

Article

Chirality as a Feature of the Crystal Structure of Lanthanide Ion Complexes—Some Simple Examples

Lioubov I. Semenova ¹, Irene Ling ²  and Alexandre N. Sobolev ^{1,*} 
¹ School of Molecular Sciences, M310, The University of Western Australia, 35 Stirling Highway, Perth, WA 6009, Australia

² School of Science, Monash University Malaysia, Jalan Lagoon Selatan, Bandar Sunway 47500, Selangor, Malaysia

* Correspondence: alexandre.sobolev@uwa.edu.au

Abstract: Single-crystal X-ray structure determinations are reported for four lanthanide complexes, [Dy(bipy)₂Cl₂(OH₂)₂]Cl·H₂O (bipy = 2,2′-bipyridine), **1**; [La₂(phen)₂(O₂CCH₃)₄(NO₃)₂] (phen = 1,10-phenanthroline), **2**; [Lu(terpy)(O₂CCH₃)₃]·NaNO₃ (terpy = 2,2′;6′,2″-terpyridine) **3**; and [Lu(phen)(O₂CH)₃(OH₂)]·H₂O, **4**. Dispersion interactions within the stacked arrays of coordinated aza-aromatic units found in all four complexes appear to be a significant structural influence in the solid state. For complex **1**, there are additional interactions beyond dispersion, which suggests that it may be the means whereby the Δ and Λ forms contribute to the overall chiral nature of the crystal. These weak intermolecular interactions were investigated in detail using the Hirshfeld surface analysis.

Keywords: lanthanide; chiral; bipyridine; phenanthroline; terpyridine



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1. Introduction

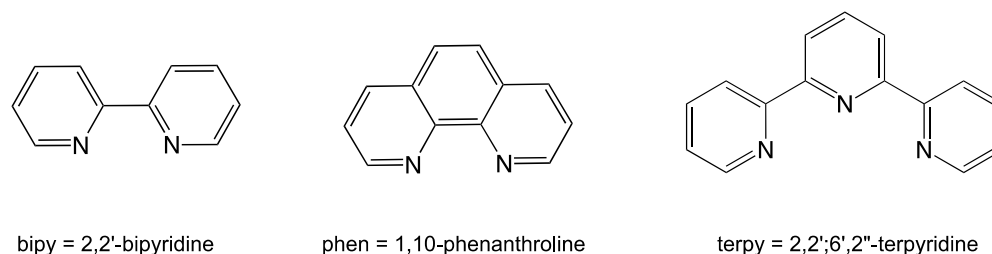
Lanthanides are strong Lewis acids that typically form complexes through coordination with ligands that have highly electronegative donor atoms, notably N- or O-, although their organometallic chemistry is also well developed [1]. The variable and commonly high coordination numbers (7 to 10), which typify lanthanide(III) ion coordination chemistry, mean that chirality (optical activity) can be an important aspect of the complex ion structures [2]. An early review article by Aspinall [3] provides numerous examples of chiral lanthanide complexes, involving a wide range of ligands, which have various applications; however, the point is made that, in most cases, the chirality of the complexes is derived from the use of stable enantiomeric forms of the ligands alone. In the solution, the lability of the lanthanide(III) cations, some of the most labile of all metal ions known [4], usually results in their rapid inversion, a factor that limits the possible applications in chiral catalysis unless a chiral ligand is used to fix the configuration at the metal ion. This approach has seen spectacular progress over the past decades [5], although it may be noted that the chirality of a ligand does not necessarily inhibit interconversion between the diastereomeric forms of its complexes [6]. Lanthanide complexes in general have well established biomedical applications, ranging from cancer diagnosis and therapy to cell imagery [7]; however, since all biological systems are chiral, complexes which are themselves also chiral offer prospects for improved targeting [8]. In the solid-state, it has been found that the use of chiral bridging ligands to form lanthanide coordination polymers has considerable prospects in the development of new photoelectronic devices [9] and even that the selectivity involved in the crystallization of the complexes of a chiral ligand (camphorate) can be used to separate the lanthanides [10]. However, because inversion processes are inhibited in the solid state, it is not necessary to use chiral ligands in order to obtain a chiral crystal, so that even stoichiometrically simple materials may be of interest in this regard. This would depend, of course, on the occurrence of “spontaneous resolution” and the deposition of crystals

belonging to the Sohncke space groups [11], a relatively rare phenomenon, though certainly not unknown [3,12–21]. Understanding the molecular properties and the formation of supramolecular assemblies involving chiral lanthanide complexes is deemed crucial because chiral interactions could lead to dramatic improvements in the sensitivity and selectivity of their applications. Thus, the phenomenon of chiral crystallization has drawn our interest and we intend to explore this area both by revisiting certain previously studied compounds and by investigating the structural properties of new lanthanide(III) complexes. In the present work, we report four crystal structures of lanthanide(III) complexes that reflect these two themes and involve quite different solid state supramolecular architectures. Of the four crystal structures presently described, one is that of a chiral crystal, one that of a crystal where the lanthanide(III) ion centre is achiral (as is the crystal) and two involve similar ways of incorporating chiral lanthanide ion units into an achiral structure. Possible reasons for such variations in behaviour are assessed through a detailed analysis of the weak interactions revealed in each structure.

