Lanthanide complexes of an oxazoline-phenoxide hybrid chelate

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Abstract: The synthesis of 2-(2'-hydroxy-3'-allylphenyl)-4,4-dimethyl-2-oxazoline, H-Allox (3), and lanthanide tris chelate complexes, *mer*-Ln(Allox)₃ (Ln = La (4), Ce (5), Sm (6), Er (7), and Y (8)), derived from it are reported. A six-coordinate mer geometry without alkene coordination was confirmed in the solid state by X-ray crystallography for 5 and 7. Variable-temperature NMR experiments suggested that this is the most stable isomer in solution as well, al-though the inequivalent ligand environments undergo rapid averaging at room temperature for all five complexes. A mechanistic investigation indicated that this fluxional process is an intramolecular six-coordinate rearrangement, but it was not possible to distinguish between a Bailar (trigonal) or Rây–Dutt (rhombic) twist. Kinetic parameters for the fluxional process were determined by line shape analysis for 8 yielding $\Delta H^{\ddagger} = 24 \pm 2$ kJ mol⁻¹ and $\Delta S^{\ddagger} = -99 \pm 10$ J mol⁻¹ K⁻¹. The structural and dynamic features of 4–8 were compared with the related In, Ga, and Al tris(2-oxazolylphenoxides).

Key words: oxazoline, phenoxide, lanthanide, Group 3, Rây–Dutt twist, Bailar twist, Eyring plot, X-ray crystallography, mer isomer, variable-temperature NMR, line shape analysis, dynamic NMR, paramagnetic NMR, bidentate ligands.

Résumé : On rapporte la synthèse de la 2-(2'-hydroxy-3'-allylphényl)-4,4-diméthyl-2-oxazoline, H-Allox (**3**) et de complexes de lanthanide trischélates, *mer*-Ln(Allox)₃ (Ln = La (**4**), Ce (**5**), Sm (**6**), Er (**7**) et Y (**8**)) qui en dérivent. Pour les complexes **5** et **7**, les données cristallographiques ont permis de confirmer que, à l'état solide, ces complexes adoptent une géométrie mer six coordinnées sans coordination d'alcène. Les données d'expériences de RMN à température variable suggèrent que, en solution, cet isomère est aussi le plus stable même si les environnements inéquivalents des ligands de chacun de ces cinq complexes sous soumis à une moyenne rapide. Une investigation mécanistique indique que ce processus fluxionnel correspond à un réarrangement intramoléculaire à six coordonnées, mais il n'a pas été possible de faire une distinction entre une torsion de Bailar (trigonale) ou de Rây–Dutt (rhombique). On a déterminé les paramètres cinétiques du processus fluxionnel par une analyse de la forme des bandes du composé **8** et on en a déduit des valeurs de $\Delta H^{\ddagger} = 24 \pm 2$ kJ mol⁻¹ et $\Delta S^{\ddagger} = -99 \pm 10$ J mol⁻¹ K⁻¹. Les caractéristiques structurales et dynamiques des composés **4–8** avec celles des composés apparentés des tris(2-oxazolylphénolates) d'indium, de gallium et d'aluminium.

Mots clés : oxazoline, phénolate, lanthanide, Groupe 3, torsion de Rây–Dutt, torsion de Bailar, courbe de Eyring, cristallographie par diffraction des rayons X, isomère mer, RMN à température variable, analyse de la forme des bandes, RMN dynamique, RMN paramagnétique, ligands bidentates.

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Introduction

The transition metal and Group 13 chemistry of chelating 2-(2'-hydroxyphenyl)-2-oxazoline ligands (H-I) has been extensively studied for two principal reasons. First, this chelate

type is found in nature as part of microbial metal transport agents, especially the Fe(III) transporting siderophores (1, 2). Second, asymmetric ligands of this kind are easily prepared from readily available chiral β -aminoalcohols and the resulting chiral metal complexes have proven useful as

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asymmetric oxidation catalysts (2). Despite the interest in 2-(2'-hydroxyphenyl)-2-oxazolines, and oxazolines in general, as ligands in transition metal chemistry, the Group 3 and lanthanide chemistry of such complexes has not been very well explored. To date, the limited oxazoline coordination chemistry that has been disclosed with these elements has been almost exclusively restricted to the neutral methylenebis(oxazolines) (II, box) (3) or their close relatives containing additional donors: pyridine-bis(oxazolines) (III, pybox) (3, 4), 2,2'-bipyridine-bis(oxazolines) (IV) (3), and dibenzofuranbis(oxazolines) (V) (3). This is remarkable considering the success of these ligands in catalytically active complexes of the d-block metals (2). Indeed, even though little work has been done so far, enantiomerically pure II-V have proven successful in Group 3 and lanthanide chemistry for asymmetric hetero-Diels-Alder (3), glyoxylate-ene (4a), Mukayama-Michael (4b), and annulation and addition reactions of allenylsilanes with aldehydes (4c).

Recently, examples of lanthanide complexes with anionic oxazoline-containing ligands (I, VI, and VII) have been reported (5–7). The tetrakis complex of 2-(2'-hydroxyphenyl)-4,4-dimethyl-2-oxazoline (I) with Ce⁴⁺ was prepared as a possible precursor to CeO₂ films by thermal decomposition. Lanthanide complexes of VI proved effective as asymmetric catalysts for the 1,3-dipolar cycloaddition of nitrones to alkenes, although the structure of the actual catalyst was not established (being formed in situ from Yb(OTf)₃ and VI) (6). The deprotonated box ligand VII has been used to prepare Ln[VII][NR₂]₂ (Ln = Y and R = SiHMe₂; Ln = La, Nd, Sm, Lu, and R = SiMe₃) and Ln[VII][CH(SiMe₃)₂]₂ (7) complexes that serve as hydroamination catalysts.

