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Synthesis and characterisation of new polynuclear copper(I) pyrazolate complexes and their catalytic activity in the cyclopropanation of olefins

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Abstract

The reaction of $[Cu(CH_3CN)_4](BF_4)$ with racemic pyrazole-3,5-dicarboxylic acid di-*sec*-butyl ester (3,5-dicarbo-*sec*-butoxypyrazole, Hdcsbpz) or with pyrazole-3,5-di-*ter*-butyl (3,5-di-*ter*-butylpyrazole, Hdtbpz) quantitatively yields the new $[Cu(dcsbpz)]_4$ and $[Cu(dtbpz)]_4$ complexes, respectively. Crystals of $[Cu(dcsbpz)]_4$ are triclinic, $P\bar{1}$, $a = 10.9748(7)$, $b = 11.8399(8)$, $c = 26.5575(17)$ Å, $\alpha = 100.605(2)$, $\beta = 90.783(2)$, $\gamma = 105.362(2)°$; $[Cu(dtbpz)]_4 \cdot CH_2Cl_2$ is monoclinic, $P2_1/n$, $a = 10.902(3)$, $b = 19.200(3)$, $c = 25.772(4)$ Å, $\beta = 93.86(2)°$. Both species contain cyclic tetrameric molecules, with the heterocyclic ligands binding in the common N,N'-*exo*-bidentate mode; however, the shape and geometry of the inner Cu_4 moiety is remarkably different, as highlighted, for example, by the absolute values of the 1,2 and 1,3 (non-bonding) Cu···Cu interactions. These polynuclear copper(I) pyrazolate complexes catalyse the conversion of alkenes into the corresponding cyclopropane derivatives with interesting diastereomeric excesses. Aiming at the evaluation of their catalytic activities, a systematic study of the cyclopropanation reactions in the presence of ethyl diazoacetate has been performed.
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Keywords: Catalysis; Cyclopropanation; Pyrazolate; Tetrameric complexes

1. Introduction

The metal-assisted decomposition of diazocompounds in the presence of alkenes is a highly effective method to convert olefins into cyclopropanes [1,2]; furthermore, if suitable complexes are employed, even diastereo- and enantio-selective cyclopropanations of the unsaturated substrates can be successfully carried out [3]. The development of new and efficient metal-based catalytic systems able to induce high diastereomeric and/or enantiomeric excesses in the conversion of alkenes into cyclopropanic rings is an important goal for chemistry, because of the key role that these derivatives play in chemical synthesis. Indeed, cyclopropanes are versatile intermediates that can be converted into a variety of useful products by cleavage of the strained three-membered ring [4]. In addition, the occurrence in nature of molecules presenting interesting physiological properties and containing the cyclopropane moiety [5] is a continuous stimulus to develop new synthetic routes to functionalised cyclopropanes.

The intermolecular cyclopropanation of olefins with elevated diastereo- and enantio-selectivity and promoted by Cu(I)- and Cu(II)-complexes containing sp^2-nitrogen based ligands, such as C_2-symmetric semicorrins [6–8], bis(oxazolines) [9,10] and optically active bipyridines [11–13], has been widely explored. Very recently, relatively high diastereomeric excesses have been also reported using polypyrazolylborate copper(I) derivatives [14,15].

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Our continuous interest in the coordination chemistry of azolate ligands boosted us to investigate the synthesis and characterisation of new copper(I) pyrazolate complexes and explore their catalytic activity in the cyclopropanation reactions of olefins with ethyl diazoacetate (EDA). The polynuclear copper(I) pyrazolate complexes presented hereafter were found to catalyse the conversion of alkenes into the corresponding cyclopropane derivatives with interesting diastereomeric excesses; therefore, in the following, we report on their synthesis, structure and detailed quantitative aspects of their catalytic activity and selectivity.

