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Article

Chiral Monomeric and Homochiral Dimeric Copper(II) Complexes of a New Chiral Ligand, *N*-(1,2-Bis(2-pyridyl)ethyl)pyridine-2-carboxamide: An Example of Molecular Self-Recognition

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Reaction of $Cu(ClO_4)_2 \cdot 6H_2O$ with a racemic mixture of the novel chiral ligand *N*-(1,2-bis(2-pyridyl)ethyl)pyridine-2-carboxamide (PEAH) affords only the homochiral dimeric copper(II) complexes $[Cu_2(^RPEA)_2](ClO_4)_2$ and $[Cu_2(^SPEA)_2]$-$(ClO_4)_2$ in a 1:1 ratio. The phenomenon of molecular self-recognition is also observed when a racemic mixture of the monomeric copper(II) complex $[Cu(^{R(S)}PEA)(Cl)(H_2O)]$ is converted into the homochiral dimeric species $[Cu_2(^{R(S)}PEA)_2](ClO_4)_2$ via reaction with Ag^+ ion. This is the first report of *direct* conversion of a racemic mixture of a chiral monomeric copper(II) complex to a mixture of the homochiral dimers.

Introduction

Determination of factors that control the process of molecular self-recognition has been an area of intense research.[1,2] The self-recognition of peptides and nucleic acids gives rise to biological macromolecules that have been studied in detail.[3,4] In recent years, the concept has also been used to synthesize supramolecular architectures[5–8] and in enantioselective organic transformations.[9] One approach to induce self-recognition in smaller coordination compounds is to develop chiral ligands that are capable of recognition in the process of formation of the complexes. In the most simplified system, a chiral ligand L forms a $[ML_2]^{n+}$ type of compound (metal:ligand ratio 1:2). When the resulting $[ML_2]^{n+}$ complex is obtained from a racemic mixture of *R*

and *S* ligands, usually both the heterochiral $[M(^RL)(^SL)]^{n+}$ and the homochiral $[M(^RL)_2]^{n+}$ (or $[M(^SL)_2]^{n+}$) species are obtained. A ligand is said to be self-recognizing if the homochiral $[M(^{R(S)}L)_2]^{n+}$ complex is formed in preference to the heterochiral one.[10,11]

A slightly more complex system of self-recognition involves a ligand-to-metal ratio of 2:2, yielding $[M_2L_2]^{n+}$-type compounds. Dimeric $[M_2L_2]^{n+}$ complexes result from chiral bridging ligands that coordinate to both metal centers. In these cases, the process of self-recognition affords the $[M_2(^RL)_2]^{n+}$ (or the $[M_2(^RL)_2]^{n+}$ species) in excess of the heterochiral $[M_2(^RL)(^RL)]^{n+}$ even when one starts with a racemic mixture of the ligand L. Recently, Stack and co-workers have reported ligand recognition in dimeric copper-(I) complexes of tetradentate ligands that have a *trans*-1,2-cyclohexane diamine frame (*trans*-1,2-cyclohexane diamine contains two chiral carbon centers and is noted as the *RR* or the *SS* enantiomer).[12] These ligands are intrinsically helical and bind two copper(I) centers in a 2 + 2 configuration to generate the $[M_2L_2]^{n+}$ complexes. Use of copper(I) salts and a racemic mixture of the ^{RR}L and ^{SS}L ligands in this case affords a crystalline solid that contains the two homochiral complexes $([Cu_2(^{RR}L_2)_2]^{2+}$ and $[Cu_2(^{SS}L_2)_2]^{2+})$ in equal amounts.

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The exclusive formation of the homochiral copper(I) dimers from the racemic mixture and the absence of the heterochiral species ($[Cu_2(^{SS}L)(^{RR}L)]^{2+}$) demonstrates ligand self-recognition during ligand coordination.

We have recently synthesized a chiral ligand, PEAH (PEAH = N-(1,2-bis(2-pyridyl)ethyl)pyridine-2-carboxamide, where H represents the dissociable amide proton), which is isolated as a racemic mixture. PEAH is a nonlinear (branched) polypyridine ligand that contains in its donor set three pyridine nitrogen atoms and a single carboxamide nitrogen atom. This ligand is very similar to Py$_3$AH,[14] another designed ligand reported by us previously, except for an additional chiral carbon center.

