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Full Paper

Preparation and Structures of Rare Earth 3-Benzoylpropanoates and 3-Phenylpropanoates*

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Rare earth (RE) complexes of 3-benzoylpropanoate (bp), $[RE(bp)_3(H_2O)_n]$ (RE = La, n = 2; RE = Y, Ce, Pr, Nd, Yb, n = 1) and 3-phenylpropanoate (pp), $[RE(pp)_3]$ (RE = Y, La, Ce, Nd, Yb), have been prepared by metathesis reactions between the corresponding rare earth chloride and the appropriate sodium carboxylate. Analysis by single-crystal X-ray diffraction finds that both RE bp and pp complexes favour formation of carboxylate-bridged 1-D coordination polymers in the solid state. Here, the former favours heteroleptic 9 or 10-coordinate complexes (splitting between Ce and La) with the carbonyl remaining uncoordinated but participating as a hydrogen bond acceptor with water in the coordination sphere. Lack of bp carbonyl coordination leaves this group available for surface interactions during corrosion inhibition and complex solubilization. The latter pp derivatives form eight-coordinate complexes for Y and Yb and are the first examples of homoleptic RE pp complexes to be reported.

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Introduction

Rare earth carboxylates are a rich source of coordination polymers with structural diversity enriched by the high coordination numbers and lack of directional effects exhibited by the rare earth ions and the many coordination modes of the carboxylate ion.^[1–5] Besides the structural and bonding interests, rare earth carboxylates have potential applications in gas absorption, as luminescent probes and light conversion devices,^[6–9] and as catalysts in artificial rubber production.^[10] One promising application is the use of rare earth arene carboxylates^[11–14] as non-toxic alternatives to increasingly restricted toxic chromate corrosion inhibitors.^[15]

Although the carboxylate structural features for optimum anticorrosion activity are not yet clear, some trends are emerging. In particular, additional unsaturation or donor capacity appears advantageous;^[11–13,16–18] see Fig. 1. Thus, good performers include cerium salicylate,^[11–13] lanthanum 3-^[19] and 4-hydroxycinnamate,^[11–13] lanthanum and cerium 3-methoxy-4-hydroxycinnamate (ferulate),^[16] and yttrium 3-(4'-methylbenzoyl)propanoate.^[17,18,20] The importance of unsaturation was shown by the far greater effectiveness of lanthanum 4-hydroxycinnamate relative to lanthanum

3-(4'-hydroxyphenyl)propanoate.^[16,21] Subtle caveats are becoming apparent though, as additional unsaturation, using 3-(4'-hydroxyphenyl)propiolate, reduced effectiveness whereas addition of a methoxy group was an improvement.^[16] Optimal inhibition also varies with the rare earth applied: with salicylate, cerium prevails; for 4-hydroxycinnamate, it is lanthanum;^[11–13] in the ferulate series, both cerium and lanthanum display excellent behaviour;^[16] and for 3-(4'-methylbenzoyl)propanoate,^[22] yttrium performs best.^[17,18]

3-(4'-Methylbenzoyl)propanoic acid (mbpH) is an established corrosion inhibitor, originally sold by Ciba as Irgacor 419 and now available as a 2 : 1 mixture with 4-ethylmorpholine as Irgacor 1405 or Rustban 1405 (Pantech Chemicals). To attempt to understand the behaviour of complexation of mbp with iron, model cage complexes have been prepared.^[23] In neither case was the carbonyl (C=O) group coordinated to iron but in one, it was involved in H-bonding. In the case of the excellent [RE(mbp)₃)(H₂O)] inhibitors,^[17,18] the structures of the complexes show no >C=O-RE interactions,^[22] and the question arises as to the significance of the carbonyl functionality. Although the [RE(mbp)₃(H₂O)] complexes are excellent inhibitors, the limited solubility (0.25 mM) of the optimum

^{*}This paper is dedicated to Professor William Roy Jackson, a great colleague, mentor and friend, whose life will never be forgotten.

yttrium complex has deterred us from pursuing a comparison with analogous complexes without the carbonyl group. We have now found that the corresponding benzoyl derivatives, i.e. of 3benzoylpropanoate (bp, Fig. 1), have greater solubility. Accordingly, we have prepared a range of rare earth complexes (RE = Y, La, Ce, Pr, Nd, Yb) of this ligand and some corresponding 3-phenylpropanoate (pp, Fig. 1) complexes (i.e. without the C=O group) as a prelude to comparing their anticorrosion properties. In this paper, we report the preparations, several X-ray structures, X-ray powder diffraction (XRPD) properties, IR spectra, and solubilities of a range of rare earth bp and pp complexes. In our earlier study of rare earth 3-(4'-methylbenzoyl)propanoate complexes,^[22] we were unable to obtain single crystals of an La complex. We now report the structure of $[La(mbp)_3(H_2O)_2]$. 3H₂O together with an understanding of the difficulties in its characterization.

Results and Discussion

Rare earth 3-benzoylpropanoates and 3-phenylpropanoates were precipitated on mixing aqueous solutions of the appropriate

sodium carboxylate and rare earth chloride. Crystals of the compounds were obtained by slow evaporation of aqueous ethanol solutions. The bulk crystals of [RE(bp)₃(H₂O)] (RE = Ce, Pr, Nd, Yb, Y) and $[RE(pp)_3]$ (RE = Yb, Y) gave microanalyses consistent with the single-crystal compositions, whereas the $[RE(pp)_3] \cdot nH_2O$ (RE = La, n = 0.5; RE = Ce, n = 1; RE = Nd, n = 3) compositions were derived by microanalysis as the crystal diffraction data were unsatisfactory. Microanalysis of the La bp complex was indicative of the composition $La(bp)_3(H_2O)_{1.5}$, whereas the low-temperature X-ray diffraction data indicated a 2:1 mixture of [La(bp)₃(H₂O)₂]·H₂O and [La(bp)₃(H₂O)₂]·2H₂O. Water is evidently readily lost at room temperature as the X-ray powder diffractogram of the bulk crystals indicates the presence of two phases, one with a powder pattern corresponding to that simulated from the X-ray structure while the other matches the pattern of [Ce(bp)₃(H₂O)], see Fig. 2a. The latter is presumably [La(bp)₃(H₂O)] isomorphous with the Ce complex and with a much lower amount of water $(-2H_2O \text{ or } -3H_2O)$ than the single crystals. Partial formation of an anhydrous La(bp)₃ species is also evident by thermogravimetric





Fig. 1. Ligands for actual and potential rare earth carboxylate corrosion inhibitors.

