Syntheses, Crystal Structures, and CD Spectra of Simple Heterobimetallic Transition Metal Binaphtholates

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The first pseudooctahedral tris(binaphtholates) of first-row transition elements, $Na_3[Fe(S\text{-binaphtholate})_3]\cdot 3Et_2O\cdot H_2O$ (**1**), $Li_3[Fe(R\text{-binaphtholate})_3]\cdot 6THF$ (**2**), and $Li_3[Cr(R\text{-binaphtholate})_3]\cdot 6THF$ (**3**), are heterobimetallic complexes incorporating alkali metal ions. **1** crystallizes in the monoclinic spacegroup $P2_1$ with $a = 11.3256(10)$ Å, $b = 20.735(3)$ Å, $c = 13.5741(15)$ Å, $\beta = 91.086(8)°$, and $Z = 2$. **2** and **3** are isomorphous, crystallizing in the hexagonal space group $P6_322$ with $a = 14.897(15)$ Å, $b = 19.2849(19)$ Å, and $Z = 2$ (**2**) and $a = 14.850(4)$ Å, $b = 19.052(7)$ Å, and $Z = 2$ (**3**). The CD and absorption spectra of the Fe(III) and Cr(III) compounds are discussed and compared with those reported for $[Fe(enterobactin)]^{3-}$ and model compounds and for $[Cr(entereobactin)]^{3-}$, respectively.

Introduction

Axially dissymmetric binaphthyl units have proved to have high chiral recognition properties, and functionalized binaphthyl subunits have been used to control the stereochemisty of several reactions over a period of many years. One of the simplest and most effective of such compounds is binaphthol, single enantiomers of which have frequently been used to modify Lewis acids in order to achieve high enantioselectivity in both stoichiometric and catalytic reactions.[1] The hard-base character of the oxygen atoms makes this compound ideal for attaching to high-oxidation-level metal ions, and binaphtholates of titanium(IV) or zirconium(IV), for example, have been used successfully as reagents or catalysts for Diels−Alder and ene reactions, producing high ee (enantiomeric excess) values.[2−9]

For the most part, these reagents have been prepared from simple transition metal salts and binaphthol and used in situ. However, the nature of the active species in many of the reactions is uncertain, as their lability has rendered their isolation and structural characterization difficult. The few examples that have been described often reveal unexpected complexities. Thus the interaction of substituted binaphthols and $[Ti(OPr^i)_4]$ produced bridged and binuclear compounds such as $[(R_2\text{-binaphtholate})Ti(OPr^i)_2]_2$ and $[(R_2\text{-binaphtholate})Ti_2(OPr^i)_6]$, as well as $[(R_2\text{-binaphtholate})Ti(OPr^i)_2]$.[10] (The authors also commented that the derivatives of the substituted binaphthols were considerably more amenable to isolation and purification than those of binaphthol itself.) [Ethylenebis(4,5,6,7-tetrahydro-1-indenyl)]titanium binaphtholate[11] and a related bridged titanocene derivative[12] have also been described, as have binaphtholate derivatives of Mo, W, and Os, often with other supporting ligands.[13−17] Complexes with the soft-acid centers Pd^{II} and Pt^{II} are also known,[16,18,19] though a potential complicating factor here is a propensity for the formation of C-bonded binaphtholates.

Seven-coordinate rare earth metal complexes of the general form $[LnM_3(\text{binaphtholate})_3(OH_2)(THF)_6]$ (M is an alkali metal and Ln is a lanthanide ion) were recently isolated and examined.[1,20,21] Described as heterobimetallic, they consist of lanthanide ions with the alkali metal ions of the three $(THF)_2M^+$ units coordinated to the oxygen atoms of adjacent binaphtholates. These compounds catalyze a number of reactions, including asymmetric nitroaldol and Michael reactions, though their performance is critically dependent on the nature of both the rare earth metal and the alkali metal ions involved.

