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Enantioselective Synthesis of Optically Active Polymeric Homo- and Bimetallic Oxalate-Bridged Networks $[M_2(ox)_3]_n$

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The synthesis of the enantiomeric forms of the two- and three-dimensional polymers: $\{[NBu_4][MnCr(ox)_3]\}_n$ (**1**) (Bu = *n*-butyl, ox = oxalate), $\{[M(bpy)_3)][LiCr(ox)_3]\}_n$ (M = Ni (**2**), Ru (**4**)) (bpy = 2,2′-bipyridine), $\{[M(bpy)_3)][Mn_2(ox)_3]\}_n$ (M = Ni (**3**), Ru (**5**)) using resolved $[Cr(ox)_3]^{3-}$ and $[M(bpy)_3]^{2+}$ (M = Ni, Ru) species as chiral building blocks, and their structural characterization are reported. The optical activity of these systems arises from the helical chirality of the tris-chelated subunits with Δ or Λ configurations. Bimetallic two-dimensional optically active network **1** results from the stacking of similar metallo-oxalate honeycomblike layers containing $[Cr(ox)_3]^{3-}$ units of the same chirality. The assembly of homochiral species leads to optically active three-dimensional 3-connected 10-gon nets **2**−**5**. Solid state circular dichroism (CD) measurements demonstrate the enantiomeric character of the obtained polymers. Absolute configurations of the metal centers have been assigned according to circular dichroism and X-ray diffraction data. Enantiomerically pure single crystals of the two enantiomeric forms, $\{[Ru_\Delta(bpy)_3)][Li_\Delta Cr_\Delta(ox)_3]H_2O\}_n$ (**4**Δ) and $\{[Ru_\Lambda(bpy)_3)][Li_\Lambda Cr_\Lambda(ox)_3]H_2O\}_n$ (**4**Λ), have been obtained and the structures determined by X-ray diffraction studies (crystals data: cubic system, space group $P2_13$, a (Å) = 15.293(8) (**4**Δ), 15.289(2) (**4**Λ), Z = 4).

Introduction

Chirality is an old and ever fascinating subject. Its powerful influence may be appreciated in a wide range of scientific disciplines, from biology and biochemistry to new materials sciences.[1] A new approach to this old subject comes by the hand of supramolecular chemistry[2] focusing on the transference of chirality from molecules to materials. Supramolecular chirality results from properties of individual components and the manner they are assembled. Synthetic strategies based on self-assembling process[1,3] of building blocks with appropriate size, charge, and shape are elegant routes to the construction of supramolecular architectures. Coordination chemistry provides a great variety of chiral mononuclear complexes as suitable candidates for building supramolecular assemblies with a predetermined stereochemistry.[4] This building block approach includes the possibility of introducing chiral centers in either metal complexes or ligands and even using achiral fragments to obtain chiral networks.[2,5−7]

Bidentate chelating ligands such as bipyridine (bpy), phenanthroline (phen) or oxalate (ox) are usually involved in helical chirality[8] of propeller-like coordination complexes. Resolution and absolute configuration determination experiments on this kind of derivatives has occupied chemists from Werner's first experiments to nowadays. The chemistry of coordination compounds containing oxalate ligands is one of the most ancient subjects in coordination chemistry,[9,10] but it has been during the past decade that the shape, charge, chelating, and bridging properties of oxalate ligands have demonstrated to be a useful tool in the spatial arrangement of spin-carrying metal ions, providing new examples of one-, two-, or three-dimensional compounds valuable candidates for experimental and theoretical studies in the field of molecule-based magnets.[11]

In 1990 Okawa and co-workers reported on the synthesis and magnetic properties of oxalate-bridged polymeric compounds of general formula $[ER_4][M^{II}M^{III}(ox)_3]$,[12] where $[ER_4]^+$ stands

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for a quaternary ammonium cation and M^{III} stands for chromium(III). It was later shown by Atovmyan et al.[13a] and then by Decurtins et al.[13b] that the structure of the above species is two-dimensional with honeycomb layers supporting the negative charge and cations located between the layers. Within each layer, all M^{III} sites have the same chirality (Δ or Λ) while all M^{II} sites adopt the opposite configuration. The available single crystal data of this kind of 2D networks are usually refined within the achiral *R*3*c* space group with the unit cell being built of six anionic and six cationic layers.[13] Three of the six anionic layers incorporate $M^{III}(\Delta)$ units whereas the other three layers incorporate $M^{III}(\Lambda)$ units, leading to a whole structure which is not optically active, as in a racemic crystal.

Chiral three-dimensional structures, obtained from racemic starting materials, have been recently reported by Decurtins et al.[14] for compounds with general formula $[M^{II}(bpy)_3][M^{I}M^{III}(ox)_3]$ and $[M^{II}(bpy)_3][M^{II}_2(ox)_3]$, finding out the assembly of homochiral propeller-like mononuclear subunits (all Δ or all Λ). These structures are described as well-defined 3D 3-connected 10-gon nets (10,3)[15] with $[M(bpy)_3]^{2+}$ cations occupying the vacancies following the same arrangement.

This specific association of homochiral subunits producing less soluble compounds has been commonly used as a method of enantiomeric resolution and determination of absolute configurations of coordination complexes. The compact packing mode of this homochiral association in solid state and its thermodynamical implications has been traditionally used to explain its preferential crystallization.[16] Although resolution of racemic mixtures into its enantiomers is in continuous development,[17,18] the most widely used resolution method remains the formation and separation of crystalline diastereomeric salts between racemic substrates and optically active resolving agents, a way of resolution discovered by Pasteur in 1853.

Diastereomer formation with the optically active complex (Δ or Λ) tris(phenanthroline)nickel(II) cation as resolving agent was shown by Dwyer and Sargeson[19] to provide a rapid general resolution method for trisoxalato complexes of Co^{III}, Cr^{III}, and Rh^{III}. It was in 1971 when the first X-ray determination of the absolute configuration of a trisoxalato complex ion, formerly represented as $K(+)_{589}[Ni(phen)_3](-)_{589}[Co(ox)_3]\cdot 2H_2O$, was reported.[20] This is in fact, the first example of a chiral 3D 3-connected 10-gon net, $\{[Ni_\Lambda(phen)_3][K_\Lambda Co_\Lambda(ox)_3]\cdot 2H_2O\}_n$, in which all metallic centers have the same Λ configuration. The extreme favorability of formation of the $Ni(\Lambda)/Co(\Lambda)$ crystals compared with the $Ni(\Lambda)/Co(\Delta)$ and $Ni(\Delta)/Co(\Lambda)$ species, in the crystallization experiments using resolved species, was pointed out. In the previous example the assembling ability of the alkaline cation plays an important role in the formation of the 3D network.

In the present work, we explore the feasibility of an enantioselective synthesis of optically active two- and three-dimensional oxalate-bridged polymeric compounds using resolved $[Cr(ox)_3]^{3-}$ and $[M(bpy)_3]^{2+}$ (M = Ni, Ru) species. We report herein the results in the synthesis and characterization of enantiomeric compounds of general formula: $\{[NBu_4][Mn^{II}{}_\Delta Cr^{III}{}_\Lambda(ox)_3]\}_n$ (**1a**), $\{[NBu_4][Mn^{II}{}_\Lambda Cr^{III}{}_\Delta(ox)_3]\}_n$ (**1b**), $\{[Ni^{II}{}_\Lambda(bpy)_3][Li^{I}{}_\Lambda Cr^{III}{}_\Lambda(ox)_3]H_2O\}_n$ (**2Λ**), $\{[Ni^{II}{}_\Delta(bpy)_3][Li^{I}{}_\Delta Cr^{III}{}_\Delta(ox)_3]H_2O\}_n$ (**2Δ**), $\{[Ni^{II}{}_\Lambda(bpy)_3][Mn^{II}{}_{\Lambda 2}(ox)_3]\}_n$ (**3Λ**), $\{[Ni^{II}{}_\Delta(bpy)_3][Mn^{II}{}_{\Delta 2}(ox)_3]\}_n$ (**3Δ**), $\{[Ru^{II}{}_\Lambda(bpy)_3][Li^{I}{}_\Lambda Cr^{III}{}_\Lambda(ox)_3]H_2O\}_n$ (**4Λ**), $\{[Ru^{II}{}_\Delta(bpy)_3][Li^{I}{}_\Delta Cr^{III}{}_\Delta(ox)_3]H_2O\}_n$ (**4Δ**), $\{[Ru^{II}{}_\Lambda(bpy)_3][Mn^{II}{}_{\Lambda 2}(ox)_3]\}_n$ (**5Λ**), and $\{[Ru^{II}{}_\Delta(bpy)_3][Mn^{II}{}_{\Delta 2}(ox)_3]\}_n$ (**5Δ**).

