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M and P Double Helical Complexes of Copper(I) with Bis-imino Bis-quinoline Enantiomerically Pure Chiral Ligands

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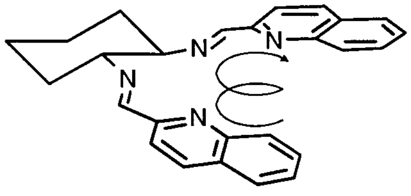
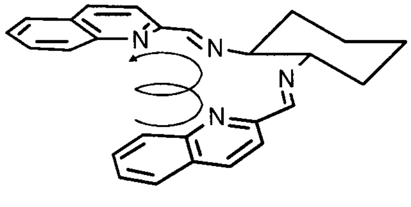
The enantiomerically pure bis-imino bis-quinoline ligands *R,R*-ImQ and *S,S*-ImQ have been prepared by Schiff condensation of 2-quinoline carboxyaldehyde with the pure *R,R* and *S,S* enantiomers of *trans*-1,2-diaminocyclohexane. Both ligands form 2:2 helical complexes with Cu^I perchlorate, and the crystal and molecular structure of $[Cu_2(R,R\text{-ImQ})_2]ClO_4 \cdot H_2O$ have been determined by X-ray diffraction methods: the $[Cu_2(R,R\text{-ImQ})_2]^{2+}$ molecular cation is a chiral double helix of M handedness, in which the two ligands are entertwined in such an arrangement that half of each ligand is not equivalent to the other half of the same ligand. Coupled circular dichroism and ^1H NMR studies reveal that in CH_3CN solution a rearrangement takes place toward a more symmetric helical structure (in which the two halves of the same ligand become equivalent), which mantains the same handedness found in the solid state and is a pure M isomer. Solid state and CH_3CN solution CD experiments confirm that $[Cu_2(S,S\text{-ImQ})_2]ClO_4 \cdot H_2O$, both in solution and in the solid state, is a pure double helix of P handedness, i.e., the enantiomer of the species containing the *R,R* ligand.

Introduction

Enriched or pure P or M double-helical coordination compounds[1,2] (i.e., double helices with a plus or minus handedness) may be obtained through metal−ligand self-assembly processes which involve chiral ligands.[3−5] We have already found[6] that the Schiff condensation of *trans*-1,2-diamino cycloexhane (*R,R* + *S,S* racemic mixture) with 2-quinoline aldehyde gives the ImQ ligand, which is capable of forming dimeric compounds with Cu^I (2:2 stoichiometry), which are of helical nature in solution and can instead assume both helical and nonhelical structures in the solid state. Of course, working with a racemic mixture of ligands, no P or M excess was obtained. On the other hand, from the pure *R,R* and *S,S* isomers of 1,2-cyclohexane diamine the couple of pure enantiomeric ligands *R,R*-ImQ and *S,S*-ImQ (Figure 1) can be obtained through Schiff condensation with 2-quinoline carboxyaldehyde. Interestingly, these ligands are preorganized along a helical path,[7] due to the reciprocal arrangement of the $C-N_{imine}$ bonds in the rigid *trans*-1,2-cyclohexyl moiety. *R,R*-ImQ and *S,S*-ImQ display M and P handedness, respectively, this supposedly favoring the formation of pure M or P double helicates when assembling with Cu^I. In this work, reaction with $[Cu(CH_3CN)_4]ClO_4$ gave the 2:2 ligand/metal double-helical $[Cu_2(R,R\text{-ImQ})_2]^{2+}$ and $[Cu_2(S,S\text{-ImQ})_2]^{2+}$ complexes, each of which is a pure diastereoisomer whose M or P nature in solution and in the solid state have been ascertained by X-ray diffraction, NMR, and CD studies.