2. Materials and Methods

2.1. Synthesis

The materials studied in the present work, $[\text{Dy}(\text{bipy})_2\text{Cl}_2(\text{OH}_2)_2]\text{Cl}\cdot\text{H}_2\text{O}$ (bipy = 2,2'-bipyridine), **1**; $[\text{La}_2(\text{phen})_2(\text{O}_2\text{CCH}_3)_4(\text{NO}_3)_2]$ (phen = 1,10-phenanthroline), **2**; $[\text{Lu}(\text{terpy})(\text{O}_2\text{CCH}_3)_3]\text{NaNO}_3$ (terpy = 2,2';6',2''-terpyridine) **3**; and $[\text{Lu}(\text{phen})(\text{O}_2\text{CH})_3(\text{OH}_2)]\cdot\text{H}_2\text{O}$, **4**, (Scheme 1) were all prepared some time ago as part of a series of systematic studies of lanthanide ion solid-state coordination chemistry [22–24] and all reagents of analytical grades were purchased from the commercial suppliers and used without further purification. The complexes were crystallized from water/ethanol solutions for their structure determinations. The complex $[\text{Er}(\text{bipy})_2\text{Cl}_2(\text{OH}_2)_2]\text{Cl}\cdot\text{H}_2\text{O}$, **5**, structurally characterized in the original work [24], was also recrystallized from water/ethanol solution and its structure was confirmed by a redetermination (CCDC number 222101).



Scheme 1. Schematic representation of the three ligands discussed in this paper.

2.2. Crystallography

Crystallographic data for the structures were measured using $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$) radiation on an Enraf-Nonius CAD four-circle single-counter diffractometer for complexes **1–3,5** and for complex **4** on a Bruker AXS CCD area-detector diffractometer. Data were corrected for Lorentz and polarization effects, and absorption correction applied using multiple symmetry equivalent reflections. The structures were solved by direct methods and refined against F^2 with full-matrix least-squares using the program suite SHELX [25]. Anisotropic displacement parameters were employed for the non-hydrogen atoms. Most of the hydrogen atoms were added at calculated positions and refined by the use of a riding model with isotropic displacement parameters based on those of the parent atom ($\text{C—H} = 0.95 \text{ \AA}$, $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}\text{C}$ for CH (aromatic)). The hydroxyl and water molecule hydrogen atoms were located from experimental data and refined with O–H distances restrained to their idealized values. The details of the data collection and processing, structure solution and refinement are summarized below and for compound **5** in Table S1. Crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre. Copies of the cifs with CCDC numbers 2204924, 2220098–2220101 can be obtained free of charge via <https://www.ccdc.cam.ac.uk/structures/> (accessed on

1 February 2023) or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax+ 441223336033; email deposit@ccdc.cam.ac.uk).

2.2.1. Crystal/Refinement Details for Complex 1: $[\text{Dy}(\text{bipy})_2\text{Cl}_2(\text{OH}_2)_2]\text{Cl}\cdot\text{H}_2\text{O}$:

Empirical formula $\text{C}_{20}\text{H}_{20}\text{Cl}_3\text{DyN}_4\text{O}_2$, $M = 617.25$, colourless prism, $0.375 \times 0.160 \times 0.138 \text{ mm}^3$, cubic, space group $I23$ (No. 197), $a = 25.932(4)$, $V = 17438(8) \text{ \AA}^3$, $Z = 24$, $D_c = 1.411 \text{ g cm}^{-3}$, $\mu = 2.865 \text{ mm}^{-1}$. $F_{000} = 7224$, diffractometer Enraf-Nonius CAD-4, $T = 297(2) \text{ K}$, $2\theta_{\text{max}} = 46.0^\circ$, 6502 reflections collected, 2175 unique ($R_{\text{int}} = 0.2331$). Final $\text{Goof} = 1.001$, $R1 = 0.0699$, $wR2 = 0.1314$, R indices based on 1184 reflections with $I > 2\sigma(I)$, largest diff. peak and hole are 0.707 and $-0.654 \text{ (e \AA}^{-3})$, 291 parameters, 195 restraints. Absolute structure parameter = 0.45(6) (Flack, H. D. *Acta Cryst.* 1983, A39, 876–881). CCDC number 2220098.

2.2.2. Crystal/Refinement Details for Complex 2: $\text{La}_2(\text{phen})_2(\text{O}_2\text{CCH}_3)_4(\text{NO}_3)_2$

Empirical formula $\text{C}_{32}\text{H}_{28}\text{La}_2\text{N}_6\text{O}_{14}$, $M = 998.42$, colourless block, $0.35 \times 0.30 \times 0.25 \text{ mm}^3$, triclinic, space group $P-1$ (No. 2), $a = 9.902(5)$, $b = 9.918(9)$, $c = 10.139(5) \text{ \AA}$, $\alpha = 108.89(7)$, $\beta = 99.89(4)$, $\gamma = 90.21(6)^\circ$, $V = 926.2(11) \text{ \AA}^3$, $Z = 1$, $D_c = 1.790 \text{ g cm}^{-3}$, $\mu = 2.349 \text{ mm}^{-1}$. $F_{000} = 488$, diffractometer Enraf-Nonius CAD-4, $T = 297(2) \text{ K}$, $2\theta_{\text{max}} = 45.9^\circ$, 5126 reflections collected, 2565 unique ($R_{\text{int}} = 0.1079$). Final $\text{Goof} = 1.002$, $R1 = 0.0838$, $wR2 = 0.1930$, R indices based on 1820 reflections with $I > 2\sigma(I)$, largest diff. peak and hole are 3.041 and $-2.255 \text{ (e \AA}^{-3})$, 246 parameters, 12 restraints. CCDC number 2220099.