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Table 1. Experimental Details of the Crystallographic Studies for **1**−**3**

	1	**2**	**3**
empirical formula	$Na_3Fe(C_{20}H_{12}O_2)_3{\cdot}3Et_2O{\cdot}H_2O$	$Li_3Fe(C_{20}H_{12}O_2)_3{\cdot}6THF$	$Li_3Cr(C_{20}H_{12}O_2)_3{\cdot}4.2THF$
fw	1218.08	1326.18	1228.54
crystal system	monoclinic	hexagonal	hexagonal
space group	$P2_1$	$P6_322$	$P6_322$
a/Å	11.3256(10)	14.897(15)	14.850(4)
b/Å	20.735(3)		
c/Å	13.5741(15)	19.2849(19)	19.052(7)
β/deg	91.086(8)		
V/Å^3	3187.1(7)	3706.4(6)	3638.5(19)
Z	2	2	2
D_c/g cm^{-3}	1.269	1.221	1.121
F(000)	1278	1438	1290
μ(Mo Kα)/mm^{-1}	0.316	0.265	0.211
T/K	291	291	291
R^a	0.0505	0.0843	0.0768
$R_w{}^b$	0.1095	0.2190	0.2012

^{a} $R = \sum(|F_o| - |F_c|)/\sum(F_o)$. ^{b} $R_w = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

Rather surprisingly, there have been no reports of first-row d-block transition metal compounds containing only binaphthol or binaphtholate ligands. A brief account of an Al analogue[22] has been published, and the preparation of W^{VI}(binaphtholate)$_3$ has been reported[17] but no crystal structure was obtained. The nearest analogues of our complexes are the tris(catecholate) complexes of Fe(III) and Cr(III) prepared by Raymond et al.[23] There is a recent report[24] of the Ga(III), Fe(III), and Cr(III) complexes of a macrobicyclic ligand based on binaphthol, but again no crystal structures are reported. We describe here the isolation, crystal structures, and CD and absorption spectra of the heterobimetallic complexes Na_3[Fe(*S*-binaphtholate)$_3$]·$3Et_2O{\cdot}H_2O$, Li_3[Fe(*R*-binaphtholate)$_3$]·6THF, and Li_3[Cr(*R*-binaphtholate)$_3$]·6THF.

Experimental Section

Reactions were carried out under an atmosphere of pure, dry nitrogen but worked up in air. Microanalyses were performed at the Glasgow University microanalytical laboratory. CD spectra were measured by the U.K. National CD Service (King's College London) (Na_3[Fe(*S*-binaphtholate)$_3$]) or on a home-built instrument [25] (Li_3[Cr(*R*-binaphtholate)$_3$]). CD spectra were calibrated against $[Co(en)_3]^{3+}$ [26] and Ni(spartein)Cl_2.[27] The magnetic moment of **1** was measured using a Faraday balance. Binaphthol was resolved enzymatically by following a known procedure.[28]

Na_3[Fe(*S*-binaphtholate)$_3$]·$3Et_2O{\cdot}H_2O$ (1). To a solution of disodium *S*-binaphtholate prepared from *S*-binaphthol (2.86 g, 0.01 mol) and sodium hydride (0.48 g, 0.02 mol) in THF (50 mL) was added anhydrous $FeCl_3$ (0.54 g, 0.003 mol). The dark red-brown mixture was stirred overnight and then refluxed for 1 h. The mixture was filtered to remove a small amount of precipitate, and the solvent was then removed under vacuum. The product was soluble in THF, ether, acetone, acetonitrile, and toluene but decomposed in protic or chlorinated solvents. It proved difficult to crystallize but was eventually obtained in small amount as the solvate Na_3[Fe(*S*-binaphtholate)$_3$]·$3Et_2O{\cdot}H_2O$ from ether. Anal. Calcd for $C_{72}H_{68}FeNa_3O_{10}$: C, 70.99; H, 5.62. Found: C, 68.07; H, 5.67. These crystals proved suitable for X-ray analysis.