Experimental Section

Materials. The following complexes were prepared according to literature methods: $K_3[Cr(ox)_3]\cdot 3H_2O$,[21] $[Ni(bpy)_3]Cl_2\cdot 6H_2O$,[22] $[Ru(bpy)_3]X_2\cdot 6H_2O$ (X = Cl, I).[23] Procedures of resolution, already described, have been followed to obtain enantiomerically pure Δ and Λ isomers of $[Cr(ox)_3]^{3-}$ [24] and $[Ru(bpy)_3]^{2+}$.[25] The other reagents are commercially available and were used as purchased.

Physical Techniques. The IR spectra were recorded on a Bio-Rad IRFT spectrophotometer as KBr pellets in the 4000−250 cm^{-1} region. Elemental analyses were completed at the SIAR-UPMC, Paris. Metal analyses were performed at the Service Central d'Analyse−CNRS, Vernaison. Specific rotations of the starting materials were measured at 20 °C, in a 1-dm tube containing the aqueous solutions, using the sodium D line in a polarimeter Ameria AA 5. The enantiomeric excess was calculated by comparison with the maximum specific rotation values found in the literature.[24] X-ray powder diffraction profiles were recorded at room temperature on an automated Philips diffractometer in reflection mode with Cu Kα radiation over the 10−60° (2θ) angular range. Circular dichroism spectra were measured with a Jasco model J-710 spectropolarimeter. Measurements were made on the resulting complexes as dispersions of 0.1−1 mg in 100 mg of oven-dried KBr. 13-mm diameter disks were made in a standard disk press. The baseline correction was performed with the spectrum of a pure KBr disk, prepared in the same conditions. The displayed absorption spectra result from subtraction of spectrum of a standard KBr disk. Spectra were recorded for the wavelength range 700−400 nm for all the disks, and extended to lower wavelengths when allowed by the quality of the less concentrated samples.

Synthesis of Optically Active Polymers. Experimental conditions similar to those reported by Okawa et al.[12b] and Decurtins et al.[14b] were used in the synthesis and crystallization of the optically active polymers. The X-ray powder diffraction profiles of optically active polymers were registered and compared to those of the corresponding nonoptically active compounds (**1**−**5**). All three-dimensional polymers have been found to be isostructural. The following synthetic procedure are representative for the preparations of the two enantiomers in every case.

Preparation of 1a and 1b. To an aqueous solution (10 cm^3) of $K_3[Cr_\Lambda(ox)_3]\cdot 3H_2O$ ($[\alpha]_D = 1481$, ee = 0.90) (0.25 g, 0.51 mmol) and $MnCl_2\cdot 4H_2O$ (82 mg, 0.51 mmol) was added NBu_4Br (0.25 g, 0.77

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mmol) with stirring at room temperature. A green microcrystalline precipitate started to appear and after 2 min, was filtered off, washed with water and ethanol, and air-dried. A 0.23 g amount of $\{[\mathrm{NBu_4}][\mathrm{Mn}_\Delta\mathrm{Cr}_\Lambda(\mathrm{ox})_3]\}_n$ (**1a**) (73%) was obtained. IR (KBr): 1629, vs; 817, w; 805, w. Anal. Calcd for $\mathrm{C_{22}H_{36}NO_{12}CrMn}$: C, 43.08; H, 5.92; N, 2.28; Cr, 8.46; Mn, 8.94. Found: C, 43.17; H, 5.96; N, 2.23; Cr, 8.40; Mn, 8.95.

Preparation of 2Δ and 2Λ. To an aqueous solution (40 $\mathrm{cm^3}$) of $[\mathrm{Ni(bpy)_3}]\mathrm{Cl_2{\cdot}6H_2O}$ (0.60 g, 0.85 mmol) and LiCl (17 mg, 0.41 mmol) was added an aqueous solution (10 $\mathrm{cm^3}$) of $\mathrm{K_3}[\mathrm{Cr}_\Delta(\mathrm{ox})_3]\mathrm{{\cdot}3H_2O}$ ($[\alpha]_D = -1603$, ee = 0.97) (0.20 g, 0.41 mmol). A green precipitate appeared and, after 1 min, was filtered off, washed with water and ethanol, and air-dried. A 0.25 g amount of $\{[\mathrm{Ni}_\Delta(\mathrm{bpy})_3][\mathrm{Li}_\Delta\mathrm{Cr}_\Delta(\mathrm{ox})_3]\mathrm{H_2O}\}_n$ (**2**Δ) (72%) was obtained. IR (KBr): 1670, vs; 1649, vs; 1392,-vs; 807, m; 778, m. Anal. Calcd for $\mathrm{C_{36}H_{26}N_6O_{13}CrLiNi}$: C, 49.80; H, 3.02; N, 9.68; Cr, 5.99; Li, 0.80; Ni, 6.76. Found: C, 50.53; H, 2.91; N, 9.90; Cr, 6.02; Li, 0.74; Ni, 6.86.

Preparation of 3Δ and 3Λ. A solution of $[\mathrm{Ni(bpy)_3}]^{2+}$ (Λ) was prepared as follows: $\mathrm{K_3}[\mathrm{Cr}_\Delta(\mathrm{ox})_3]\mathrm{{\cdot}3H_2O}$ ($[\alpha]_D = -1603$, ee = 0.97) (0.25 g; 0.51 mmol) was added, with stirring, to an aqueous solution (40 $\mathrm{cm^3}$) of racemic $[\mathrm{Ni(bpy)_3}]\mathrm{Cl_2{\cdot}6H_2O}$ (0.60 g, 0.85 mmol) and LiCl (0.1 g, excess). The immediate precipitate (**2**Δ, 0.35 g) was filtered off, and $\mathrm{MnCl_2\ 4H_2O}$ (0.13 g, 0.85 mmol) and $\mathrm{K_2C_2O_4{\cdot}H_2O}$ (0.24 g, 1.3 mmol) were then added to the filtrate ($[\mathrm{Ni}_\Lambda(\mathrm{bpy})_3]^{2+}$). A pink precipitate appeared. After 1 min it was filtered off, washed with water and ethanol, and air-dried to yield 0.25 g of $\{[\mathrm{Ni}_\Lambda(\mathrm{bpy})_3][\mathrm{Mn}_{\Lambda 2}(\mathrm{ox})_3]\}_n$ (**3**Λ) (65%). IR (KBr): 1631, s; 1608, vs; 1442, m; 1310, m; 798, m; 780, m. Anal. Calcd for $\mathrm{C_{36}H_{24}N_6O_{12}Mn_2Ni}$: C, 47.98; H, 2.68; N, 9.32; Mn, 12.19; Ni, 6.51. Found: C, 46.54; H, 2.68; N, 9.12; Mn, 11.53; Ni, 5.71.

Preparation of 4Δ and 4Λ. $[\mathrm{Ru}_\Delta(\mathrm{bpy})_3]\mathrm{I_2{\cdot}6H_2O}$ ($[\alpha]_D = -734$, ee = 0.89) (93 mg, 0.1 mmol) was dissolved in a LiCl (0.1 g, excess) aqueous solution (40 $\mathrm{cm^3}$). A solution of racemic $\mathrm{K_3[Cr(ox)_3]{\cdot}3H_2O}$ (97 mg, 0.2 mmol) in 10 $\mathrm{cm^3}$ of water was then added with stirring, giving in a few minutes a dark red precipitate which was filtered off, washed with water and ethanol, and air-dried. A 76 mg amount of $\{[\mathrm{Ru}_\Delta(\mathrm{bpy})_3][\mathrm{Li}_\Delta\mathrm{Cr}_\Delta(\mathrm{ox})_3]\mathrm{H_2O}\}_n$ (**4**Δ) (85%) was obtained. IR (KBr): 1670, vs; 1648, vs;1393, s; 1262, m; 808, m; 777, s. Anal. Calcd for $\mathrm{C_{36}H_{26}N_6O_{13}CrLiRu}$: C, 47.48; H, 2.88; N, 9.23; Cr, 5.72; Li, 0.76; Ru, 11.10. Found: C, 47.50; H, 2.66; N, 9.45; Cr, 5.55; Li, 0.67; Ru, 9.74.

