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ARTICLE

Spontaneous resolution of **P** and **M** helical copper(II) MOFs built from achiral precursors

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Two enantiomeric (**P** and **M**) helical coordination polymers of $[Cu(\mu_{1,3}\text{-}N_3)(L)]_n$ {*HL* = 2-(dimethylamino)ethyliminomethylnaphthalen-2-ol} have been synthesized by the self-assembly of the achiral precursors via spontaneous resolution. The structures have been confirmed by single crystal X-ray crystallography. Solid-state circular dichroism spectra have confirmed the chirality of both **P** and **M** helical chains.

Introduction

A rich diversity of architectures of coordination polymers could be produced by linking transition metal centers with bridging ligands.¹ These coordination polymers could have potential applications in molecular-based ferromagnets, non-linear optics and ferroelectrics.² Among them, the helical coordination polymers constitute a special class and deserve a special mentioning because of their potential applications in material science, chemical sensing, chiral magnets, enantio-selective catalysis, non-linear optical materials and biomimetic chemistry.³ A variety of bridging groups have been employed for the synthesis of coordination polymers; among them the pseudo-halide bridged complexes have attracted the attention of coordination chemists for their versatile modes of binding the metal centres.⁴ Several N_2O donor Schiff bases are popularly used as blocking ligands in preparing such complexes.⁵ Focusing to copper(II), the pseudo-halide bridged copper(II) complexes have received considerable attention because of their potential application in bioinorganic modeling chemistry,⁶ magnetic materials⁷ and catalysis.⁸ Great efforts have been made to design and construct coordination polymers with single-, double- or multi-strand helical structures by several groups.⁹ The helical structures induce chirality, but due to the presence of both **P** (right-handed) and **M** (left handed) helices, they are usually optically inactive.¹⁰ However, if the complexes belong to chiral space groups, either **P** or **M** helix is present in it and consequently, the complex is chiral as well as optically active. The most effective method for the synthesis of chiral helix is to use a chiral molecule as the primary linker or as an auxiliary ligand.¹¹ However, it is highly desirable to create chiral compounds from achiral precursors by spontaneous resolution because of the limitation of the chiral pool and very often the high cost of chiral ligands.¹²

For any chiral solid, its absolute configuration (the left- or right-handedness) is usually determined by looking at the Flack parameter¹³, the value of which usually falls between 0 and 1. If the value is near 0, with a small standard uncertainty, the absolute structure given by the structure refinement is likely correct, and if the value is near 1, then the inverted structure is likely correct. If the value is near 0.5, the crystal may be racemic or twinned. On the other hand, inorganic chiral materials often form racemic conglomerate containing both the left- and right-handed variants in the bulk solid.

Our attempts with a N_2O donor Schiff base, 2-(dimethylamino)ethyliminomethylnaphthalen-2-ol (*HL*) afforded copper(II) helices, $[Cu(\mu_{1,3}\text{-}N_3)(L)]_n$, with end-to-end azide bridges. Single crystal X-ray data, values of Flack parameter and Solid state CD spectra support the presence of both **P** and **M** helices in the bulk material leading to the formation of racemic conglomerate. Herein, we report the synthesis, spectroscopic characterization and crystal structures of these **P** and **M** helical chains obtained by the self-assembly of achiral precursors via spontaneous resolution.

Experimental Details

All materials were commercially available, reagent grade and used as purchased from Sigma-Aldrich without further purification. Although no problems were encountered in this work, organic ligands containing azides are potentially explosive. Only a small amount of the material should be prepared and they should be handled with care.

Synthesis of the Complex

A methanol solution of *N,N*-dimethyl-1,2-diaminoethane (0.10 ml, 1 mmol) and 2-hydroxy-1-naphthaldehyde (172 mg, 1 mmol) was refluxed for ca. 1 h to form the tridentate Schiff base ligand *HL*. The ligand was not isolated. A methanol (10

ml) solution of copper(II) acetate monohydrate (200 mg, 1 mmol) was added into the methanol solution of the ligand *HL* to get a dark blue solution. A methanol-water solution of sodium azide (65 mg, 1 mmol) was added into the reaction mixture with constant stirring. The stirring was continued to get dark blue single crystals, suitable for X-ray diffraction.

