,*O*′)copper(II) crystallises in both its *cis*- and *trans*-isomers within the same crystal. Copper(II) exhibits square pyramidal coordination geometry in both isomers with weak coordination of pyridine. The square planes of the isomers are mutually orthogonal, forming a square grid, in the channels of which the pyridine molecules are stacked, approximately perpendicular to the c-axis. Pyridine is readily lost from crystals unprotected by pyridine solvent, forming a crystalline powder. This powder absorbs pyridine vapour to reform microcrystalline bis(benzoylacetonato)pyridinecopper(II).

Five-coordinate metal complexes can be square pyramidal, trigonal bipyramidal, or intermediate between these two extremes; the parameter τ quantifying the degree of distortion from the ideal polyhedron.[1] The term *allogons* has been coined to describe this type of isomerism,[2] *i.e.* geometrical isomers of a metal complex that have different coordination geometries.[3–6] If both allogons are present in the same crystal, the term *interallogons* has been proposed.[2] Elegant examples of interallogons of copper(II) have been described in recent work by Kelly *et al.*[7] In a wider context, geometrical isomerism includes the occurrence of *cis*- and *trans*-isomers (and, in six-coordination, *fac*- and *mer*-isomers), *i.e.* metal complexes with the same coordination polyhedron but with a different juxtaposition of identical ligand atoms. The existence of distinct, ordered, geometrical isomers (diastereoisomers) with identical coordination polyhedra in the same crystal is, however, rare and appears to be limited to bis(thiosemicarbazido)nickel(II) sulfate[8] and (benzoylacetonato-*O*,*O*′)(carbonyl)(triphenylphosphine)rhodium(I).[9] In addition, disordered isomers that differ in the way in which the chelate rings span the lateral and square edges of the square antiprism in eight-coordinate adducts of tris(dipivaloylmethanato)lanthanide(III) with 2,9-dimethyl-1,10-phenanthroline have been reported.[10] Recently, topological isomerism exhibited by coordination polymers within the same crystal has attracted attention.[11,12]

β-Diketones, such as acetylacetone (Hacac) and benzoylacetone (Hbzac), form well-known chelating ligands; the bzac ligand being of interest because of its capacity to produce geometrical isomers. [Cu(bzac)$_2$] has been shown to exist as the *trans*-isomer in the solid state.[13,14] In adducts of [Cu(bzac)$_2$] with N-donor ligands, the methyl and phenyl substituents of the benzoylacetonate ligands are also mutually *trans*.[14–16] It would seem that when the ligands bond in the same plane in the coordination polyhedron, the *trans*-isomer is that which is preferentially found in the solid state, regardless of the nature of the metal.[17] In [Ti(bzac)$_2$(OEt)$_2$] and [Ti(bzac)$_2$Cl$_2$], the benzoylacetonate ligands occupy positions *cis* to one another in the octahedral coordination sphere, but, even so, the acetyl ends of the ligands are in a *trans* arrangement.[18] Higher coordination numbers allow a greater degree of complexity with respect to ligand placement, and the resulting complexes are therefore not directly comparable with the planar bis(benzoylacetonate) arrangement.

We now report co-crystallisation of the *cis*- and *trans*-isomers of bis(benzoylacetonato)pyridinecopper(II); *i.e.*, the occurrence of both geometrical isomers in the same crystal. Moreover, the investigation provides a rare example of two benzoylacetonate ligands bonding *cis* to one another in the same plane of a metal coordination polyhedron.

The isomers, together with the crystallographic numbering of the atoms, are depicted in Fig. 1 and Fig. 2. A summary of key bond lengths and angles is given in Table 1. Both isomers exhibit close to ideal square pyramidal geometries, with τ_{trans} = 0.022 and τ_{cis} = 0.048. Cu(1) is displaced 0.2004(7) Å towards N(1) from the best plane through O(1), O(2), O(3) and O(4), while Cu(2) is displaced 0.2079(7) Å towards N(2) from the best plane through O(5), O(6), O(7) and O(8). The

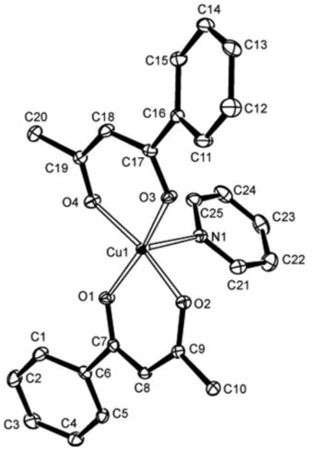

Fig. 1 The *trans*-isomer of bis(benzoylacetonato)pyridinecopper(II) showing the crystallographic numbering. Thermal ellipsoids enclose 50% probability.