Preparation of 5Δ and 5Λ. $[\mathrm{Ru}_\Lambda(\mathrm{bpy})_3]\mathrm{I_2{\cdot}6H_2O}$ ($[\alpha]_D = 813$, ee = 0.99) (93 mg, 0.1 mmol) was dissolved in a LiCl (0.1 g, excess) aqueous solution (40 $\mathrm{cm^3}$). $\mathrm{MnCl_2\ 4H_2O}$ (32 mg, 0.20 mmol) was added with stirring. $\mathrm{K_2C_2O_4{\cdot}H_2O}$ (55 mg, 0.30 mmol) was dissolved in the minimum amount of water and added to the above solution, giving in a few minutes a bright orange precipitate. It was filtered off, washed with water and ethanol, and air-dried. A 76 mg amount of $\{[\mathrm{Ru}_\Lambda(\mathrm{bpy})_3][\mathrm{Mn}_{\Lambda 2}(\mathrm{ox})_3]\}_n$ (**5**Λ) (81%) was obtained. IR (KBr): 1632, s; 1607, vs; 1598, vs; 1308, m; 799, m; 777, m. Anal. Calcd for $\mathrm{C_{36}H_{24}N_6O_{12}Mn_2Ru}$: C, 45.82; H, 2.56; N, 8.90; Mn, 11.64; Ru, 10.71. Found: C, 44.91; H, 2.57; N, 8.98; Mn, 11.32, Ru, 9.39.

Single Crystal Growth. A typical experiment of crystallization consists on formation of a tetramethoxysilane gel by mixing $\mathrm{Si(OCH_3)_4}$ (5 $\mathrm{cm^3}$) and $\mathrm{CH_3OH}$ (5 $\mathrm{cm^3}$) and posterior addition of an aqueous solution (5 $\mathrm{cm^3}$, 0.005 M) of $\mathrm{K_3Cr(ox)_3{\cdot}3H_2O}$. The resulting pale violet solution is homogenized and placed in a test tube. After a few days the gel is formed and an aqueous solution (4 $\mathrm{cm^3}$) with the stoichiometric quantities of $\mathrm{Li^+}$ and $[\mathrm{M(bpy)_3}]^{2+}$ species is added. After 1 week the tetrahedric shaped crystals are formed.

X-ray Crystallographic Analysis for 2Δ, 4Δ, and 4Λ. Accurate cell dimensions and orientation matrixes were obtained by least-squares refinements of 25 accurately centered reflections. No significant variations were observed in the intensities of two checked reflections during data collections. The data were corrected for Lorentz and polarization effects. Computations were performed by using the PC version of CRYSTALS.[26] Scattering factors and corrections for anomalous absorption were taken from ref 27. The structures were solved by direct method (SHELXS[28]). Data were collected for both positive and negative set of *hkl* values in order to determine unambiguously the correct chirality for each enantiomer. All last refinements were carried out by full-matrix least-squares using anisotropic displacement parameters for all non hydrogen atoms. Hydrogen atoms were introduced in calculated positions and only one overall isotropic displacement parameter was refined.

Results and Discussion

2D Optically Active Polymers. Compounds with general formula $[\mathrm{ER_4}]\ [\mathrm{M^{II}M^{III}(ox)_3}]$ constitute a very extensive series formed by a wide range of organic cations as well as di- and trivalent transition metal ions. Cross-linking of $[\mathrm{M^{III}(ox)_3}]^{3-}$ by $\mathrm{M^{II}}$ in two dimensions produces a honeycomb structure with alternating layers separated by the organic cations. The structure of each honeycomb layer ($\{[\mathrm{M^{II}M^{III}(ox)_3}]^-\}_n$) is defined by two restrictions: the two metal ions, $\mathrm{M^{II}}$ and $\mathrm{M^{III}}$, have opposite chirality and ions of the same type have the same chirality (all Δ or all Λ). These two conditions make the structure bidimensional, and render each layer chiral. If this statement can be extended to the whole structure, it will be also chiral. That is, if one type of metal ions maintains the same Δ or Λ configuration, all over the structure, then the whole structure will be optically active.

The synthetic strategy to control the overall chirality requires the use of resolved chiral building blocks. As it has been reported,[12] the synthesis of the above 2D polymers can be made in conditions of rapid precipitation, leading in a few minutes to the isolation of a microcrystalline solid. Such reaction conditions are suitable for using, as one of the starting reagents, the Δ or Λ enantiomers of the easily racemizable $[\mathrm{Cr(ox)_3}]^{3-}$.[9,29] Mixing solutions of optically active $[\mathrm{Cr(ox)_3}]^{3-}$ (Δ or Λ) and the corresponding achiral $\mathrm{Mn^{2+}}$ and $\mathrm{NBu_4^+}$ salts causes the immediate precipitation of dark green microcrystalline solids characterized as the optically active $\{[\mathrm{NBu_4}][\mathrm{Mn}_\Delta\mathrm{Cr}_\Lambda(\mathrm{ox})_3]\}_n$ (**1a**) or $\{[\mathrm{NBu_4}][\mathrm{Mn}_\Lambda\mathrm{Cr}_\Delta(\mathrm{ox})_3]\}_n$ (**1b**) polymers.

Circular dichroism measurements were used to demonstrate the enantiomeric nature of the two species and to determine the absolute configurations of the metallic centers. Absolute configurations for Cr centers were determined by comparison of their CD spectra with those of Δ and Λ enantiomers of potassium tris(oxalato)chromate(III), following the principle that two related optically active molecules have the same absolute configuration if they give a Cotton effect of the same sign in the absorption wavelength region of an electronic transition common to both molecules.[30] Due to the extremely low solubility of the obtained polymers, solid state circular dichroism was imposed. This technique has been used to allow CD measurements in the case of compounds which racemize rapidly in solution. This method is useful mainly for qualitative comparisons because of the intensities in general vary with the individual samples.[31]

Polymers **1a** and **1b** showed optical activity, displaying circular dichroism curves of the two opposite types. The CD

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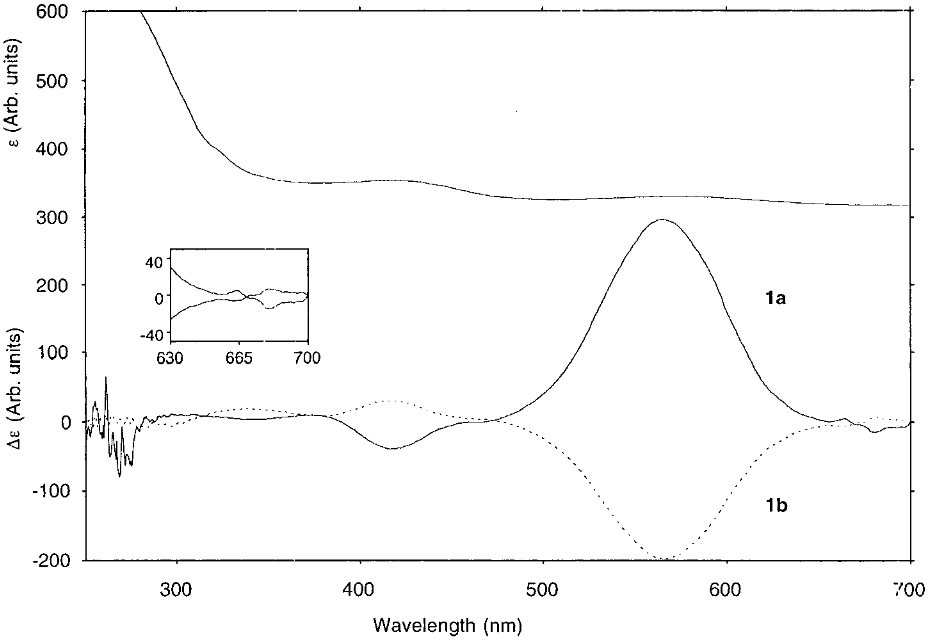

Figure 1. Absorption (top) and circular dichroism (bottom) spectra of **1a** and **1b** polymers in KBr dispersions. The inset shows the spin-forbidden bands of Cr(III).

spectra of both compounds (Figure 1) exhibit Cotton effects of bands in the visible region, easily assigned to chromium(III) d→d transitions (characteristic very weak spin-forbidden bands can be also observed).[30b,31]

Polymer **1a** obtained from $[Cr_{\Lambda}(ox)_3]^{3-}$ ($\lambda_{max} = 550$ nm) shows the same positive Cotton effect at $\lambda_{max} = 565$ nm. Polymer **1b**, obtained from $[Cr_{\Delta}(ox)_3]^{3-}$, displays the corresponding negative Cotton effect at the same wavelength. The bands due to the Mn(II) ion are too weak to be observed and probably hidden by the more intense bands due to chromium. If the same 2D arrangement is maintained by these enantiomers, as it is expected to be, in accordance with the structural data, the configuration of Mn centers is imposed to be the opposite one of Cr centers.