(Yield: 274 mg, 79%) Anal. Calc. for $C_{15}H_{17}CuN_5O$ (346.89): C, 51.94; H, 4.94; N, 20.19 %. Found: C, 51.7; H, 4.8; N, 20.4 %. FT-IR (KBr, cm^{-1}): 1622 (C=N); 2067 (N_3). λ_{max} (nm) [ϵ_{max} (lit $mol^{-1} cm^{-1}$)] (acetonitrile): 298 (3.96×10^4); 383 (2.23×10^4); 584 (3.05×10^2).

X-ray Crystallography

Eleven suitable crystals of the complex were used for data collection using a 'Bruker SMART APEX II' diffractometer equipped with graphite-monochromated Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at 293 K. The molecular structures were solved by direct method and refined by full-matrix least squares on F^2 using the SHELX-97 package.¹⁴ Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. Multi-scan empirical absorption corrections were applied to the data using the program SADABS.¹⁵ Details of crystallographic data and refinements of one **M** and one **P** helical MOFs are given in Table 1. CCDC reference numbers are 999066 and 1039159 respectively for the **M** and **P** helices. Data for other **M** and **P** helices are gathered in Table S1; Electronic Supplementary Information.

Table 1: Crystallographic data and refinement details of one **M** and one **P** helical MOFs.

Complex	M	P
Formula	$C_{15}H_{17}CuN_5O$	$C_{15}H_{17}CuN_5O$
Formula Weight	346.89	346.89
Temperature (K)	293	293
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1$	$P2_1$
a (\AA)	8.011(5)	8.0058(3)
b (\AA)	6.852(5)	6.8434(2)
c (\AA)	14.033(5)	14.0474(5)
β (deg)	103.777(5)	103.658(2)
Z	2	2
d_{calc} ($g\ cm^{-3}$)	1.540	1.541
μ (mm^{-1})	1.469	1.469
F(000)	358	358
Flack Parameter	0.06(6)	0.033(14)
Total Reflections	2717	10888
Unique Reflections	1548	2842
Observed data [$I > 2\ \sigma(I)$]	1487	2552
No. of parameters	157	199
R(int)	0.063	0.039
R1, wR2 (all data)	0.0883, 0.2097	0.0366, 0.0642
R1, wR2 [$I > 2\ \sigma(I)$]	0.0759, 0.1880	0.0309, 0.0623

Details of Instrumentation

Elemental analyses (carbon, hydrogen and nitrogen) were performed using a PerkinElmer 240C elemental analyzer. IR spectra in KBr ($4500\text{--}500\ cm^{-1}$) were recorded with a PerkinElmer Spectrum Two spectrophotometer. Electronic spectra in acetonitrile were recorded on a PerkinElmer Lambda

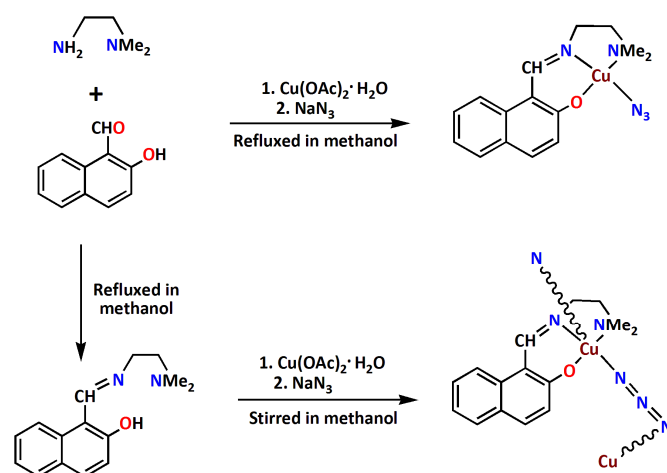
35 UV-visible spectrophotometer. Solid state (KBr pellets) circular dichroism (CD) spectrum was recorded on a JASCO J-810 spectropolarimeter. Powder X-ray diffraction was performed on a Bruker D8 instrument with Cu-K α radiation. Steady state photoluminescence spectra in acetonitrile were obtained in Shimadzu RF-5301PC spectrofluorometer at room temperature. Time dependent photoluminescence measurements were done using Hamamatsu MCP photomultiplier (R3809) and were analyzed by using IBHDAS6 software.