2.2.3. Crystal/Refinement Details for Complex 3: $\text{Lu}(\text{terpy})(\text{O}_2\text{CCH}_3)_3\cdot\text{NaNO}_3$

Empirical formula $\text{C}_{21}\text{H}_{20}\text{LuN}_4\text{NaO}_9$, $M = 670.37$, colourless prism, $0.225 \times 0.100 \times 0.030 \text{ mm}^3$, triclinic, space group $P\bar{1}$ (No. 2), $a = 9.724(12)$, $b = 11.536(4)$, $c = 12.108(17) \text{ \AA}$, $\alpha = 69.44(9)$, $\beta = 69.72(12)$, $\gamma = 86.15(9)^\circ$, $V = 1191(3) \text{ \AA}^3$, $Z = 2$, $D_c = 1.870 \text{ g cm}^{-3}$, $\mu = 4.223 \text{ mm}^{-1}$. $F_{000} = 656$, diffractometer Enraf-Nonius CAD-4, $T = 297(2) \text{ K}$, $2\theta_{\text{max}} = 50.0^\circ$, 4444 reflections collected, 4178 unique ($R_{\text{int}} = 0.0673$). Final $\text{Goof} = 1.279$, $R1 = 0.0967$, $wR2 = 0.2124$, R indices based on 2877 reflections with $I > 2\sigma(I)$, largest diff. peak and hole are 6.115 and $-3.097 \text{ (e \AA}^{-3})$, 328 parameters, 18 restraints. CCDC number 2220100.

2.2.4. Crystal/Refinement Details for Complex 4: $\text{Lu}(\text{phen})(\text{O}_2\text{CH})_3(\text{OH}_2)]\cdot\text{H}_2\text{O}$

Empirical formula $\text{C}_{15}\text{H}_{15}\text{LuN}_2\text{O}_8$, $M = 526.26$, colourless plate, $0.40 \times 0.20 \times 0.07 \text{ mm}^3$, monoclinic, space group $P2_1/m$ (No. 11), $a = 10.665(1)$, $b = 6.5735(7)$, $c = 12.465(1) \text{ \AA}$, $\beta = 109.257(2)^\circ$, $V = 824.98(13) \text{ \AA}^3$, $Z = 2$, $D_c = 2.119 \text{ g cm}^{-3}$, $\mu = 6.032 \text{ mm}^{-1}$. $F_{000} = 508$, diffractometer Bruker ASX CCD, $T = 150(2) \text{ K}$, $2\theta_{\text{max}} = 52.7^\circ$, 8127 reflections collected, 1837 unique ($R_{\text{int}} = 0.0422$). Final $\text{Goof} = 1.002$, $R1 = 0.0271$, $wR2 = 0.0813$, R indices based on 1823 reflections with $I > 2\sigma(I)$, largest diff. peak and hole are 1.001 and $-1.552 \text{ (e \AA}^{-3})$, 190 parameters, 97 restraints. CCDC number 2204924.

3. Results

As all the complexes presently described are members of families that were subjected to structural characterization [22–24] some time ago and present no anomalies with respect to composition or connectivity, we focus here only on ways they reflect the importance of chirality of Ln(III) centres, an issue of general significance but not a real focus of the earlier work.

The complex $[\text{Dy}(\text{bipy})_2\text{Cl}_2(\text{OH}_2)_2]\text{Cl}\cdot\text{H}_2\text{O}$, **1**, forms chiral crystals in cubic crystal system, space group $I23$ and is isomorphous with its Er(III) analogue (CCDC refcode: RIRLUB) [24]. The intervening lanthanide between Dy(III) and Er(III) is Ho(III), and thus it might be considered surprising that the Ho(III) complex, which is of similar stoichiometry, does not have the same structure [23], although the capricious nature of lanthanide(III) complexes' crystallisation is rather well known [24]. We have, however, confirmed the reproducibility of the crystallisation of the Dy(III) and Er(III) complexes in their $I23$ form. The cation present in **1** has C_2 symmetry and for present purposes it is sufficient to specify

its chirality in terms of the projection of the edges spanned by the 2,2'-bipyridine ligands on the C_2 axis (Figure 1). In the crystal chosen for the structure determination, only the enantiomer designated as Λ is present (as is the case for the Er(III) complex determinations).

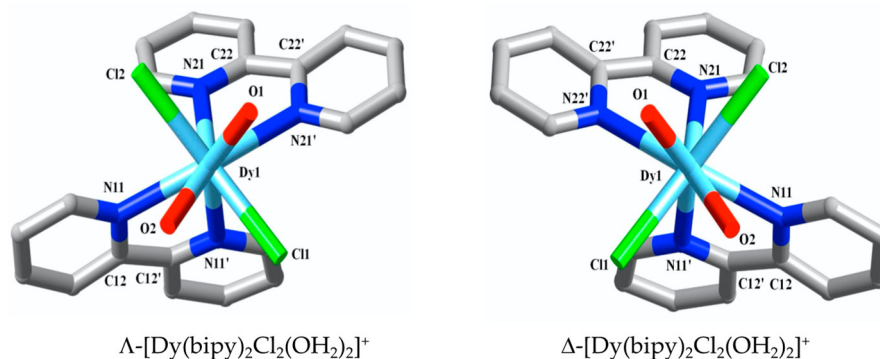


Figure 1. Enantiomeric forms of [Dy(bipy)₂Cl₂(OH₂)₂]⁺, viewed down the C_2 axis of the cation, only the Λ enantiomer being found in the structure of **1**. Stick representation; colour code: C = grey, N = dark blue, O = red, Cl = green, Dy = light blue. H-atoms are omitted for clarity.

The symmetry of the crystal structure is such that the cations assemble in groups of three, with the Dy(III) atoms forming an equilateral triangle, Dy...Dy 6.474(2) Å, and with the C_2 axes and the chloro and aqua ligands directed to the centroid of that triangle. Each Dy(III) is eight-coordinated. The possibility that this association might be due to the O-H...O bonding of the aqua ligands is denied by the long O...O separations (shortest, O1...O2ⁱ 3.55(3) Å; $i = 1 - y, 1 - z, x$), and bound-Cl...O separations are in fact much shorter (O1...Cl1ⁱ 3.26(2) Å; Cl2...O2ⁱ 3.21(2) Å), consistent with Cl...H-O bonding being the dominant influence (Figure 2a). The strong Cl...H-O interaction is evident on the d_{norm} -mapped Hirshfeld surface as highlighted by the deep red spots (Figure 2b), which covers 32.1% of the total surface, as obtained using CrystalExplorer17 [26,27].