Fig. 2. (a) XRPD of the bulk $La(bp)_3$ sample and simulated XRPD patterns for $[La(bp)_3(H_2O)_2] \cdot 1 \ 1/3H_2O$ and $[Ce(bp)_3(H_2O)]$. (b) XRPD of bulk RE(mbp)_3 samples (RE = La, Ce) and simulated XRPD pattern of $[La(mbp)_3 (H_2O)_2] \cdot 3H_2O$. Simulated patterns obtained from single-crystal data.

analysis (TGA) of the bulk sampled for microanalysis (~1.1 H₂O loss). Heating a fresh sample of $[La(bp)_3(H_2O)_2] \cdot 11/3H_2O$ shows, by IR and XRPD, water loss, residual $[La(bp)_3(H_2O)_2] \cdot 11/3H_2O$ and a species of low crystallinity, presumably anhydrous $La(bp)_3$. From a lengthy crystallization procedure, single crystals of $[La(mbp)_3(H_2O)_2] \cdot 3H_2O$ were obtained. This compound could not be satisfactorily crystallized previously. On standing, the crystals lost water to give a powder pattern corresponding to overlapping patterns derived from the crystal and that of $[Ce(mbp)_3(H_2O)]$; see Fig. 2b. Correspondence of the latter is attributable to formation of isomorphous $[La(mbp)_3(H_2O)]$ by loss of four H₂O from the efflorescent single crystals. The ready water loss explains the previous crystallographic problems.

Solubilities

Solubilities (see Table 1) were determined by dissolution in boiling aqueous ethanol, boiling off the ethanol, cooling, and standing at room temperature while part of the complex deposited (2–3 h). This was collected and weighed to determine what remained in solution. The values indicated an approximate 3-fold increase in solubility for the bp complexes over the corresponding mbp complexes (solubility ~ 0.25 mM); hence, the bp complexes are potentially more useful than the mbp derivatives. Although low solubility in water is attractive for use in coatings, a somewhat higher solubility would enable concentrations to be varied for electrochemical measurements of inhibition and to be tailored for different uses in aqueous solution, such as for protection of cooling towers or radiators.

Structural Studies

The structures of $[La(bp)_3(H_2O)_2] \cdot 1 \ 1/3H_2O$, $[RE(bp)_3(H_2O)]$ (RE = Ce, Yb, Y) and $[RE(pp)_3]$ (RE = Yb, Y) were determined. Rare earth coordination bond lengths can be found in Table 2 and crystal refinement data are given in the *Experimental* section. Unit cell data (*Experimental* section) show that $[RE(bp)_3(H_2O)]$ (RE = Nd, Pr) are isomorphous with the Ce, Yb, and Y analogues but the data could not be refined satisfactorily owing to twinning that could not be resolved.

The lanthanum complex was modelled as a mixed crystal of $[La(bp)_3(H_2O)_2] \cdot H_2O$ and $[La(bp)_3(H_2O)_2] \cdot 2H_2O$ in a 2 : 1 ratio. As the variation in water of crystallization only has effects at the periphery of the molecules, the lanthanum coordination spheres are the same in both components. The complex is a polymer with 10-coordinate lanthanum. The molecular array is shown in Fig. 3a, the lanthanum coordination sphere in Fig. 3b, and the coordination polymer in Fig. 3c. Each La atom is coordinated by a chelating $1\kappa(O,O')$ carboxylate, two chelating components of two μ -1 κ (O,O'):2 κ (O) ligands, two unidentate components of two μ -1 κ (O):2 κ (O,O') ligands, and two *cisoid* water ligands $(O(10)-La(1)-O(11): 68.61(5)^{\circ})$. The coordinated aqua ligands form O-H…O hydrogen bonds with a carboxylate or carbonyl oxygen; see Fig. 3b, d. The shortest RE-O bond lengths, La– $O(4^1,7^n)$ by >0.1 Å, involve bridging oxygens rather than any of the four terminal oxygens. The three chelate rings vary from symmetrical to quite unsymmetrical (0.14 Å) binding, presumably reflecting steric strain and/or H-bonding effects. The carbonyl group is not coordinated but is involved in hydrogen bonding.

The isomorphous series of complexes $[RE(bp)_3(H_2O)]$ (RE = Y, Ce, Nd, Pr, Yb) have polymeric structures with ninecoordinate rare earth ions. A representative structure of $[Ce(bp)_3$ (H₂O)] can be found in Fig. 4. Bond lengths for the cerium coordination sphere and crystal refinement data are given in Table 2 and the *Experimental* section, respectively. The coordination environment comprises two *transoid* chelating $\kappa(O,O')$ carboxylates of μ -1 $\kappa(O,O')$:2 $\kappa(O)$ ligands, two single oxygens of μ -1 $\kappa(O)$;2 $\kappa(O,O')$ ligands, an oxygen from each of two separate μ -1 $\kappa(O)$:2 $\kappa(O')$ ligands, and an aqua ligand. Chelation is more symmetrical than in [La(bp)_3(H_2O)_2]·1 1/3H_2O and the two shortest RE–O bonds again involve bridging, not terminal, oxygen atoms (Table 2). RE–OH₂ bond lengths in the [RE(bp)_3 (H₂O)] complexes are shorter than those of [La(bp)_3(H_2O)_2]·1 1/3H_2O by considerably more than expected for the change in