PEAH   Py$_3$AH
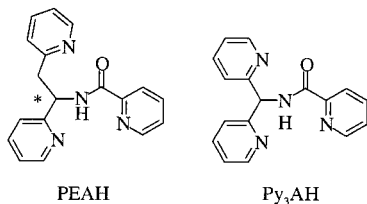
In this paper, the synthesis of the chiral ligand PEAH along with the monomeric and dimeric copper(II) complexes derived from PEA$^-$ (PEA$^-$ is the deprotonated form of PEAH) is reported.[15] It is interesting to note at the very beginning that although a racemic mixture of PEAH is employed, the isolated dimeric complex $[Cu_2(PEA)_2](ClO_4)_2$ comprises only homochiral dimers $[Cu_2(^RPEA)_2](ClO_4)_2$ and $[Cu_2(^SPEA)_2](ClO_4)_2$ in the crystalline state. Since no trace of the heterochiral species $[Cu_2(^SPEA)(^RPEA)](ClO_4)_2$ is found, chiral recognition in the process of complexation is evident. This result is similar to that reported by Stack and co-workers.[12] The present system however goes beyond this initial recognition process. When the monomeric complex $[Cu(PEA)(Cl)(H_2O)]$ (isolated as a racemic mixture) is converted to the dimeric species via reaction with Ag$^+$, one only obtains the homochiral dimers $[Cu_2(^RPEA)_2](ClO_4)_2$ and $[Cu_2(^SPEA)_2](ClO_4)_2$ as the final product. It is therefore evident that the recognition process remains active during the monomer–dimer conversion. This is the first report of

direct conversion of a racemic mixture of a chiral monomeric copper(II) complex to a homochiral dimeric complex. The dimerization is best described as a process of molecular self-recognition since both the monomeric R and S copper complexes are present during the dimerization step. As described below, the formation of the homochiral dimer $[Cu_2(^{R(S)}PEA)_2](ClO_4)_2$ from two $[Cu(^{R(S)}PEA)(Cl)(H_2O)]$ units resembles a molecular handshake.

Experimental Section

Materials. Copper(II) chloride dihydrate (CuCl$_2$·2H$_2$O) and copper(II) perchlorate hexahydrate (Cu(ClO$_4$)$_2$·6H$_2$O) were purchased from Aldrich Chemical Co. and used without further purification. The acid chloride of picolinic acid was synthesized by heating 2-picolinic acid in excess thionyl chloride followed by the removal of the unreacted thionyl chloride under vacuum. 1,2-Bis(2-pyridine)ethylamine was synthesized by following published procedures.[16,17] Triethylamine (Et$_3$N) was distilled fresh from NaOH prior to use. Dichloromethane (CH$_2$Cl$_2$), N,N'-dimethylformamide (DMF), acetonitrile (CH$_3$CN), and diethyl ether (Et$_2$O) were distilled from CaCl$_2$, BaO, CaH$_2$, and Na, respectively, prior to use.

Caution! Although no explosion was encountered in this work, perchlorate salts could detonate upon heating and should be handled with caution and in small amounts.

Preparation of Compounds. PEAH. A solution of 0.909 g (4.6 mmol) of 1,2-bis(2-pyridyl)ethylamine in 15 mL of tetrahydrofuran (THF) was added dropwise at 0 °C to a solution of 0.649 g (4.6 mmol) of 2-picolinic acid chloride and 0.928 g (9.2 mmol) of Et$_3$N in 50 mL of THF. The mixture was stirred for 20 min at 0 °C followed by 15 min of gentle heating (35 °C). Next the solution was cooled to 0 °C and filtered to remove Et$_3$N·HCl(s). Crude PEAH was obtained as a light brown colored oil upon removal of the THF in vacuo. The ligand was further purified by dissolving the resulting oil in CH$_2$Cl$_2$ and washing the solution with portions of aqueous NaOH (3 × 10 mL). The CH$_2$Cl$_2$ was collected and dried over MgSO$_4$ and the solvent removed in vacuo to yield PEAH as a light brown solid. Crystalline PEAH was obtained from warm Et$_2$O. Yield: 75%. ^{1}H NMR (303 K, CDCl$_3$, 250 MHz): δ (ppm from TMS) 9.45 (d, 1H) 8.60 (d, 2H) 8.52 (d, 1H) 8.12 (d, 1H) 7.80 (t, 1H) 7.40 (m, 3H) 7.10 (m, 4) 5.70 (q, 1H) 3.49 (t, 2H). Selected IR frequencies (KBr disk, cm^{-1}): 3340 (m), 1664 (s, ν_{CO}) 1518 (s), 1435 (s) 1152 (m), 996 (m), 901 (m), 753 (s).