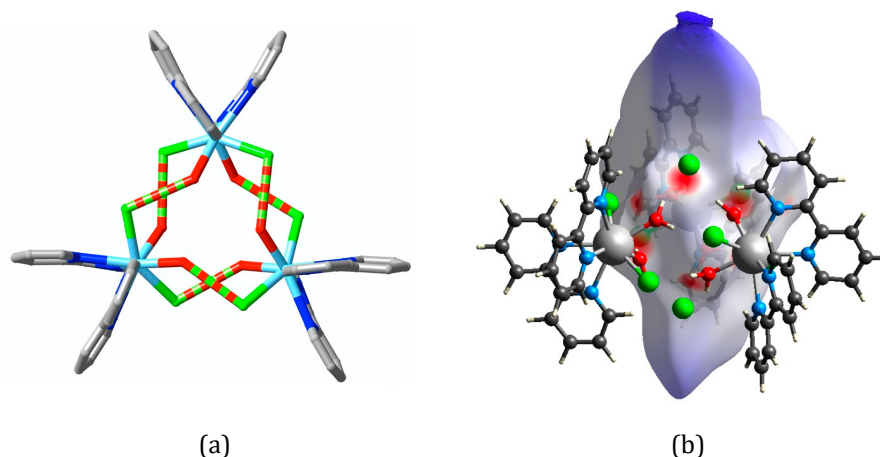


Figure 2. Proposed Cl...HO interactions (red–green dashed lines (a) and deep red spots on the Hirshfeld surface mapped using d_{norm} (b)) in one of the trinuclear groups of [Dy(bipy)₂Cl₂(OH₂)₂]⁺ cations present in the crystal of [Dy(bipy)₂Cl₂(OH₂)₂]Cl·H₂O, here as seen in the view down [111]. Some H-atoms are omitted for clarity.

While it is difficult to predict exactly what the consequences of replacing one in three Λ cations by a Δ might be (equivalent, of course, to replacing one in three Δ by Λ , so that only two situations need be considered), the simple inversion at one Dy(III) in the species shown in Figure 2 would disrupt four of the Cl...H-O interactions and thus we assume that the presence of six equivalent Cl...H-O bonds in the homochiral species is the reason it is homochiral. Note that the uncoordinated chloride also appears to have a role in stabilising the trinuclear species, although its distribution in partial occupancy over five

sites complicates any comparison of its influence with that of the coordinated chlorides. Cl3 and Cl4, each with a site occupancy of 1/3, are found within hydrogen bonding distance of three bound water molecules in the cation groups (Cl3...O1 3.11(2) Å; Cl4...O2 3.13(2) Å), but the closest contacts to Cl5, Cl6 and Cl7 (populations 1/6, 1/12 and 1/12; this is the main difference from the results published earlier for the Er(III) analogue) are CH atoms, presumably involved in very weak interactions. These interactions alone do not explain why only Λ cations are found in the entire crystal, so that extended interactions of the trinuclear units must be carefully examined.

In any complexes of aza-aromatic ligands, an obvious factor to be considered as an influence on their solid-state structure, is the stacking of the aza-aromatic units [28,29]. In complex **1**, stacking of both 2,2'-bipyridine ligands of the one enantiomer of the cations is involved in the formation of the right-handed helical arrays, which extend throughout the crystal, and the examination of the Hirshfeld surface for the structure, shows that at least one interaction exceeding dispersion (C14'...C25 3.19(3) Å) occurs within this supramolecular polymeric unit (Figure 3). In combination, C...C and Cl...O interactions give three-dimensionality to a lattice based on a single enantiomer of the complex and explain the formation of a chiral crystal. The disposition of the molecules in the cubic crystal lattice comprising aggregates of an eight-cation grouping in a cluster about a site of 222 symmetry at (1/2, 1/2, 0), (1/2, 0, 1/2) and (0, 1/2, 1/2) in a projection down the three axes with restricted hydrogen bonding between clusters. The arrangement of the clusters (Figure 4) resulted in a rather interesting assembly in the overall structure with interstices/channels between the aggregates filled with chloride ions (estimated to be 15.9% of the total unit cell volume).

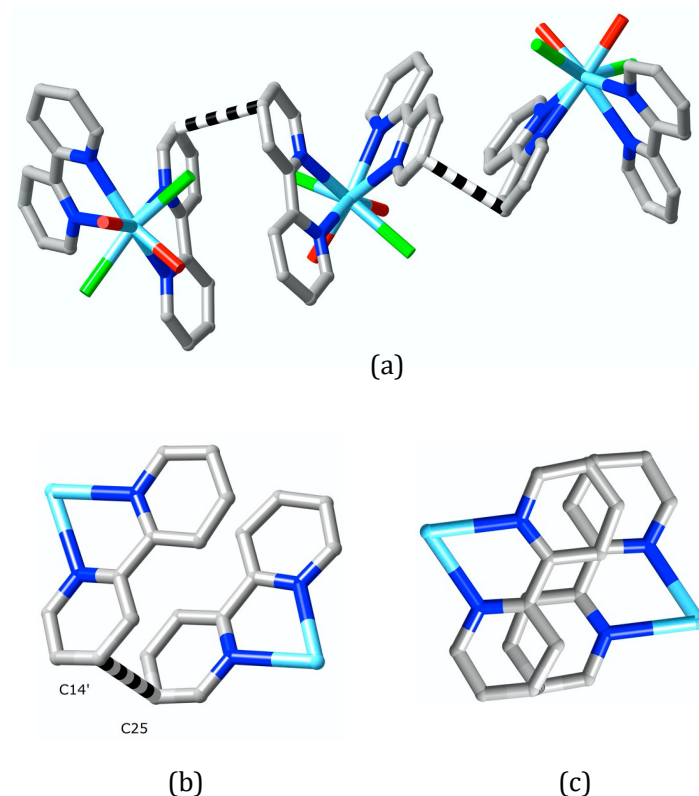


Figure 3. Stick representation of (a) a portion of the right-handed helical chain involving C...C interactions of the 2,2'-bipyridine ligands of the Λ -[Dy(bipy)₂Cl₂(OH₂)₂]⁺ cations found in complex **1**; (b) atom numbering of the interacting units; (c) overlap in the projection of the interacting ligands, indicating the extent of pure dispersion interactions (also involving the H-atoms, which are not shown).