The emission of the complex is tentatively attributed to the intra ligand transitions modified by metal coordination. Intensity decay profile was fitted to the sum of exponentials series $I(t) = \sum_i \alpha_i \exp(-t/\tau_i)$, where α_i was a factor representing the

fractional contribution to the time-resolved decay of the component with a lifetime of τ_i . Bi-exponential function was used to fit the decay profile for the complex, with obtaining χ^2 close to 1. The intensity-averaged life time (τ_{av}) was determined from the result of

the exponential model using $\tau_{av} = \frac{\sum_i \alpha_i \tau_i^2}{\sum_i \alpha_i \tau_i}$, where α_i and τ_i are the

pre-exponential factors and excited-state luminescence decay time associated with the i -th component, respectively.



Scheme 1: Synthesis route to the helical coordination polymer and its mononuclear analogue.

Result and Discussion

Synthesis

The tridentate Schiff base ligand, *HL*, was prepared by the 1:1 condensation of *N,N*-dimethyl-1,2-diaminoethane with 2-hydroxy-1-naphthaldehyde in methanol following the literature method.¹⁴ The methanol solution of *HL* was then made to react with copper(II) acetate monohydrate along with sodium azide to prepare **M** and **P** helices of $[Cu(\mu_{1,3}\text{-}N_3)(L)]_n$. Eleven crystals from the same reaction were randomly picked and characterized by single-crystal X-ray diffraction analyses, which showed that the bulk material contained single crystals of both **M** and its

enantiomorph **P** helices almost in equal proportions. Each single crystal belonging to chiral $P2_1$ space group, suggesting that spontaneous resolution occurred during the crystal growth process. The Flack parameters of all crystals are all close to zero (Table 1 and S1; ESI). The results demonstrate that each individual crystal is homochiral while the bulk material is a racemic conglomerate consisting of more or less 50% **P** and 50% **M** helices. It is to be noted here that a mononuclear complex, $[Cu(N_3)(L)]$, could be crystallized from an unstirred solution. The structure of this complex was reported by a different group.¹⁶ The formation of both complexes is shown in Scheme 1.

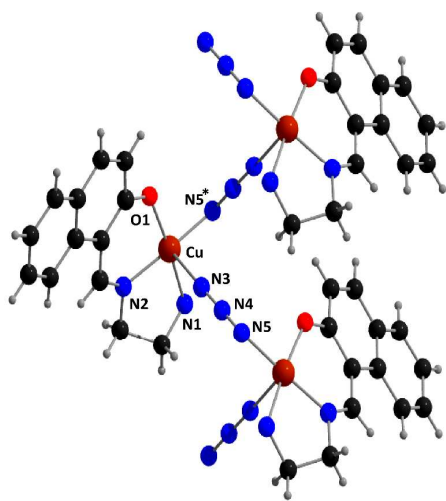


Fig. 1: Perspective view of **M** helix with selective atom numbering scheme. Methyl groups of the amine nitrogen atoms have been omitted for clarity. Symmetry transformation: * = $-x, -1/2+y, 1-z$.

Structure Description

The fundamental building units for both **M** and **P** helices consist of a copper(II) centre, one deprotonated Schiff base ligand, (L^-), and an azide ion. Taking one **M** helix as an example, a perspective view of the complex with the selective atom-numbering scheme is shown in Fig. 1. Copper(II) centres are bridged singly by end-to-end (EE) azides with the formation of the helix. Each copper(II) centre is coordinated equatorially by one amine nitrogen atom, N(1), one imine nitrogen atom, N(2), and one oxygen atom, O(1), of the tridentate deprotonated Schiff base, (L^-), and a nitrogen atom, N(3), of the EE bridged azide; this defines the basal plane. An nitrogen atom, N(5)*, from a symmetry related ($-x, -1/2+y, 1-z$) bridging azide coordinates axially at a rather long distance furnishing an elongated square-pyramidal (4+1) geometry for each copper(II) center. The value of Addison parameter (τ)¹⁷ is 0.047, which also suggests a slightly distorted square pyramidal geometry. In the equatorial plane, the Cu-N_{imine} distance {1.933(13) Å} is shorter than the Cu-N_{amine} {2.032(13) Å} distance, as was also observed in similar systems.¹⁸ The deviations of the coordinating atoms N(1), N(2), O(1) and N(3) from the least square mean plane through them are -0.001(13), 0.047(13),