[Cu($^{R(S)}$PEA)(H$_2$O)(Cl)]. A solution of 0.1182 g (0.388 mmol) of PEAH and 0.0118 g (0.492 mmol) of NaH in 10 mL of DMF was added dropwise to a solution of 0.0662 g (0.388 mmol) of CuCl$_2$·2H$_2$O dissolved in 15 mL of DMF. After 1 h, the solvent was removed, and the resulting blue oil was dissolved in CH$_3$CN and filtered to remove NaCl(s). The filtrate was concentrated to 4 mL and stored at −28 °C following the addition of 6 mL of Et$_2$O. Crystalline [Cu($^{R(S)}$PEA)(H$_2$O)(Cl)] was obtained within 24 h (yield 45%). Anal. Calcd for [Cu($^{R(S)}$PEA)(H$_2$O)(Cl)]: C$_{18}$H$_{17}$-ClCuN$_4$O$_2$: C 51.43, H 4.08, O 7.61. Found: C 51.39, H 4.12, O 7.95. Selected IR frequencies (KBr disk, cm^{-1}): 3255 (s), 1625 (s, ν_{CO}), 1595 (s), 1567 (s), 1411 (s), 1050 (m), 1024 (m), 1005 (m), 756 (s), 648 (m). Absorption spectrum in CH$_3$CN: λ_{max} nm (ϵ, M^{-1} cm^{-1}) 625 (100). EPR spectrum in 7:3 CH$_3$CN/DMF (v/v) glass (85 K): $g_{||}$ = 2.224, $g_{\perp}$ = 2.052, and $A_{||}$ = 173G.

[Cu$_2$($^{R(S)}$PEA)$_2$](ClO$_4$)$_2$·2.5CH$_3$CN. A slurry of 0.0139 g (0.579 mmol) of NaH in 1 mL DMF was added to a solution of 0.1470 g

(13) Zema and co-workers have synthesized similar ligands in enantiomerically pure forms and have isolated pure homochiral [Cu$_2$(^{RR}L)$_2$]$^{2+}$ or [Cu$_2$(^{SS}L)$_2$]$^{2+}$ complexes that form exclusively as P or M double helices (See: Amendola, V.; Fabbrizzi, L.; Mangano, C.; Pallavicini, P.; Roboli, E.; Zema, M. *Inorg. Chem.* **2000**, *39*, 5803). When a racemic mixture of the ligand is used, the homochiral [Cu$_2$(^{RR}L)$_2$]$^{2+}$ and [Cu$_2$(^{SS}L)$_2$]$^{2+}$ complexes are isolated in addition to the heterochiral, nonhelical [Cu$_2$(^{SS}L)(^{RR}L)]$^{2+}$ complex. In this case, all three possible combinations of [Cu$_2$(^{RR}L)$_2$]$^{2+}$ or [Cu$_2$(^{SS}L)$_2$]$^{2+}$ and [Cu(^{SS}L)(^{RR}L)]$^{2+}$ are obtained (See: Amendola, V.; Fabbrizzi, L.; Linati, L.; Mangano, C.; Pallavicini, P.; Pedrazzini, V.; Zema, M. *Chem. Eur. J.* **1999**, *5*, 3679).

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(15) Abbreviations used throughout the text to indicate stereochemistry are as follows: PEAH is the racemic mixture of ^{R}PEAH and ^{S}PEAH. Stereochemical assignment (R or S) of the chiral carbon center in the copper(II) complexes has not been completed in our structural analysis. However, the centrosymmetric space groups of the two compounds confirm that the R and S enantiomers are present in a 1:1 ratio. Therefore, the abbreviation for the racemic mixture of [Cu$_2$(^{R}PEA)$_2$]$^{2+}$ and [Cu$_2$(^{S}PEA)$_2$]$^{2+}$ is denoted as [Cu$_2$($^{R(S)}$PEA)$_2$]$^{2+}$. Likewise, the racemic mixture of [Cu(^{R}PEA)(Cl)(H$_2$O)] and [Cu(^{S}PEA)(Cl)(H$_2$O)] is denoted as [Cu($^{R(S)}$PEA)(Cl)(H$_2$O)].