Li_3[Fe(*R*-binaphtholate)$_3$]·6THF (2). The preparation was performed as above by the reaction between dilithium *R*-binaphtholate, prepared from *R*-binaphthol (0.5 g, 1.75 mmol) and lithium hydride (0.0278 g, 3.47 mmol), and anhydrous $FeCl_3$ (0.0946 g, 0.58 mmol) in THF (50 mL). The red-brown product was crystallized from THF as the solvate Li_3[Fe(*R*-binaphtholate)$_3$]·6THF in a form suitable for X-ray analysis, but these crystals readily lost THF on standing. Slow recrystallization from ether also produced red crystals of Li_3[Fe(*R*-binaphtholate)$_3$]·$3Et_2O{\cdot}H_2O$, analogous to the sodium salt above. Anal. Calcd for $C_{72}H_{68}FeLi_3O_{10}$: C, 73.98; H, 5.85. Found: C, 73.85; H, 5.5.

Li_3[Cr(*R*-binaphtholate)$_3$]·6THF (3). This was prepared as above from *R*-binaphthol (1.43 g, 5 mmol), LiH (0.079 g, 10 mmol), and $CrCl_3{\cdot}3THF$ (0.624 g, 1.67 mmol). The deep green product proved difficult to crystallize. The complex was eventually obtained as a THF solvate which readily lost THF on standing, and satisfactory microanalyses could not be obtained. An NMR spectrum of the product recorded in CD_3CN, although broad, integrated to a ratio of six THF molecules per Li_3[Cr(*R*-binaphtholate)$_3$] unit. The crystal structure was obtained by coating the crystals with epoxy resin.

Structure Determinations. Details of the data collection and analysis of **1**−**3** are given in Table 1. Compounds **1**−**3** were obtained as red, red, and green crystals, respectively. Single crystals of suitable size were attached to a glass fiber using acrylic resin and mounted on a goniometer head in a general position. Crystals of **2** and **3** were coated with epoxy resin to minimize solvent loss. Data were collected on an Enraf-Nonius TurboCAD4 instrument using graphite-monochromated X-radiation ($\lambda = 0.710\,73$ Å). Precise unit cell dimensions were determined by refinement of the setting angles of 25 high-angle reflections which were flagged during data collection. Standard reflections were measured every 2 h during data collection. Small decays of ca. 11% (**1**), 3% (**2**), and 5% (**3**) were noted, and interpolated corrections were applied to the reflection data. Lorentz−polarization corrections were then applied to the reflection data. ψ-Scans indicated that no absorption corrections were necessary. The structures were solved by direct methods (SIR92).[29] All non-H atoms were allowed anisotropic thermal motion. Aliphatic CH hydrogen atoms were included at calculated positions, with C−H = 0.96 Å. Refinement (SHELXL97)[30] was accomplished by full-matrix least-squares calculations on F^2. The weighting scheme $w = [\sigma^2(F_o)^2 + (AP)^2 + BP]^{-1}$ where $P = (F_o^2/3 + 2F_c^2/3]$ was used, with values of A and $B = 0.0703$ and 0.0 for **1**, 0.0610 and 0.2733 for **2**, and 0.0591 and 0.8873 for **3**. Counting statistics were used to estimate $\sigma(F_o)^2$. Neutral-atom scattering factors, coefficients of anomalous dispersion, and absorption coefficients

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Table 2. Comparison of the Salient Structural Features of Compounds **1**−**3** with Those of Related Compounds (Bond Lengths, Å; Bond Angles, deg)

	1[a]	**2**	**3**	$Li_3Al(binaphtholate)_3$[22]	$K_3Fe(cat)_3$[23]	$K_3Cr(cat)_3$[23]
r_{M-O}	2.013(3)	2.006(3)	1.977(3)	1.891(3)	2.015	1.986
$r_{M-(Na,Li)}$	3.233(3)	2.995(13)	2.955(13)			
$r_{(Na,Li)-O}$	2.249(5)	1.963(12)	1.925(10)	1.944(11)		
O−M−O	86.80(14)	80.2(2)	80.25(19)		81.26	83.56
O−(Na,Li)−O	75.83(15)	83.0(5)	82.84(5)			
M−O−(Na,Li)	98.44(16)	98.4(3)	98.43(3)			
(Na,Li)−M−(Na,Li)	119.77(10)	120.0	120.0			

[a] Average values.