In this paper, we report the synthesis, solid-state structure, and solution behaviour of lanthanide complexes containing deprotonated 2-(2'-hydroxy-3'-allylphenyl)-4,4-dimethyl-2oxazoline (Allox). The goal of this work is to understand the structural chemistry of tris(oxazoline-phenoxide) complexes of the lanthanides in solid state and solution. Although the present complexes are achiral, their solution behaviour should provide useful information about the suitability of enantiomerically pure variants as asymmetric Lewis acid catalysts. Besides providing some additional steric bulk, the allyl substituent was deliberately incorporated to assess whether coordination of the tethered alkene can occur. We have previously observed rare examples of alkene coordination with lanthanide centres for a phenoxide ligand bearing a tethered allyl group so it was of interest to see if this also occurred with Allox.²

Experimental

General procedures

All manipulations were carried out under an argon or nitrogen atmosphere, with the rigorous exclusion of oxygen and water, using standard glovebox (Braun MB150-GII) or



Schlenk techniques. Tetrahydrofuran (THF), hexane, and toluene were dried by distillation from sodium benzophenone ketyl under argon immediately prior to use. The appropriate lanthanide tris(silylamides), Ln[N(SiMe₃)₂]₃, were prepared according to literature procedures (8). All NMR spectra (¹H, ¹³C) including variable-temperature experiments were recorded on a Bruker AMX-360 MHz spectrometer and referenced to residual solvent resonances. All deuterated solvents were dried over activated 4 Å molecular sieves and spectra were recorded using 5 mm tubes fitted with a Teflon® valve (Brunfeldt). Variable-temperature NMR spectra and plots of δ vs. 1/*T* for paramagnetic complexes 5–7 are included in the Supplementary material,³ while a representative hightemperature spectrum is included in the experimental data for each complex given below. Melting points were recorded using a Büchi melting point apparatus and are not corrected. Elemental analyses were performed by Canadian Microanalytical, Delta, British Columbia. Mass spectra were recorded on a Kratos Concept H spectrometer using electron impact (70 eV) ionization. The molecular ion simulation for complex 6 is shown in Fig. 1; simulations for 4-7 are included in the Supplementary material.³

2-(2'-Hydroxyphenyl)-4,4-dimethyl-2-oxazoline (1)

2-Cyanophenol (10.0 g, 0.0840 mol), $Yb(CF_3SO_3)_3$ (0.52 g, 1.0 mol%), and 2-amino-2-methylpropanol (11.22 g,

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³Supplementary data for this article are available on the Web site or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada. DUD 3656. For more information on obtaining material refer to http://cisti-icist.nrc-cnrc.gc.ca/irm/unpub_e.shtml. CCDC 260761 and 260762 contain the crystallographic data for this manuscript. These data can be obtained, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax +44 1223 336033; or deposit@ccdc.cam.ac.uk).





0.126 mol) were suspended in dry 1,2-dichlorochlorobenzene (150 mL) in a Kontes flask under argon. The flask was sealed and the reaction mixture was heated to 170 °C for 24 h; all solids dissolved upon heating. After cooling, the flask was opened and the contents were poured onto ice (200 g). Dichloromethane (200 mL) was added and the twophase mixture was separated. The organic layer was washed repeatedly with water, dried over anhydr. MgSO₄, filtered, and the solvent removed from the filtrate under vacuum to afford 2-(2'-hydroxyphenyl)-4,4-dimethyl-2-oxazoline (9) as white crystals. Yield: 12.5 g (78%); mp 58-60 °C. ¹H NMR (d-chloroform) δ: 12.17 (br s, 1H, OH), 7.65 (d, 1H, 6'aryl*H*, *J* = 7.5 Hz), 7.34 (t, 1H, 4'-aryl*H*, *J* = 7.5 Hz), 6.98 (d, 1H, 3'-arylH, J = 8.0 Hz), 6.83 (t, 1H, 5'-arylH, J =7.8 Hz), 4.07 (s, 2H, CH₂), 1.37 (s, 6H, CH₃). ¹³C NMR (dchloroform) δ: 164.2 (C=N), 159.9 (2'-arylC), 133.2, 127.9, 118.6, 116.7 (arylCH), 112.4 (1'-arylC), 78.4 (CMe₂CH₂O), 67.1 (CMe₂), 28.5 (CH₃).

2-(2'-Allyloxyphenyl)-4,4-dimethyl-2-oxazoline (2)

The crude 2-(2'-hydroxyphenyl)-4,4-dimethyloxazoline (4.0 g, 0.021 mol) was placed in a round bottomed flask and dissolved in 100 mL of acetone. Excess allylbromide (3.19 g, 0.0264 mol), K₂CO₃ (12.1 g, 0.0872 mol), and n-Bu₄N⁺Br⁻ (0.34 g, 0.0017 mol), as a phase-transfer catalyst, were added. The suspension was stirred vigorously at room temperature for 6 days. The salts were removed by filtration and the solvent was stripped under vacuum. The residue was redissolved in diethyl ether (100 mL), filtered to remove further solids, and again taken to dryness under vacuum. The residue was columned on silica gel (hexane) and the pure allyl ether was isolated as a yellow oil. Yield: 4.11 g (85%). ¹H NMR (*d*-chloroform) δ : 7.61 (d, 1H, 6'-aryl*H*, *J* = 7.8 Hz), 7.24 (t, 1H, 4'-arylH, J = 7.6 Hz), 6.87 (d, 1H, 3'-arylH, J = 7.9 Hz), 6.81 (t, 1H, 5'-arylH, J = 7.8 Hz), 5.95 (m, 1H, $CH=CH_2$), 5.46 (d, 1H, $CH=CH_{trans}$, J = 16.9 Hz), 5.17 (d, 1H, CH= CH_{cis} , J = 11.1 Hz), 4.46 (d, 2H, OC H_2 CH=CH₂, J = 6.6 Hz), 3.98 (s, 2H, CH₂), 1.32 (s, 6H, CH₃). HR-MS (EI) calcd.: M⁺ 231.1259; found: 231.1271.