Crystallization of the enantiomers to determine the X-ray structure is not possible because of the rapid racemization of $[Cr(ox)_3]^{3-}$ in solution. The X-ray powder diffraction patterns of **1a** and **1b** have been found to be strictly the same, but different when compared to that of the corresponding racemic $\{[NBu_4][MnCr(ox)_3]\}_n$ (**1**). The enantiomeric forms must be described in chiral space groups. Up to date, only two crystal data reported on $[NBu_4][MnFe(ox)_3]$ (space group $P6_3$)[13f] and $[NPn_4][MnFe(ox)_3]$ (space group $C222_1$)[32] reveal a chiral crystalline structure probably as a consequence of the unusual selection of a single isomer from a racemate in assembling the bimetallic layers.[33]

3D Optically Active Polymers. Compounds of general formula $[M(bpy)_3][M'M''(ox)_3]$ are representative of 3-dimensional homo- and bimetallic oxalate-bridged networks, usually described as 3D 3-connected 10-gon nets (10, 3). The enantioselective self-assembly of homochiral building blocks is necessary to afford the overall helical chirality of this kind of networks, giving rise to only two possible assemblies with all metallic center configurations Δ (M(Δ), M′(Δ), M″(Δ)) or Λ (M(Λ), M′(Λ), M″(Λ)) and the corresponding left- (M) or right- (P) handed supramolecular helicity. Such a high level of organization may be related to the fact that the conglomerate is the preferred crystalline form, allowing the growth of enantiomerically pure single crystals.[14,34]

On the basis of these observations, the use of optically active reagents was explored either in conditions of rapid precipitation or slow crystallization. In the case of the compound $[Ni(bpy)_3][LiCr(ox)_3]$ (**2**), optically active tris(oxalato)chromate(III) (Δ or Λ) was used as the only resolved building block. In conditions of fast precipitation racemization is avoided and the reaction yields the corresponding enantiomers $\{[Ni_{\Delta}(bpy)_3][Li_{\Delta}Cr_{\Delta}(ox)_3]H_2O\}_n$ (**2Δ**) or $\{[Ni_{\Lambda}(bpy)_3][Li_{\Lambda}Cr_{\Lambda}(ox)_3]H_2O\}_n$ (**2Λ**).

The CD spectra of the enantiomeric compounds (Figure 2) exhibit typical excitonic interactions of the bipyridine $\pi\rightarrow\pi^*$ intraligand transitions in UV region and the expected Cotton effects of chromium d→d bands in the visible region. These two sets of signals in UV and visible regions are related to Ni and Cr configurations, respectively.[30b,31,35]

Polymer **2Λ** obtained from $[Cr_{\Lambda}(ox)_3]^{3-}$ shows a positive Cotton effect ($\lambda_{max} = 560$ nm) in the same region as the initial building block. In the high energy transitions region, associated to Ni configuration ($\lambda_{max} = 318$ nm), the same positive Cotton effect is found. The sign of these bands are representative of the Ni(Λ) and Cr(Λ) configurations. The corresponding negative Cotton effects were found for polymer **2Δ** obtained from $[Cr_{\Delta}(ox)_3]^{3-}$. The interpretation of the spectra agrees with the homochirality of Cr and Ni centers within each enantiomer. To corroborate this relationship other experiments were made.

The use of enantiomerically pure solutions of $[Cr(ox)_3]^{3-}$ in these reactions requires 2-fold concentrated solutions of racemic $[Ni(bpy)_3]^{2+}$. Precipitation of the corresponding optically active polymer renders the solution enriched in the opposite enantiomer of $[Ni(bpy)_3]^{2+}$. If tris(oxalato)chromate(III) (Δ) is used, the polymer **2Δ** precipitates and the resulting solution becomes enriched in $[Ni_{\Lambda}(bpy)_3]^{2+}$. Addition, after filtration, of a second solution of racemic $[Cr(ox)_3]^{3-}$ leads to a new precipitate which

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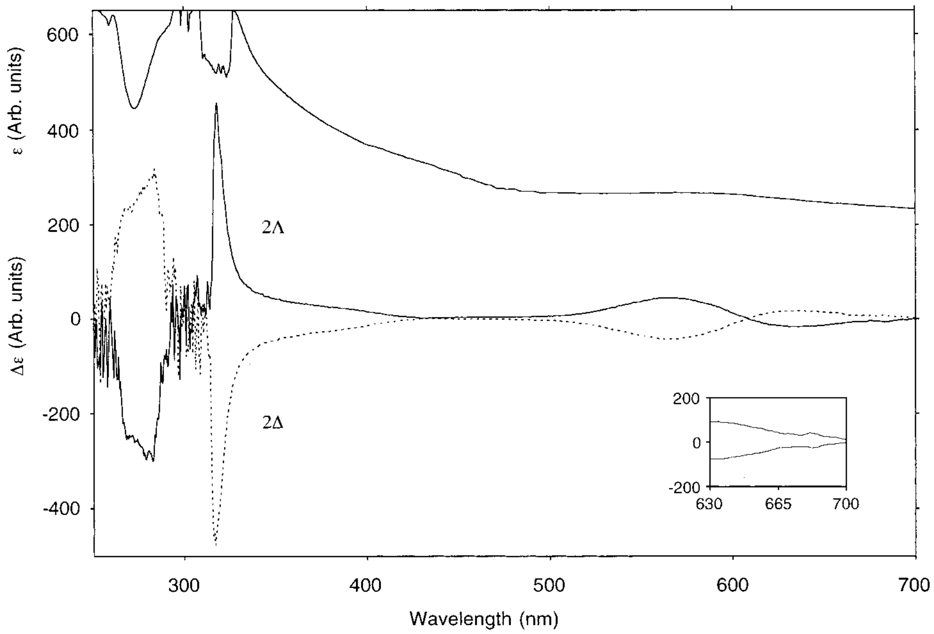

Figure 2. Absorption (top) and circular dichroism (bottom) spectra of **2Δ** and **2Λ** polymers in KBr dispersions.

shows the opposite CD spectrum to that of the first precipitate (**2Δ**), and is therefore identified as **2Λ**.

Different experiments of crystallization of $[Ni(bpy)_3][LiCr(ox)_3]$ (**2**) were performed using racemic $[Cr(ox)_3]^{3-}$. Gel technique of crystallization[36] allows the slow diffusion of reagents, leading to well formed crystals suitable for X-ray diffraction studies. Crystallization requires several days and in such conditions the control over the chirality of the easily racemizable reagents is not possible, but very interesting information has been obtained.

Two single crystals were analyzed by X-ray diffraction and the same structure corresponding to the enantiomer **2Δ** was found. It is not possible to distinguish the enantiomers by optical methods due to the isomorphism of levo and dextro crystals, and determination of each crystalline structure of the enantiomers by single-crystal X-ray diffraction is random. The X-ray diffraction data confirmed the homochiral association between metallic centers in the crystal network and the enantiomeric purity of single crystals.