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Table 1. Summary of Crystal Data and Intensity Collection and Structure Refinement Parameters for the Structure of [Cu$_2$($^{R(S)}$PEA)$_2$](ClO$_4$)$_2$·2.5CH$_3$CN and [Cu($^{R(S)}$PEA)(Cl)(H$_2$O)]

	[Cu$_2$($^{R(S)}$PEA)$_2$](ClO$_4$)2· 2.5CH$_0$CN	[Cu($^{R(S)}$PEA)(Cl)(H$_2$O)]
empirical formula	C$_{41}$H$_{37.50}$Cl$_2$Cu$_2$N$_{10.50}$O$_{10}$	C$_{18}$H$_{17}$ClCuN$_4$O$_2$
mol wt	1035.30	420.35
cryst color, habit	blue, prism	blue, plate
T, K	90(2)	130(2)
cryst syst	monoclinic	orthorhombic
space group	$P2_1/n$	Pbca
a, Å	12.4124(7)	8.8580(7)
b, Å	13.6347(8)	17.1000(14)
c, Å	25.7106(15)	23.528(2)
α, deg	90	90
β, deg	90.8930(10)	90
γ, deg	90	90
vol, Å^3	4350.7(4)	3563.85(5)
Z	4	8
density(calcd), g cm^{-3}	1.581	1.567
abs coeff, mm^{-1}	1.171	3.286
GOF^a on F^2	1.088	1.029
R1,^{b} %	5.11	4.16
wR2,^{c} %	13.27	10.98

^{a} GOF = $[\sum[w(F_o^2 - F_c^2)^2]/(M - N)]^{1/2}$ (M = number of reflections, N = number of parameters refined). ^{b} R1 = $\sum||F_o| - |F_c||/\sum|F_o|$. ^{c} wR2 = $[\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

(0.483 mmol) of PEAH in 7 mL of DMF. To this solution of deprotonated ligand was then added with stirring a solution of 0.1790 g (0.483 mmol) of Cu(ClO$_4$)$_2$·6H$_2$O in 5 mL of DMF. The resulting blue solution was allowed to stir for 1 h, and the DMF was removed in vacuo. The resulting blue oil was dissolved in 10 mL of warm CH$_3$CN, and the solution was stored at room temperature following the addition of 3 mL of Et$_2$O. Blue crystals of [Cu$_2$($^{R(S)}$PEA)$_2$](ClO$_4$)$_2$·2.5CH$_3$CN were obtained within 4 h (yield 70%). Anal. Calcd for [Cu$_2$($^{R(S)}$PEA)$_2$](ClO$_4$)$_2$·2.5CH$_3$CN: C$_{41}$H$_{37.5}$Cl$_2$Cu$_2$N$_{10.5}$O$_{10}$: C 47.57, H 3.65, O 15.45. Found: C 47.60, H 3.67, O 15.49. Selected IR frequencies (KBr disk, cm^{-1}): 1636 (s, ν_{CO}), 1602 (s), 1569 (s), 1378 (m), 1104 (vs ν_{ClO4}), 758 (m), 624 (m). Absorption spectrum in CH$_3$CN: λ_{max} nm (ϵ, M^{-1} cm^{-1}) 590 (150).

X-ray Data Collection and Structure Solution and Refinement. Diffraction data for [Cu($^{R(S)}$PEA)(H$_2$O)(Cl)] were collected at 130 K on a Siemens P4 diffractometer with Cu Kα radiation (λ = 1.54184 Å). Data for [Cu$_2$($^{R(S)}$PEA)$_2$](ClO$_4$)$_2$·2.5CH$_3$CN were collected at 90 K on a Bruker SMART 1000 system using Mo Kα (0.71073 Å) radiation. Both data sets were corrected for absorption effects. The intensities of two standard reflections showed only random fluctuations of less than 1% during the course of data collection in the first case. The structures were solved by using the standard SHELXS-97 package. Machine parameters, crystal data, and data collection parameters are summarized in Table 1. Selected bond distances and angles are listed in Table 2. Complete crystallographic data for the two complexes have been submitted as Supporting Information.

Other Physical Measurements. Absorption spectra were recorded on a Perkin-Elmer Lambda 9 spectrophotometer. A Perkin-Elmer 1600 FTIR spectrophotometer was used to monitor the infrared (IR) spectra. EPR spectra at X-band frequencies were obtained with a Bruker ESP-300 spectrometer.