R,R-ImQ – helicity: M



S,S-ImQ – helicity: P

Figure 1. Sketch of a possible conformation of *R,R*-ImQ and *S,S*-ImQ ligands and of their intrinsic helicity. Free rotation is obviously possible around the bond between the CH groups of the cyclohexyl ring and the imino nitrogens. However, the fixed reciprocal disposition of the HC−N=C bonds imparts to the whole molecule M or P helicity.

Results and Discussion

Crystal and Molecular Structure of $[Cu_2(R,R-ImQ)_2](ClO_4)_2 \cdot H_2O$. We have already found[6] that the racemic mixture of the *R,R*-ImQ and *S,S*-ImQ ligands gave with $Cu(CF_3SO_3)$ crystals containing a 2:2 ligand/metal molecular cation of helical nature, while on replacing $CF_3SO_3^-$ with ClO_4^-, crystals were

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(1) Knof, U.; von Zelewsky, A. *Angew. Chem., Int. Ed.* **1999**, *38*, 302.

(2) Piguet, C.; Berardinelli, G.; Hopfgartner, G. *Chem. Rev.* **1997**, *97*, 2005.

(3) Baum, G.; Constable, E. C.; Fenske, D.; Housecroft, C. E.; Kulke, T. *Chem. Eur. J.* **1999**, *5*, 1862.

(4) Zarges, W.; Hall, J.; Lehn, J.-M. *Helv. Chem. Acta* **1991**, *74*, 1843.

(5) Masood, M. A.; Enemark, E. J.; Stack., T. D. P. *Angew. Chem., Int. Ed.* **1998**, *37*, 928.

(6) Amendola, V.; Fabbrizzi, L.; Linati, L.; Mangano, C.; Pallavicini, P.; Pedrazzini, V.; Zema, M. *Chem. Eur. J.* **1999**, *5*, 3679.

(7) Gargiulo, D.; Ikemoto, N.; Odingo, J.; Bozhkova, N.; Iwashita, T.; Berova, N.; Nakanishi, K. *J. Am. Chem. Soc.* **1994**, *116*, 3760.

10.1021/ic0005700 CCC: \$19.00

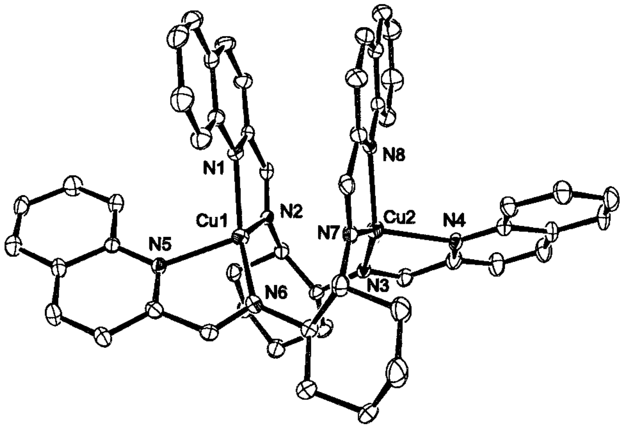

Figure 2. ORTEP view of the [Cu$_2$(*R*,*R*-ImQ)$_2$]$^{2+}$ molecular cation, with 20% probability displacement ellipsoids. The perchlorate anions, the water molecule, and the H atoms have been omitted for the sake of clarity. Selected bond distances (Å) and angles (deg): Cu1−N1 2.087(5), Cu2−N3 2.012(5), Cu1−N2 2.000(6), Cu2−N4 2.115(5), Cu1−N5 2.116(5), Cu2−N7 2.002(6), Cu1−N6 2.017(5), Cu2−N8 2.117(5). N1−Cu1−N2 80.6(2), N3−Cu2−N4 81.3(2), N1−Cu1−N5 106.4(2), N3−Cu2−N7 136.6(2), N1−Cu1−N6 138.8(2), N3−Cu2−N8 132.4(2), N2−Cu1−N5 118.1(2), N4−Cu2−N7 121.5(2), N2−Cu1−N6 132.5(2), N4−Cu2−N8 104.3(2), N5−Cu1−N6 81.0(2), N7−Cu2−N8 81.0(2).