2. Results and discussion

2.1. Synthesis

The reaction of $[Cu(CH_3CN)_4](BF_4)$ with racemic pyrazole-3,5-dicarboxylic acid di-*sec*-butyl ester (3,5-dicarbo-*sec*-butoxypyrazole, Hdcsbpz) or with pyrazole-3,5-di-*ter*-butyl (3,5-di-*ter*-butylpyrazole, Hdtbpz) in methanol and in the presence of triethylamine (Section 4) yields quantitatively the new $[Cu(dcsbpz)]_4$ [1] and $[Cu(dtbpz)]_4$ [2] complexes, respectively, as insoluble white products (Eq. (1))

$$4[Cu(CH_3CN)_4]BF_4 + 4Hpz* \xrightarrow[-CH_3CN]{Et_3N}$$
$$[Cu(pz*)]_4 + 4(Et_3NH)BF_4 \qquad (1)$$
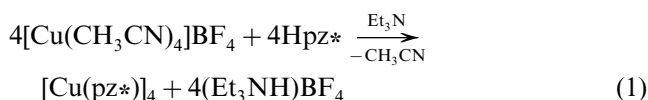
where Hpz* = Hdcsbpz, **1**; Hdtbpz, **2**.

The synthetic method employed (Eq. (1)) has been verified to work well for a large series of pyrazoles, affording derivatives of general formula $[Cu(3,5-R_2pz)]_n$ (R = H, Me, COOMe, COO-*t*-Bu) [16]. Actually, it is well known that group 11 metals in the +1 oxidation state, in the absence of ancillary ligands (e.g. phosphines or isocyanides), form neutral complexes presenting singly bridged M(μ-pz*)M units with the deprotonated form of several pyrazoles (Hpz*). The structurally characterised $[M(pz*)]_n$ systems (M = Cu, Ag and Au) have been found to possess a variety of molecular arrangements (*n* ranging from 3 to ∞), with a definite tendency of forming cyclic oligomeric species [17].

The IR spectrum of **1** recorded in the solid state shows only one strong carbonyl absorption at 1709 cm^{-1}, comparable to the ν(CO) value found for the free ligand, which is due to the CO stretching of the COO-*s*-Bu arms and suggests the presence of two equivalent carbonyl groups not coordinated to the copper(I) metal centres.

The ^{1}H-NMR spectrum of **1** registered in CD$_2$Cl$_2$ at room temperature shows, beside a singlet centred at 7.3 ppm attributable to the C(4)–*H* of the pyrazolate rings, only one set of signals attributable to the aliphatic protons of the carbo-*sec*-butoxy groups in the 3 and 5 positions of the pyrazolate ligand. On lowering the temperature down to 173 K, the spectral features do not significantly change. These observations demonstrate that no, or little, stereochemical information of one (*S*