Table 1. Solubility of rare earth bp and pp complexes in water

Compound	Y(bp) ₃	La(bp) ₃	Ce(bp) ₃	Pr(bp) ₃	Nd(bp) ₃	Yb(bp) ₃	Y(pp) ₃	La(pp) ₃	Ce(pp) ₃	Nd(pp) ₃	Yb(pp) ₃
Solubility	0.80 mM	0.70 mM	0.73 mM	0.57 mM	0.76 mM	0.95 mM	0.72 mM	0.67 mM	0.69 mM	0.93 mM	0.39 mM
	530 ppm	470 ppm	490 ppm	380 ppm	510 ppm	685 ppm	380 ppm	390 ppm	410 ppm	550 ppm	240 ppm

Table 2.	Selected bond	distances	(Å) for	rare earth	bp and	pp complexes
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Atoms	La(bp) ₃	Atoms	Y(bp) ₃	Ce(bp) ₃	Yb(bp) ₃	Atoms	Y(pp) ₃	Yb(pp) ₃
M-O(1)	2.5836(13)	M-O(1)	2.467(5)	2.587(3)	2.434(4)	M-O(1)	2.372(4)	2.342(5)
M-O(2)	2.6642(14)	$M-O(1)^{ii}$	2.439(4)	2.537(3)	2.397(4)	M-O(2)	2.462(4)	2.438(5)
M-O(4)	2.6342(12)	M-O(2)	2.518(4)	2.632(3)	2.511(3)	$M-O(2)^{i}$	2.353(4)	2.321(5)
$M-O(4)^i$	2.4835(12)	M-O(4)	2.425(4)	2.536(3)	2.398(3)	M-O(3)	2.307(4)	2.273(4)
M-O(5)	2.6285(13)	M-O(5)	2.436(4)	2.565(3)	2.395(4)	M-O(4)	2.716(4)	2.772(5)
M-O(7)	2.7370(12)	$M-O(5)^{i}$	2.318(4)	2.443(3)	2.288(4)	$M-O(4)^{i}$	2.343(4)	2.305(4)
$M-O(7)^{ii}$	2.4616(12)	M-O(7)	2.321(4)	2.446(3)	2.295(3)	M-O(5)	2.252(4)	2.216(5)
M-O(8)	2.6007(13)	M–O(8) ⁱⁱ	2.404(4)	2.517(3)	2.376(3)	$M-O(6)^{i}$	2.235(4)	2.202(5)
M-O(10)	2.5777(14)	M-O(10)	2.351(4)	2.486(3)	2.312(3)			
M-O(11)	2.6426(14)							

Symmetry operators: La(bp)₃, ⁱ-*x*, 1-*y*, 1-*z*, ⁱⁱ 1-*x*, 1-*y*, 1-*z*; Y(bp)₃, ⁱ*x*, 11/2-*y*, 1/2+*z*, ⁱⁱ*x*, 11/2-*y*, *z*-1/2; Ce(bp)₃, ⁱ*x*, 11/2-*y*, 1/2+*z*, ⁱⁱ*x*, 11/2-

Rare Earth Carboxylate Complexes



Fig. 3. (a) Molecular diagram; (b) lanthanum coordination environment; (c) 1-D coordination polymer chain along the *a* axis; and (d) intra and intermolecular hydrogen bonding of $[La(bp)_3(H_2O)_2] \cdot H_2O$. Atoms generated by symmetry operators: i -x, 1 - y, 1 - z; ii -x, 1 - y, 1 - z.



Fig. 4. (a) Molecular diagram; (b) cerium coordination environment; (c) 1-D coordination polymer chain along the *c* axis; and (d) intra and intermolecular hydrogen bonding of [Ce(bp)₃(H₂O)]. Atoms generated by symmetry operators: ⁱ x, 1 1/2 - y, 1/2 + z; ⁱⁱ x, 1 1/2 - y, z - 1/2.

coordination number and of rare earth element, thereby implying relief of steric strain. For the coordinated water, there are $O-H\cdots O$ hydrogen bonds to a carboxylate oxygen in the same polymer chain and to a carbonyl oxygen of an adjacent chain. Again, the carbonyl groups are not coordinated. Only two 3-phenylpropanoate complexes could be obtained as crystals suitable for structure determination. $[RE(pp)_3]$ with RE = Y, Yb were isolated without coordinated or lattice water and are isomorphous. The structure of the Yb complex is shown in Fig. 5. Bond lengths and crystal refinement data can be found in



Fig. 5. (a) Molecular diagram; (b) ytterbium coordination environment; and (c) 1-D coordination polymer chain of $[Yb(pp)_3]$. Atoms generated by symmetry operators: i 1/2 + x, 1 - y, z.

Table 2 and the Experimental section, respectively. The isomorphous pair contain eight-coordinate rare earth ions. In the coordination sphere, there are two *cisoid* (\sim 91–92°) chelating groups from μ -1 κ (O,O'):2 κ (O') ligands, two single oxygen donors from μ -1 κ (O):2 κ (O,O') ligands, and two single oxygens from μ -1 κ (O):2 κ (O') ligands, as observed in [RE(bp)₃(H₂O)] though without coordinated water. In addition, the chelate rings are cisoid compared with transoid in the bp complexes. A striking feature is the asymmetry of the O(3)-RE-O(4) chelate ring, where RE–O(4) is longer than RE–O(3) by ~ 0.5 Å (Yb) or 0.4 Å (Y). This bond is also $\sim 0.4 \text{ Å}$ longer than in corresponding bonds of nine-coordinate [RE(bp)₃(H₂O)] complexes. Despite this, <RE–O> for the pp complexes is slightly smaller than for the bp analogues, though by less than expected for a change of coordination number. In the [RE(pp)3] series, the shortest RE-O bonds are those of the μ -1 κ (O):2 κ (O') ligands. Although there are several rare earth 3-phenylpropanoate structures reported, the current complexes are the first homoleptic derivatives to be structurally characterized. The sole structures of aqua complexes of the unsubstituted 3-phenylpropanoate ion are five isomorphous monomeric nine-coordinate [RE(pp)₃(H₂O)₂]. Hpp (RE = Eu, Gd, Tb, Dy, Er) species, which crystallize with lattice 3-phenylpropanoic acid and have terminal chelating pp ligands^[24] that are not observed in our $[RE(pp)_3]$ complexes. Other reported aqua complexes are of substituted 3-phenylpropanoates, mainly 2-hydroxy^[25] or 4-hydroxy^[21] derivatives. There are also several structures of 2,2'-bipyridine and 1,10-phenanthroline complexes of both the simple 3-phenylpropanoate and also 2- and 4-hydroxy derivatives in which the coligands completely displace aqua ligands.^[26-31]