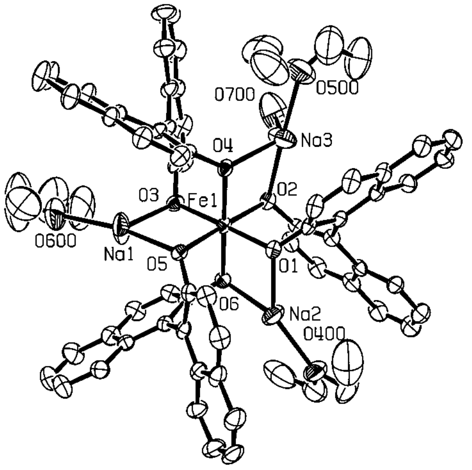

Figure 1. Ortep for Windows[43] drawing of the structure of $Na_3[Fe(S\text{-binaphtholate})_3]\cdot 3Et_2O\cdot H_2O$ (**1**). Thermal ellipsoids are shown at 30% probability.

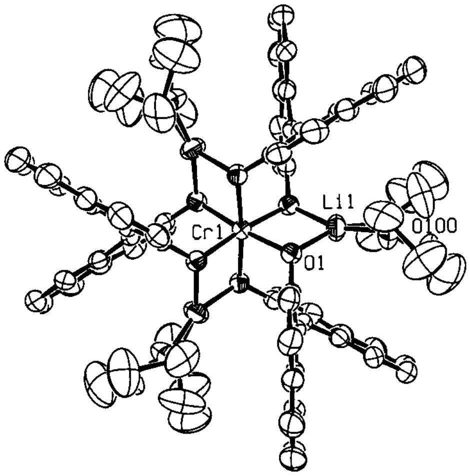

Figure 2. Ortep for Windows[43] drawing of the structure of $Li_3[Cr(R\text{-binaphtholate})_3]\cdot 6THF$ (**2**). Thermal ellipsoids are shown at 30% probability.

were obtained from ref 31. All structures contained solvent molecules of crystallization. For **3**, the refinement indicated a partial occupancy of 4.2 mol of THF per formula of coordination complex. Structural diagrams were drawn using Ortep for Windows.[32]

Results and Discussion

Syntheses and Structures. The complexes were readily prepared from Na_2(binaphtholate) or Li_2(binaphtholate) and the transition metal trichlorides in dry THF. All were soluble in most organic solvents but decomposed in chlorinated media. They proved very difficult to crystallize. However, crystals suitable for X-ray analysis were eventually obtained as solvates from ether or THF. On prolonged standing in moist air, the sodium salts reacted to liberate binaphthol. The structures of all the molecules incorporate solvated Na^+ or Li^+ ions coordinated to the ligand O atoms of adjacent binaphtholate groups. They are thus best described as heterobimetallic species, like the lanthanide complexes,[20,21] rather than anionic transition metal complexes. This does not imply the presence of a metal−metal bond (the M−Na or M−Li distances are much larger than the sum of the appropriate covalent radii). We have no direct evidence that the solid state structures are retained in solution, but the fact that the complexes are soluble in nonpolar solvents such as toluene does suggest this. The solvent molecules are readily lost in air, leading to crystal degradation and decomposition.