2-(2'-Hydroxy-3'-allylphenyl)-4,4-dimethyl-2-oxazoline (H-Allox, 3)

Neat allyl ether 2 (3.3 g, 0.014 mol) was placed in a Kontes flask and heated with rapid stirring at 160 °C for 36 h. The resulting brown oil was chromatographed on silica gel (hexane - diethyl ether, 30:1) to afford 3 as a strawcolored oil. Carrying out the Claissen rearrangement at higher temperatures decreases the time required, but results in considerable production of the 4'-allyl isomer that is difficult to remove chromatographically. Yield: 2.9 g (88%). ¹H NMR (d-chloroform) δ : 12.42 (br s, 1H, OH), 7.43 (d, 1H, 6'-arylH, J = 7.7 Hz), 7.18 (d, 1H, 4'-aryl*H*, J = 7.8 Hz), 6.72 (t, 1H, 5'-arylH, J = 7.7 Hz), 5.95 (m, 1H, CH=CH₂), 5.05 (d, 1H, $CH=CH_{trans}, J = 16.5 Hz$, 5.02 (d, 1H, $CH=CH_{cis}, J =$ 10.1 Hz), 4.01 (s, 2H, CH₂), 3.39 (d, 2H, CH₂CH=CH₂, J =6.7 Hz), 1.30 (s, 6H, CH_3). ¹³C NMR (*d*-chloroform) δ : 164.1 (C=N), 158.0 (2'-arylC), 136.9 (CH=CH₂), 133.6 (arylCH), 127.8 (3'-arylC), 126.2, 118.4 (arylCH), 115.8 $(CH=CH_2)$, 112.4 (1'-arylC), 78.6 (CMe_2CH_2O) , 67.3 (CMe_2) , 34.3 $(CH_2CH=CH_2)$, 28.8 (CH_3) . HR-MS (EI) calcd.: M⁺ 231.1259; found: 231.1265.

$La(Allox)_3$ (4)

A solution of **3** (0.069 g, 0.30 mmol) in 4 mL of toluene was added to a solution of $La[N(SiMe_3)_2]_3$ (0.062 g, 0.10 mmol) in 4 mL of toluene in the glovebox. The solution immediately turned pale yellow and all solids dissolved. The solution was stirred overnight at room temperature and the solvent was removed under reduced pressure to yield a granular white solid. The solid was redissolved in a minimum of hot hexane–toluene (80:20), filtered though a Celite[®] pad, and the filtrate was then allowed to slowly cool to room tem-

perature. The clear, colorless blocks of 4 that deposited from solution were collected by vacuum filtration and dried under vacuum. Yield: 0.061 g (73%); mp 180–182 °C. ¹H NMR $(d_8$ -toluene) δ : 7.90 (dd, 1H, 6'-aryl*H*, J = 7.7, 1.8 Hz), 7.20 (dd, 1H, 4'-arylH, J = 7.2, 1.8 Hz), 6.59 (t, 1H, 5'-arylH, J = 7.5 Hz), 5.98 (m, 1H, CH=CH₂), 5.00 (d, 1H, $CH=CH_{trans}$, J = 17.1 Hz), 4.90 (d, 1H, $CH=CH_{cis}$, J =10.3 Hz), 3.47 (s, 2H, OCH₂), 3.45 (d, 2H, CH₂CH=CH₂, J = 6.7 Hz), 1.27 (s, 6H, CMe_2). ¹³C NMR (d_8 -toluene) δ : 168.0 (C=N), 157.8 (2'-arylC), 137.6 (CH=CH₂), 135.1 (arylCH), 130.9 (arylC), 115.3 (arylCH), 115.0 (CH=CH₂), 112.0 (1'-arylC), 78.0 (CMe₂CH₂O), 67.4 (CMe₂), 35.5 (CH₂CH=CH₂), 28.5 (CH₃). The remaining aryl C resonance was not discernible. MS (EI) m/z (amu): 829 (M^{+ 139}La, 44%), 599 (M⁺ – L, 10%), 527 (M⁺ – L – (C₄H₈O), 7%), 455 $(M^+ - L - 2(C_4H_8O), 100\%)$. Anal. calcd. for C₄₂H₄₈N₃O₆La (%): C 60.80, H 5.83, N 5.06; found: C 61.22, H 5.52, N 5.00.

Ce(Allox)₃ (5)

Complex **5** was prepared using a procedure analogous to **4** from Ce[N(SiMe₃)₂]₃ (0.062 g, 0.10 mmol) and 3 equiv. of **3**. Small, bright yellow blocks of **5** were isolated by allowing a warm (60 °C) hexane-toluene solution to cool to room temperature. Yield: 0.072 g (87%); mp 196–199 °C. ¹H NMR (d_8 -toluene, 323 K) δ : 11.86 (d, 3H, 6'-aryl*H*, J = 7.4 Hz), 10.63 (d, 3H, 4'-aryl*H*, J = 6.8 Hz), 9.37 (t, 3H, 5'-aryl*H*, J = 6.3 Hz), 8.06 (m, 3H, CH=CH₂), 5.65 (d, 3H, CH=CH_{trans}, J = 14 Hz), 5.39 (d, 3H, CH=CH_{cis}, J = 8 Hz), 4.27 (br s, $v_{1/2} = 18$ Hz, 6H, CH₂CH=CH₂), 1.00 (s, $v_{1/2} = 8$ Hz, 6H, CH₂), -9.48 (br s, $v_{1/2} = 34$ Hz, 18H, CH₃). MS (EI) m/z (amu): 830 (M^{+ 140}Ce, 43%), 516 (100%). Anal. calcd. for C₄₂H₄₈N₃O₆Ce (%): C 60.71, H 5.82, N 5.06; found: C 61.05, H 5.71, N 4.92.