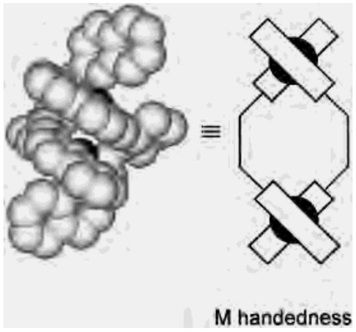

Figure 3. CPK rendering of the molecular structure, stressing the M handedness of the [Cu$_2$(*R*,*R*-ImQ)2]$^{2+}$ double helix.

obtained containing *both* a 2:2 ligand/metal helical species with a different conformation *and* a second, nonhelical species with the same stoichiometry. This nonhelical structure featured one *R*,*R* and one *S*,*S* ligand, i.e., it had to be formulated as [Cu$_2$(*R*,*R*-ImQ)(*S*,*S*-ImQ)]$^{2+}$, while the two helical forms contained two ligands of the same handedness. In this work, crystals suitable for structural determination were obtained by slow evaporation at low temperatures of acetonitrile solutions containing [Cu(CH$_3$CN)$_4$](ClO$_4$) and *R*,*R*-ImQ in a 1:1 molar ratio. X-ray diffraction demonstrated that the crystals contained only the molecular cation depicted in Figure 2, which is almost perfectly isostructural to the helical molecular cation found in ref 6 for [Cu$_2$(ImQ)$_2$](ClO$_4$)$_2$·H$_2$O,[8] indicating that, with ClO$_4^-$ as the counteranion, this helical form is the preferred one even in the absence of the packing effects exerted by [Cu$_2$(*R*,*R*-ImQ)(*S*,*S*-ImQ)]$^{2+}$. An M handedness can be clearly assigned to the found [Cu$_2$(*R*,*R*-ImQ)$_2$]$^{2+}$ molecular cation, as sketched in Figure 3, and a Λ configuration can be found at each copper center.