The crystal structure of $Na_3[Fe(S\text{-binaphtholate})_3]\cdot 3Et_2O\cdot H_2O$ is shown in Figure 1, with salient bond lengths and angles in Table 2. The molecule is a tris-chelate in which the three $[\text{binaphtholate}]^{2-}$ ions coordinate to an Fe(III) core. The binaphtholate oxygens are further coordinated to three Na^+ ions, each of which is also coordinated to a single Et_2O molecule. In addition, one of the Na^+ ions is coordinated to a water molecule, thus lowering the symmetry of the complex from the idealized D_3. The *S* stereochemistry of the binaphthol imposes the Λ absolute configuration at the metal center. The coordination about the Fe is very close to octahedral; there is a slight trigonal compression (average O−Fe−O angle 86.53°), but surprisingly, in view of the fairly large charge transfer and metal-based CD, a very small (average ∼ 1.5°) twist away from octahedral geometry (the trigonal twist as defined by Kepert[33] is 58.5°). The coordinated ethers at both the 3- and 4-coordinated sodium ions have the rather unusual "W" conformation.

$Li_3[Fe(R\text{-binaphtholate})_3]\cdot 6THF$ (**2**) and $Li_3[Cr(R\text{-binaphtholate})_3]\cdot 4.2THF$ (**3**) are isomorphous. The structure of $Li_3[Cr(R\text{-binaphtholate})_3]\cdot 4.2THF$ is shown in Figure 2, with a stereodiagram in Figure 3. Salient bond lengths and angles for the two complexes are listed in Table 2. The main difference between the two Li^+ complexes and **1** is that each lithium ion is solvated by two THF molecules instead of one Et_2O and there is no coordinated water molecule; thus they have strict D_3 symmetry. In **3**, there is only partial occupancy of the THF molecules. The *R*-binaphtholate ion imposes a Δ stereochemistry at the metal, and in contrast to the case of **1**, there is a pronounced anticlockwise twist from octahedral toward trigonal prismatic geometry (7.5° in the Cr(III) and 4.5° in the Fe(III) complex). The trigonal compression in **2** is essentially the same as that in **1** (86.29°) while **3** is slightly closer to octahedral (88.96°).

Comparison of the structures of the two Fe(III) complexes shows that the alkali metal ion has an effect on the FeO_6 coordination polyhedron. In particular, the Fe−O bond length is slightly larger and the O−Fe−O angle is significantly larger

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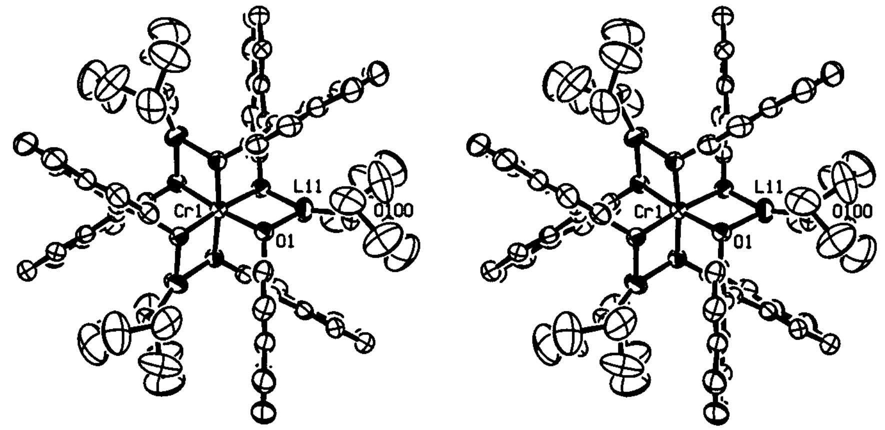

Figure 3. Ortep for Windows[43] stereo drawing of the structure of $Li_3[Cr(R\text{-binaphtholate})_3]$.

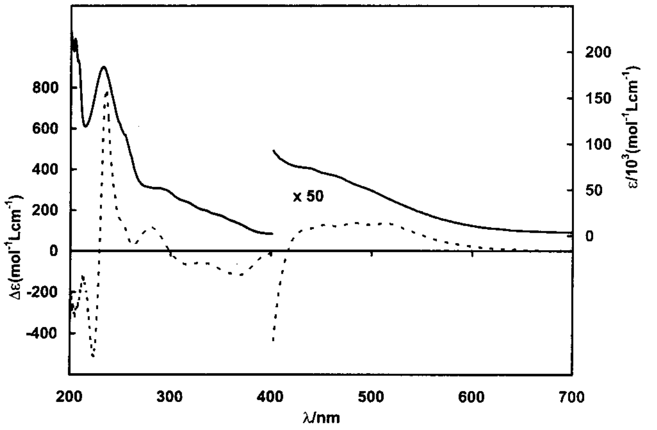

Figure 4. Absorption (full line) and CD (dashed line) spectra of a diethyl ether solution of $Na_3[Fe(S\text{-binaphtholate})_3]$.