A set of crystallizations was performed and, for each crystallization, CD measurements were made over a representative number of crystals (60−70% of the calculated mass for quantitative reaction). Optical activity was always found for the individual samples. CD spectra corresponding to the two enantiomers (**2Δ** and **2Λ**) were recorded. The signals displayed have, in many cases, comparable intensities to those of the spectra registered for optically active polymers obtained by fast precipitation. These facts evidence a phenomenon of partial spontaneous resolution. The theoretical maximum yield in a resolution cannot exceed 50% for each of the two pure enantiomers. However, when racemization or formation of interconvertible diastereomers in solution occurs, then preferential crystallization of one of the two enantiomeric species and displacement of the resulting equilibrium can lead to a total transformation of the initial racemate into a single enantiomer.[16,37] In such kind of asymmetric transformation, a rare phenomenon, experimental conditions of crystallization are critical. Experiments with gels have been suggested to be valuable for investigation of deviations from the 1:1 distribution of levo and dextro crystals.[36a]

Optically Active Cations $[M(bpy)_3]^{2+}$ as Templates. The role of dipositive, tris-chelated transition-metal bipyridine complexes as templates in the formation of three-dimensional homo- and bimetallic oxalate-bridged networks is well-established.[14] The synthesis of $\{[Ni(bpy)_3][Mn_2(ox)_3]\}_n$ (**3**) is an example of construction of a highly organized 3D structure induced by $[M(bpy)_3]^{2+}$ fragments.[14b] We extended these observations by the synthesis of the optically active forms of **3**, using $[Ni(bpy)_3]^{2+}$ as the only chiral reagent. The other reagents were manganese dichloride and potassium oxalate. Solutions of optically active $[Ni(bpy)_3]^{2+}$ were first obtained by precipitation of **2Λ** or **2Δ** with resolved $[Cr(ox)_3]^{3-}$ (Λ or Δ), and rapidly mixed with the other reagents (Mn^{2+}, $(ox)^{2-}$) to produce immediate precipitation of the corresponding optically active polymers $\{[Ni_{\Delta}(bpy)_3][Mn_{\Delta 2}(ox)_3]\}_n$ (**3Δ**) or $\{[Ni_{\Lambda}(bpy)_3][Mn_{\Lambda 2}(ox)_3]\}_n$ (**3Λ**). These compounds display opposite curves in the CD spectra. Absolute configurations were assigned by comparison of the CD spectra (Figure 3) with those of **2Δ** and **2Λ**. Higher intensity signals appear in the UV region (λ = 314 nm) associated to the $\pi \rightarrow \pi^*$ bipyridine ligand transitions. A very weak signal at 560 nm is tentatively assigned to Mn(II) ions. A positive Cotton effect at these wavelengths is representative of the Λ configuration of Ni and Mn centers in **3Λ**. The opposite curve is assigned to the enantiomer **3Δ**.

At this point the use of an optically active cation, stable enough to keep its configuration unchanging, was attempted. It is well-known that ruthenium compounds are configurationally stable even in boiling aqueous solution.[38] First trials with racemic $[Ru(bpy)_3]^{2+}$ showed its adequate characteristics (charge, size and shape) for the obtention of desired polymers

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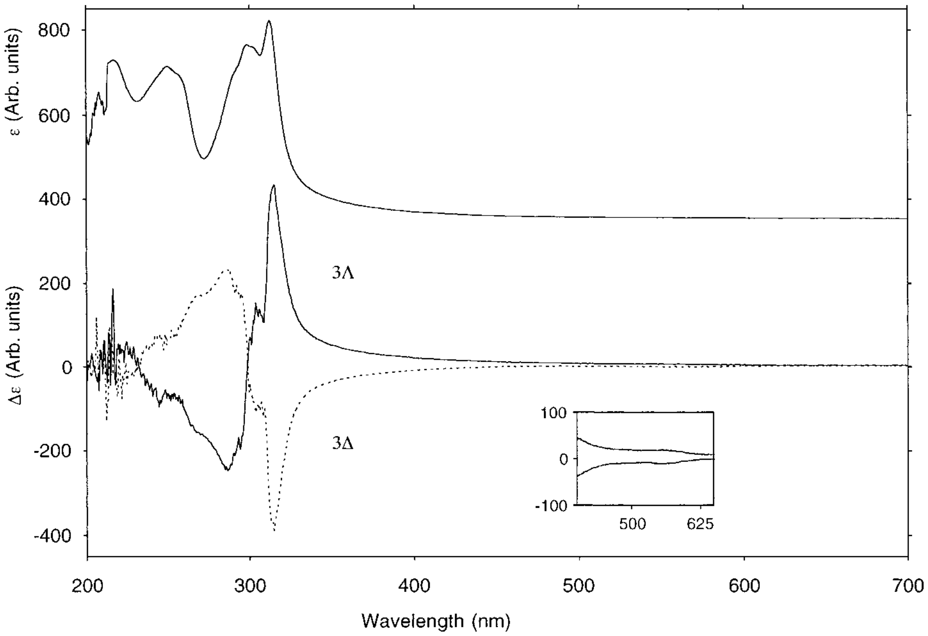

Figure 3. Absorption (top) and circular dichroism (bottom) spectra of **3**Δ and **3**Λ polymers in KBr dispersions.

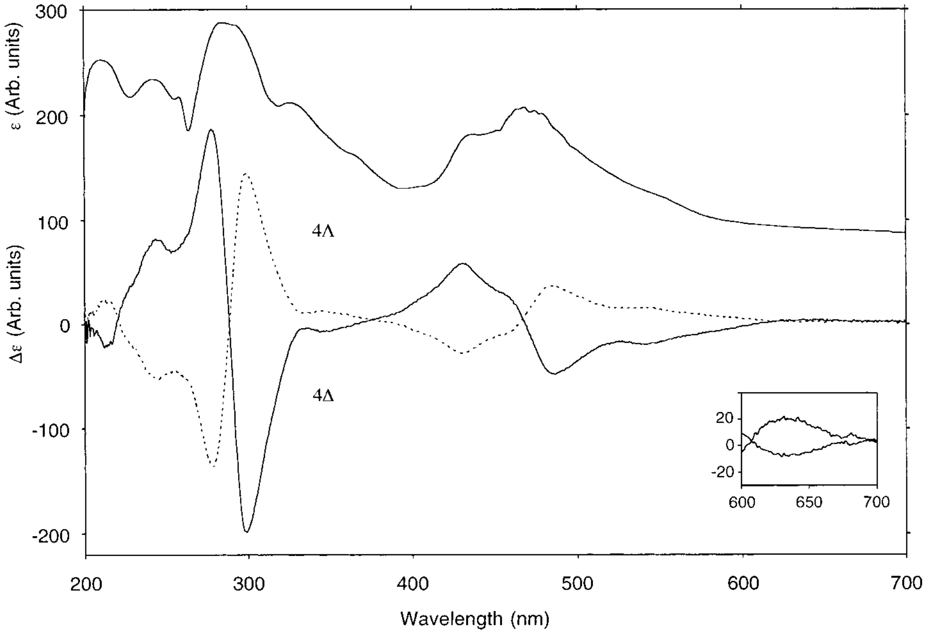

Figure 4. Absorption (top) and circular dichroism (bottom) spectra of **4**Δ and **4**Λ polymers in KBr dispersions.

$\{[Ru(bpy)_3][LiCr(ox)_3]\}_n$ (**4**) and $\{[Ru(bpy)_3][Mn_2(ox)_3]\}_n$ (**5**). The racemic cation $[Ru(bpy)_3]^{2+}$ was resolved into its Δ and Λ configurationally stable enantiomers and used to synthesize the optically active polymers **4**Δ, **4**Λ, **5**Δ, and **5**Λ, by reaction with the corresponding racemic or achiral mixtures of the other reagents. CD spectra (Figures 4 and 5) were registered and used for absolute configuration assignments. In all cases the spectra are dominated by intense bands at $\lambda = 298$ nm ($\pi \rightarrow \pi^*$ intraligand transitions) and $\lambda = 484$ nm (MLCT transitions), unambiguously assigned to $[Ru(bpy)_3]^{2+}$ fragments.[39] In the case of **4**Δ and **4**Λ typical signals of a Cr(III) complex (shoulder at $\lambda = 570$ nm and weak spin-forbidden bands) can also be observed in the high wavelength region. Positive Cotton effects of these signals are representative of the Λ configuration.

Crystallization of **4**Δ and **4**Λ was performed by gel technique and crystals suitable for X-ray diffraction studies were obtained. The enantiomeric purity of single crystals and the homochiral relationship between metallic centers were confirmed. The configuration stability of starting $[Ru(bpy)_3]^{2+}$ was corroborated and the predicted absolute configurations found for each enantiomer. Crystals of **4**Λ, obtained from $[Ru_\Lambda(bpy)_3]^{2+}$, showed the expected same Λ configuration for each metallic center in the crystal lattice and the corresponding right-handed (P) supramolecular helicity. The opposite helicity has been found for crystals of **4**Δ, obtained from $[Ru_\Delta(bpy)_3]^{2+}$. The CD spectra of samples prepared with a relevant number of crystals of **4** obtained from racemic configurationally stable $[Ru(bpy)_3]^{2+}$ did not show optical activity, as expected for an equal proportion of crystals of each enantiomer. No attempt was made to determine the optical purity of the solids. In the case of **4**Λ and **4**Δ, the intensities of signals for polymers obtained by

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(39) McCaffery, A. J.; Mason, S. F.; Norman, B. J. *J. Chem. Soc. (A)* **1969**, 1428.