Table 1
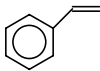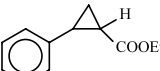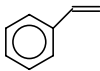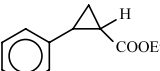Catalytic cyclopropanations by copper(I) pyrazolate complexes **1**, **2** and **3**
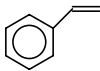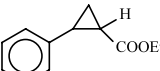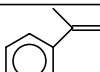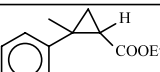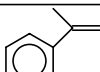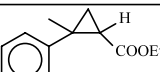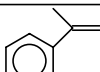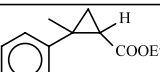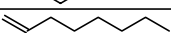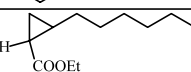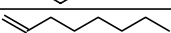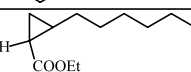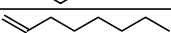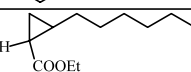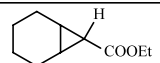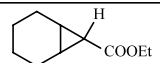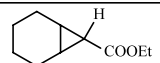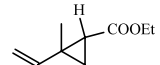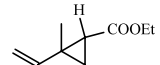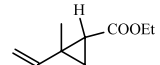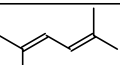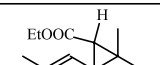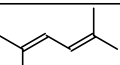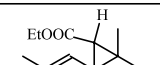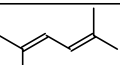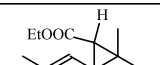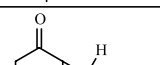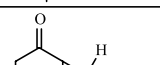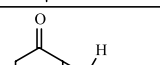
entry	Complex	substrate	product	*trans:cis*	yield %
1	**1**		H COOEt	80:20	75
2	**2**			88:12	82
3	**3**			72:28	75
4	**1**		H COOEt	59:41	90
5	**2**			78:22	81
6	**3**			71:29	90
7	**1**		H COOEt	58:42	71
8	**2**			63:37	86
9	**3**			56:44	71
10	**1**		H COOEt	87:13	85
11	**2**			79:21	92
12	**3**			54:46	85
13	**1**		H COOEt	60:40	83
14	**2**			56:44	93
15	**3**			60:40	83
16	**1**		H EtOOC	65:35	88
17	**2**			60:40	89
18	**3**			65:35	88
19	**1**	O	O H COOEt	84:16	87
20	**2**			86:14	91
21	**3**			85:15	87

Table 2
Synoptic table containing relevant stereochemical data for **1**, **2a** and **3** [18]

	[Cu(dcsbpz)]$_4$ (**1**)	[Cu(dtbpz)]$_4$ (**2a**)	[Cu(dppz)]$_4$ (**3**)
Cu1–Cu2	3.480(2)	2.963(1)	3.119(2)
Cu2–Cu3	3.400(2)	2.989(1)	3.131(2)
Cu3–Cu4	3.403(2)	2.964(1)	3.088(2)
Cu4–Cu1	3.535(2)	2.972(1)	3.132(2)
Average Cu···Cu	3.455	2.972	3.118
Short Cu···Cu diagonal(s)	4.702 (2), 5.061(2)	3.393(1)	4.366(2), 4.451(2)
Cu···Cu···Cu angles	86.22(4), 96.20(4), 85.30(4), 92.28(4)	69.73(3), 108.89(4), 69.50(3), 109,32(4)	89.19(4), 90.83(4), 88,61(4), 91.38(4)
Idealized Cu$_4$ shape	Parallelogram	Rhombus	Square
Average Cu–N	1.870	1.855	1.847
Average N–Cu–N	175.2	171.6	179.1

Distances in Å, angles in degree (e.s.d.'s in parentheses).

or *R*) residue is transferred to its partner located on the opposite COOR branch. In the case of **2**, the ^{1}H-NMR spectrum recorded in CD$_2$Cl$_2$ at room temperature exhibits only two singlets ($\delta = 5.9$ and 1.4 ppm in a 1:18 ratio), clearly attributable to the C(4)–*H* (upfield signal) and to the equivalent aliphatic protons of the *ter*-butyl residues.

Spectroscopic data for compounds **1** and **2** are consistent with those of polynuclear copper(I) complexes containing metal centres bridged by the heterocycles in the common *N*,*N′-exo*-bidentate fashion. The formulations of both complexes **1** and **2** as tetranuclear species have been definitively settled by X-ray crystal structure analyses.

2.2. Crystal structures

The crystal structures of **1** and **2a** (**2·CH$_2$Cl$_2$**) contain discrete cyclic copper pyrazolate tetramers, with the heterocyclic ligands binding in the common *N*,*N′-exo*-bidentate mode and weakly interacting with the neighbouring molecules through van der Waals contacts. In **2a**, one crystallographically independent CH$_2$Cl$_2$ molecule is found to be hosted in the crystal lattice. Each copper atom is nearly linearly coordinated by two