The structure of $[La(mbp)_3(H_2O)_2]\cdot 3H_2O$ was determined but there were problems with the refinement (see *Experimental*); hence, the structure is discussed in terms of connectivity only. The crystal and refinement data, and lanthanum coordination bond lengths are given in the supplementary material. The complex is a polymer with ten-coordinate lanthanum (see Fig. 6) that differs from [La(bp)₃(H₂O)₂]·1 1/3H₂O in several regards, thereby showing the considerable effect of the 4-Me group on the overall array. As in the bp analogue, there are two oxygens coordinated from each of two μ -1 κ (O,O'):2 κ (O') ligands and the chelate rings are *transoid* ($\sim 156^{\circ}$), and two oxygens from two μ -1 κ (O'):2 κ (O,O') ligands. However, the two aqua ligands are *transoid* $(O(10)-La-O(11) = 131.8(2)^{\circ})$ as distinct from *cisoid* in the bp analogue. The chief difference is that the chelating bp ligand is replaced by oxygen atoms from two μ -1 κ (O):2 κ (O') mbp ligands. Thus, the polymer is more tightly connected than in the bp complex. Dehydration to give the La analogue of the crystallographically defined [Ce(mbp)₃ (H₂O)]^[22] (see characterization above) involves no rearrangement of the carboxylate binding modes.

Infrared Spectroscopy (Table 3)

The IR spectra of the $[\text{RE}(bp)_3(\text{H}_2\text{O})_n]$ complexes show v(CO) absorptions at 1693–1672 cm⁻¹ arising from the hydrogen-bonded carbonyl group. The values are similar to those of $[\text{RE}(\text{mbp})_3$ (H₂O)] complexes,^[22] but the feature is more complex. In addition, a $\delta(\text{CO})$ band was identified at 662–663 cm⁻¹, a feature not assigned in $[\text{RE}(\text{mbp})_3(\text{H}_2\text{O})]$ spectra.^[22] As expected, this region is clear in the spectra of $[\text{RE}(\text{pp})_3] \cdot n\text{H}_2\text{O}$ (n = 0–3) complexes (see *Experimental*). The $v_{as}(\text{CO}_2)$ and $v_s(\text{CO}_2)$ absorptions of both $[\text{RE}(bp)_3(\text{H}_2\text{O})_n]$ and $[\text{RE}(pp)_3] \cdot n\text{H}_2\text{O}$ (n = 0–3) complexes are complicated features in the expected regions (~1580–1500 and 1420–1390 cm⁻¹ respectively), the complexity reflecting the multiple coordination modes of the



Fig. 6. Extended 1-D coordination polymer chain showing the lanthanum coordination environment of [La(mbp)₃(H₂O)₂]·3H₂O.

Assignment	$Y(bp)_3$	La(bp) ₃	$Ce(bp)_3$	$Pr(bp)_3$	$Nd(bp)_3$	Yb(bp) ₃	$Y(pp)_3$	La(pp) ₃	$Ce(pp)_3$	$Nd(pp)_3$	$Yb(pp)_3$
v(OH)	3490	3455	3449	3461	3461	3496		3391	3392	3330	
	3283	3166		3174	3283	3279		3236	3230		
	3157				3164	3158					
v(CO) of	1693	1691	1687	1692	1691	1692					
isolated	1684	1686	1672	1687	1686	1684					
C=O	1674	1673		1674	1673	1675					
$v_{\rm as}(\rm CO_2)$	1591	1597	1596	1597	1596	1591	1542	1527	1525	1540	1542
	1579	1574	1574	1575	1575	1579	1520	1509	1510	1524	1521
	1560	1548	1559	1560	1561	1560	1509			1510	1509
	1554	1534	1552	1551	1552	1555					
	1535		1535	1536	1534	1536					
$v_{\rm s}({\rm CO}_2)$	1421	1412	1413	1421	1420	1421	1418	1416	1419	1421	1417
	1401	1400	1400	1414	1400	1401	1404	1407	1406	1408	1404
				1401							
$\delta(CO_2)$	-	678	678	678	679		669	670	670	669	670
δ(CO ₂) of isolated C=O	663	663	662	662	662	663					

Table 3. Selected infrared bands (cm⁻¹) for bp and pp rare earth coordination compounds

ligands. The v(OH) bands of the bp complexes are weak, broad, and split into several features, as expected for the extensive Hbonding, whereas the pp complexes have fewer v(OH) bands and the unsolvated Y and Yb complexes have no absorptions above aromatic v(CH) at $\sim 3100 \text{ cm}^{-1}$. All complexes show the expected features associated with monosubstituted benzenes (*Experimental* section).