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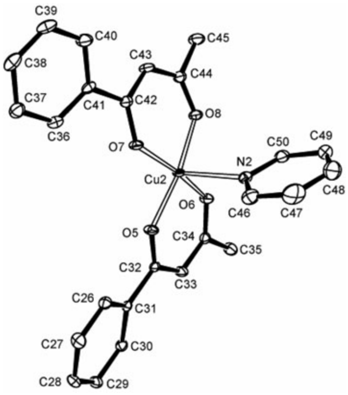

Fig. 2 The *cis*-isomer of bis(benzoylacetonato)pyridinecopper(II) showing the crystallographic numbering. Thermal ellipsoids enclose 50% probability.

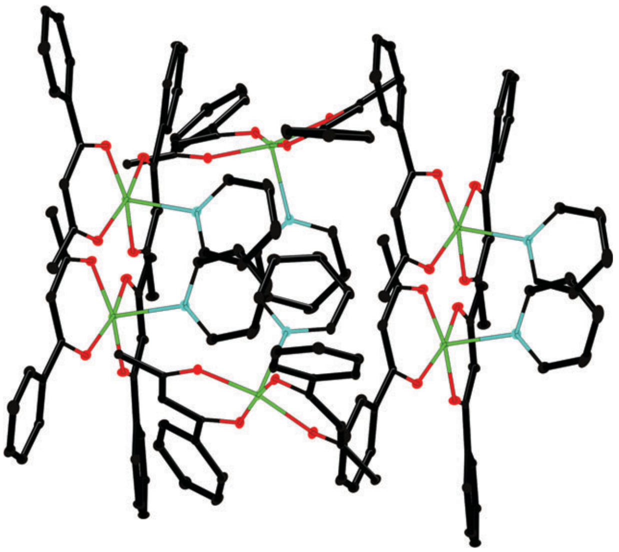

Fig. 3 Illustration of the square grid formed by the isomers, which encloses four columns of pyridine molecules, stacked approximately perpendicular to the c-axis; *cis*-isomers are vertical while *trans*-isomers are horizontal.

planes formed by Cu(1), O(1), C(7), C(8), C(9), O(2) and Cu(1), O(3), C(17), C(18), C(19), O(4) are inclined by 20.88(6)°, and those formed by Cu(2), O(5), C(32), C(33), C(34), O(6) and Cu(2), O(7), C(42), C(43), C(44), O(8) are inclined by 18.76(7)°. The dihedral angles between the phenyl rings and the Cu, O, C, C, C, O groups to which they are bound are: 29.79(7)° [ring 1], 29.92(5)° [ring 2], 10.98(5)° [ring 3] and 21.97(7)° [ring 4]. The *cis*-isomer is less symmetrical than the *trans*-isomer in this respect.

Pyridine is weakly bonded to Cu(II) [Cu(1)–N(1) = 2.283(1) Å and Cu(2)–N(2) = 2.271(2) Å] and is lost when the dry crystals are exposed to the atmosphere. This is in accordance with earlier magnetic field-dependent electron spin echo envelope modulation (ESEEM) spectroscopic studies, which indicated that little of the electron density is removed from the nitrogen lone pair σ-orbital upon coordination to Cu(II).[19] The square planes of the complexes are mutually orthogonal [81.82(4)° between the best planes through O(1), O(2), O(3), O(4) and O(5), O(6), O(7), O(8)]. The isomers thus form a square grid, with the pyridine molecules in the cavities, stacked approximately perpendicular to the c-axis. Four columns of pyridine molecules are accommodated within each grid (see Fig. 3), such that the centroids of the pyridine molecules within a column form a zigzag chain along the c-axis, with alternating *cis*···*trans*···*cis* distances of 4.206 and 5.145 Å. The shortest carbon···carbon distance between adjacent pyridine rings is C(21)···C(50) = 3.29 Å. Despite this π···π ring interaction, pyridine is readily lost from the channels once the crystals are unprotected by an excess of pyridine solvent, the situation being similar to that observed for complexes of copper(I) chloride with nitrogen donor ligands containing acetonitrile solvent coordinated to the metal.[20]