NMR Studies. The ^{1}H NMR spectra of the two Cu^I complexes (CD$_3$CN as solvent) are identical, and besides the different chemical shifts, the number and multiplicity of the signals are the same as in the free ligands. For [Cu$_2$(*R*,*R*-ImQ)$_2$](ClO$_4$)$_2$ signals are found at δ 8.60 (s, 4H, −C*H*═N−); 8.14 (d, 4H), 7.72 (d, 4H), 7.39 (t, 4H), 7.21 (t, 4H), 7.13 (d, 4H), 6.93 (d, 4H), H of the quinoline rings; 4.09 (m, 4H, N−C*H*(R)−C*H*(R)-N of the cyclohexane ring); 2.2−1.3 (m, C*H*$_2$ of the cyclohexane ring + C*H*$_3$CN solvent impurity). The X-ray structure of the enantiomeric pure [Cu$_2$(*R*,*R*-ImQ)$_2$](ClO$_4$)$_2$·H$_2$O (Figure 2) shows that the molecular cation does not fit D_2 symmetry as, although the two ligands can be interconverted through a C_2-axis passing through the midpoints between Cu1−Cu2, N1−N8, N2−N7, and N3−N6, no other C_2-axis can be defined. Each ligand can be subdivided into two halves, each experiencing a different environment: one iminoquinoline half of the first ligand is in face-to-face disposition with the corresponding iminoquinoline half of the second ligand (they form an angle of 8.7°), whereas the other half is isolated. Thus, if the configuration found in the crystal structure for [Cu$_2$(*R*,*R*-ImQ)$_2$]$^{2+}$ is mantained also in solution, a set of aromatic signals split into two is to be expected. However, the found single-set NMR spectrum indicates that in acetonitrile the molecular cation adopts a more symmetric conformation.[9] It has to be pointed out that for the enantiomeric mixture of the two ligands (see ref 6) when the NMR spectrum of the Cu^I complex was carried out, a further, much less intense set of aromatic signals was recorded, indicating the presence of another species in solution. In this second set, the signals were split into two subsets of identical intensity, and this second species reached 13% at 293 K. On the basis of the splitting into two twin subsets of the aromatic signals in the NMR spectrum and on what was found by X-ray diffraction, it has been proposed that this second less abundant species was of asymmetric helical nature; that is, the two halves of each ImQ ligand had to experience different environments. With the enantiomerically pure complexes no trace of a second, less intense set of signals for the aromatic protons is observed. However, an equimolar mixture of [Cu$_2$(*R*,*R*-ImQ)$_2$](ClO$_4$)$_2$·H$_2$O and [Cu$_2$(*S*,*S*-ImQ)$_2$](ClO$_4$)$_2$·H$_2$O displays a second, less intense set of signals, which is split into two (in particular, the two C*H*═N signals are at 9.21 and 8.93 ppm and have the same intensity). As a matter of fact, it is the same spectrum recorded for the complex between Cu^I and the enantiomeric mixture of ligands synthesized starting from the commercially available mixture of *R*,*R*- and *S*,*S*-1,2-diaminocyclohexane. This new result (i) confirms that the second set of signals observed in ref 6 was not the consequence of some kind of impurity contained in the commercially available isomeric mixture of *R*,*R*+*S*,*S*-*trans*-1,2-diaminocyclohexane, but it was a real feature of the system; (ii) throws a new light on the nature of the species responsible for the second, less intense set of signals, which must be formulated as [Cu$_2$(*R*,*R*-ImQ)(*S*,*S*-ImQ)]$^{2+}$; and (iii) merged with the already stressed X-ray structure results of ref 6, suggests that the conformation of the 2:2 metal/ligand complex [Cu$_2$(*R*,*R*-ImQ)(*S*,*S*-ImQ)]$^{2+}$ is not necessarily helical, although it must be such that the two halves of the same ligand experience remarkably different environments. Finally, the fact that in the equimolar mixture of [Cu$_2$(*R*,*R*-ImQ)$_2$]$^{2+}$ and [Cu$_2$(*S*,*S*-ImQ)$_2$]$^{2+}$ the prevailing spectrum is coincident with that observed for the Cu^I complexes with the enantiomerically pure ligands demonstrates that *RR*-ImQ and *SS*-ImQ are self-recognizing (at least partially) when

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(8) In the structure reported in ref 6, the centrosymmetric space group obviously allowed the coexistence within the unit cell of both [Cu$_2$(*R*,*R*-ImQ)$_2$]$^{2+}$ and [Cu$_2$(*S*,*S*-ImQ)$_2$]$^{2+}$ molecular cations in a 1:1 ratio.

(9) The configuration change takes place in the few seconds required to transfer the freshly prepared solutions to the NMR apparatus This agrees with the fast rearrangement motions already found for these systems, e.g., in the electrochemically driven Cu^{II}-monomer/Cu^I-dimer interconversion;[6] moreover, it has to be noted that spectra recorded after 48 h on the same solutions do not display any further variation.