in the Na^+ salt. In addition, as mentioned above, the twist away from octahedral geometry toward trigonal prismatic is smaller in the Na^+ salt. The Fe−O and Cr−O bond lengths of **1**/**2** and **3** are similar to those for $K_3Fe(cat)_3$ and $K_3Cr(cat)_3$ (cat = catecholate dianion), respectively.[23] Structural diagrams were drawn using Ortep for Windows.[32]

Absorption and CD Spectra. (a) $Na_3[Fe(S\text{-binaphtholate})_3]$. The CD (circular dichroism) spectrum of *R*-binaphthol consists of an exciton couplet ($\Delta\epsilon = +150$ at 224 nm, -200 at 235 nm) under the higher energy, long-axis polarized ^1B_b band and a weak ($\Delta\epsilon = +13$ at ~320 nm) monosignate CD under the lower short-axis polarized ^1L_a band.[34] The CD spectrum of the *S*-binaphthol used to prepare the metal complex was identical to the published spectrum apart from reversal of sign. The exciton coupling in binaphtholates has been discussed in detail,[35] and the sign of the couplet under the ^1B_b band is routinely used to establish the absolute configuration of derivatized organic molecules.[36] The ^1B_b, ^1L_a nomenclature is explained in ref 35, pp 41−42.

The absorption and CD spectra of $Na_3[Fe(S\text{-binaphtholate})_3]$ are shown in Figure 4. Starting from highest energy, we see an exciton couplet ($\Delta\epsilon = -500$ at 220.5 nm, $+780$ at 235 nm) centered on 229 nm due to the long-axis polarized transitions (^1B_b band) of the binaphtholate dianion. This has essentially the same energy and the same sign pattern as *S*-binaphthol and slightly more than three times the intensity of free *S*-binaphthol. This is expected since the transient electric dipole moments of the three binaphthol units are directed toward the metal atom and therefore cannot couple with each other. The slight increase in intensity of the couplet compared to that of the three free binaphthol units is presumably due to the fact that in the complex the angle between the two naphthol units is slightly larger than that adopted by binaphthol in solution. The CD spectrum of free *S*-binaphthol is available as Supporting Information.

The next couplet ($\Delta\epsilon = +115$ at 280 nm, -70 at 318 nm) centered on 300 nm is, we believe, due to the short-axis polarized transitions (^1L_a band) of the binaphtholate dianion. In binaphthol itself, the two short-axis transitions couple to give rise to a single short-axis transition polarized in a direction parallel to the bond connecting the two naphthalene units. In twisted binaphthol, this cannot give rise to first-order CD, and so, in free binaphthol, the ^1L_a band has weak, monosignate, second-order CD. In the complex, however, the three short-axis polarized ligand transitions **can** couple to give A_2 and E polarized components, which have opposite CD's. The higher energy (A_2) component has a +ve CD, indicating that the three short-axis transitions form a right-handed helix. Inspection of the structure shows that the three C−C bonds connecting the naphthalene units do indeed form a right-handed helix.

The remaining transitions are assigned as ligand → Fe(III) charge-transfer transitions.[37] The lower energy one (550 nm) shows a pronounced vibronic structure ($1250\ cm^{-1}$) in both the absorption and (especially) the CD even at room temperature. The interval is that of an aromatic C−C stretch and suggests that the LUMO contains some admixture of (aromatic) ligand orbitals.