Results and Discussion

The monomeric complex [Cu($^{R(S)}$PEA)(Cl)(H$_2$O)] is readily formed in the reaction of CuCl$_2$·2H$_2$O with the deprotonated ligand (PEA$^-$) in DMF. The presence of Cl$^-$ ions in the reaction mixture prevents any dimer formation in this

Table 2. Selected Bond Distances (Å) and Angles (deg) for [Cu$_2$($^{R(S)}$PEA)$_2$](ClO$_4$)$_2$·2.5CH$_3$CN and [Cu($^{R(S)}$PEA)(Cl)(H$_2$O)]

[Cu$_2$($^{R(S)}$PEA)$_2$](ClO$_4$)$_2$·2.5CH$_3$CN			
Cu1−N1	2.025(2)	Cu2−N4	1.9895(19)
Cu1−N2	1.9154(18)	Cu2−N5	2.044(2)
Cu1−N3	2.000(2)	Cu2−N6	1.902(2)
Cu1−N8	1.9868(19)	Cu2−N7	2.026(2)
Cu1−O3	2.707(2)	Cu2−O7	2.737(2)
N1−Cu1−N2	82.89(8)	N4−Cu2−N5	100.07(8)
N1−Cu1−N3	154.05	N4−Cu2−N6	167.46(9)
N1−Cu1−N8	100.23(8)	N4−Cu2−N7	98.59(9)
N1−Cu1−O3	81.24(8)	N4−Cu2−O7	91.77(7)
N2−Cu1−N3	82.62(8)	N5−Cu2−N6	82.65(9)
N2−Cu1−N8	169.23(9)	N5−Cu2−N7	155.61(9)
N2−Cu1−O3	94.31(8)	N5−Cu2−O7	75.26(7)
N3−Cu1−N8	98.00(8)	N6−Cu2−N7	82.53(9)
N3−Cu1−O3	78.52	N6−Cu2−O7	100.75(8)
N8−Cu1−O3	96.35(8)	N7−Cu2−O7	88.64
[Cu($^{R(S)}$PEA)(Cl)(H$_2$O)]			
Cu−N1	2.038(3)	Cu−Cl	2.2466(10)
Cu−N2	1.930(3)	Cu−O2	2.245(3)
Cu−N3	2.014(3)	N2−C6	1.318(5)
N1−Cu−N2	80.00(12)	N2−Cu−Cl	159.91(10)
N1−Cu−N3	160.68(12)	N2−Cu−O2	101.00(11)
N1−Cu−Cl	98.84(9)	N3−Cu−Cl	99.02(9)
N1−Cu−O2	93.20(11)	N3−Cu−O2	91.18(11)
N2−Cu−N3	80.70(12)	Cl−Cu−O2	99.09(7)

reaction. We have observed similar behavior in the synthesis of [Cu(Py$_3$A)(Cl)], the copper(II) complex of Py$_3$AH.[14] Since we employed racemic PEAH, the complex is isolated as a racemic mixture of [Cu(^{R}PEA)(Cl)(H$_2$O)] and [Cu(^{S}PEA)-(Cl)(H$_2$O)]. Reaction of Cu(ClO$_4$)$_2$·6H$_2$O with deprotonated PEA$^-$ affords the dimer [Cu$_2$($^{R(S)}$PEA)$_2$](ClO$_4$)$_2$ in high yield. It is interesting to note that just a simple change in the starting copper salt results in the exclusive formation of the dimeric species. The crystalline form of this dimeric complex comprises only of the homochiral dimers [Cu$_2$(^{R}PEA)$_2$]-(ClO$_4$)$_2$ and [Cu$_2$(^{S}PEA)$_2$](ClO$_4$)$_2$. This complex can also be synthesized by the addition of AgClO$_4$ to a solution of [Cu-($^{R(S)}$PEA)(Cl)(H$_2$O)] in acetonitrile. Coordination of the carboxamido nitrogen of PEA$^-$ to the copper(II) center in [Cu($^{R(S)}$PEA)(Cl)(H$_2$O)] and [Cu$_2$($^{R(S)}$PEA)$_2$](ClO$_4$)$_2$ is indicated by the red shift of the carbonyl stretching frequency (1625 and 1636 cm^{-1}, respectively) in the IR spectra of these complexes.