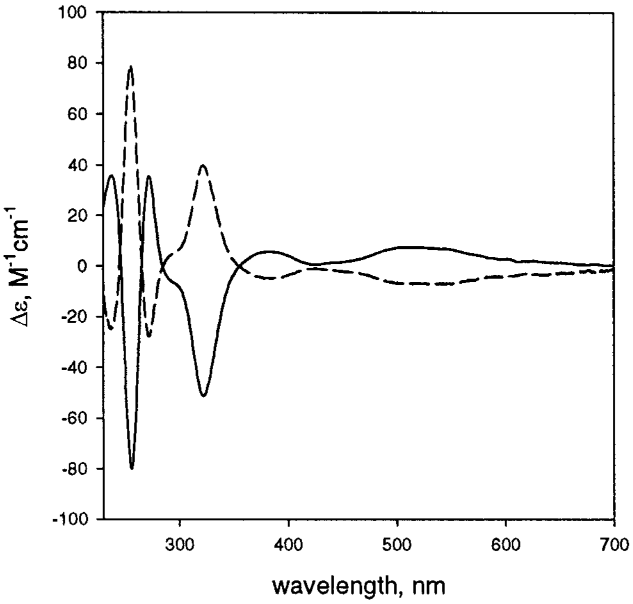

Figure 4. CD spectra of $[Cu_2(R,R\text{-}ImQ)_2]ClO_4{\cdot}H_2O$ (solid line) and $[Cu_2(S,S\text{-}ImQ)_2]ClO_4{\cdot}H_2O$ (dashed line), in CH_3CN as solvent. Concentration = 2×10^{-4} M.

assembling around Cu^+ cations: the heterochiral $[Cu_2(R,R\text{-}ImQ)(S,S\text{-}ImQ)]^{2+}$ species reaches 12%[10] in acetonitrile at 20 °C, while the homochiral $[Cu_2(R,R\text{-}ImQ)]^{2+}$ and $[Cu_2(S,S\text{-}ImQ)]^{2+}$ are both at 44% (i.e., in solution there is 88% of homochiral self-recognized species).

Circular Dichroism. NMR spectra show that the $[Cu_2(R,R\text{-}ImQ)_2]^{2+}$ molecular cation changes its conformation on dissolving in CH_3CN. This raises the question whether the same helical handedness is mantained or not by $[Cu_2(R,R\text{-}ImQ)_2]^{2+}$ after rearrangement. CD spectra on the free *R*,*R*-ImQ ligand in CH_3CN display an intense positive band at 240 nm ($\Delta\epsilon = +124$ $M^{-1} \times cm^{-1}$) with a symmetrical negative one at 253 nm ($\Delta\epsilon = -122$ $M^{-1} \times cm^{-1}$), which correspond to the $\pi-\pi^*$ UV band found for the ligand, in the same solvent, at 242 nm ($\epsilon = 71\,000$ $M^{-1} \times cm^{-1}$); at 293 nm the free *R*,*R*-ImQ ligand displays also a positive, less intense band ($\Delta\epsilon = +16$ $M^{-1} \times cm^{-1}$), which corresponds to the $n-\pi^*$ UV band centered at 284 nm ($\epsilon = 17\,800$ $M^{-1} \times cm^{-1}$, in CH_3CN). Acetonitrile solutions of $[Cu_2(R,R\text{-}ImQ)_2](ClO_4)_2{\cdot}H_2O$ display UV/vis spectra, with a MLCT band centered at 540 nm ($\epsilon = 8420$ $M^{-1} \times cm^{-1}$), plus a shoulder at 392 nm ($\epsilon = 5180$ $M^{-1} \times cm^{-1}$), and ligand-centered bands at 316 nm ($\epsilon = 27\,000$ $M^{-1} \times cm^{-1}$) and 250 nm ($\epsilon = 98\,000$ $M^{-1} \times cm^{-1}$). Interestingly, CH_3CN solutions of $[Cu_2(R,R\text{-}ImQ)_2](ClO_4)_2{\cdot}H_2O$ display CD spectra with $\pi-\pi^*$ bands centered at almost the same wavelength as in the free ligand (Figure 4), while the $n-\pi^*$ band shifts to longer wavelength (322 nm),[11] changes its sign, and increases in intensity ($\Delta\epsilon = -52$ $M^{-1} \times cm^{-1}$). Moreover two positive mlct bands are found at 385 and 522 nm ($\Delta\epsilon = +6$ and $+8$ $M^{-1} \times cm^{-1}$, respectively).