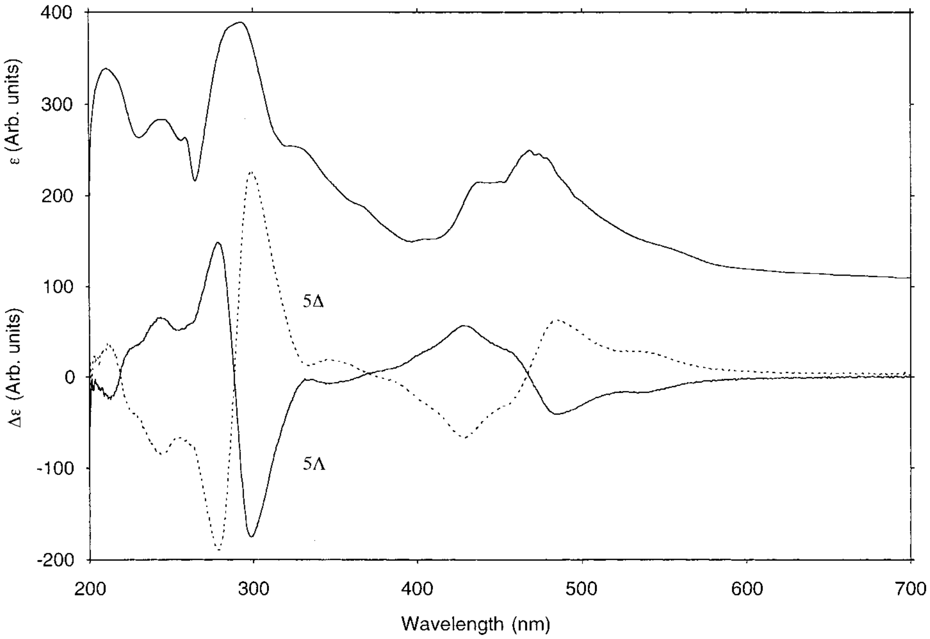

Figure 5. Absorption (top) and circular dichroism (bottom) spectra of **5Δ** and **5Λ** polymers in KBr dispersions.

Table 1. Crystal Data and Structure Determination Parameters[a] of **2Δ**, **4Δ**, and **4Λ**

	$\{[Ni(bpy)_3][LiCr(ox)_3]H_2O\}_n$, **2Δ**	$\{[Ru(bpy)_3][LiCr(ox)_3]H_2O\}_n$, **4Δ**	$\{[Ru(bpy)_3][LiCr(ox)_3]H_2O\}_n$, **4Λ**
formula	$C_{36}H_{26}O_{13}N_6NiCrLi$	$C_{36}H_{26}O_{13}N_6RuCrLi$	$C_{36}H_{26}O_{13}N_6RuCrLi$
fw	868.1	910.5	910.5
temperature	295 K	295 K	295 K
crystal system	cubic	cubic	cubic
space group	$P2_13$	$P2_13$	$P2_13$
a (Å)	15.380(5)	15.293(8)	15.289(2)
V (Å^3)	3638(2)	3576(4)	3573.9(8)
Z	4	4	4
linear abs coef μ (cm^{-1})	8.8	7.84	7.85
density ρ (g cm^{-3})	1.58	1.69	1.69
crystal size (mm)	0.12 × 0.12 × 0.12	0.18 × 0.18 × 0.18	0.15 × 0.15 × 0.15
diffractometer	CAD4 Enraf-Nonius	CAD4 Enraf-Nonius	CAD4 Enraf-Nonius
radiation	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.710 69 Å)
scan type	$\omega/2\theta$	$\omega/2\theta$	$\omega/2\theta$
scan range (deg)	$0.8 + 0.345 \tan \theta$	$0.8 + 0.345 \tan \theta$	$0.8 + 0.345 \tan \theta$
θ range (deg)	1−25	1−25	1−25
index range, *h*, *k*, *l*	0, ±18; 0, ±18; 0, ±18	0, ±18; 0, ±18; 0, ±18	0, ±18; 0, ±18; 0, ±18
no. of data collected	7194	7116	7124
no. of unique data collected	2145	2119	2119
no. of unique data used	844 $(F_o)^2 > 3\sigma(F_o)^2$	1411 $(F_o)^2 > 3\sigma(F_o)^2$	1391 $(F_o)^2 > 3\sigma(F_o)^2$
no. of variables	84	176	176
R_1[b], wR_2[c] ($I > 3\sigma(I)$)	0.0476, 0.0578	0.0256, 0.0287	0.0305, 0.0351
R_1, wR_2 (all data)	0.114, 0.0699	0.0487, 0.0313	0.0558, 0.0369
weight coefficients[d]	3.39, 0.647, 2.03	1.19, 0.210, 0.513	2.89, −0.308, 1.98
goodness of fit on *F*	0.95	1.14	1.11
2nd extinction parameter	none	none	none
enantiopole parameter[e]	0.06	0.012	−0.02
max shift/esd	0.102	0.0031	0.0019
$\Delta\rho$ min, max (e Å^{-3})	−0.60, 0.82	−0.62, 0.44	−0.48, 0.58

[a] For all three compounds: data were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer; unit cell parameters and orientation matrixes were obtained from the least-squares refinements of the θ angles of 25 reflections with $12 < \theta < 12.3$ for **2Δ**, $14 < \theta < 14.5$ for **4Δ**, and $11.9 < \theta < 12.3$ for **4Λ**; structures were solved by direct methods (SHELXS) and refined by full-matrix least-squares on F using the PC version of CRYSTALS. Because of the small and homogeneous dimensions of the crystals no absorption corrections were applied. [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $wR_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$. [d] $w = w'[1 - ((||F_o| - |F_c||)/6.\sigma(F_o))^2]^2$ with $w' = 1/\sum_r A_rT_r(X)$ with three coefficients for a Chebyshev series, for which X is $F_c/F_c(\max)$. [e] $F_c = ((1 - x)F(H)^2 + xF(-H)^2)^{1/2}$, $x = 0$ for correct and +1 for inverted absolute structure.

crystallization (enantiomerically pure single crystals) or by rapid precipitation are comparable within the limitations of the solid-state CD technique.

Description of the Structures. Relevant crystallographic data and structure determination parameters obtained by X-ray diffraction studies of enantiomerically pure single crystals of complexes **2Δ**, **4Δ**, and **4Λ** are given in Table 1.

The topology of these compounds shows the expected chiral three-dimensional 3-connected 10-gon (10, 3) network configuration with the formal $[M(ox)_{3/2}]$ units representing three-connecting nodes. An exhaustive structural analysis of similar networks has been previously reported by Decurtins et al.[14]

The oxalate ligands repeatedly bridge adjacent Li and Cr ions in all three dimensions leading to polymeric nets. $[M^{II}(bpy)_3]^{2+}$

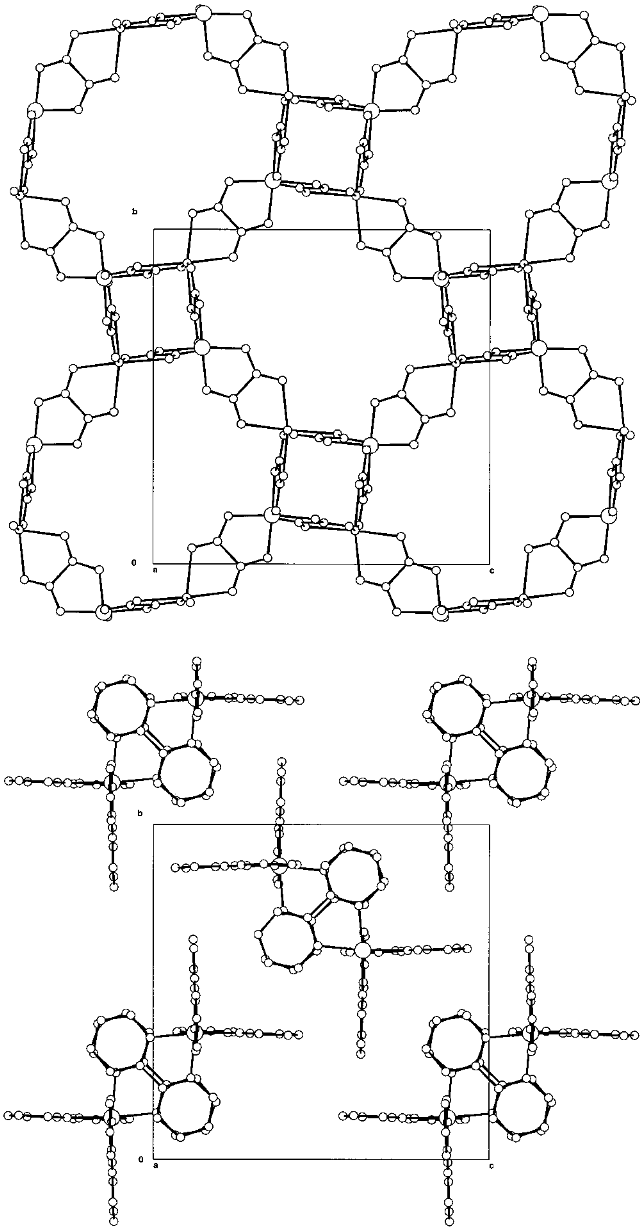

Figure 6. [100] projection of $\{[LiCr(ox)_3]^{2-}\}_n$ (top) and $[Ru(bpy)_3]^{2+}$ (bottom) for compound **4Δ**.