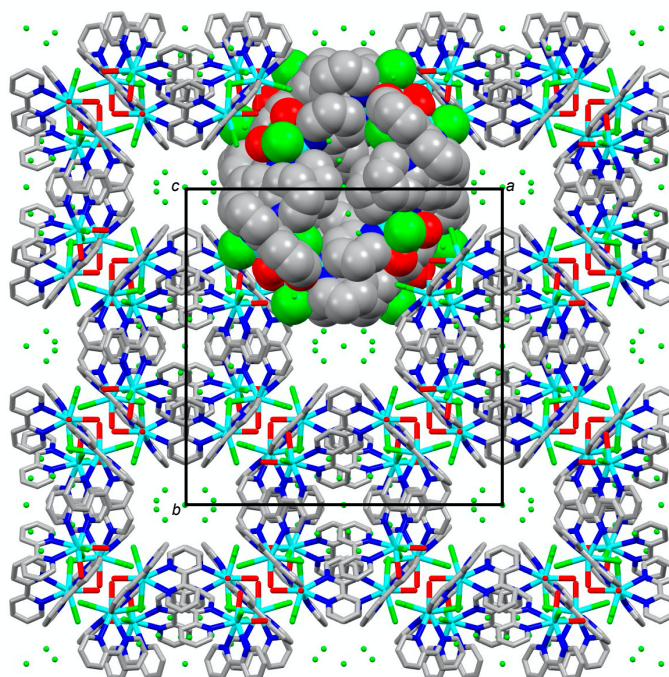


Figure 4. The unit cell contents of complex **1**, projected down *c*-axis, comprising an overlay of the aggregates (each of eight molecules in space-filling representation).

Early studies of the synthesis of aza-aromatic ligand complexes of lanthanide(III) carboxylates, surveyed in reference [22], showed that the use of commercially available lanthanide(III) nitrates as reactants could lead to the isolation of mixed nitrate–acetates. When initially following these procedures [22], such materials were obtained and were recrystallized as part of the present work in order to obtain $[\text{La}_2(\text{phen})_2(\text{O}_2\text{CCH}_3)_4(\text{NO}_3)_2]$, **2**, and $[\text{Lu}(\text{terpy})(\text{O}_2\text{CCH}_3)_3]\cdot\text{NaNO}_3$, **3**.

The ligands bipy, phen and terpy (Scheme 1) are all relatively large chelating species which are inherently achiral, although bipy can adopt a chiral conformation by twisting about the 1,1' bond. In 1:1 complexes, phen and terpy provide no particular bias in favour of a chiral form and chirality can only result from interactions with other ligands within the primary coordination sphere, possibly influenced by interactions beyond that sphere. In $[\text{La}_2(\text{phen})_2(\text{O}_2\text{CCH}_3)_4(\text{NO}_3)_2]$, the other ligands are acetate and nitrate, both species are capable of forming compact, four-membered chelate rings expected to be favoured on relatively large cations, such as the lanthanide(III) ions [30]. Indeed, in binuclear $[\text{La}_2(\text{phen})_2(\text{O}_2\text{CCH}_3)_4(\text{NO}_3)_2]$, the phen and nitrate ligands are simply chelating, while two acetates are $\mu^2\text{-}\kappa^2\text{O},\text{O}';\kappa^1\text{O}'$ bridging and two are $\mu^2\text{-}\kappa^1\text{O},\kappa^1\text{O}'$ bridging (Figure 5a); however, any influence of one upon the other appears to be symmetrical, so that the nine-coordinated La(III) primary coordination sphere is achiral and the complex is centrosymmetric. Indeed, the environment of the phen ligands in particular is rather sparse, a fact which may be explained by the capacity of acetate, as a much stronger base than nitrate, to satisfy the demand for high coordination numbers of La(III) by acting as a bridge to form the binuclear complex and thus being localised between the two metal ions. However, another reason for the apparent isolation of phen from the nitrate and acetate ligands, is the fact that it is not isolated from the phen ligands of adjacent complex molecules. The chains of complexes running parallel to [101] involve phen unit stacking that contributes approximately 3.7% to the total interaction surface. This part of the whole assembly is apparently the result of purely dispersive forces, again involving important overlap in projection of each pair and resulting in one possibly significant acetate–O...H–C contact, O32...H14' 2.56(6) Å. An interesting possibility is that it is the centrosymmetric nature of each stacked (phen)₂ unit which determines the centrosymmetric form of the dimeric complex, meaning that as for complex **1**, extended interactions throughout the

structure may be the determinants of local coordination geometry. This may be an explanation of why there are various examples reported that pertain to the different coordination behaviours of lanthanide(III) centres in the solid-state and solution [31–33].