Assignation of absolute configuration of helical systems in solution has been proposed on the basis of the sign of either $n-\pi^*$[3] or, more frequently, mlct bands[4,12] in the CD spectrum. In both cases, a P handedness has been proposed for complexes displaying positive signs for these bands. In the case of our complex interpretation is controversial, due to the change in the sign on passing from $n-\pi^*$ to mlct bands. In particular, the sign of the mlct bands is positive, while a minus (M) handedness is found in the solid state. Although the hypothesis of a M-to-P fast conversion in solution cannot be excluded for the double-helical $[Cu_2(R,R\text{-}ImQ)_2]^{2+}$ complex, this contrasts with the orientation imposed by the ImQ ligand, which has a "built-in" M handedness (see Figure 1), which cannot be overcome unless serious structural modifications take place (e.g., *E*-to-*Z* isomerization at one C═N bond).[7] To ascertain if the same handedness (M) is mantained on dissolving $[Cu_2(R,R\text{-}ImQ)_2](ClO_4)_2{\cdot}H_2O$ in acetonitrile, CD spectra were recorded also on thin pellets of KCl containing crystalline $[Cu_2(R,R\text{-}ImQ)_2](ClO_4)_2{\cdot}H_2O$ (~100:2 in weight); see Figure 5.

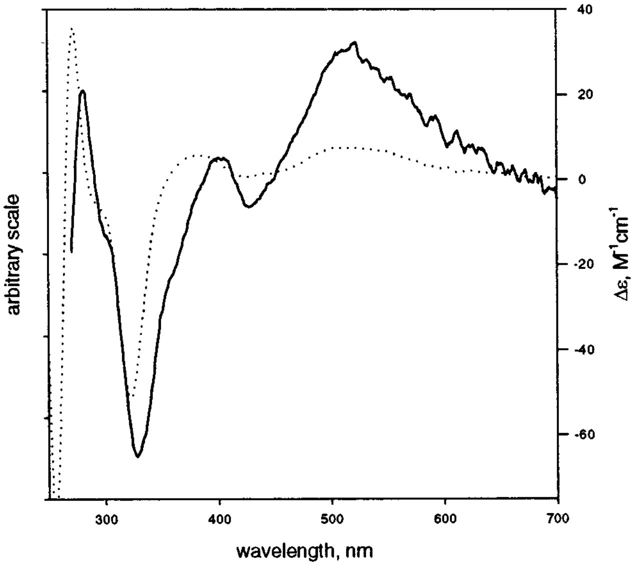

Figure 5. CD spectrum on KCl pellets containing solid $[Cu_2(R,R\text{-}ImQ)_2]ClO_4{\cdot}H_2O$ (solid line, left vertical axis in arbitary units). The spectrum of $[Cu_2(R,R\text{-}ImQ)_2]ClO_4{\cdot}H_2O$ in CH_3CN solution (dotted line, right vertical axis; same spectrum as solid line in Figure 5) is reproduced for the sake of comparison.

Although the values on the $\Delta\epsilon$ scale are meaningless,[13] the sign and position of the CD bands are reliable and significant: with respect to CH_3CN solution, a slight shift in the band position is observed (which parallels the shift found for UV/vis spectra measured on the same pellet).[14] In particular, the mlct bands are found in the solid at 401 and 517 nm, while the $n-\pi^*$ band is at 325 nm. On the other hand, the sign of both $n-\pi^*$ and mlct bands is the same found in solution (minus and plus, respectively), this strongly suggesting that the M helicity is mantained on dissolving $[Cu_2(R,R\text{-}ImQ)_2](ClO_4)_2{\cdot}H_2O$ in CH_3CN.[15]

Experimental Section

Materials and Syntheses. The *R*,*R*-ImQ and *S*,*S*-ImQ ligands can be prepared according to the procedure already described for the ImQ

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(10) Calculated on the basis of the $-CH{=}N$ integrals, remeasured in this work on the spectrum of the 1:1 mixture of $[Cu_2(R,R\text{-}ImQ)_2]^{2+}$ and $[Cu_2(S,S\text{-}ImQ)_2]^{2+}$.