0.002(11) and 0.047(13) Å respectively. As usual for a square pyramid structure, the copper(II) is slightly pulled out of this mean square plane towards the apical donor atom at a distance 0.0944(16) Å. The closest conformation of the five-membered chelate ring, Cu(1)-N(1)-C(3)-C(4)-N(2), is envelope with puckering parameters $q(2) = 0.430(15)$ Å and $\phi(2) = 71.8(16)^\circ$.¹⁹ The bridging azides are quasi-linear; the N-N-N angle is $174.3(16)^\circ$. The shortest Cu...Cu distance is 5.838(3) Å in the helix. Selected bond lengths and angles are gathered in Table 2.

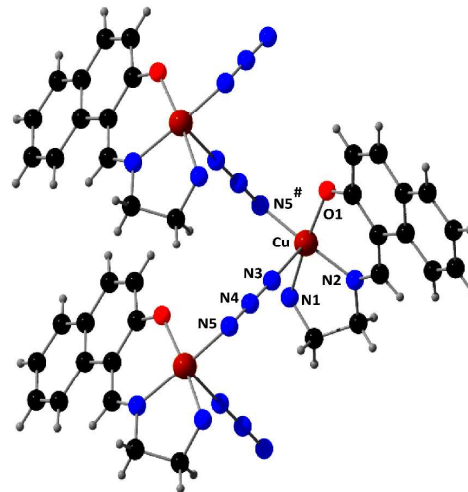


Fig. 2: Perspective view of **P** helix with selective atom numbering scheme. Methyl groups of the amine nitrogen atoms have been omitted for clarity. Symmetry transformation: # = $1-x, 1/2+y, 2-z$.

On the other hand, the **P** helix has a very similar structure (Figure 2) in which each square-pyramidal (Addison parameter = 0.034) copper(II) centre is coordinated equatorially by one amine nitrogen atom, N(1), one imine nitrogen atom, N(2), and one oxygen atom, O(1), of the tridentate deprotonated Schiff base, (L^-), and a nitrogen atom, N(3), of the EE bridged azide; and axially by an nitrogen atom, N(5)#, from a symmetry related ($1-x, 1/2+y, 2-z$) end-to-end bridging azide. Cu-N_{imine} distance {1.939(2) Å} is shorter than the Cu-N_{amine} {2.042(2) Å} distance, as was also observed in **M** helical chain. The deviations of the coordinating atoms N(1), N(2), O(1) and N(3) from the least square mean plane through them are -0.018(2), 0.019(2), -0.019(2) and 0.018(2) Å respectively and that of copper(II) from the same plane -0.1362(3) Å. The closest conformation of the five-membered chelate ring, Cu(1)-N(1)-C(3)-C(4)-N(2), is envelope with puckering parameters $q(2) = 0.427(3)$ Å and $\phi(2) = 250.1(3)^\circ$.¹⁹ The N-N-N angle in the bridging azide is $175.4(6)^\circ$. The shortest intra-helix Cu...Cu distance is 5.8362(5) Å. Selected bond lengths and angles of both **M** and **P** helices are gathered in Table 2. A closer look at the both **P** and **M** helical chains are shown in Fig. 3.

The hydrogen atom H(1A), attached with a methyl carbon, C(1), in the **M** helix is involved in C-H... π interaction with a

symmetry related (1+x,y,z) phenyl ring [C(7)–C(8)–C(9)–C(10)–C(11)–C(12)] from a neighbouring helix to form supra-molecular two-dimensional sheet as shown in Fig. 4. C–H... π interactions in the **P** helix also form similar supra-molecular two-dimensional sheet.

CD Spectroscopy

Additional evidence for the occurrence of spontaneous resolution comes from CD spectroscopy performed on the single crystals obtained in the same crystallization. Each and every single crystal of the complex that was used for single crystal X-ray diffraction analysis, are also used for collection of CD spectrum. The results gave the expected opposite Cotton effects, positive or negative (at 298, 383 and 584 nm), revealing the formation of either **M** or **P** helices in the bulk sample under spontaneous resolution (Fig. 5).