Structure of [Cu($^{R(S)}$PEA)(Cl)(H$_2$O)]. The structure of [Cu($^{R(S)}$PEA)(Cl)(H$_2$O)] is shown in Figure 1. The crystals comprise a racemic mixture of [Cu(^{R}PEA)(Cl)(H$_2$O)] and [Cu(^{S}PEA)(Cl)(H$_2$O)] units which are related by inversion. In [Cu($^{R(S)}$PEA)(Cl)(H$_2$O)], the geometry around the copper-(II) center is square pyramidal. Two pyridine rings (one connected to the chiral carbon C7 and one next to the carboxamide moiety), the carboxamido nitrogen and a chloride ion define the basal plane while the apical position is occupied by a molecule of water. Thus, coordination of the PEA$^-$ ligand to copper in [Cu($^{R(S)}$PEA)(Cl)(H$_2$O)] gives rise to two five-membered chelate rings and a pendant arm containing the third pyridine.[18] The Cu(II)−N$_{amido}$ distance in [Cu($^{R(S)}$PEA)(Cl)(H$_2$O)] (1.930(3) Å) is within the range of Cu(II)−N$_{amido}$ distances noted in similar complexes.[14,19−22]

The crystal structure of [Cu($^{R(S)}$PEA)(Cl)(H$_2$O)] is stabilized by an ordered network of intermolecular hydrogen
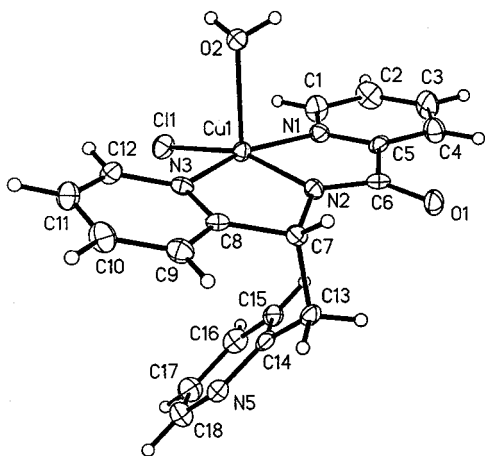
Figure 1. Thermal ellipsoid plot (probability level 50%) of [Cu($^{R(S)}$PEA)-(Cl)(H$_2$O)] with the atom labeling scheme. The chiral carbon center is given the label C7.
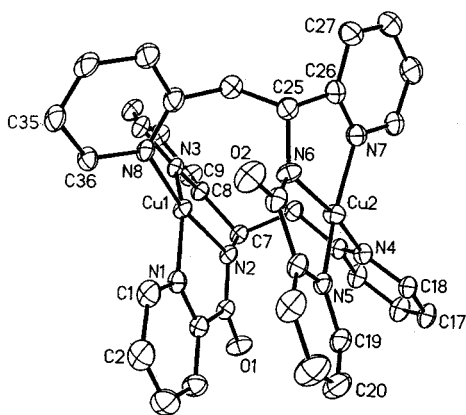

Figure 2. Thermal ellipsoid (probability level 50%) plot of [Cu$_2$-($^{R(S)}$PEA)$_2$]$^{2+}$ with the atom labeling scheme. H atoms are omitted for the sake of clarity. Only the atoms of the first coordination sphere of the copper-(II) centers have been labeled for the sake of clarity.

bonds that exist between the hydrogen atoms of the axially bound water molecules and the nitrogen atoms of the noncoordinating pyridine rings. The water molecules are also hydrogen bonded to the oxygen atom of the carboxamido groups of the neighboring complexes (Figure S1, Supporting Information).

Structure of [Cu$_2$($^{R(S)}$PEA)$_2$](ClO$_4$)$_2$. The structure of [Cu$_2$($^{R(S)}$PEA)$_2$](ClO$_4$)$_2$ (structure of the cation shown in Figure 2) demonstrates that the homochiral dimers [Cu$_2$-(^{R}PEA)$_2$](ClO$_4$)$_2$ and [Cu$_2$(^{S}PEA)$_2$](ClO$_4$)$_2$ are present in equal amounts in the solid state and are related by inversion. The dimeric structure results from 3 + 1 ligand sharing