Conclusions

The successful synthesis and characterization of a comparable set of rare earth 3-benzoylpropanoate and 3-phenylpropanoate complexes provide a basis for determining the importance of the carbonyl group of the 3-benzoyl substituent on corrosion inhibitor properties. As the bp complexes are more soluble than the excellent inhibitor $[Y(mbp)_3(H_2O)]$, the comparison can be made over a wider solubility range than would be possible with the mbp system. To assess the corrosion inhibiting properties of

the compounds, electrochemical methods such as potentiodynamic polarization and impedance spectroscopy will be used. Polarization probes the effect of a compound on cathodic and anodic reaction rates as well as the overall corrosion current, whereas impedance spectroscopy also provides information on the surface effects. Imaging of immersed surfaces is also used to determine the effect on corrosion mechanisms such as pit growth. An isomorphous series of $[RE(bp)_3(H_2O)]$ (RE = Ce, Pr, Nd, Yb, Y) complexes crystallize as coordination polymers with nine-coordinate RE atoms, whereas [La(bp)3(H2O)2]·11/3H2O is a cocrystallized 2:1 mono-hydrate or dihydrate, both of which are polymeric with 10-coordinate La, and readily dehydrate to an isotype of [Ce(bp)₃(H₂O)]. [La(mbp)₃(H₂O)₂]·3H₂O has also been crystallized as a polymer with 10-coordinate La, but the coordination differs from that of the bp analogue. It also readily dehydrates. Five pp complexes were prepared (RE = La, Ce, Nd, Yb, Y), but only $[RE(pp)_3]$ (RE = Y, Yb) were obtained

Complex	Y(bp) ₃ ^A	La(bp) ₃ ^B	Ce(bp) ₃	Pr(bp) ₃ ^C	Nd(bp) ₃ ^C	Yb(bp) ₃ ^A	Y(pp) ₃	Yb(pp) ₃
Empirical formula	C ₃₀ H ₂₉ O ₁₀ Y	C ₃₀ H _{33 2/3} O _{12 1/3} La	C ₃₀ H ₂₉ O ₁₀ Ce	C30H29O10Pr	C30H29O10Nd	C ₃₀ H ₂₀ O ₁₀ Yb	C ₂₇ H ₂₇ O ₉ Y	C ₂₇ H ₂₇ O ₉ Yb
Formula weight	638.44	730.47	689.65	690.44	693.80	722.57	536.39	620.52
Crystal system	Monoclinic	Triclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$PP\overline{1}$	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2_1/c$	Ia	Ia
Colour	Colourless	Colourless	Colourless	Pale green	Colourless	Colourless	Colourless	Colourless
a [Å]	30.1795(7)	8.6328(2)	29.1035(3)	29.1811(8)	29.2275(3)	30.0406(6)	8.0242(2)	7.9985(2)
<i>b</i> [Å]	11.9946(2)	13.2306(2)	12.0352(1)	12.0334(3)	12.0285(2)	11.9398(3)	22.5750(6)	22.5212(5)
c [Å]	7.6267(2)	13.6590(3)	7.9365(1)	7.8786(2)	7.8367(1)	7.5382(2)	13.3057(4)	13.3096(3)
α [°]	90	93.090(2)	90	90	90	90	90	90
β [°]	94.032(2)	98.428(2)	94.911(1)	94.759(2)	94.544(1)	93.782(2)	98.697(3)	98.603
γ[°]	90	104.207(2)	90	90	90	90	90	90
V [Å ³]	2753.96(11)	1489.46(5)	2769.68(5)	2756.99(13)	2746.41(6)	2697.90(11)	2382.56(11)	2370.56(10)
Ζ	4	2	4			4	4	4
λ [Å]	1.54184	0.71073	1.54184	0.71073	1.54184	1.54184	0.71073	0.71073
Temperature [K]	123	123	123	123	123	123	123	123
$\mu [\mathrm{mm}^{-1}]$	3.494	1.499	13.208			6.932	2.488	3.986
T _{min/max}	0.274, 1.000	0.526, 1.000	0.568, 1.000			0.613, 1.000	0.164, 1.000	0.256, 1.000
$2\theta_{\rm max}$ [°]	153.7	57.4	153.7			153.9	55.0	55.8
N _t	18769	41145	27258			25553	26820	15722
N, R _{int}	6486, 0.082	7704, 0.054	5668, 0.042			8013, 0.051	5435, 0.068	4960, 0.041
$N_o(I \ge 2\sigma(I))$	5937	7072	5393			7648	4779	4257
Parameters	379	488	469			379	316	316
$R_1 (I > 2\sigma(I))$	0.061	0.024	0.037			0.038	0.044	0.029
wR_2 (all data)	0.188	0.057	0.097			0.107	0.101	0.078
GoF	1.096	1.084	1.156			1.034	1.091	1.073
$\Delta e_{\min,\max} [e \text{ Å}^{-3}]$	-1.73, 1.26	-0.72, 1.25	-1.27, 1.21			-1.91, 2.24	-0.87, 0.92	-1.30, 2.28
CCDC no.	2009222	2009226	2009223			2009221	2009224	2009225

Table 4. Crystallographic data and structure refinement for rare earth bp and pp complexes

^AData treated as a two-component non-merohedral twin.

^BThe structural model comprises a disordered 2:1 mixture of [La(bp)₃(H₂O)₂]·H₂O and [La(bp)₃(H₂O)₂]·2H₂O.

^CFull structure refinements not obtained as crystal samples examined showed evidence of twinning that could not be resolved.

as structurally viable single crystals. They are polymeric with eight-coordinate rare earth atoms and are the first homoleptic pp complexes.

Experimental

General

Solvents and chemicals were purchased from Sigma–Aldrich and used without further purification. Microanalyses (C, H) were obtained from Galbraith Laboratories (Knoxville, TN, USA). IR spectra were recorded using an Agilent Cary 630 (FT)IR spectrophotometer equipped with a single-reflection diamond attenuated total reflectance accessory. TGA was recorded on a TA Instruments SDT 650 using a temperature range of 25–400°C (ramp 10°C min⁻¹), standard 40 µL Al metal pan and N₂ gas (50 mL min⁻¹). Powder diffraction data were recorded at room temperature using a Bruker D8 ADVANCE Eco fitted with a Lynxeye detector, Cu source (wavelength 1.54059 Å), and Ni filter.