$Sm(Allox)_3$ (6)

Complex 6 was isolated as colorless crystals in the same manner as 4 and 5 previously starting from $Sm[N(SiMe_3)_2]_3$ (0.063 g, 0.10 mmol) and 3 equiv. of 3. Yield: 0.052 g (62%); mp 173–176 °C. IR (Nujol, NaCl, cm⁻¹): 1652 (vw), 1635 (sh w), 1597 (s), 1558 (w), 1345 (w), 1260 (s), 1226 (vw), 1190 (w), 1160 (w), 1132 (m), 1096 (m), 1065 (w), 1055 (w), 862 (w), 822 (w), 768 (m), 750 (w), 720 (w), 667 (m). The IR spectra of complexes 4, 5, 7, and 8 were superimposable with that of 6. ¹H NMR (d_8 -toluene, 373 K) δ: 9.23 (d, 3H, 6'-arylH, J = 8.7 Hz), 7.87 (d, 3H, 4'-arylH, J = 6.5 Hz), 7.68 (t, 3H, 5'-arylH, J = 8.5 Hz), 6.10 (m, 3H, $CH=CH_2$), 4.97 (d, 3H, $CH=CH_{trans}$, J = 16 Hz), 4.85 (d, 3H, $CH=CH_{cis}$, J = 11 Hz), 2.83 (d, 6H, $CH_2CH=CH_2$, J = 11 Hz), 2.83 (d, 6H, $CH_2CH=CH_2$, J = 11 Hz), 2.83 (d, 6H, $CH_2CH=CH_2$), J = 11 Hz), 2.83 (d, 6H, $CH_2CH=CH_2$), J = 10 Hz), 2.83 (d, 6H, CH_2CH=CH_2), J = 10 Hz), 2.83 (d, 6H, CH_2CH=CH_2CH=CH_2), J = 10 Hz), 2.83 (d, 6H, CH_2CH= 6.4 Hz), 2.73 (s, 6H, CH₂), -2.94 (br s, $v_{1/2}$ = 4 Hz, 18H, CH₃). MS (EI) *m*/*z* (amu): 842 (M^{+ 152}Sm, 68%), 612 (M⁺ -L, 10%), 540 (M⁺ – L – (C₄H₈O), 16%), 468 (M⁺ – L – 2(C₄H₈O), 100%). Anal. calcd. for $C_{42}H_{48}N_3O_6Sm$ (%): C 59.97, H 5.75, N 5.00; found: C 60.30, H 5.58, N 5.01.

Er(Allox)₃ (7)

Complex 7 was obtained as well-formed, bright pink prisms using the procedure outlined for 4 previously starting from Er[N(SiMe₃)₂]₃ (0.065 g, 0.10 mmol) and 3 equiv. of 3. Yield: 0.077 g (90%); mp 168–170 °C. ¹H NMR (d_8 -toluene, 373 K, all resonances are broad singlets) δ : 80.1 ($v_{1/2}$ =

4400 Hz, 18H, *CH*₃), 37.8 ($v_{1/2}$ = 480 Hz, 6H, *CH*₂), -1.51 ($v_{1/2}$ = 68 Hz, 3H, alkene*H*), -7.0 ($v_{1/2}$ = 180 Hz, 3H, alkene*H*), -12.1 ($v_{1/2}$ = 50 Hz, 3H, aryl*H*), -15.3 ($v_{1/2}$ = 35 Hz, 3H, aryl*H*), -20.8 ($v_{1/2}$ = 80 Hz, 3H, aryl*H*). One CH₂ (6H) resonance was not observable. MS (EI) *m*/*z* (amu): 858 (M⁺ ¹⁶⁸Er, 100%), 628 (M⁺ - L, 7%), 554 (M⁺ - L - (C₄H₈O), 12%), 482 (M⁺ - L - 2(C₄H₈O), 43%). Anal. calcd. for C₄₂H₄₈N₃O₆Er (%): C 58.79, H 5.64, N 4.90; found: C 60.71, H 5.92, N 4.62.

Y(Allox)₃ (8)

Complex 8 was isolated as colorless crystals using the procedure described for 4 starting from $Y[N(SiMe_3)_2]_3$ (0.057 g, 0.10 mmol) and 3 equiv. of 3. Yield: 0.036 g (63%); mp 185 to 186 °C. ¹H NMR (d_8 -toluene) δ : 7.90 (dd, 3H, 6'-arylH, J = 8.0, 1.9 Hz), 7.16 (dd, 3H, 4'-arylH, J =7.3, 1.9 Hz), 6.57 (t, 3H, 5'-arylH, J = 7.7 Hz), 5.89 (m, 3H, $CH=CH_2$), 4.95 (d, 3H, $CH=CH_{trans}$, J = 17.0 Hz), 4.86 (d, 3H, CH=C H_{cis} , J = 10.0 Hz), 3.51 (s, 6H, C H_2), 3.40 (d, 6H, $CH_2CH=CH_2$, J = 6.7 Hz), 1.25 (s, 18H, CMe_2). ¹³C NMR $(d_8$ -toluene) δ : 138.1 (CH=CH₂), 134.8 (arylCH), 132.2 (arylC), 115.1 (arylCH), 114.7 (CH=CH₂), 112.5 (1'-arylC), 78.1 (CMe₂CH₂O), 67.8 (CMe₂), 35.4 (CH₂CH=CH₂), 28.4 (CH_3) . The remaining aryl C resonances and the oxazoline C=N resonance were not discernible. MS (EI) m/z (amu): 779 (M^{+ 89}Y, 100%), 405 (M⁺ – L – 2(C₄H₈O), 26%). Anal. calcd. for C42H48N3O6Y (%): C 64.69, H 6.20, N 5.39; found: C 65.01, H 6.44, N 5.15.