are located in the vacancies of the polymeric anionic framework. [100] projections showing the anionic host ($[LiCr(ox)_3]^{2-}$) and the guests ($[Ru(bpy)_3]^{2+}$), in the case of **4Δ**, are depicted in Figure 6.

Three adjacent $[M^{II}(bpy)_3]^{2+}$ cations form a sufficiently large cavity to accommodate additional molecules.[14,20,34] In the present case a water molecule is hosted in each cavity. The environment of each metallic ion in the net can be described as a trigonally distorted octahedron. The main distortion in such a polymeric Cr and Li combination is showed by Li centers with two sets of different Li−O distances which vary between 2.119(9) and 2.288(8) Å in the case of **4Δ**. Selected bond lengths and angles for **2Δ**, **4Λ**, and **4Δ** are listed in Tables 2, 3, and 4.

All metallic centers show the same configuration within each crystal, all Δ in **2Δ** and **4Δ** and all Λ in **4Λ**. The configuration of Cr and Li centers within the **4Δ** and **4Λ** networks is showed in Figure 7. The view on top, corresponding to **4Δ**, shows the Δ configuration of both metallic centers. It can easily seen in the case of Cr center. Just below, the Λ configuration of Cr and Li, in **4Λ**, is showed. In this case the Λ configuration appears more clearly for Li center. This representation of the two fragments can be seen as the typical mirror image of two enantiomeric forms.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **2Δ**

Ni(II) environment		Cr(III) environment	
Ni(1)−N(1)	2.068(8)	Cr(1)−O(1)	1.977(7)
Ni(1)−N(2)	2.067(8)	Cr(1)−O(2)	1.973(7)
N(1)[a]−Ni(1)−N(1)	94.5(3)	O(1)[c]−Cr(1)−O(1)	91.0(3)
N(1)−Ni(1)−N(2)	79.3(3)	O(1)−Cr(1)−O(2)	82.2(3)
N(1)[a]−Ni(1)−N(2)	92.3(3)	O(1)[c]−Cr(1)−O(2)	172.4(3)
N(1)[b]−Ni(1)−N(2)	171.1(3)	O(1)[d]−Cr(1)−O(2)	92.4(3)
N(2)[a]−Ni(1)−N(2)	94.5(4)	O(2)[c]−Cr(1)−O(2)	94.8(3)
Li(I) environment		**oxalate ligand**	
Li(1)−O(3)	2.24(2)	O(1)−C(11)	1.27(1)
Li(1)−O(4)	2.23(1)	O(3)−C(11)	1.20(1)
O(3)[a]−Li(1)−O(3)	88.6(8)	O(2)−C(12)	1.28(1)
O(3)[a]−Li(1)−O(4)	163.3(9)	O(4)−C(12)	1.22(1)
O(4)[a]−Li(1)−O(4)	104.7(7)	C(11)−C(12)	1.58(1)
O(3)−Li(1)−O(4)	74.8(3)		
O(3)[b]−Li(1)−O(4)	91.3(3)		

[a] $1/2 + z, 3/2 - x, 1 - y$. [b] $3/2 - y, 1 - z, -1/2 + x$. [c] $1 - y, 1/2 + z, 1/2 - x$. [d] $1/2 - z, 1 - x, -1/2 + y$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **4Λ**

Ru(II) environment		Cr(III) environment	
Ru(1)−N(1)	2.046(4)	Cr(1)−O(1)	1.977(4)
Ru(1)−N(2)	2.054(4)	Cr(1)−O(2)	1.972(4)
N(1)[a]−Ru(1)−N(1)	95.3(2)	O(1)[c]−Cr(1)−O(1)	94.5(2)
N(1)−Ru(1)−N(2)	78.9(2)	O(1)−Cr(1)−O(2)	82.4(1)
N(1)[a]−Ru(1)−N(2)	172.0(2)	O(1)[c]−Cr(1)−O(2)	172.8(2)
N(1)[b]−Ru(1)−N(2)	90.7(2)	O(1)[d]−Cr(1)−O(2)	92.2(2)
N(2)[a]−Ru(1)−N(2)	95.6(2)	O(2)[c]−Cr(1)−O(2)	91.2(2)
Li(I) environment		**oxalate ligand**	
Li(1)−O(3)	2.28(1)	O(1)−C(11)	1.282(7)
Li(1)−O(4)	2.14(1)	O(3)−C(11)	1.221(7)
O(3)[e]−Li(1)−O(3)	100.6(6)	O(2)−C(12)	1.274(6)
O(3)[e]−Li(1)−O(4)	168.0(5)	O(4)−C(12)	1.231(6)
O(4)[e]−Li(1)−O(4)	92.1(6)	C(11)−C(12)	1.538(7)
O(3)−Li(1)−O(4)	76.3(2)		
O(3)[f]−Li(1)−O(4)	91.4(2)		

[a] $-1/2 + y, 3/2 - z, 1 - x$. [b] $1 - z, 1/2 + x, 3/2 - y$. [c] $1 - y, -1/2 + z, 3/2 - x$. [d] $3/2 - z, 1 - x, 1/2 + y$. [e] $-1/2 + z, 1/2 - x, 1 - y$. [f] $1/2 - y, 1 - z, 1/2 + x$.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **4Δ**

Ru(II) environment		Cr(III) environment	
Ru(1)−N(1)	2.057(4)	Cr(1)−O(1)	1.972(3)
Ru(1)−N(2)	2.047(4)	Cr(1)−O(2)	1.981(3)
N(1)−Ru(1)−N(1)[a]	95.3(1)	O(1)−Cr(1)−O(1)[c]	91.4(1)
N(1)−Ru(1)−N(2)	78.9(1)	O(1)−Cr(1)−O(2)	82.5(1)
N(1)[a]−Ru(1)−N(2)	90.9(2)	O(1)[c]−Cr(1)−O(2)	173.2(1)
N(1)[b]−Ru(1)−N(2)	171.9(1)	O(1)[d]−Cr(1)−O(2)	91.7(2)
N(2)−Ru(1)−N(2)[a]	95.4(2)	O(2)−Cr(1)−O(2)[c]	94.7(2)
Li(I) environment		**oxalate ligand**	
Li(1)−O(3)	2.119(9)	O(1)−C(11)	1.289(5)
Li(1)−O(4)	2.288(8)	O(2)−C(12)	1.279(6)
O(3)−Li(1)−O(3)[e]	92.8(5)	O(3)−C(11)	1.223(5)
O(3)−Li(1)−O(4)	76.3(1)	O(4)−C(12)	1.221(5)
O(4)−Li(1)−O(4)[e]	99.8(5)	C(11)−C(12)	1.545(6)
O(3)[e]−Li(1)−O(4)	168.4(3)		
O(3)[f]−Li(1)−O(4)	91.7(2)		

[a] $1 - y, 1/2 + z, 1/2 - x$. [b] $1/2 - z, 1 - x, -1/2 + y$. [c] $-1/2 + z, 1/2 - x, 1 - y$. [d] $1/2 - y, 1 - z, 1/2 + x$. [e] $-y, -1/2 + z, 1/2 - x$. [f] $1/2 - z, -x, 1/2 + y$.