Preparation of Sodium 3-Benzoylpropanoate and Phenylpropanoate

bpH or ppH (1.5 g) in ethanol (15 mL) was added to an equimolar amount of NaHCO₃ in water (20 mL) and stirred for 20 min. Solutions were then filtered, evaporated to dryness under a stream of air at room temperature, and the resulting solid dried in a vacuum desiccator for 24 h.

Preparation of Rare Earth bp and pp Complexes

Three molar equiv. of aqueous sodium 3-benzoylpropanoate and 3-phenylpropanoate were filtered into 1 molar equiv. of stirred aqueous rare earth chloride, affording immediate precipitate formation. The resulting suspensions were stirred for 2 h before the precipitates were isolated, washed with water followed by ethanol, and dried to constant mass under vacuum (24-48 h). Crystals were prepared by partial dissolution of the bulk rare earth complexes in a boiling water/ethanol mixture (80: 20, 200-400 mL) before being filtered and concentrated by slow evaporation of solvent over 1–2 weeks.

Dehydration of La(bp)3

Crystalline La(bp)₃ was homogenized with a spatula and sampled for IR and XRPD before being heated to 60°C for 30 min under a circulated N₂ atmosphere. After 30 min, the temperature was ramped to 100°C (ramp 1°C min⁻¹) with periodic mixing of the sample. Once 100°C was reached, the sample was cooled to room temperature under N₂ before being sampled for IR and XRPD.

$[Y(bp)_3(H_2O)]$

Colourless crystals; yield 41 %. v_{max} (ATR)/cm⁻¹ 3490wbr, 3157vwbr, 3089vw, 3074vwsh, 3062w, 3028vw, 2983vw, 2955vw, 2914wsh, 2903w, 1693m, 1684m, 1674m, 1656w, 1648vw, 1626w, 1617w, 1591s, 1579s, 1560vssh, 1554vsbr, 1535msh, 1509w, 1500w, 1491w, 1474wsh, 1458w, 1446ssh, 1434vs, 1421ssh, 1401vs, 1390ssh, 1357vs, 1310m, 1296s,

1267m, 1253msh, 1240s, 1201s, 1181s, 1151m, 1102w, 1080w, 1064w, 1027vw, 1018w, 1000w, 990w, 972m, 956msh, 952m, 931w, 925wsh, 895w, 884m, 856vwsh, 848w, 836vwsh, 827vw, 799vw, 763s, 747vs, 691vs, 685vs, 670msh, 663m. Anal. Calc. for $C_{30}H_{29}O_{10}Y$: C 56.43, H 4.58. Found: C 56.10, H 4.05%.

$[La(bp)_3(H_2O)_2] \cdot 1 \ 1/3H_2O \ ([La(bp)_3(H_2O)_2] \cdot 2H_2O: \\ [La(bp)_3(H_2O)_2] \cdot H_2O \ 1:2)$

Colourless crystals; yield 45 %. TGA weight loss calculated for: $0.5H_2O$, 1.31 %; $1.1H_2O$, 2.84 %. Found in the range of 50–80°C: 2.81 %. v_{max} (ATR)/cm⁻¹ 3455vwbr, 3166vwbr, 3088vw, 3061vw, 3028vw, 2977vw, 2945vw, 2920vwsh, 2905vw, 1691msh, 1686m, 1673s, 1656vwsh, 1648vwsh, 1631vw, 1597m, 1574vs, 1548vsbr, 1534ssh, 1509wsh, 1499vwsh, 1491vw, 1475vw, 1441msh, 1424vs, 1412vssh, 1400vs, 1389ssh, 1358vs, 1314wsh, 1293vs, 1267m, 1240s, 1202s, 1182s, 1171msh, 1151wsh, 1100vw, 1078vwsh, 1064w, 1028vw, 1017vw, 1001w, 988w, 977w, 969m, 951m, 932vw, 923vwsh, 886w, 879m, 857vw, 846vw, 836vwsh, 822vw 798vw, 759s, 748vs, 688vs, 678ssh, 663m. Anal. Calc. for C₃₀H₂₉LaO₁₀: C 52.34, H 4.25. Anal. Calc. for C₃₀H₃₀LaO_{10.5}: C 51.66, H 4.34. Anal. Calc. for C₃₀H_{33.66}LaO_{12.33}: C 49.33, H 4.65. Found: C 51.53, H 4.62 %.

$[Ce(bp)_{3}(H_{2}O)]$

Colourless crystals; yield 31 %. ν_{max} (ATR)/cm⁻¹ 3449wbr, 3087vw, 3061w, 3029vw, 2980vw, 2904w, 1687s, 1672s, 1655w, 1648w, 1636wsh, 1632w, 1618wsh, 1596s, 1576s, 1559ssh, 1552ssh, 1544s, 1535ssh, 1508w, 1499vwsh, 1491vw, 1449wsh, 1441msh, 1423vs, 1413vs, 1400vs, 1389vssh, 1354vs, 1313m, 1292vs, 1266s, 1236vs, 1202vs, 1180s, 1164msh, 1153msh, 1099w, 1077w, 1065m, 1027w, 1018w, 1000m, 987m, 978m, 968m, 951s, 932w, 924w, 888m, 879m, 853w, 825wsh, 795w, 758s, 748vs, 686vs, 678ssh, 662m. Anal. Calc. for C₃₀CeH₂₉O₁₀: C 52.24, H 4.24. Found: C 52.19, H 4.33 %.

$[Pr(bp)_{3}(H_{2}O)]$

Pale green crystals; yield 49 %. v_{max} (ATR)/cm⁻¹ 3461vwbr, 3174vwbr, 3087vw, 3060vw, 3028vw, 2981vw, 2942vw, 2927vwsh, 2905vw, 1692m, 1687m, 1674m, 1655w, 1648vw, 1637vw, 1631vw, 1625vwsh, 1619vw, 1597m, 1575s, 1560s, 1551vssh, 1543vs, 1536ssh, 1524msh, 1509w, 1500w, 1491vw, 1475vw, 1466vw, 1458w, 1446msh, 1427vs, 1421vssh, 1414ssh, 1401vs, 1390msh, 1357s, 1313wsh, 1295s, 1268w, 1239s, 1203m, 1182m, 1154w, 1103vwsh, 1078vw, 1065vw, 1028vw, 1018vw, 1001w, 990w, 978w, 969w, 953w, 932vw, 924vwsh, 890w, 881m, 854vw, 846vwsh, 837vwsh, 827vw, 798vw, 760m, 749vs, 717vw, 688vs, 678msh, 662w. Anal. Calc. for $C_{30}H_{29}PrO_{10}$: C 52.19, H 4.41. Found: C 52.17, H 4.23 %.