(11) A parallel shift of the $n-\pi^*$ band is actually observed during UV/vis spectrophotometric titration of the free ligand with substoichiometric quantities of $[Cu(CH_3CN)_4]ClO_4$ in CH_3CN. The shift stops at 1.0 *R*,*R*-ImQ/Cu^+ molar ratio.

(12) Ziegler, M.; von Zelewsky, A. *Coord. Chem. Rev.* **1998**, *177*, 257.

(13) Subtraction of a blank spectrum was not performed, and unpredictable and irreproducible light absorption came from the KCl pellet, e.g., depending on its thickness. However, even if the values recorded on the $\Delta\epsilon$ scale were not reproducible (more experiments were carried out on different pellets), the position, shape, and sign of the bands were the same in each experiment.

(14) Bands were found at 534, 405, and 320 nm; measurements were carried out on a Varian Cary 2300 instrument, with a pellet of pure KCl in the reference beam.

racemate,[6] starting from commercial (Aldrich) (1*R*,2*R*)-1,2-diaminocyclohexane, (1*S*,2*S*)-1,2-diaminocyclohexane, and 2-quinoline carboxyaldehyde.

$[Cu_2(R,R\text{-ImQ})_2](ClO_4)_2 \cdot H_2O$ and $[Cu_2(S,S\text{-ImQ})_2](ClO_4)_2 \cdot H_2O$. A sample of the chosen ligand (100 mg, 0.254 mmol) was dissolved in CH_3CN (5 cm^3) and treated with $[Cu(CH_3CN)_4]ClO_4$ (85 mg, 0.254 mmol). The deep purple solution was slowly evaporated in air, while refrigerated at 0 °C in an ice bath. Black purple crystals were obtained, which in the case of the $[Cu_2(R,R\text{-ImQ})_2](ClO_4)_2 \cdot H_2O$ complex were found suitable for X-ray diffraction studies. Yield: ∼50% and ∼45%, for the *R*,*R* and *S*,*S* enantiomer, respectively. Anal. Calcd for $C_{52}H_{50}Cl_2Cu_2N_8O_9$: C 55.34, H 4.43, N 9.92. Found: C 55.31, H 4.42, N 9.94 ($[Cu_2(R,R\text{-ImQ})_2](ClO_4)_2 \cdot H_2O$) and C 55.30, H 4.44, N 9.88 ($[Cu_2(S,S\text{-ImQ})_2](ClO_4)_2 \cdot H_2O$). IR (NaCl cells, Nujol mull): ν 1664 (imine C=N stretch), 1593 cm^{-1} (quinoline C=N stretch). Mass spectra (ESI), for the two complexes: 1010, for $\{[Cu_2(ImQ)_2]ClO_4\}^+$.

Physical Measurements. Mass spectra (ESI) were recorded on a Finnigan MAT TSQ 700 instrument, NMR spectra on a Bruker AMX 400 spectrometer, IR on a Mattson 5000 FT-IR instrument, UV/vis spectra on a Hewlett-Packard HP8453 diode array spectrophotometer, and CD spectra on a JASCO J-710 instrument.

Crystallographic Studies. Crystal data and details on the crystallographic study are reported in Table 1. Intensity data were obtained on an Enraf-Nonius CAD4 diffractometer, using graphite-monochromated Mo Kα radiation. Unit cell parameters were obtained by least-squares fitting of 25 centered reflections monitored in the range $5.95° < \theta < 8.66°$. Calculations were performed with the WinGX-97 software.[16] Corrections for *Lp* and empirical absorption were applied.[17] Friedel opposites were collected and not merged to enable refinement of the Flack parameter[18] in order to determine the absolute structure. The *P*1 space group is rather unusual, but any attempt of describing the structure with a higher symmetry was unsatisfactory. The acentric space group is of course substantiated by the presence in the structure of a chiral molecule. The structure was solved by direct methods (SHELXS-97)[19] and refined by full-matrix least-squares using SHELXL-97[19] with anisotropic displacement parameters for all non-hydrogen atoms. Hydrogen atoms were inserted in calculated positions with isotropic displacement parameters proportional to those of their neighboring atoms. H atoms of the water molecule were not located in the ΔF maps and were then disregarded. Atomic scattering factors and the values of $\Delta f'$ and $\Delta f''$ were taken from International Tables for X-ray Crystallography.[20] Diagrams of the molecular structures were produced by the ORTEP program.[21] Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-142432. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223 336−033; e-mail: deposit@ccdc.cam.ac.uk).