Figure 8 emphasizes the 2-fold screw axis in the enantiomeric forms **4Δ** and **4Λ**, by exhibiting one of the helical strands, which

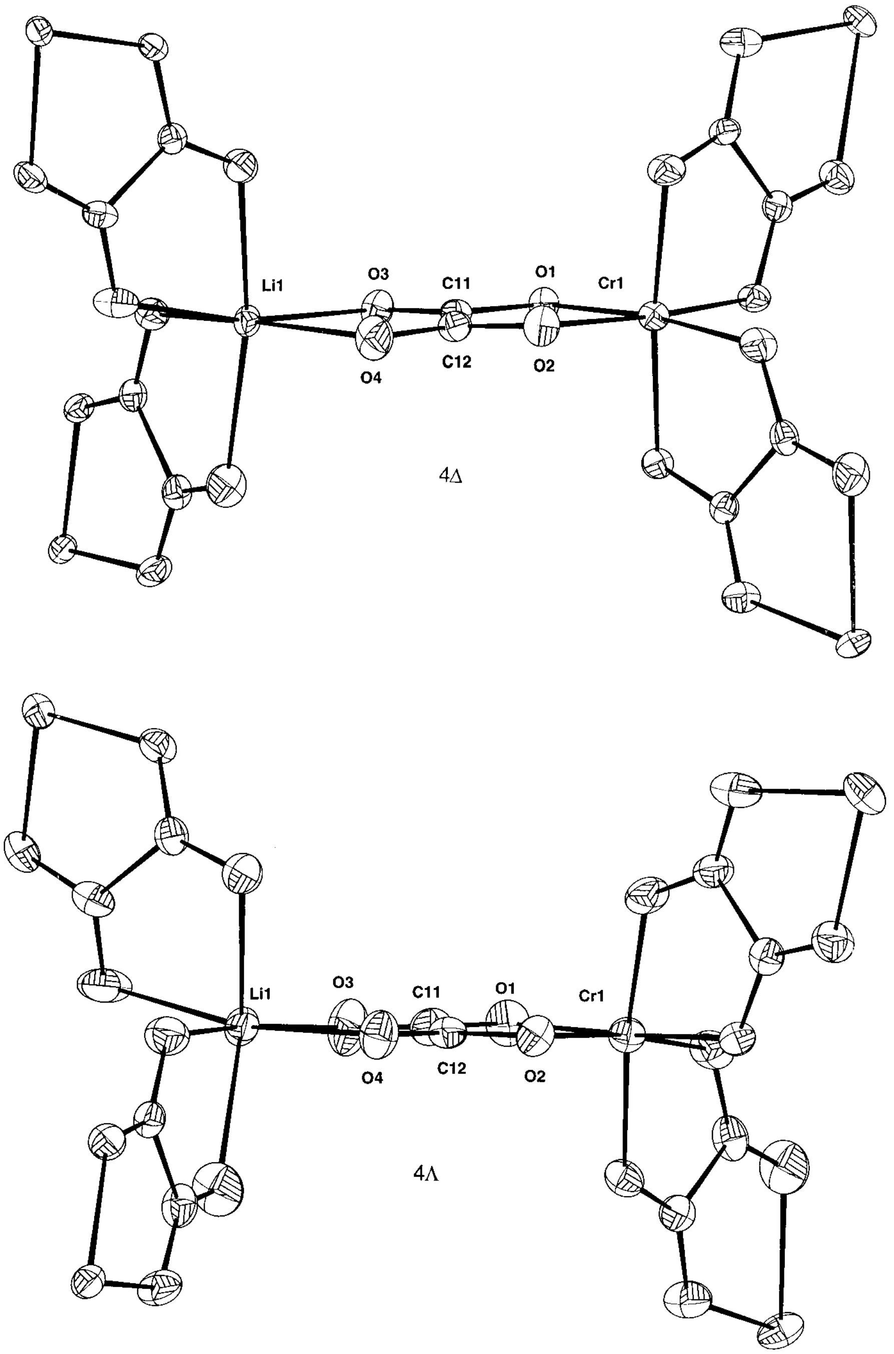

Figure 7. View of the Cr and Li coordination in the three-dimensional oxalate-bridged networks **4**Δ (top) and **4**Λ (bottom). Thermal ellipsoids are drawn at the 30% probability level.

all together form the 3D network. The Λ-configuration of the chiral subunits produces a right-handed (P) helical strands in **4**Λ. Correspondingly, subunits with a Δ-configuration bring out a left-handed (M) helicity in **4**Δ.

Concluding Remarks

In this paper, we have described the simple and effective synthesis of optically active homo- and bimetallic oxalate-bridged networks $[M_2(ox)_3]_n$, using optically active tris-chelate complexes (anionic $[Cr(ox)_3]^{3-}$ or cationic $[M(bpy)_3]^{2+}$, M = Ni, Ru) as building blocks.

Formation of these polymers is highly enantioselective. The control over chirality of only one type of the building blocks leads to the selective formation of the corresponding enantiomer. Adequate experimental conditions leading to optimal optical activity can be achieved either by using configurationally stable chiral building blocks or by using easily racemizable species in conditions of rapid precipitation of polymers. Solid-state circular dichroism is a useful tool in the characterization of the enantiomeric polymers.

A phenomenon of partial spontaneous resolution has been observed when preparation of $\{[Ni(bpy)_3][LiCr(ox)_3]\}_n$ (**2**) takes place in slow reaction conditions, as it is for the crystallization in gel.

In the case of two-dimensional polymers, the use of enantiomerically pure building blocks causes structural modifications in the crystal lattice. A complete analysis of the structure and the magnetic behavior of this kind of optically active polymers are now under study. Monocationic complexes possessing a propeller-like chirality should be able to operate as template

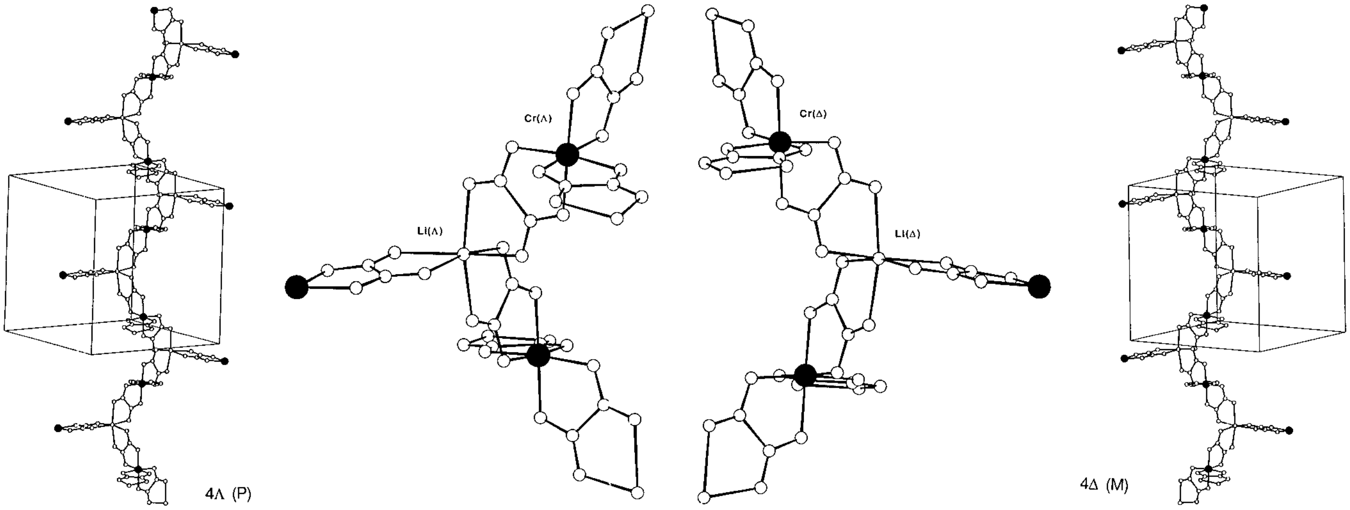

Figure 8. Comparative view of helical strands along 2-fold screw axis within the enantiomeric 3D (10, 3) networks **4Λ** (left) and **4Δ** (right).

counterion in building three-dimensional optically active [M^{III}-(ox)M^{II}] networks. These studies are currently in progress in our laboratory.

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Supporting Information Available: Tables of fractional parameters, anisotropic thermal parameters, interatomic distances, and angles for **2Δ**, **4Δ**, and **4Λ**. This material is available free of charge via the Internet at http://pubs.acs.org.

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