$[Nd(bp)_3(H_2O)]$

Colourless crystals; yield 48 %. ν_{max} (ATR)/cm⁻¹ 3461wbr, 3164vwbr, 3087vw, 3062w, 3029vw, 2983vw, 2905w, 1691m, 1686m, 1673s, 1656w, 1648w, 1637w, 1630w, 1619w, 1596m, 1576s, 1561ssh, 1543vs, 1534vssh, 1509m, 1500w, 1491w, 1474w, 1465wsh, 1458w, 1445msh, 1428vs, 1420vssh, 1400vs, 1390ssh, 1356vs, 1313msh, 1293s, 1267m, 1238s, 1202s, 1181s, 1153m, 1101wsh, 1078w, 1065w, 1027w, 1017w, 1001m, 990m, 977m, 969m, 952m, 932w, 924wsh, 890m, 881m, 853w, 847wsh, 826vw, 798w, 759s, 748vs, 716wsh, 686vs, 679ssh, 662m. Anal. Calc. for C₃₀H₂₉NdO₁₀: C 51.93, H 4.21. Found: C 51.75, H 4.34%.

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$[Yb(bp)_{3}(H_{2}O)]$

Colourless crystals; yield 20 %. v_{max} (ATR)/cm⁻¹ 3496vwbr, 3158vwbr, 3090vw, 3074vw, 3062vw, 3027vw, 2984vw, 2915vwsh, 2903w, 1692m, 1684m, 1675s, 1656vw, 1648vw, 1624wsh, 1620w, 1591s, 1579s, 1560vssh, 1555vs, 1542ssh, 1536msh, 1508w, 1499vw, 1491vw, 1474vwsh, 1460w, 1446ssh, 1435vs, 1401vs, 1389ssh, 1356vs, 1311m, 1295s, 1267m, 1253m, 1239s, 1201s, 1181s, 1151m, 1102m, 1080w, 1064w, 1027vw, 1018w, 1007vwsh, 1001w, 991w, 972m, 956m, 952m, 936w, 924wsh, 897w, 885m, 855vwsh, 848vw, 827vw, 798vw, 763s, 747vs, 692vs, 684vs, 663m. Anal. Calc. for C₃₀H₂₉O₁₀Yb: C 49.86, H 4.05. Found: C 49.82, H 4.05 %.

$[Y(pp)_3]$

Colourless crystals; yield 42 %. v_{max} (ATR)/cm⁻¹ 3105vw, 3083vw, 3057vw, 3042vwsh, 3028vw, 3003vw, 2968vwsh, 2928vw, 2861vw, 1601vw, 1543wsh, 1520s, 1494s, 1451ssh, 1433vs, 1417vs, 1402vs, 1345m, 1334m, 1272m, 1242m, 1206w, 1182w, 1167w, 1152w, 1111vw, 1080w, 1047vw, 1027w, 1006w, 999wsh, 988vw, 971vw, 954w, 915vw, 856vw, 851vw, 836w, 814vw, 788w, 755m, 743msh, 722s, 698vs, 669wsh. Anal. Calc. for C₂₇H₂₇O₆Y: C 60.40, H 4.81. Found: C 60.45, H 5.07 %.

$[La(pp)_{3}] \cdot 0.5H_{2}O$

Colourless crystals; yield 55 %. v_{max} (ATR)/cm⁻¹ 3391wbr, 3087vw, 3060vw, 3027w, 3005vw, 2956vw, 2933vw, 2870vw, 1603vw, 1555msh, 1527vs, 1509ssh, 1494s, 1475w, 1440vssh, 1417vs, 1407vs, 1338s, 1329s, 1276m, 1247msh, 1238m, 1234m, 1180w, 1161w, 1153w, 1110vw, 1078w, 1044w, 1028w, 1002w, 983vw, 968vw, 952w, 944w, 910wsh, 904w, 871vw, 832w, 786w, 747s, 695vs, 685ssh, 670s. Anal. Calc. for C₂₇H₂₈LaO_{6.5}: C 54.46, H 4.74. Found: C 54.46, H 4.62 %.

$[Ce(pp)_3] \cdot H_2O$

Colourless crystals yield: 45 %. v_{max} (ATR)/cm⁻¹ 3392wbr, 3086vw, 3061w, 3027w, 3005vwsh, 2956vw, 2933w, 2870vw, 1655vw, 1638vw, 1602vw, 1554msh, 1525vs, 1510ssh, 1495s, 1437ssh, 1419vssh, 1406vs, 1338s, 1329s, 1276m, 1249msh, 1237m, 1232msh, 1179w, 1161wsh, 1153w, 1110w, 1077w, 1044w, 1027w, 1001w, 983vwsh, 967vwsh, 952w, 945w, 908wsh, 904w, 872vw, 832w, 809vwsh, 785w, 747m, 717msh, 695vs, 670msh. Anal. Calc. for C₂₇H₂₉CeO₇: C 53.54, H 4.83. Found: C 53.65, H 4.41 %.