nitrogen atoms (average Cu–N 1.870 and 1.855 Å; average N–Cu–N 175.2 and 171.6°, for **1** and **2a**, respectively). (Substituted) pyrazolates alternatively lie on the different sides of roughly planar Cu$_4$ moieties. Table 2 contains a summary of chemically relevant bond distances and angles. With reference to Fig. 1, where the molecular structures of **1** and **2a** are shown [together with that of [Cu(dppz)]$_4$ (**3**), characterised some years ago [18] (Hdppz = 3,5-diphenylpyrazole)], one can see that these species markedly differ in the shape and size of the basic Cu$_4$ framework: it roughly approximates an ideal rhombus in **2**, with very short (< 3.0 Å) Cu···Cu interactions and a diagonal Cu···Cu contact of only 3.393(1) Å, lower that the shortest (intramolecular) intermetallic interaction found in **1** [3.400(2), Å with the Cu$_4$ moiety arranged as a slightly bent square]. Differently, in **3**, the Cu$_4$ fragment is nearly square, and the molecule (neglecting phenyls orientations) closely approaches D_{2d} symmetry.

The extreme variety of the Cu···Cu contacts in these isoelectronic systems (Table 2), reflected by the local changes in the Cu–N stereochemistry, may suggest that, in **1** and **2a**, markedly different interactions are present (including, possibly, d^{10}–d^{10} contacts of the aurophilic type). Actually, invoking subtle steric effects at work in

Fig. 1. Schakal drawing of the tetrameric [Cu(dscbpz)]$_4$, [Cu(dtbpz)]$_4$ and [Cu(dppz)]$_4$ species (**1**, **2a** and **3**, left to right). Copper atoms in light grey. Nitrogen and carbon atoms in dark grey, labelled and unlabelled, respectively. For the sake of clarity, (disordered) aliphatic residues have been omitted in **2a**.
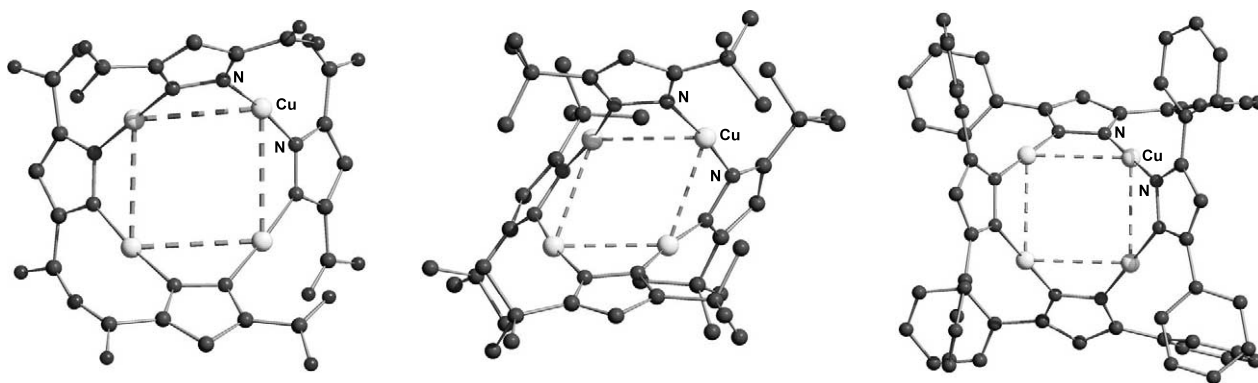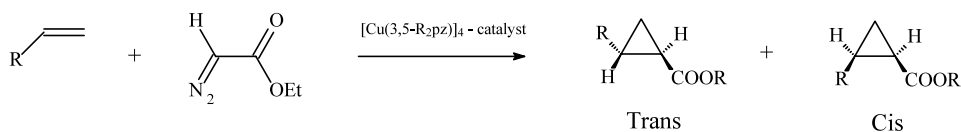
Chart 1. Cyclopropanation of alkenes.

the 'squeezed' **2a** species, which contains the substituents with the largest cone angle, contrasts with the observation of its very short intermetallic distances; consequently, we have no explanation available for such geometrical versatility.