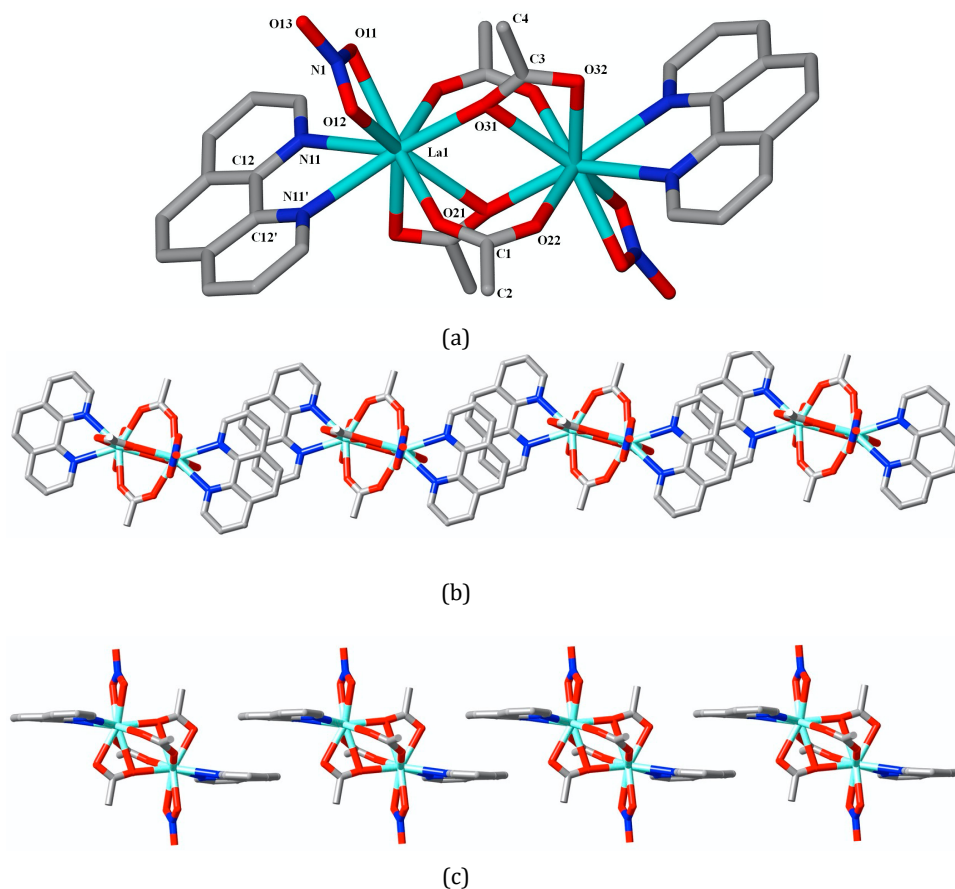


Figure 5. Stick representations showing (a) the centrosymmetric binuclear complex $[\text{La}_2(\text{phen})_2(\text{O}_2\text{CCH}_3)_4(\text{NO}_3)_2]$, and (b) orthogonal views of part of one chain of complexes involving phen stacking; (c) same view rotated by 90° . H-atoms not shown for clarity; colour code C = grey, N = blue, O = red, La = pale greenish-blue.

Complex **3**, $[\text{Lu}(\text{terpy})(\text{O}_2\text{CCH}_3)_3]\cdot\text{NaNO}_3$, has certain similarities to complex **2**, in that while the nine-coordinated lanthanide component, triacetatolutetium(III), is binuclear and centrosymmetric, it is in fact a heterometallic coordination polymer, due to the lutetium acetate units being linked by centrosymmetric, binuclear $\text{Na}_2(\text{NO}_3)_2$ bridges (Figure 6). Unsurprisingly, stacking of the larger 2,2',6',2''-terpyridine units is a more prominent feature of the structure (Figure 6d), here being associated with contact of four Lu_2Na_2 polymer chains running parallel to $[100]$ with any other. The chains therefore extend both along $[100]$ and $[010]$, and as a result of their cross linking through the dimeric lutetium acetate units, they generate the tridimensional nature of the complete structure. Within both chains, there are two types of overlap, depending upon whether one or two pyridine rings are involved, but any one pair of adjacent terpyridines is centrosymmetric, possibly explaining why both the lutetium and sodium dimers are also centrosymmetric. A centrosymmetric dimer can be formed from enantiomeric chiral components, and this is the case for both dimers here, marking another point of distinction from complex **2**. For both, however, rather minor bond rotations can convert them into achiral forms, so the influences here are presumably rather subtle.