Table 2: Selected bond lengths (Å) and bond angles (°) in **M** and **P** helices of the complex.

	M	P
Cu(1)–O(1)	1.936(10)	1.914(2)
Cu(1)–N(1)	2.032(13)	2.042(2)
Cu(1)–N(2)	1.933(13)	1.939(2)
Cu(1)–N(3)	1.945(13)	1.962(3)
Cu(1)–N(5) ^{#*}	2.495(13)	2.471(4)
O(1)–Cu(1)–N(1)	173.7(5)	172.36(10)
O(1)–Cu(1)–N(2)	90.9(5)	90.89(10)
O(1)–Cu(1)–N(3)	92.3(5)	91.80(11)
O(1)–Cu(1)–N(5) ^{#*}	92.9(4)	92.85(12)
N(1)–Cu(1)–N(2)	85.6(5)	85.15(10)
N(1)–Cu(1)–N(3)	90.4(5)	91.09(11)
N(1)–Cu(1)–N(5) ^{#*}	92.2(5)	93.50(12)
N(2)–Cu(1)–N(3)	170.9(5)	170.34(12)
N(2)–Cu(1)–N(5) ^{#*}	87.9(5)	87.43(12)
N(3)–Cu(1)–N(5) ^{#*}	100.5(5)	101.70(13)

Symmetry transformations: * = -x, -1/2+y, 1-z (For **M**) and # = 1-x, 1/2+y, 2-z (For **P**).

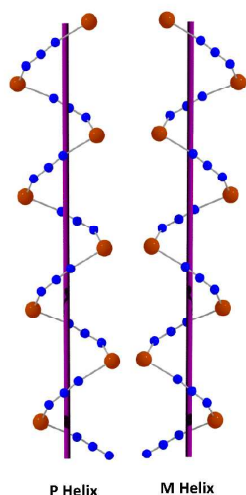


Fig. 3: A closer look at the **P** and **M** helical chains of the complex.

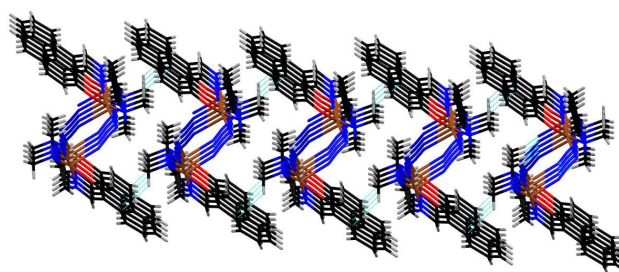


Fig. 4: Perspective view of the two dimensional supra-molecular network formed via C–H... π interactions in the **M** helix.

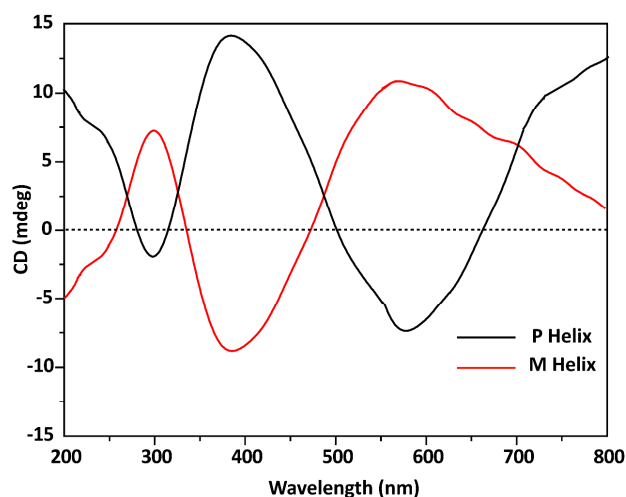


Fig. 5: Solid state (KBr pellet) CD spectra of **P** and **M** helices showing the opposite cotton effects.