A dissymmetry factor plot confirms that the CD between 350 and 750 nm is mainly due to electric dipole allowed (charge transfer) transitions: $|\Delta\epsilon/\epsilon| < 4 \times 10^{-3}$. It also reveals a transition at 380 nm, however, with a much larger dissymmetry factor ($\Delta\epsilon/\epsilon = 1.5 \times 10^{-2}$). This is likely to be a magnetic dipole allowed d ↔ d transition. The only candidate is the spin-forbidden $^6A_1 \rightarrow {}^2T_1$ transition. If this assignment is correct, an energy of $26\,315\ cm^{-1}$ for the $^6A_1 \rightarrow {}^2T_1$ transition corresponds to a Δ_0/B value (from the Tanabe−Sugano diagram for d^5 ions[38]) of ~27, which puts it close to the high-spin/low-spin crossover ($\Delta_0/B = 28$). The magnetic moment ($5.95\ \mu_B$) corresponds to high-spin Fe(III).

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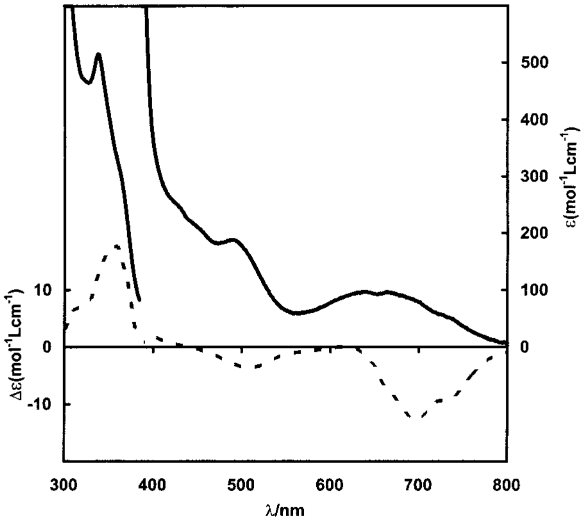

Figure 5. Absorption (full line) and CD (dashed line) spectra of a THF solution of $Li_3[Cr(R\text{-binaphtholate})_3]$.

The positive CD under the ∼500 nm charge-transfer transition for the Λ absolute configuration is in agreement with the sign/configuration correlations found for $[Fe(enterobactin)]^{3-}$ (Ent_{Fe}) and model compounds.[39] The magnitude of the CD (+4.0 mol L^{-1} dm^3 at 514 nm) is essentially the same as that for Ent_{Fe}.

(b) $Li_3[Cr(R\text{-binaphtholate})_3]$. The absorption and CD spectra of $Li_3[Cr(R\text{-binaphtholate})_3]$ in the visible/near-UV region are shown in Figure 5. The lowest energy d ↔ d band, and thus Δ_0, is at slightly lower energy for our compound (655 nm, 15 270 cm^{-1}) than for $K_3[Cr(cat)_3]$ and $[NH_4]_3[Cr(enterobactin)]$ (592 and 586 nm, respectively).[40] The magnitude of the CD is very much larger ($\Delta\epsilon = 13.5$) then that of the last two complexes and is indeed one of the largest Cr(III) CD's ever reported, being larger than those of $Cr(pd)_3$[25] [pd = 2,4-pentanedione], $[Cr(oxalate)_3]^{3-}$,[41] $[Cr(en)_3]^{3+}$,[42] and $[Cr(bipy)_3]^{3+}$,[43] for example. This is probably due to the extremely polarizable nature of the ligand.[26]

Conclusions

We have prepared and crystallographically characterized the first transition metal tris(binaphtholate) complexes and shown that they are structurally very similar to the series of catalytically active lanthanide binaphtholate compounds. Related transition metal binaphtholates have already been established as valuable in situ catalysts for a variety of chiral organic transformations.[1] The complexes provide convenient models for a set of Fe(III) and Cr(III) macrobicyclic ligand complexes recently reported.[24]

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Supporting Information Available: A CD spectrum of free binaphthol and X-ray crystallographic files, in CIF format, for the structure determinations of **1**−**3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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