$[Nd(pp)_3] \cdot 3H_2O$

Colourless crystals; yield 56 %. v_{max} (ATR)/cm⁻¹ 3339vwbr, 3086vw, 3061vw, 3027vw, 3003vwsh, 2960vwsh, 2926vw, 2863vw, 1603wsh, 1524vs, 1510vssh, 1497s, 1452ssh, 1438vssh, 1431vssh, 1421vssh, 1408vs, 1341m, 1331m, 1304m, 1273msh, 1240m, 1180w, 1163w, 1155w, 1109vw, 1078w, 1029w, 1003w, 981vw, 966wsh, 951w, 906w, 874vw, 839w, 830wsh, 786w, 775wsh, 748m, 716m, 695vs, 669s, 663m. Anal. Calc. for C₂₇H₂₇NdO₆: C 50.22, H 5.15. Found: C 50.37, H 4.83 %.

$[Yb(pp)_3]$

Colourless crystals; yield 51 %. I ν_{max} (ATR)/cm⁻¹ 3085vw, 3058vw, 3040vwsh, 3029vw, 3003vw, 2970vwsh, 2929vw, 2862vw, 1601vw, 1542msh, 1521s, 1509ssh, 1494s, 1474msh, 1452ssh, 1434vs, 1417vs, 1404vs, 1346s, 1334m, 1319msh, 1282msh, 1272m, 1242m, 1205w, 1182w, 1166w, 1152w, 1111w, 1080m, 1045w, 1027w, 1006w, 1000wsh, 989ws, 972w, 956w, 914vw, 857vw, 851vw, 837w, 815vw, 788w,

754s, 744msh, 723s, 698vs, 670wsh. Anal. Calc. for $C_{27}H_{27}O_6$ Yb: C 52.26, H 4.39. Found: C 52.34, H 4.22 %.

$[La(mbp)_3(H_2O)_2] \cdot 3H_2O$

Colourless single crystals of the *title compound* were prepared by slow mixing of aqueous lanthanum chloride and Na(mbp) solutions from opposite arms of an H-tube assembly. Precipitation commenced where the solutions met in the crossarm and, after several months of standing at room temperature, single crystals were found among the precipitate and separated for structural examination.

X-Ray Crystallographic Data and Refinement of Structures (*Table 4*)

Representative needle-shaped crystals of $RE(bp)_3$ and $RE(pp)_3$ compounds were mounted onto nylon loops and placed in the cold nitrogen stream of a Rigaku Synergy S diffractometer fitted with a Hypix6000HE hybrid photon counting detector. Diffraction data were collected using MoK α ([La(bp)₃(H₂O)₂]·1 1/3H₂O, $[Yb(pp)_3]$, and $[Y(pp)_3]$) or CuK α ($[RE(bp)_3(H_2O)]$, RE = Ce, Yb, Y) radiation and processed, including an empirical (multiscan) absorption correction, with the proprietary software CrysAlisPro.^[32] Data for [RE(bp)₃(H₂O)] (RE = Pr, Nd) were obtained similarly but showed evidence of significant twinning that could not be resolved; only the unit cell parameters are reported here. Crystals of [La(mbp)₃(H₂O)] yielded problematic data using laboratory instruments. Consequently, the final dataset was obtained on the MX1 beamline at the Australian Synchrotron and processed with the XDS software program.^[33] All structures were solved and refined by conventional methods using the SHELX2018 software suite.^[34] Non-hydrogen atoms were refined with anisotropic displacement parameter forms and hydrogen atoms attached to carbon were placed in calculated positions using a riding model (d(C-H) = 0.95-0.99 Å), $U_{\rm iso}({\rm H}) = 1.2 \times U_{\rm eq}({\rm C})$). For the water molecules, suitable difference-density peaks were assigned as hydrogen and either freely refined or refined with a restrained geometry (d(O-H = 0.86(2) Å, $H = -O = 109(4)^{\circ}$. Data for $[Yb(bp)_3(H_2O)]$ and $[Y(bp)_3(H_2O)]$ were each processed as two non-merohedral twin domains related by a 180° rotation about [1 0 0] (reciprocal cell axis) using the twinning tools in CrysAlisPro. Twin data statistics are listed in the appropriate CIF files. The structure of $[La(bp)_3(H_2O)_2] \cdot 1 / 3H_2O$ was modelled with one of the bp groups disordered over two positions, with occupancies fixed at 0.66:0.33 after a trial refinement. The minor component has additionally an associated water molecule (occupancy 0.33) not present in the major component. Thus, the overall structural model comprises a 2:1 mixture of [La(bp)₃(H₂O)₂]·H₂O and $[La(bp)_3(H_2O)_2] \cdot 2H_2O$. The structure of $[Ce(bp)_3(H_2O)]$ was modelled with one of the $CH_2C(O)Ph$ groups disordered over two positions, corresponding to a 180° rotation relative to the Ce-O₂CR fragment. Relative occupancies were refined to 0.77: 0.23, and the minor component was refined with restrained anisotropic displacement parameters (ISOR command). Both the structures of [Yb(pp)₃] and [Y(pp)₃] were modelled with one of the propanoate carbon atoms as disordered over two positions ~ 0.60 Å apart and refined with occupancies fixed at 0.5:0.5, and with restrained geometry and anisotropic displacement parameters (SADI, ISOR commands). For the structure of [La(mbp)₃(H₂O)₂], the final refinement cycles yielded a symmetrical pattern of significant residual difference-density peaks

and holes (approximately $<5.5 \text{ e} \text{ Å}^{-3}$) within ~1 Å of the La position, contributing to the high *R* values. The final structural model shows no evidence of disorder and the peaks are in chemically non-sensible positions. Consequently, the residual electron density peaks are presumed to be artefacts resulting from systemic errors in the data. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Centre (CCDC) as supplementary numbers CCDC 2009221–2009227. Crystallographic data can be obtained free of charge from https://www.ccdc.cam.ac.uk/structures/, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223 336 033; email: deposit@ccdc.cam.ac.uk.

Supplementary Material

Infrared spectra, the La(bp)₃ TGA profile, and La(bp)₃ thermal conversion, XRPD, and crystallographic and structure refinement data for $[La(mbp)_3(H_2O)_2]\cdot 3H_2O$ are available on the Journal's website.

Conflicts of Interest

The authors declare no conflicts of interest.

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