X-ray crystallographic studies

Crystals of 5 and 7 suitable for X-ray crystallography were grown by allowing a hot, concentrated, toluene-hexane solution to slowly cool to room temperature. Typical crystallographic procedures are illustrated for compound 5 in the following section. Crystals of 5 suitable for X-ray diffraction were removed from the flask, covered with a layer of hydrocarbon oil, attached to a glass fiber, and placed in the lowtemperature nitrogen stream (10). Data was collected at 83(2) K using a Bruker/Siemens SMART APEX instrument (Mo K α radiation, $\lambda = 0.71073$ Å) equipped with a Cryocool NeverIce low-temperature device. Data were measured using ω scans of 0.3° per frame for 30 s, and a full sphere of data was collected. A total of 2132 frames were collected with a final resolution of 0.77 Å. The first 50 frames were recollected at the end of data collection to monitor for decay. Cell parameters were retrieved using SMART (11) software and refined using SAINTPlus (12) on all observed reflections. Data reduction and correction for Lorentzian polarization and decay were performed using the SAINTPlus (12) software. Absorption corrections were applied using SADABS (13). The structure was solved by direct methods and refined by the least-squares method on F^2 using the SHELXTL program package (14). The structure was solved in the space group $P2_1/n$ (No. 14) by analysis of systematic absences. All atoms were refined anisotropically. One of the terminal vinyl groups was disordered. This was modeled with an occupancy of 66% for the major fraction. Soft restraints were applied to maintain the correct geometry. No decomposition was observed during data collection. Details of the data collection and refinement are given in Ta-

Table 1. Crystallographic data for Ln(Allox)₃ (5 (Ce), 7 (Er)).

Empirical formula	C ₄₂ H ₄₈ CeN ₃ O ₆	C ₄₂ H ₄₈ ErN ₃ O ₆
Formula weight	831.0	858.1
Temperature (K)	83	223
Wavelength (Å)	0.710 73	0.710 73
Crystal system	Monoclinic	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i> (No. 14)	$P2_1/n$ (No. 14)
<i>a</i> (Å)	14.641 1(10)	14.426(3)
<i>b</i> (Å)	15.057 6(10)	15.186(3)
<i>c</i> (Å)	17.102 3(11)	17.065(4)
β (°)	94.976(1)	93.849(4)
Volume (Å ³)	3756.2(4)	3781.5(13)
Ζ	4	4
Density (calcd., g/cm ³)	1.47	1.51
Absorption coeff. (μ , mm ⁻¹)	1.264	2.27
<i>F</i> (000)	1708	1748
Crystal size (mm)	$0.13 \times 0.08 \times 0.07$	$0.16 \times 0.17 \times 0.37$
Crystal color and habit	Yellow needle	Pink needle
Diffractometer	Bruker Smart APEX	Bruker Smart 1000
θ range (°)	1.80-27.50	2.0-25.0
Reflections collect., independent	48 791, 8 624	19 548, 6 679
Max and min transmission	0.92 and 0.85	1.00 and 0.85
Data / restraints / parameters	8 624 / 7 / 482	6 679 / 2 / 488
Goodness-of-fit on F^2	1.01	0.92
Final <i>R</i> indices $(I > 2\sigma(I))$	R1 = 0.045, wR2 = 0.093	R1 = 0.024, wR2 = 0.046
R (all data)	R1 = 0.092	R1 = 0.057
Largest diff. peak and hole $(e/Å^3)$	2.351 and -0.745	0.50 and -0.29

ble 1. Further details are provided in the Supplementary material.³

Results and discussion

Synthesis and characterization

The chelating neutral ligand 2-(2'-hydroxy-3'-allylphenyl)-4,4-dimethyl-2-oxazoline (HAllox, **3**) was prepared in three steps from 2-cyanophenol as illustrated in Scheme 1. The oxazoline ring was first introduced by the Lewis-acidcatalyzed cyclization of 2-cyanophenol and 2-amino-2methylpropanol using ytterbium triflate as the catalyst. Although this reaction proceeds slowly at 170 °C in 1,2dichlorobenzene, we prefer this route to the ZnCl₂-catalyzed cyclization (9) because the product is cleaner and yields are comparable. Introduction of the 3'-allyl group was achieved in two steps by the Claissen rearrangement of the allyl phenyl ether **2**.

Lanthanide complexes **4–8** of the new oxazoline-phenoxide ligand were most readily prepared by an acid–base reaction between the neutral ligand **3** and $Ln[N(SiMe_3)_2]_3$ in toluene (Scheme 1: Ln = La **4**, Ce **5**, Sm **6**, Er **7**, Y **8**). Metathesis reactions between the lithium salt LiAllox and YCl₃ or LaCl₃ in THF produced **4** or **8**, respectively, but the yields were much lower by this route (20%–30%). The complexes displayed the characteristic colour of each ion (Ce yellow, Er pink, La, Sm, Y colourless). Complexes **4–8** display similar melting points and their IR spectra as Nujol mulls are superimposable suggesting that these complexes are isostructural in the solid state. This observation was confirmed for **5** and **7** by X-ray crystallography (vide infra). All complexes gave an acceptable elemental analysis, but the carbon percentage was slightly high in all cases, possibly indicating retention of toluene solvent (from recrystallization).

All of the Ln(Allox)₃ complexes prepared gave wellbehaved mass spectra with molecular ions as the base peaks for complexes of the smaller metals (Er 7 and Y 8). Simulation of the molecular ion pattern provided unequivocal evidence for the formation of the tris chelate complexes, especially for 4–7, since these metals have distinctive isotopic patterns. An example of the match between the experimental and calculated molecular ion pattern is shown in Fig. 1 for Sm(Allox)₃ (6). The dominant fragments in the mass spectra of 4–8 represent the loss of one or two ligands and the loss of C₄H₈O, presumably from cleavage of the oxazoline ring. The latter has been observed previously during the thermal decomposition of Ce(Me₂-phenox)₄ (Me₂phenox, ligand I) (5).

Solid-state structures

Crystallographic data for **5** and **7** are summarized in Table 1. Selected distances and angles are given in Table 2, and ORTEP3 (15) plots of the structures are shown in Figs. 2 (**5**, Ce) and 3 (**7**, Er). The structures of **5** and **7** are very similar to one another, showing a distorted octahedral coordination environment and a mer arrangement of the three chelating Allox ligands. The allyl groups clearly are not within bonding distance of the metal as the closest contacts between the internal or terminal alkene carbons and the metals are more than 4 Å.

