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Heterometallic Ce^{III}–Fe^{III}–salicylate networks: models for corrosion mitigation of steel surfaces by the 'Green' inhibitor, Ce(salicylate)$_3$

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The syntheses and structures of the novel Ce–Fe bimetallic complexes $[\{Fe(sal)_2(bpy)\}_2Ce(NO_3)(H_2O)_3]\cdot EtOH$ and $[\{Fe(sal)_2(bpy)\}_4Ce_2(H_2O)_{11}][salH]_2\cdot EtOH\cdot 3H_2O$ ($salH_2$ = salicylic acid) suggest Fe^{3+}–sal^{2-} units and Ce–OC(R)O–Fe bridging contribute to the formation of corrosion inhibitive layers on steel surfaces exposed to $[Ce(salH)_3(H_2O)]$.

Recent developments in chemical mitigation of corrosion of metal surfaces (*e.g.* iron), driven by the need to replace current extremely toxic treatments (*e.g.* chromates),[1] have yielded highly effective 'Green' inhibitors based on Rare Earth compounds such as $Ce(salH)_3$ (salH = salicylate).[2] A key feature has been the synergistic combination of Ce^{3+}, a known inhibitor,[3] with an organic inhibitor component $salH^-$.[4] Analyses of steel surfaces exposed to solutions containing $Ce(salH)_3$,[2,5] clearly showed the deposition of a protective film that was not merely adsorbed inhibitor, but most likely an inert chemically bonded material containing Ce^{3+}, $Fe^{2+/3+}$, and $salH^-$ (or sal^{2-}). However, a more precise molecular picture, particularly of the role of the salicylic acid residue, remained uncertain. We have now synthesised bimetallic Ce/Fe complexes with salicylate ligands to chemically model these protective layers. Known bimetallic (f/d) carboxylate species (see ref. 6 for recent examples) do not incorporate Fe and $salH^-$ (or sal^{2-}).

Reactions of $CeCl_3$, $FeCl_3$, and Na(salH) (mole ratio 1:1:6 or 1:2:4) resulted in precipitation of significant quantities of dark red–brown solids (**1a**,**b**)† of a similar colour to materials deposited on steel surfaces. Furthermore, the ATR FTIR spectra of these materials (Table 1) matched those obtained from the protected steel surfaces.[5] Elemental analyses (C,H,Ce,Fe) indicated Ce:Fe:sal^{2-} (or $salH^-$) ratios of 1:1:1.7 (**1a**) or 2:5:3 (**1b**) suggesting a range of compositions is possible. However, crystallisation of either solid from a variety of solvents failed, precluding X-ray structural characterisation. In an attempt to produce crystalline complexes, mixtures of CeX_3, FeX_3, (X = Cl, NO_3) and $salH_2$, were neutralised in the presence of a neutral donor, bpy. These preparations gave red–purple crystals of $[\{Fe(sal)_2(bpy)\}_2Ce(NO_3)(H_2O)_3]\cdot EtOH$ (**2**) or $[\{Fe(sal)_2(bpy)\}_4Ce_2(H_2O)_{11}][salH]_2\cdot EtOH\cdot 3H_2O$ (**3**) from EtOH,† with Ce:Fe ratios between those of **1a** and **1b**. Solid state *vis.* spectra of **1a** and **2** are similar to those of Fe^{III}/phenolate species[7] consistent with the presence of Fe^{III} in the current complexes. Moreover, $salH^-$ does not reduce Fe^{III} at neutral pH.[7]

The basic structural units‡ of both **2** (Fig. 1) and **3** (Fig. 2) are octahedral $Fe^{III}(sal)_2(bpy)^-$ moieties, each with one chelating bipy ligand and two doubly deprotonated salicylic acid residues chelated to the iron through the phenolate and one of the carboxylate oxygen atoms (Fig. 3), and Ce^{3+} sites surrounded

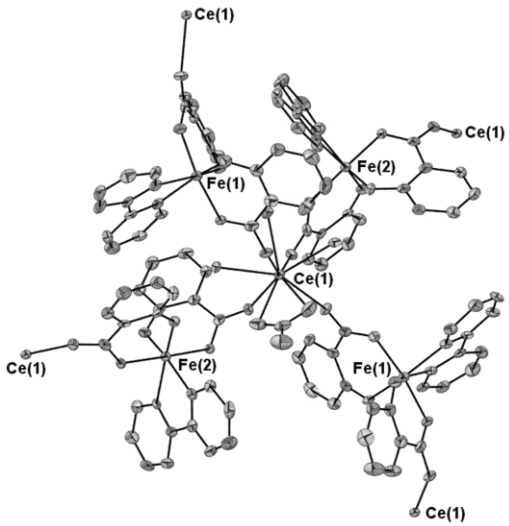

Fig. 1 The solid-state structure of **2** showing one complete Ce^{3+} environment and connectivity to neighbouring Ce^{3+}. Selected bond distances (Å): Ce–O(NO_3) 2.584(5), 2.642(5), Ce–O(CO_2) 2.445(4)–2.517(4), Ce–O(H_2O) 2.517(4)–2.584(5), Fe–O(CO_2) 1.967(4)–2.002(4), Fe–O(OPh) 1.910(5)–1.953(4), Fe–N 2.171(5)–2.207(5).