IR, UV-VIS, Fluorescence spectroscopy and PXRD

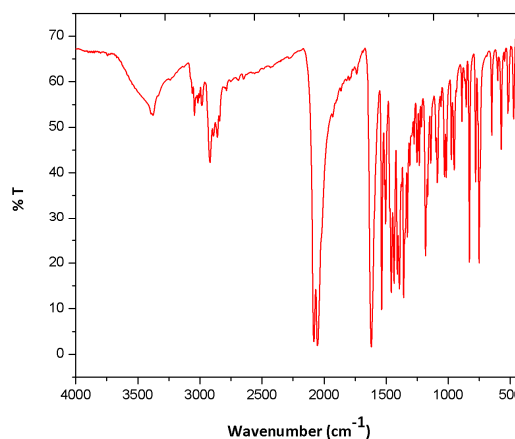


Fig. 6: IR spectrum (KBr pellet) of the bulk material.

In the IR spectrum of the complex, distinct band due to the azomethine (C=N) group at 1622 cm^{-1} (Fig. 6) is routinely noticed.^{1(f)} The appearance of a strong band at 2067 cm^{-1} indicates the presence of $\mu_{1,3}$ -bridged azide in the complex.²⁰ The UV-Vis absorption spectrum (Fig. 7) of the complex in acetonitrile shows a d-d transition band at 584 nm, as expected for a square pyramidal copper(II) environment with N_2O donor

tridentate Schiff bases along with nitrogen donor monodentate ligands.^{21(a)} The intense absorption bands below 400 nm may be assigned to ligand to metal ion charge transfer bands (LMCT).^{21(a)} On the other hand, the absorption spectrum of its mononuclear analogue, $[Cu(N_3)(L)]$, shows only one d-d transition band at 604 nm along with the intense absorption bands below 400 nm due to LMCT transitions in acetonitrile solution. Although both square planar and square pyramidal complexes exhibit single symmetric bands due to the $d_z^2 \rightarrow d_{x^2-y^2}$ transitions, the positions of the absorption maxima should differ.^{21(b)} Therefore, the difference in the value of the λ_{max} of the mononuclear complex containing square planar copper(II) and the helical polynuclear one with square pyramidal copper(II) indicates their independent existence in solution.

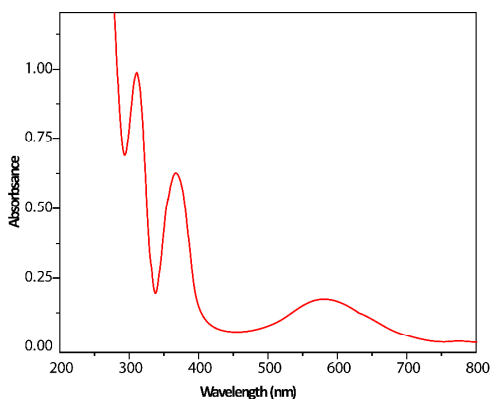


Fig. 7: UV spectrum (KBr pellete) of the bulk material.

The complex exhibits luminescence in acetonitrile medium at 425 nm on exciting at 380 nm and may be assigned to intra-ligand ($\pi-\pi^*$) fluorescence.²¹ The mean lifetime (τ_{av}) of the excited state is 2.72 ns at room temperature and the lifetime decay profile is shown in Fig. S1; ESI. The experimental P-XRD pattern of the bulk product is in good agreement with the simulated XRD pattern from single-crystal X-ray diffraction, indicating consistency of the bulk sample (Fig. S2; ESI). The simulated patterns of the complexes are calculated from the single crystal structural data (cif files) using the CCDC Mercury software.

Conclusion

The synthesis of chiral compounds from achiral precursors by spontaneous resolution is an interesting research topic nowadays. In the present work, an achiral tridentate N_2O donor Schiff base was used to prepare new helical chains of a copper(II) MOF via spontaneous chiral resolution. Solid state CD spectra and single crystal X-ray diffraction studies show that each individual crystal is homochiral while the bulk material is a racemic conglomerate containing both **P** and **M** helices.

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Spontaneous resolution of P and M helical copper(II) MOFs built from achiral precursors

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Enantiomeric **P** and **M** helices have been synthesized by the self-assembly of the achiral precursors via spontaneous resolution and structures have been confirmed by single crystal X-ray crystallography and sSolid-state circular dichroism spectra.