2.3. Catalysis

In order to carry out useful comparisons, along with the two newly synthesised copper(I) derivatives **1** and **2**, the already known tetranuclear pyrazolate derivative [Cu(dppz)]$_4$ **3**, was included in the present catalytic experiments.

When complexes **1**–**3** were dissolved in dichloromethane under a dinitrogen atmosphere, at room temperature, in the presence of EDA, the conversion of olefins into the corresponding cyclopropanes derivatives (Chart 1) was detected (Table 1). With the aim of minimising EDA decomposition, a large excess of olefin was employed (Cu:EDA:olefin = 1:400:1000 molar ratio). Although diethyl maleate and diethyl fumarate were inevitably observed, the yields in cyclopropanes esters were good in all examined cases.

Complexes **1** and **2** were found to be active catalysts in the cyclopropanation of styrene by EDA. The terminal olefin was transformed into the corresponding cyclopropane ester by both copper(I) derivatives with good yields and moderately high *trans*-diastereoselectivity (88:12 = *trans*:*cis* ratio). On the contrary, only a low(er) *trans*:*cis* ratio was observed in the cyclopropanation of styrene and α-methylstyrene with compound **3**. However, when the EDA:olefin molar ratio was raised (for example, with Cu:EDA:olefin in 1:400:400 ratio), the diastereoselectivity remarkably increased (up to a *trans*:*cis* ratio of 89:11 for the conversion of α-methylstyrene into the corresponding cyclopropane ester). In styrene cyclopropanation reactions, the *trans*-isomer is generally the main product [19]: the vast majority of reported copper catalysts have provided *trans*:*cis* ratios from 50:50 to 75:25. Increasing the size of R on N$_2$CH$_2$COOR generally enhances enantiocontrol; at variance, for diastereoselectivity, only a small increase is observed, except when very bulky substituents are used, as in the case of 2,6-di-*ter*-butyl-4-methyl phenyl (DBA) and dicyclohexylmethyl diazoacetates [9].

Interestingly, complexes **1**–**3** were also found to be active catalyst in the cyclopropanation of electron-poor olefins such as cyclohexen-1-one. In all cases, good

trans:*cis* ratios (85:15) and conversion yields were obtained.

Consistently with the behaviour observed for mono-olefins, when compounds **1**–**3** were employed to catalyse the conversion of conjugated diolefins in the presence of EDA, the *trans*-isomer was always favoured. Indeed, on running parallel experiments with rhodium(II) acetate (in the same experimental conditions *but* at 0 °C), similar selectivities were obtained (GC–MS evidences).

3. Conclusions

The syntheses and structural characterisations of the new homoleptic [Cu(dcsbpz)]$_4$ and [Cu(dtbpz)]$_4$ copper(I) pyrazolate derivatives have been described. The compounds reported have been found to possess catalytic activity in the cyclopropanation reactions of alkenes with interesting diastereoselectivities, the *trans*-diastereoisomeric products being favoured in all the examined cases. The results reported in this paper hearten us to investigate the synthesis and characterisation of new copper(I) azolate complexes employing chiral pyrazoles as ligands, with the aim of obtaining new Cu(I) chiral catalysts suitable for asymmetric homogeneous catalytic transformations.