Table 1 Selected bond distances (Å) and angles (°) for *trans*- and *cis*-[Cu(bzac)$_2$py]

trans		*cis*	
Cu(1)–O(1)	1.951(1)	Cu(2)–O(5)	1.931(1)
Cu(1)–O(2)	1.962(1)	Cu(2)–O(6)	1.959(1)
Cu(1)–O(3)	1.956(1)	Cu(2)–O(7)	1.948(1)
Cu(1)–O(4)	1.950(1)	Cu(2)–O(8)	1.947(1)
Cu(1)–N(1)	2.283(2)	Cu(2)–N(2)	2.271(2)
O(1)–Cu(1)–O(2)	92.70(5)	O(5)–Cu(2)–O(6)	92.48(5)
O(1)–Cu(1)–O(3)	168.74(5)	O(5)–Cu(2)–O(7)	85.40(5)
O(1)–Cu(1)–O(4)	84.78(5)	O(5)–Cu(2)–O(8)	169.17(6)
O(1)–Cu(1)–N(1)	92.34(5)	O(5)–Cu(2)–N(2)	99.28(6)
O(2)–Cu(1)–O(3)	88.43(5)	O(6)–Cu(2)–O(7)	166.27(6)
O(2)–Cu(1)–O(4)	167.41(5)	O(6)–Cu(2)–O(8)	86.99(5)
O(2)–Cu(1)–N(1)	95.38(5)	O(6)–Cu(2)–N(2)	91.74(6)
O(3)–Cu(1)–O(4)	91.69(5)	O(7)–Cu(2)–O(8)	92.55(5)
O(3)–Cu(1)–N(1)	98.72(5)	O(7)–Cu(2)–N(2)	101.99(5)
O(4)–Cu(1)–N(1)	97.05(5)	O(8)–Cu(2)–N(2)	91.55(6)

The co-crystallisation of *cis*- and *trans*-benzoylacetonatocarbonyltriphenylphosphinerhodium(I) was attributed in part[9] to the nearly equal electronegativities of the methyl and phenyl substituents of the β-diketonate ligand.[21] It is, nevertheless, somewhat surprising that co-crystallisation of geometrical isomers of bis(bzac)$_2$ metals and their adducts is not more frequent, and that crystal structure determinations of their *cis*-isomers are lacking. It would seem likely that the square grid, formed in solid bis(benzoylacetonato)pyridinecopper(II) in the presence of pyridine and stabilised by the presence of π···π pyridine interactions within the ensuing channels, assists the crystallisation of both isomers in the same crystal.

Loss of pyridine results in a grey desolvated microcrystalline (Fig. 4a) powder. However, on exposure to pyridine vapour, this reverts from grey to green, with the re-emergence of the X-ray powder diffraction pattern calculated for [Cu(bzac)$_2$py] (see Fig. 4c and d). It is clear from Fig. 4 that the structure of desolvated [Cu(bzac)$_2$py] differs from that of the parent compound. This is an example of a reversible transformation with retention of crystallinity, but not of a single-crystal to single-crystal transformation.[22–25] As has been pointed out,[25] many applications, such as catalysis and storage, do not require single-crystal transformations, but retention of single-crystallinity would be essential if a crystal were to be incorporated into a device such as a substrate-triggered sensor.[25]

A further point of interest is the question of porosity.[26] When a powder diffraction pattern is calculated for crystalline

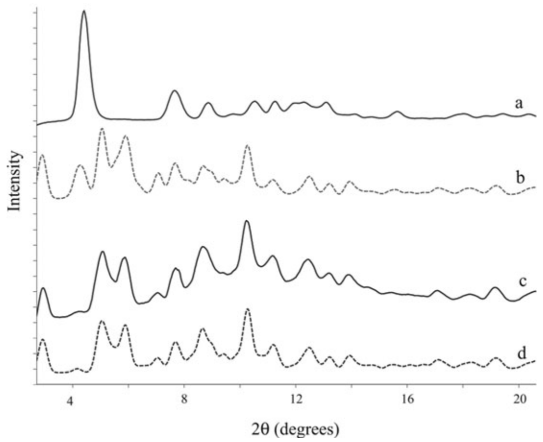

Fig. 4 X-Ray powder diffraction patterns obtained for *cis*- and *trans*-[Cu(bzac)$_2$py]. (a) The grey product after loss of pyridine. (b) Calculated for crystalline [Cu(bzac)$_2$py], omitting the contribution from pyridine. (c) The microcrystalline green powder after re-absorption of pyridine. (d) Calculated for crystalline [Cu(bzac)$_2$py].