Table 1. Crystal and Refinement Data

formula	$Cu_2N_8C_{52}H_{48}Cl_2O_9$
fw	1127.0
cryst syst	triclinic
space group	*P*1
a (Å)	11.056(6)
b (Å)	11.366(4)
c (Å)	11.398(3)
α (deg)	99.72(3)
β (deg)	95.10(3)
γ (deg)	113.82(4)
V ($Å^3$)	1271.8
Z	1
D_{calc} (g cm^{-3})	1.471
T (K)	293(3)
μ (mm^{-1})	1.01
scan type	$\omega - 2\theta$
θ range (deg)	2−25
abs corr method	ψ-scan
index ranges	$-13 \le h \le 13, -13 \le k \le 13, -13 \le l \le 13$
total no. of reflns measd	8966
refinement type	F^2
R_1[a]	0.0519
R_{all}	0.1019
wR_2	0.1325
GOF[b]	1.030
Flack param[c]	0.0028(165)
no. of refined params	658
weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0558P)^2 + 0.4158P]$ where $P = (F_o^2 + 2F_c^2)/3$
(shift/esd)$_{max}$	0.000
max, min $\Delta\rho$ (e $Å^{-3}$)	0.43, −0.46

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ (calculated on 6101 reflections with $I > 2\sigma_I$). [b] GOF $= S = [\sum[w(F_o^2 - F_c^2)^2]/(n - p)]^{0.5}$, where *n* is the number of reflections and *p* is the total number of parameters refined. [c] For inverted structure 0.993(20) and $R_1 = 0.0639$.

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Supporting Information Available: Listings of final atomic coordinates, anisotropic thermal parameters, all bond lengths and angles, intermolecular contacts, least-squares planes, and unit cell and packing diagrams.

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(15) The CD spectra in CH_3CN of $[Cu_2(S,S\text{-ImQ})_2](ClO_4)_2 \cdot H_2O$ was checked and found to be the mirror image of that of $[Cu_2(R,R\text{-ImQ})_2](ClO_4)_2 \cdot H_2O$ (Figure 4). In CH_3CN, $[Cu_2(S,S\text{-ImQ})_2](ClO_4)_2 \cdot H_2O$ is thus a helical complex of P handedness. The same helicity is maintained in the solid state, with a structure that should be of the same nature as for $[Cu_2(R,R\text{-ImQ})_2](ClO_4)_2 \cdot H_2O$: CD spectra on KCl pellets containing ∼2% of solid complex display bands in the same position and with opposite sign with respect to $[Cu_2(R,R\text{-ImQ})_2](ClO_4)_2 \cdot H_2O$.

(16) Farrugia, L. J. *WinGX-97*, A Windows Program for Crystal Structure Analysis; University of Glasgow: Glasgow, 1998.

(17) North, A. C. T.; Philips, D. C.; Mathews, F. S. *Acta Crystallogr*. **1968**, *A24*, 351.

(18) Flack, H. D. *Acta Crystallogr*. **1983**, *A39*, 876.

(19) Sheldrick, G. M. *SHELX97*, Programs for Crystal Structure Analysis; University of Goettingen: Germany, 1998.

(20) *International Tables for X-ray Crystallography*; Kynoch Press, Birmingham, England, 1974: Vol. 4.

(21) Farrugia, L. J. *J. Appl. Crystallogr*. **1997**, *30*, 565.