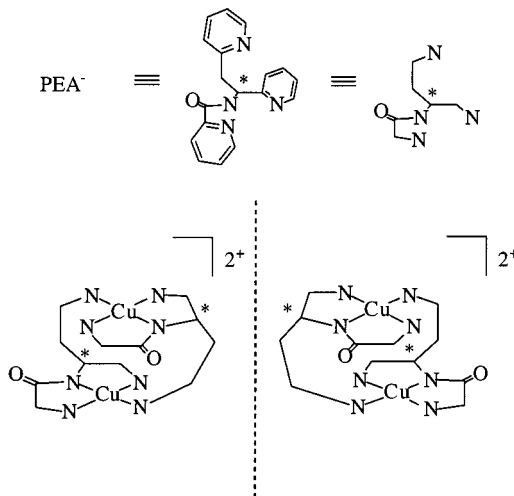(18) The mode of binding of the PEA$^-$ ligand to copper in [Cu($^{R(S)}$PEA)-(Cl)(H$_2$O)] is very similar to that of the Py$_3$A$^-$ ligand in [Cu(Py$_3$A)-(Cl)]. For example, the angle generated by the two pyridine nitrogen atoms that occupy trans positions in the base of the square pyramid of [Cu($^{R(S)}$PEA)(Cl)(H$_2$O)] is 160.68(12)°. The corresponding angle in [Cu(Py$_3$A)(Cl)] is 160.28(10)°.
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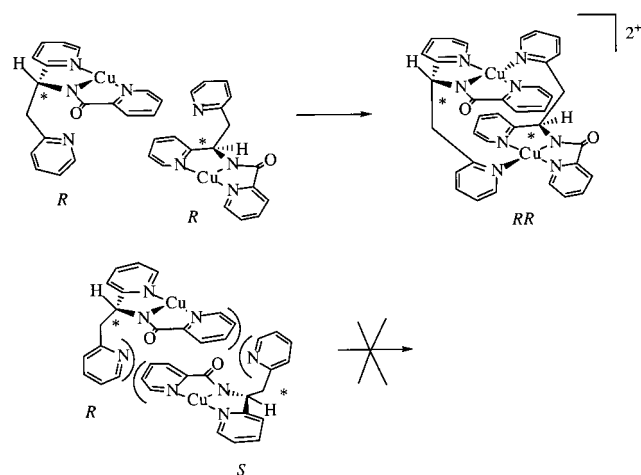
Figure 3. Schematic representation of [Cu$_2$(^{R}PEA)$_2$]$^{2+}$ and [Cu$_2$(^{S}PEA)$_2$]$^{2+}$.

pattern exhibited by the PEA$^-$ ligand. The geometry around both copper(II) centers is distorted square planer with the basal plane defined by three nitrogen donor atoms from one PEA$^-$ ligand and the pendant pyridine of a second [Cu-(PEA)]$^+$ unit. Thus the mode of binding of the PEA$^-$ ligand to copper does not change from [Cu($^{R(S)}$PEA)(Cl)(H$_2$O)] to [Cu$_2$($^{R(S)}$PEA)$_2$]$^{2+}$ except for the fact that the pendant (and noncoordinating) arm of the ligand in the monomer is involved in coordination in the dimeric species. The Cu-(II)−N$_{amido}$ bond lengths in [Cu$_2$($^{R(S)}$PEA)$_2$]$^{2+}$ (1.9154(18) and 1.902(2) Å) are slightly shorter than the Cu(II)-N$_{amido}$ bond length found in [Cu($^{R(S)}$PEA)(Cl)(H$_2$O)]. The Cu−Cu distance in [Cu$_2$($^{R(S)}$PEA)$_2$]$^{2+}$ is 3.606 Å. Finally, weak interaction between the outer axial positions of the copper(II) centers and the oxygens of the perchlorate anion is indicated by the Cu(II)−O distances of 2.707(2) and 2.737(2) Å in [Cu$_2$-($^{R(S)}$PEA)$_2$](ClO$_4$)$_2$.

Chiral Recognition during the Formation of the Homochiral Dimeric Complex. The fact that only the homochiral dimeric species [Cu$_2$(^{R}PEA)$_2$](ClO$_4$)$_2$ and [Cu$_2$(^{S}PEA)$_2$]-(ClO$_4$)$_2$ are obtained from racemic mixtures of PEA$^-$ and Cu(ClO$_4$)$_2$·6H$_2$O suggests that a process of self-recognition is involved during assembly of the two homochiral dimers.