[Cu(bzac)$_2$py], omitting the contribution from pyridine (*cf.* Fig. 4b), it is seen to resemble that of [Cu(bzac)$_2$py], and it is very different from that actually obtained for desolvated [Cu(bzac)$_2$py] (*cf.* Fig. 4a). This indicates that, despite the square grids formed by the isomers, [Cu(bzac)$_2$py] is not porous, but that the material assumes a different structure upon loss of pyridine. The desolvated material is, however, permeable in that it re-absorbs pyridine to form a microcrystalline product with a powder pattern characteristic of [Cu(bzac)$_2$py] (*cf.* Fig. 4). It might therefore be considered to fall into the category of "porosity without pores".[26] One could conceive that the isomers act in concert[22–26] during pyridine uptake so as to preserve crystallinity, but as a microcrystalline powder rather than a single crystal.

Experimental

Synthesis of bis(benzoylacetonato)pyridinecopper(II)

All operations were performed under nitrogen atmosphere using standard Schlenk techniques at ambient temperature or using a special low temperature methodology.[27] Benzoylacetone (Fluka), copper(II) oxide (E. Merck) and pyridine (Prolabo) were used without further purification.

Copper(II) oxide (0.795 g, 10 mmol) and benzoylacetone (3.24 g, 20 mmol) were mixed together and heated at 60 °C for 1 h. Pyridine (4 ml) was added and the heating continued for another 2 h. The mixture was cooled to ambient temperature and transferred to a centrifuge tube. The reaction flask was rinsed with pyridine (3 ml), the mixture centrifuged (2 min at 3500 rpm) and the clear green solution layered with hexane (20 ml). Green crystals formed within 2 d. The mixture was filtered and the crystals washed with hexane. Yield: 3.2 g (67%). The mother liquor was diluted with hexane (50 ml) and cooled to −20 °C overnight, whereupon a second crop of green crystals formed (0.75 g, 17%), leaving the mother liquor almost colourless. Crystals moisturised with pyridine were stable at low temperature, but they decomposed rapidly at ambient temperature, forming a grey powder.

Crystal structure determination

A crystal of [Cu(bzac)$_2$py] was selected, mounted under nitrogen in a glass capillary at low temperature[27] and transferred to a Rigaku R-AXIS IIc image plate system. Diffracted intensities were measured at 100(2) K using graphite-monochromated Mo-K$_\alpha$ radiation (λ = 0.71073 Å) from a RU-H3R rotating anode operated at 50 kV and 90 mA. Ninety oscillation photographs with a rotation angle of 2° were collected and processed using the CrystalClear software package. Empirical corrections were applied for the effects of absorption using the REQAB program under CrystalClear. The structures was solved† by direct methods[28] and refined using full-matrix least-squares calculations on F^2 (SHELXL-97)[29] on all reflections, both programs operating under the WinGX program package.[30] Anisotropic thermal displacement parameters were refined for all non-hydrogen atoms, and the hydrogen atoms were included using a riding model. Structural illustrations have been drawn with ORTEP-3 for Windows[31] operating under WinGX.[30]

Loss of pyridine

A crystal of [Cu(bzac)$_2$py] was mounted in an open capillary and intensity data measured on a Rigaku R-AXIS IIc image plate system at room temperature. The loss of pyridine was manifested in the disappearance of discrete reflections and the concomitant appearance of powder diffraction rings, during which transformation the crystal changed colour from green to grey. The rings on the five final frames were evaluated using the AreaMax software package to give the powder diffraction pattern shown in Fig. 4a. The desolvated product outwardly resembled a "crystal", as in the study by van Koten *et al.*[22,23] The capillary containing the desolvated product was exposed to pyridine vapour for a few minutes, during which time a colour change from grey to green took place, and the powder diffraction pattern shown in Fig. 4c was obtained. The desorption and absorption of pyridine vapour by the bulk material resulted in powder patterns identical to those of Fig. 4a and c.

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† [Cu(OC(CH$_3$)CHC(C$_6$H$_5$)O)$_2$(C$_5$H$_5$N)]: C$_{25}$H$_{23}$CuNO$_4$, M_r = 465.0, monoclinic, space group $P2_1/c$, a = 9.7867(10), b = 28.1721(26), c = 15.7764(16) Å, β = 94.616(4)°, U = 4335.6(7) Å^3, Z = 8, D_c = 1.42 g cm^{-3}, μ = 1.039 mm^{-1}. Green prism, 0.2 × 0.2 × 0.2 mm, 27 034 reflections measured, 7818 unique (R_{int} = 0.036), 563 parameters, R_1 = 0.030 and wR_2 = 0.072 for the 7288 reflections for which $I > 2\sigma(I)$, R_1 = 0.033 and wR_2 = 0.074 for all 7818 reflections, maximum and minimum residual electron density: 0.37 and −0.30 e Å^{-3}. CCDC reference number 604740. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b615579k

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