4. Experimental

All preparations and manipulations were carried out under dinitrogen atmosphere using conventional Schlenk techniques. Alkenes employed in catalytic reactions were taken from new bottles kept at −25 °C and their purity grade was confirmed by GC–MS control analysis. Solvents were purified and dried by standard methods. Hdtbpz [20] and [Cu(dppz)]$_4$ [18] were prepared according to literature procedures. [Cu(CH$_3$CN)$_4$]BF$_4$ was prepared by following a procedure analogous to that reported for the synthesis of [Cu(CH$_3$CN)$_4$]PF$_6$ [21], but using aqueous HBF$_4$ instead of HPF$_6$. Infrared spectra were recorded on a BIO RAD FTIR 7 instrument while ^{1}H-NMR spectra were acquired on a Bruker spectrometer operating at 400 MHz. Quantitative analyses of products were performed on a Shimadzu GC-17A instrument with a capillary column PS255 (25 m, 0.25 mm) and coupled with a QP5000 mass selective detector. X-ray structural determinations were carried out at the Dipartimento di

Chimica Strutturale e Stereochimica Inorganica at the University of Milan. Elemental analyses were carried out at the Microanalytical Laboratory of the latter University.

4.1. Synthesis of pyrazole-3,5-dicarbonyl dichloride

In a 250-ml two-necked round bottom flask, 5 g (29 mmol) of pyrazole-3,5-dicarboxylic acid monohydrate were suspended in 80 ml of thionyl chloride. The suspension was refluxed at 120 °C for 6 h; then, exceeding $SOCl_2$ was removed by distillation and the precipitation of a white solid took place. The precipitate was suspended in hexane, the suspension filtered and the product dried under vacuum and kept under dinitrogen atmosphere. (Yield: 85%)—IR: strong absorption at 1764 cm^{-1}, ν(CO)—^{1}H-NMR (CD$_3$CN) δ (ppm): 8.0, C(4)–H.

4.2. Synthesis of pyrazole-3,5-dicarboxylic acid di-sec-butyl ester (3,5-dicarbo-sec-butoxypyrazole-Hdcsbpz) [as a mixture of meso-(R,S) and (R,R)/(S,S) forms]

Pyrazole-3,5-dicarbonyl dichloride (2.0 g; 10.4 mmol) and (rac)-2-butanol (4 ml; $d = 0.808$ g ml^{-1}; 43.6 mmol) were suspended in degassed dioxane (30 ml), previously dried with molecular sieves and passed through an Al$_2$O$_3$ column. A large excess of triethylamine was then added. The pale yellow suspension was heated at 95 °C for 8 h. The solvent was then removed under reduced pressure and the crude solid suspended in diethyl ether. The clear yellow solution was then evaporated under vacuum and the oil obtained was re-crystallised by slow addition of an aqueous solution of CH$_3$COONa. The suspension was eventually filtered and the white precipitate dried under vacuum. (Yield: 59%)—C$_{13}$H$_{20}$N$_2$O$_4$ (268.14 g mol^{-1}): Calc. C 58.19, H 7.51, N 10.44; Found: C 58.21, H 7.46, N 10.45%—m.p. 101 °C—IR: strong absorption at 1719 cm^{-1}—^{1}H-NMR (CD$_2$Cl$_2$) d (ppm): 11 (s, 1H, N–H), 7.33 [s, 1H, C(4)$_{pz}$–H], 5.13 [m, 1H, CH(CH$_2$CH$_3$)(CH$_3$)], 1.71 [m, 2H, CH(CH_2CH$_3$)(CH$_3$)], 1.37 [d, 3H, CH(CH$_2$CH$_3$)(CH_3)], 1.0 [t, 3H, CH(CH$_2$CH_3)(CH$_3$)]—^{13}C-NMR (CD$_2$Cl$_2$) d (ppm): 160.0 (COOR), 140.8 [C$_{pz}$(3,5)], 111.0 [C$_{pz}$(4)], 74.3 [CH(CH$_2$CH$_3$)(CH$_3$)], 29.1 [CH(CH_2CH$_3$)(CH$_3$)], 19.6 [CH(CH$_2$-CH_3)(CH$_3$)], 9.8 [CH(CH$_2$CH$_3$)(CH_3)]. *It is worth noting that the material obtained (mix-Hdcsbpz) consists of a mixture of three diastereoisomers: the (S,S)-, the (R,R)- and the meso-(R,S)-Hdcsbpz species*. ^{1}H-, ^{13}C-NMR and IR spectra of mix-Hdcsbpz were found to be identical to those measured on pure (S,S)-Hdcsbpz (m.p. 100 °C), obtained in a parallel synthesis with pure (S)-sec-butanol, demonstrating the negligible influence of the absolute stereochemistry at one COOR residue on the opposite branch. Preliminary X-ray