More than 40 structures have been reported of metal complexes containing derivatives of the 2-oxazolylphenoxide chelate unit. These structures span all groups of the d-block and the Group 13 metals, but there are no examples containScheme 1.



Table 2. Selected distances and angles for Ln(Allox)₃ (5 (Ce), 7 (Er)).^a

5		7	
Bond distances (Å)			
Ce(1)—N(1A)	2.697(3)	Er(1) - N(1)	2.420(3)
Ce(1)—N(1B)	2.584(4)	Er(1) - N(2)	2.433(3)
Ce(1)—N(1C)	2.577(4)	Er(1)—N(3)	2.541(3)
Ce(1)—O(1A)	2.260(3)	Er(1) - O(1)	2.148(2)
Ce(1)—O(1B)	2.251(3)	Er(1)—O(3)	2.124(3)
Ce(1)—O(1C)	2.275(3)	Er(1)—O(5)	2.140(2)
Bond angles (°)			
Ce(1)-O(1A)-C(1A)	148.9(3)	Er(1)-O(1)-C(1)	142.7(2)
Ce(1)-O(1B)-C(1B)	147.3(3)	Er(1)-O(3)-C(15)	143.9(2)
Ce(1)-O(1C)-C(1C)	146.2(3)	Er(1)-O(5)-C(29)	146.4(2)
N(1A)-Ce(1)-N(1B)	107.79(11)	N(1)-Er(1)-N(2)	160.7(9)
N(1A)-Ce(1)-N(1C)	92.92(11)	N(1)-Er(1)-N(3)	91.02(10)
N(1A)-Ce(1)-O(1A)	68.62(11)	N(1)- $Er(1)$ - $O(1)$	75.41(9)
N(1A)-Ce(1)-O(1B)	161.41(11)	N(1)-Er(1)-O(3)	90.72(9)
N(1A)-Ce(1)-O(1C)	92.23(11)	N(1)-Er(1)-O(5)	100.61(9)
N(1B)-Ce(1)-N(1C)	156.48(12)	N(2)-Er(1)-N(3)	105.77(10)
N(1B)-Ce(1)-O(1A)	95.78(11)	N(2)-Er(1)-O(1)	94.46(9)
N(1B)-Ce(1)-O(1B)	69.94(11)	N(2)-Er(1)-O(3)	75.14(10)
N(1B)-Ce(1)-O(1C)	97.49(10)	N(2)-Er(1)-O(5)	93.50(9)
N(1C)-Ce(1)-O(1A)	102.22(11)	N(3)-Er(1)-O(1)	90.87(9)
N(1C)-Ce(1)-O(1B)	93.90(11)	N(3)-Er(1)-O(3)	166.86(9)
N(1C)-Ce(1)-O(1C)	70.02(11)	N(3)-Er(1)-O(5)	73.24(9)
O(1A)-Ce(1)-O(1B)	93.01(11)	O(1)-Er(1)-O(3)	102.16(9)
O(1A)-Ce(1)-O(1C)	159.36(11)	O(1)-Er(1)-O(5)	163.67(9)
O(1B)-Ce(1)-O(1C)	106.36(11)	O(3)-Er(1)-O(5)	93.65(9)

^aEstimated standard deviations are in parentheses.

ing Group 3, lanthanide, (or actinide) ions.⁴ Of the published structures, the best comparisons to 5 and 7 are the six-coordinate, tris chelate complexes of Al, Ga, and In, all of which also adopt a mer geometry (16). In fact, the other known tris chelates of this ligand type, three for Mn (2d, 2h)

and one for Fe (17), crystallize exclusively in the mer geometry. There appears to be a pronounced trans influence operative in **5** and **7** as the M—N distance trans to oxygen is ca. 0.12 Å longer than that trans to nitrogen in both cases. A similar, but much smaller, effect is observed in the tris che-

⁴A complete listing of these structures and a table summarizing important metrical parameters is given in the Supplementary material.³

Fig. 2. ORTEP3 (16) plot (30% probability) of $Ce(Allox)_3$ (5).



Fig. 3. ORTEP3 (16) plot (30% probability) of Er(Allox)₃ (7).



late complexes of Group 13 where the average difference is only ca. 0.03 Å (16). The Ln—O bond lengths in **5** and **7** are 0.07 Å *shorter* than predicted from $In(Phox)_3$ (PhoxH = 2-(2'-hydroxyphenyl)-2-oxazoline) (16*a*) after adjustment for differences in ionic radii⁵ (18). In contrast, the Ln—N distances are 0.20 (**5**, Ce) and 0.17 (**7**, Er) Å *longer* than expected using this same comparison. All of these observations are consistent with a greater affinity for oxygen vs. nitrogen for the lanthanides.

There are only two structures reported of any type that contain a neutral oxazoline ring bonded to a Group 3 or lanthanide ion and both complexes contain the oxazoline ring as part of a chiral, tridentate "pybox" ligand (Sc(Ph $pybox)(OTf)_3(H_2O)$ (4c) and $[La(Ph_2-pybox)(OTf)_2(H_2O)_4]^+$ $[OTf]^-$ (4b)). The Sc—N(ox) distances in the sevencoordinate Sc complex predict Ce-N and Er-N distances of 2.56 and 2.44 Å, respectively, almost exactly matching those observed in 5 and 7 for the trans pair of oxazoline Ln-N bonds.⁵ The La-N(ox) distances in the ninecoordinate La complex predict Ce-N and Er-N distances of 2.47 and 2.35 Å, respectively, far shorter than those actually observed. However, the La comparison is based on the nine-coordinate radius of La³⁺ and since the La centre is bound by four small water molecules, this radius is likely an overestimation of the size of the metal ion.