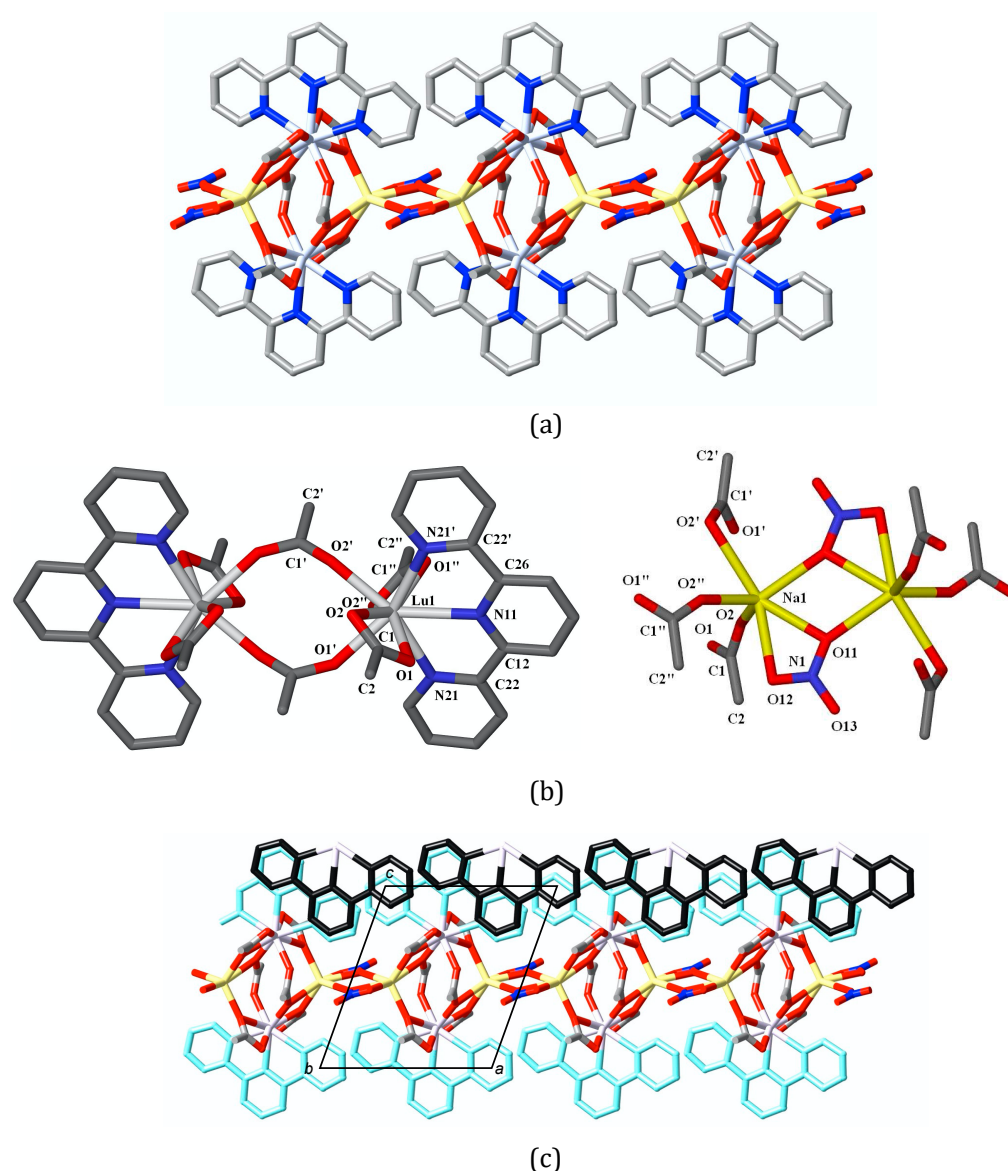


Figure 6. Stick representations showing (a) part of the monoperoxidic, heterometallic coordination polymer forming chains along [010] in the structure of $[\text{Lu}(\text{terpy})(\text{O}_2\text{CCH}_3)_3]\cdot\text{NaNO}_3$; (b) the two centrosymmetric units found in the coordination polymer; (c) part of one polymer chain with its terpyridine atoms shown in blue and those of one of the four adjacent strands shown in black to highlight the two-ring, one-ring alternation in the stacking pattern projected down the b -axis.

Complex 4, $[\text{Lu}(\text{phen})(\text{O}_2\text{CH})_3(\text{OH}_2)]\cdot\text{H}_2\text{O}$, is a double-stranded, monoperoxidic, homometallic coordination polymer. Each eight-coordinated Lu(III) centre has no (C_1) symmetry and is therefore chiral, but the crystal is achiral due to the polymer being formed as a racemic mixture of right- and left-handed helical chains involving just one of the two enantiomeric Lu(III) centres in each of the two enantiomeric chains (Figure 7). Once again, stacking of the aza-aromatic ligands is a prominent feature of the structure, with the phen groups to each side of the polymer chains interdigitating along [010] (Figure 7b), contributing 11.0% to the overall surface (Figure S8).

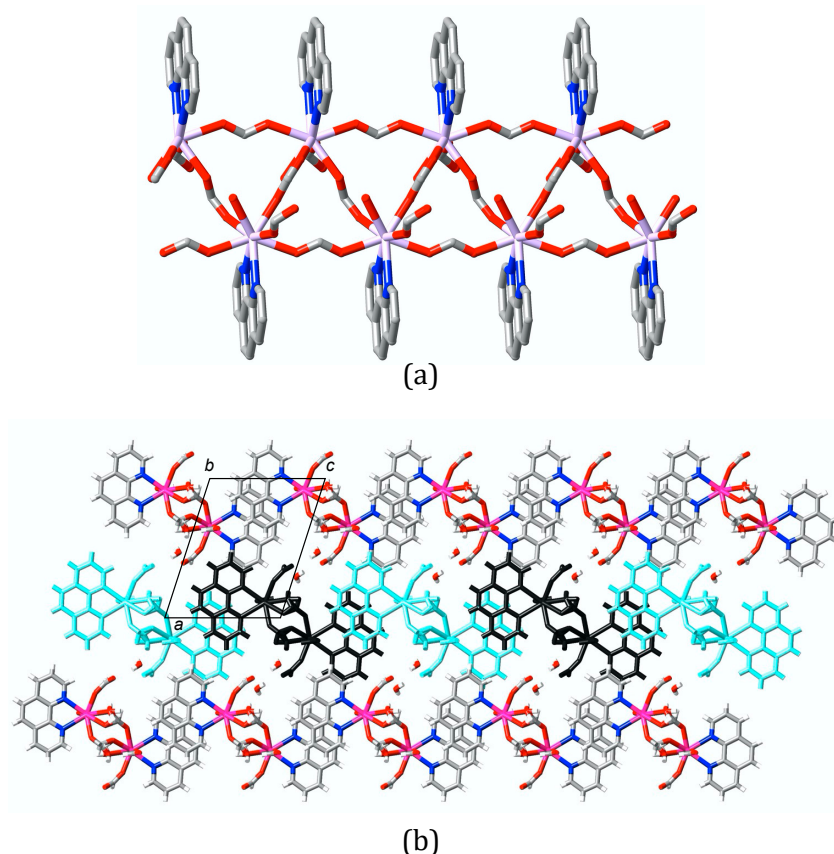


Figure 7. Stick representations showing (a) partial view of one of the left-handed helical chains of the coordination polymer in $[\text{Lu}(\text{phen})(\text{O}_2\text{CH})_3(\text{OH}_2)] \cdot \text{H}_2\text{O}$, the helix axis being parallel to $[010]$; (b) viewed down $[010]$, of part of the structure ($[001]$ horizontal) with some of the polymer units coloured alternately in blue and black to highlight the overlap in projection of the phen units. The detailed atomic numbering scheme of this complicated structure can be found in Figure S4 of SI.