diffraction data showed that, in the solid, the three diastereoisomers coexist in disordered tetragonal $I4_1/a$ crystals where hydrogen bonded tetramers are found [22]. However, mix-Hdcsbpz and pure (S,S)-Hdcsbpz can be distinguished by means of X-ray powder diffraction (XRPD). The unit cells obtained by a Le Bail treatment of the XRPD spectra of the two materials are actually somewhat different ($a = 21.635(1)$, $c = 13.789(1)$ Å, $V = 6454(1)$ Å^3 for mix-Hdcsbpz; $a = 21.603(1)$, $c = 13.895(1)$ Å, $V = 6485(1)$ Å^3 for (S,S)-) [23].

4.3. [Cu(dcsbpz)]$_4$ **1**

To a stirred solution of [Cu(CH$_3$CN)$_4$](BF$_4$) (0.252 g; 0.8 mmol) in methanol (4 ml) at room temperature and under inert atmosphere, the nitrogen ligand Hdcsbpz (0.223 g; 0.85 mmol) was added in one portion. After 3 min, Et$_3$N was added dropwise. The white solid was stirred under dinitrogen atmosphere for 2 h, then filtered under inert atmosphere, washed with cold methanol and dried under vacuum. (Yield: 90%)—C$_{13}$H$_{19}$CuN$_2$O$_4$ (330.85 g mol^{-1}): Calc. C 47.19, H 5.79, N 8.47; Found: C 47.24, H 5.95, N 8.38%—m.p. 166 °C (dec.)—IR (nujol): absorption at 1709 cm^{-1}. Crystals suitable for an X-ray structure determination were obtained by slow evaporation of a saturated pentane solution of **1**. *Strictly speaking, such material is a mixture of stereochemically different molecules*: also in this case, (S)- and (R)-sec-butylic residues are likely to be present in a statistical distribution, leading to a total of $2^8 = 256$ possible stereoisomers, which (if idealized D_{2d} symmetry is chosen) result in 27 different diastereoisomers (most of them occurring as enantiomeric pairs) [24]. As later described, this is reflected by the extreme disorder affecting, in the crystals, *all* methyl–ethyl fragments of the aliphatic residues.

The corresponding chiral [Cu((S,S)-dcsbpz)]$_4$ species, **1a**, has been synthesised in the same way.

4.4. [Cu(dtbpz)]$_4$ **2**

The pyrazolate complex **2** was obtained following the same synthetic procedure used for complex **1**, but employing 3,5-di-ter-butylpyrazole (Hdtbpz) instead of 3,5-dicarbo-sec-butoxypyrazole (Yield: 94%)—C$_{11}$H$_{19}$CuN$_2$ (242.08 g mol^{-1}): Calc. C 54.41, H 7.89, N 11.54; Found: C 54.01, H 7.98, N 11.54%—m.p. 295 °C (dec.). The crystal used in the X-ray structure determination was obtained by slow evaporation, under dinitrogen, of a dichloromethane solution of **2** and was shown to contain clathrated CH$_2$Cl$_2$.

4.5. Procedure for copper-catalyzed cyclopropanations

To a solution of copper(I) pyrazolate complex (10^{-2} mmol) in dichloromethane (15 ml), at room temperature and under inert atmosphere, EDA and olefin were added (catalyst:EDA:olefin molar ratio = 1:400:1000). Both reagents were added in one portion. The reaction mixture was kept under stirring until total disappearance of the diazo-compound from solution. The consumption of EDA was monitored by infrared spectroscopy. The mixture was then worked up by removing the solvent and the crude product was purified by column chromatography (dichloromethane:-hexane = 6:4). All the cyclopropanes obtained were characterised by ^{1}H-NMR and GC–MS. Diastereoselectivities (*trans*:*cis* ratios) were measured by ^{1}H-NMR of the reaction bulk.