Subtle differences are detectable between the structures of **5** and **7**. In particular, although the difference in Ln—O bond lengths in the two structures (0.125 Å) matches the difference in ionic radii for the two metals (18), the difference in Ln—N bond distance (0.155 Å) is slightly larger than expected. Thus, the Er—N(oxazoline) distance in **7** is rela-

tively short compared to that in **5**. Since Er is the smaller of the two metals, this runs counter to steric arguments; stronger oxazoline binding owing to the higher charge to size ratio of Er may explain this effect. In any case, it seems quite clear from the foregoing discussion that these complexes are not significantly crowded, as we might expect for a sixcoordinate lanthanide center and relatively small ligand substituents.

The Ln-O-C angles of the phenoxide group are considerably less bent in **5** (146.2(3)°–148.9(3)°) and **7** (142.7(2)°– 146.4(2)°) than those in the Group 13 tris chelates (122°– 135°) (16), and only complexes of the Group 4 metals show M-O-C angles of more than 140° (19). Terminal Ln-O-C(aryl) angles are usually greater than 160° (20) so the observed angles are in fact more bent than usual because of the constraints of the chelate geometry.⁶ The chelate bite itself (O-Ln-N (**5** (68.62(11)°–70.02(11)°), **7** (73.24(9)°–75.41(9)°)) is the smallest of any reported 2-oxazolylphenoxide structure (range (76°–96°), median (87°)),⁴ but this is primarily a reflection of the fact that Ce and Er are the largest metals to which this ligand has been complexed.

Solution behaviour

The NMR spectra of **4–8** in d_8 -toluene each show a single set of nine resonances for the Allox ligand consistent with average $C_{3\nu}$ molecular symmetry. Since this symmetry is unlikely in a static structure, we investigated the variabletemperature ¹H NMR spectra of all complexes at both high and low temperature. In all cases, lowering the temperature resulted in decoalescence into at least 17, and usually more, resonances (vide infra). The resonances for paramagnetic complexes **5–7** showed good linear behaviour in δ vs. 1/*T*

⁵ Ionic radii from ref. 18: coordination number (CN) = 6 for In³⁺ 0.800 Å, Ce³⁺ 1.01 Å, Y³⁺ 0.90 Å, Er³⁺ 0.89 Å; CN = 7, Sc³⁺ 0.81 Å; CN = 9, La³⁺ 1.22 Å.

⁶The mean Ln-O-C angle in terminal phenoxides bearing only H or Me groups in the ortho positions is 167° with a standard deviation of 8° and an overall range of 144°–180°. Some typical examples are given in ref. 20.

Fig. 4. ¹H NMR chemical shift (δ) vs. the inverse temperature (1/*T*) plot for Er(Allox)₃ (**7**) above coalescence (d_8 -toluene, 360 MHz).



plots above and below coalescence, consistent with a single species in each temperature regime. A sample plot for 7 above coalescence is shown in Fig. 4; remaining plots are included in the Supplementary material.³ The line widths below coalescence were quite broad for Er, but the wider chemical shift window made it possible to distinguish 30 peaks in the low-temperature spectra. This is consistent with the low symmetry environment found in the solid-state structure since 36 resonances are expected if the molecule possesses C_1 symmetry.

In the case of Ce and Sm, resonances clearly overlap with one another, but the observation of six methyl signals in the low-temperature spectra of **6** indicates that the lowtemperature limiting structure of this complex also possesses C_1 symmetry (Fig. 5). Addition of d_8 -THF to a d_8 -toluene solution of **6** had a minor effect on the chemical shifts observed, but did not alter the coalescence behaviour. Changing the concentration of **6** over a fivefold range also caused no changes in dynamic behaviour. Taken together, the observation of linear δ vs. 1/T behaviour above or below coalescence and the lack of concentration or coordinating solvent effects strongly imply that an intramolecular fluxional process is operative.

The diamagnetic complexes **4** and **8** show similar behaviour to their paramagnetic counterparts except that the smaller spectral dispersion leads to a much lower coalescence temperature and more overlap in the low-temperature spectra. The full VT NMR spectra of **8** are shown in Fig. 6 and an expansion of the most downfield aryl resonance is shown in Fig. 7. Most of the resonances that have decoalesced in the 193 K spectrum (Fig. 6) appear to be in 2:1 intensity ratio (resonances near 6.0 and 8.2 ppm, for example). However, closer inspection reveals that this is most likely due to accidental overlap of resonances. This is clear in the expansion of the downfield aryl resonance (6'-aryl H) because this proton cannot give rise to a true triplet given the coupling constants involved for this aryl position. The observation of an **Fig. 5.** A portion of the low temperature ¹H NMR spectrum of $Sm(Allox)_3$ (6, d_8 -toluene, 500 MHz, diamagnetic peaks between 0 and 1 ppm suppressed).



Fig. 6. Variable-temperature ¹H NMR spectra of $Y(Allox)_3$ (8) (d_8 -toluene, 360 MHz, T = toluene, * = impurity).







apparent triplet can only be explained by the overlap of two doublets (a doublet of doublets pattern is expected, but the smaller coupling is not resolvable given the line widths in this spectrum). The four methyl resonances between 1.0– 1.8 ppm in the 193 K spectrum integrate as 3:3:3:9, which also can only be explained by accidental overlap of three (of the six) inequivalent methyl groups at 1.0 ppm.

The VT behaviour of the downfield aryl resonance was simulated by DNMR3 assuming that a single process exchanges all three inequivalent resonances; a subset of the simulated and observed spectra is shown in Fig. 8. The Eyring plot for this process (Fig. 9) gave $\Delta H^{\ddagger} = 24 \pm 2 \text{ kJ mol}^{-1}$ and $\Delta S^{\ddagger} = -99 \pm 15 \text{ J mol}^{-1} \text{ K}^{-1}$. While the errors in these parameters are admittedly quite large, the large negative entropy of activation is inconsistent with a dissociative mechanism (21). An associative process to produce a seven-coordinate complex is also highly unlikely given the lack of solvent and concentration dependence. A process involving a "hinged" five-coordinate intermediate cannot be entirely excluded, but most examples of rearrangements proceeding by partial dissociation of a chelate ligand show positive activation entropies (22). Conversely, a six-coordinate rearrange-

Fig. 8. Experimental and simulated (DNMR3) lineshapes for the 6'-aryl resonance of Y(Allox)₃ (8) at selected temperatures.