4. Discussion

The four complexes presently are all considered to be members of larger, isostructural families and thus need only be considered as illustrating the frequent occurrence of chirality at Ln(III) in lanthanide ion complexes. The observation in general of various coordination numbers and geometry renders the development of a nomenclature for the description of their absolute configuration as particularly complicated [2] and our description of complex 1 as having Δ and Λ forms, though adequate for the present discussion, does not include the designation of the location of the bound pairs of chloride and water ligands, which could, for example, each be in a cisoid array rather than the observed transoid. For complexes formed with achiral ligands, chirality has long been recognized as an important feature in species of higher symmetry, such as the D_3 -symmetric $[\text{Ln}(\text{oda})_3]^{3-}$ anions [18,21,34] (oda = oxydiacetate); however, in many other instances of relatively simple species, such as in $[\text{Eu}(\text{terpy})(\text{NO}_3)_3\text{OH}_2]$ [35], where the lanthanide ion is found at a site with no point symmetry but within an achiral crystal, the focus has been on the coordination number and geometry rather than definition of the absolute configuration. While it is, in general, conventional to analyse the crystal structure of a metal ion complex in terms of the bonding selectivity and the stereochemical preferences of the metal ion, for lanthanide(III) complexes of aza-aromatic ligands, in particular one of the reasons crystal structure determinations are essential, is that it is often found that such ligands are incorporated into the crystal without being bound to the lanthanide ion [36], testifying to an influence of aromatic–aromatic interactions—not just between coordinated species [28,29] in determining the crystal structures. The four present structures illustrate only the stacking arrays of coordinated aza-aromatics, where dispersive interactions appear to be dominant,

although in the case of complex **1**, there are additional interactions beyond dispersion which we have suggested may be the cause of the overall chiral nature of the crystal. The fact that $[\text{Dy}(\text{bipy})_2\text{Cl}_2(\text{OH}_2)_2]\text{Cl}\cdot\text{H}_2\text{O}$ and its Er(III) analogue are the only members of the family of the bis(2,2'-bipyridine) complexes of hydrated lanthanide(III) chlorides [23,24] to form chiral crystals is possibly a sign of another subtle influence on the structures and the difference in Ln-(donor atom) bond lengths even for neighbouring elements. That more remote members of the lanthanide series may show that differences are unsurprising, but it is nonetheless remarkable that the crystalline complexes of $\text{La}(\text{O}_3\text{SCF}_3)_3$ and $\text{Yb}(\text{O}_3\text{SCF}_3)_3$ with an achiral cyclic triamide [19] both incorporate diperiodic, chiral and cationic coordination polymers, but in the La(III) complex, space group $P\bar{6}$, the chirality of the polymer sheets, alternates from one to the next, giving an achiral crystal, whereas in the Yb(III) complex, space group $P1$, the sheets all have the same chirality, giving a polar chiral crystal. The alliance of chirality with other properties specific to a given lanthanide(III) ion, such as its paramagnetism, is another issue that must be considered in relation to any application [37]. One characteristic shared by most lanthanide(III) ions is that of luminescence and this, coupled with chirality, renders appropriate complexes as useful sources of circularly polarised radiation, seemingly a subtle aspect to be exploited but one considered to be potentially more valuable than simple luminescence measurements [38].

5. Conclusions

The structures of four different complexes resulting from the complexation of three lanthanides(III) (Ln(III) = Dy(III), La(III) and Lu(III)) with different polypyridines (2,2'-bipyridine, 1,10-phenanthroline and 2,2':6',2''-terpyridine) represent an important extension of earlier work with the emphasis on the ways these complexes reflect on the chirality of Ln(III) centres and comprises the focus in the present work. The structural analysis revealed that dispersive interaction appears to be dominant in all structures. Additionally, the stacking arrays of the coordinated aza-aromatics appear to be an important factor in the self-assembly and may explain why a chiral crystal is obtained in one of the structures.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/cryst13020337/s1>, Table S1: Crystal and structure refinement data for the redefined $\text{Er}(\text{bipy})_2\text{Cl}_2(\text{OH}_2)_2]\text{Cl}\cdot\text{H}_2\text{O}$ structure described in the reference [24]; Table S2: Metal atom environment for $\text{Dy}(\text{bipy})_2\text{Cl}_2(\text{OH}_2)_2]\text{Cl}\cdot\text{H}_2\text{O}$, **1**; Table S3: Metal atom environment for $\text{La}_2(\text{phen})_2(\text{O}_2\text{CCH}_3)_4(\text{NO}_3)_2$, **2**; Table S4: Metal atom environment for $\text{Lu}(\text{terpy})(\text{O}_2\text{CCH}_3)_3]\cdot\text{NaNO}_3$, **3**; Table S5: Metal atom environment for $\text{Lu}(\text{phen})(\text{O}_2\text{CH})_3(\text{OH}_2)]\cdot\text{H}_2\text{O}$, **4**; Figures S1–S4: Details of atom numbering in each complex; Figures S5–S8: Two-dimensional fingerprint plots generated from the Hirshfeld surfaces, using CrystalExplorer17.

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