4.6. Crystallography

Single crystal data for compounds **1** and **2a** (**2·CH$_2$Cl$_2$**) were collected at room temperature on a Bruker AXS SMART and an Enraf Nonius CAD4 systems, respectively, equipped with graphite-monochromatized Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). Intensity data were corrected for Lorentz, polarization and absorption effects (SADABS [25] for **1**, ψ-scans [26] for **2a**). The structures were solved by direct methods [27] and refined with full-matrix least squares calculations on F^2 [28]. Anisotropic temperature factors were assigned to all non-disordered (vide infra) atoms but hydrogens, riding their parent atoms with a common isotropic displacement parameter chosen as 1.2 times that of the pertinent parent. The above mentioned *racemic* nature of the starting material (*sec*-butylic alcohol) is reflected, in the crystals of **1**, by the high disorder affecting the aliphatic residues of *all* esteric 3,5-substituents. A thorough analysis of the geometrical models potentially describing such complex disorder, assisted by restrained refinements of half-occupancy methyl and ethyl residues, did not converge to any significantly stable minimum and was therefore discarded. Thus, the model presented above is truncated at the methylene groups (see Fig. 1), which, together with their neighbouring oxygen atoms, show rather large adp's, probably due to *static* disorder; nevertheless, since the inner portion of the molecule (up to the carboxylic residues) is well defined, the structural discussion presented remains fully valid.

4.7. Crystal data for 1

C$_{52}$H$_{76}$Cu$_4$N$_{16}$O$_{16}$, $M = 1323.4$ g mol^{-1}; colourless plate ($0.36 \times 0.26 \times 0.07$ mm); triclinic, $P\bar{1}$, $a = 10.9748(7)$, $b = 11.8399(8)$, $c = 26.5575(17)$ Å, $\alpha = 100.605(2)$, $\beta = 90.783(2)$, $\gamma = 105.362(2)^\circ$, $V = 3263.7(6)$ Å^3, $Z = 2$; $T = 298(2)$ K, $\rho_{calc} = 1.350$ g cm^{-3}, μ(Mo–K$_\alpha$) = 1.35 mm^{-1}, minimum relative transmission factor 0.84, $F(0\,0\,0) = 1376$. 29753 reflections (8750 unique) measured, of which 5310 with $F_o^2 > 4\sigma(F_o^2)$ observed and used to refine 649 parameters to $wR_2 = 0.264$, R_1(obs) = 0.078, Gof = 1.066 and highest peak in difference map = 1.10 e Å^{-3}.

4.8. Crystal data for 2a

C$_{45}$H$_{78}$Cl$_2$Cu$_4$N$_8$, $M = 1056.21$ g mol^{-1}, colourless needle ($0.30 \times 0.08 \times 0.03$ mm), monoclinic, $P2_1/n$, $a = 10.902(3)$, $b = 19.200(3)$, $c = 25.772(4)$ Å, $\beta = 93.86(2)^\circ$, $V = 5382(2)$ Å^3, $Z = 4$; $T = 298(2)$ K, $\rho_{calc} = 1.303$ g cm^{-3}, μ(Mo–K$_\alpha$) = 1.69 mm^{-1}, minimum relative transmission factor 0.87, $F(0\,0\,0) = 2216$. All 9417 unique reflections measured, of which 4440 with $F_o^2 > 4\sigma(F_o^2)$ observed and used to refine 532 parameters to $wR_2 = 0.124$, R_1(obs) = 0.070, Gof = 1.002 and highest peak in difference map = 0.34 e Å^{-3}.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre supplementary publication nos. CCDC 199 105 and 199 106. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

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