Fig. 9. Eyring plot for the exchange process of $Y(Allox)_3$ (8).



ment of the anion in $K_3[Ga(catecholate)_3]$ has been established that shows a negative activation entropy of -20 to -47 J mol⁻¹ K⁻¹ depending on the solvent and conditions (23).

The foregoing discussion suggests that 4-8 undergo a sixcoordinate fluxional process in solution. The options include the familiar Bailar (trigonal) or Rây–Dutt (rhombic) twists (Figs. 10 and 11) (24). Negative entropies of activation are often associated with both of these processes (23, 25).

The Bailar twist cannot interconvert mer and fac isomers, but it can scramble ligands between sites within the mer geometry and cause racemization (*mer*- Δ with *mer*- Λ). The Rây–Dutt twist can interconvert all four isomers (*mer*- Δ , *mer*- Λ , *fac*- Λ) (26). We cannot distinguish between these two possibilities because we would need to observe fac and mer exchange to confirm a Rây–Dutt twist (26) and the fac isomer is not observed in the low-temperature NMR spectra of **4–8**.

Theoretically, it is also possible to distinguish between these two mechanisms kinetically since the Bailar twist exchanges ligand environments at different rates $[\mathbf{A} \rightarrow \mathbf{C}, \mathbf{B} \rightarrow$ $\mathbf{B}, \mathbf{C} \rightarrow \mathbf{A}]$ while a Rây–Dutt twist permutes ligand environments at an equal rate $[\mathbf{A} \rightarrow \mathbf{C}, \mathbf{B} \rightarrow \mathbf{A}, \mathbf{C} \rightarrow \mathbf{B}]$ (Figs. 10*a*– 10*c*) (26, 27). Unfortunately, the spectral dispersion in the VT NMR of diamagnetic complexes **4** and **8** is not sufficient to model exchange by anything more than a single process.



Fig. 10. Interconversion of geometric and optical isomers by the Rây–Dutt (rhombic) twist mechanism.

Fig. 11. The trigonal prismatic Rây–Dutt intermediate.

mer Δ



(Trigonal prism)

If the fac isomer is present and exchanging with the mer isomer, it must be in low concentration at all temperatures or we would not observe linear behaviour in plots of δ vs. 1/*T* for 5–7.⁷

The relative energetics of the Rây–Dutt and Bailar twist mechanisms have been assessed theoretically by Rodger and Johnson (28). They suggest that the Bailar twist will generally be favoured if the ratio of chelate bite angle (*b*) to hard sphere contact distance (*l*) between adjacent ligand atoms (not part of the same chelate) is small ($b/l \approx 0.5$), and the Rây–Dutt twist will be favoured if this ratio is large ($b/l \approx 1.5$). According to these calculations, there is no energetic difference between the two mechanisms at b/l = 0.914. This ratio is 0.76 (Ce) and 0.82 (Er) in complexes 5 and 7. It should also be pointed out that a recent experimental study

on *mer*-Ga(fox)₃ (Hfox = 5-fluoro-8-hydroxyquinoline) using 2D EXSY NMR was able to kinetically distinguish between the two twist mechanisms and found that *both* contributed to the fluxional behaviour of this compound (27). Interestingly, the *b/l* ratio for *mer*-Ga(ox)₃ (Hox = 8hydroxyquinoline) is 0.90 (29), almost exactly the value predicted by Rodger and Johnson to give equal energetics for either twist mechanism. Thus, while theoretical treatments suggest that **4–8** should undergo a Bailar rather than a Rây– Dutt twist, the mechanisms may be close enough in energy that both are operative.⁸

The fluxional Group 13 tris chelates $(M(3'-MePhox)_3)$ M = Al, Ga, In) were previously investigated by VT NMR spectroscopy (16a). These complexes also undergo intramolecular rearrangement of inequivalent ligands within the mer geometry on the NMR timescale at, or just above, room temperature. In the case of In, there was some evidence for formation of the fac isomer as a distinct (nonexchanging) species at high temperature. The authors did not determine ΔS^{\ddagger} and were unable to rule out a bond rupture (fivecoordinate Berry pseudorotation) mechanism. However, ΔG^{\ddagger} values were calculated at the coalescence temperatures and as might be expected, they decrease in the order Al $(72 \text{ kJ mol}^{-1}) > \text{Ga} (64 \text{ kJ mol}^{-1}) > \text{In} (<42 \text{ kJ mol}^{-1})$. The value reported for In was based on the lowest temperature attained of 213 K; using the activation parameters for **8**, we calculate a value of $\Delta G^{\ddagger} = 45 \text{ kJ mol}^{-1}$ at this temperature. While it might seem surprising that the much larger⁴ Y complex has a larger ΔG^{\ddagger} value, the oxazoline rings in the In structure are unsubstituted while those in 8 bear two methyl groups in the 4 position. These methyl groups are relatively close to the metal centre (avg. 3.89 Å in 7) and may well increase the barrier to a six-coordinate rearrangement.

Concluding remarks

C

fac A

Lanthanide complexes of the hybrid oxazoline-phenoxide chelating ligand Allox are readily accessible and adopt a sixcoordinate mer geometry in the solid state without coordination of the pendant allyl substituents. NMR evidence suggests that this structure is maintained in solution over a wide temperature range, but exchange of inequivalent ligands within the mer geometry occurs rapidly on the NMR timescale at room temperature for all complexes studied. A more detailed study of the exchange process for Y complex 8 supports an intramolecular six-coordinate rearrangement, although it is not possible to distinguish between a Bailar (trigonal) or Rây–Dutt (rhombic) twist mechanism.

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⁷Assuming that the ratio of fac and mer isomers varies significantly with temperature.

⁸For a discussion of electronic factors in six-coordinate rearrangements see ref. 30.

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