$$4PEA^- + 4Cu(II) \rightarrow [Cu_2(^RPEA)_2]^{2+} + [Cu_2(^SPEA)_2]^{2+}$$
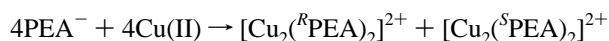
[Cu$_2$(^{R}PEA)$_2$]$^{2+}$ and [Cu$_2$(^{S}PEA)$_2$]$^{2+}$ form nonsuperimposable mirror images as represented schematically in Figure 3. Formation of only homochiral dimeric complexes from racemic mixtures of PEAH can be rationalized by the orientation of the pendant pyridine ring attached to the chiral carbon of the [Cu(PEA)]$^+$ unit. When two [Cu(^{R}PEA)]$^+$ monomeric units are brought together to form a dimeric [Cu$_2$(^{R}PEA)$_2$]$^{2+}$ molecule, the chiral center holds the pendant pyridine ring in the correct position for ligand sharing. In this configuration, the pyridine-2-carboxamido units are coplanar and the ethylene linkage of the ligand allows the remaining pyridine rings to coordinate to the neighboring copper(II) centers while maintaining chirality and adequate space for dimerization. Likewise, two [Cu(^{S}PEA)]$^+$ monomeric units form the [Cu$_2$(^{S}PEA)$_2$]$^{2+}$ species. Significant $\pi-\pi$

Figure 4. Schematic representation of the dimerization of two [Cu-(^{R}PEA)]$^+$ units to afford [Cu$_2$(^{R}PEA)$_2$]$^{2+}$ (top panel). Molecules of [Cu-(^{S}PEA)]$^+$ and [Cu(^{R}PEA)]$^+$ do not dimerize to yield [Cu$_2$(^{S}PEA)(^{R}PEA)]$^{2+}$ (bottom panel).

stacking between the pyridine-2-carboxamido rings is observed in the structure of [Cu$_2$($^{R(S)}$PEA)$_2$]$^{2+}$ and may further stabilize the dimeric structure. The situation is very different when one attempts to form the hetrochiral dimeric complex [Cu$_2$(^{R}PEA)(^{S}PEA)]$^{2+}$ from monomeric [Cu(PEA)]$^+$ units of different chirality. The chiral carbon of the ethylene linkage now places the pendant pyridine ring in a position where it either points at the wrong direction or fails to ligate the neighboring copper(II) center due to steric congestion (Figure 4). The situation is much like a handshake attempted between a right and a left hand.

This mechanism of molecular self-recognition by [Cu-($^{R(S)}$PEA)]$^+$ units is further supported by the direct conversion of the racemic mixture of copper(II) monomeric units to the homochiral dimeric complexes. When AgClO$_4$ is added to CH$_3$CN solutions of [Cu($^{R(S)}$PEA)(Cl)(H$_2$O)], displacement of Cl$^-$ and subsequent dimerization afford only the homochiral complexes [Cu$_2$(^{R}PEA)$_2$](ClO$_4$)$_2$ and [Cu$_2$(^{S}PEA)$_2$]-

(ClO$_4$)$_2$.[23] This is the first report of monomer to dimer conversion involving metal complexes that are capable of self-recognition. The homochiral dimers are therefore obtained not only from the reaction mixture of the racemic ligand and Cu(ClO$_4$)$_2$·6H$_2$O but also from self-assembly of the racemic mixture of the monomeric copper(II) complexes in solution.
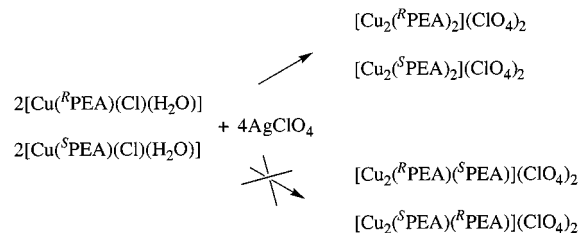
In conclusion, we have shown that the chirality of the monomeric complex [Cu(PEA)(Cl)(H$_2$O)] is recognized during dimer formation. Dimers are formed only when the chirality of the two monomeric units is the same. Spatial positioning of the pendant pyridine ring connected to the chiral carbon atom leads to this process of recognition.

Supporting Information Available: An illustration of the hydrogen bond network in the structure of [Cu($^{R(S)}$PEA)(Cl)(H$_2$O)] (Figure S1), the X-ray crystallographic files (in CIF format), and tables for the structure determination of [Cu($^{R(S)}$PEA)(Cl)(H$_2$O)] and [Cu$_2$($^{R(S)}$PEA)$_2$](ClO$_4$)$_2$·2.5CH$_3$CN. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) This product was crystallized and characterized fully by X-ray crystallography.