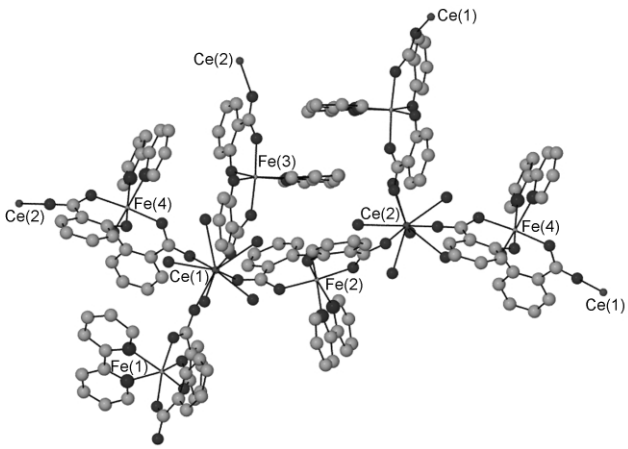

Fig. 2 The solid-state structure of **3** showing the two complete Ce^{3+} environments and connectivity to neighbouring Ce^{3+}. Selected bond distances (Å): Ce–O(CO_2) 2.412(6)–2.571(7), Ce–O(H_2O) 2.460(6)–2.648(7), Fe–O(CO_2) 1.955(6)–2.009(7), Fe–O(OPh) 1.914(7)–1.943(7), Fe–N 2.109(6)–2.235(11).

Table 1 Comparative IR frequencies (cm^{-1}) for **1a**,**b**, **2**, and **3**

	$\nu_{as}(CO_2)/\nu(CC)_{ar}$					$\nu_s(CO_2)$	ν(OAr)
Steel coupon[5]	1601	1566	1504		1454	1377	1238
1a	1599	1562	1502		1458	1386	1237
1b	1598	1564	1509		1454	1379	1236
2	1601	1565		1467	1455[a]	1362	1241
3	1598	1564		1463	1456[a]	1366	1250
Goethite-sal[11]	1600	1568	1524	1468	1455	1369	1241

[a] Coincident with ν(CC) of bpy.

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by nine oxygen atoms (Fig. 3). The donor array surrounding Fe is similar to that of the neutral Mn^{IV} complex $[Mn(sal)_2(bpy)]$[8] with the two carboxylate groups in a *trans* disposition. The Fe–O(phenolate) and Fe–O(benzoate) distances are comparable with those of 3-Mesal^{2-} in [Fe(Mesal)(L)(Me-im)$_2$] (L = 2-(benzimidazol-2-ylmethyl)phenolate).[9] In **2** and **3** most of the Fe(sal)$_2$(bipy)$^-$ units are bound to two nine coordinate Ce^{3+} cations through sal^{2-} carboxylate oxygen atoms (Fig. 1 and 2) forming either a 3-D (**2**) or 2-D (**3**) network. Thus carboxylate groups are usually bridging bidentate (Fe–OC(R)O–Ce), but one sal^{2-} ligand in **3** has a unidentate carboxylate (bound to Fe(1) only). There is one unique Ce^{3+} in **2** which is bound to four Fe(sal)$_2$(bipy)$^-$ units, each through a single carboxylate oxygen atom, a bidentate NO_3^- and three water molecules, whereas in **3** there are two distinct Ce sites, Ce(1) having four Fe(sal)$_2$(bipy)$^-$ units and five water molecules whilst Ce(2) has three and six, respectively. The Ce coordination geometries do not fit a regular polyhedron, but are remarkably similar. All three unique Ce sites have an approximately pentagonal equatorial girdle of five oxygen atoms (Fig. 3, Oa, Ob), with a single oxygen atom on one side (Fig. 3 Oc) and, surprisingly, three oxygen atoms on the other (Fig.3, Od). The Ce atom is displaced *ca*. 0.7 Å towards the three. At Ce(1) (in both **2** and **3**) Oc and Od are carboxylate oxygen atoms, whereas, at Ce(2) (**3**), Oc is from a water molecule. The five equatorial oxygen atoms comprise three water molecules and a bidentate NO_3^- anion in **2**, or five water molecules at both Ce sites in **3**. The observed Ce–O distances are not unusual.[10] Charge balance in **3** is achieved by two salH$^-$ anions (not shown) that are hydrogen bonded to coordinated water molecules.

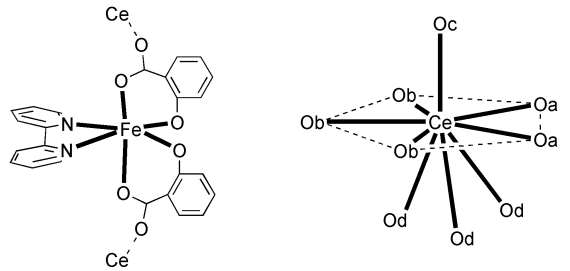

Fig. 3 Fe and Ce structural units in **2** and **3** (**2**: Ce(1), Oa = O(NO_3^-), Ob = OH_2, Oc,Od = O(RCO_2^-), **3**: Ce(1), Oa,Ob = OH_2, Oc,Od = O(RCO_2^-); Ce(2), Oa,Ob,Oc = OH_2, Od = O(RCO_2^-)).

Chelating Fe-(sal^{2-}) structural units have been proposed for the coordination of salicylate to iron(III) oxides (Goethite and Lepidocrocite) based on IR spectroscopy.[11] This proposal is given a stronger basis by the structures of **2** and **3** and by IR peak correlations in the $\nu_{as}(CO_2)/\nu(CC)_{ar}$, $\nu_s(CO_2)$ and $\nu(CO)$ frequency regions (Table 1). Some differences can be attributed to carboxylate bridging to Ce^{3+} in **2** and **3**. The IR spectra of the protective Ce/Fe/sal films on steel surfaces and the model solids **1a**,**b** have several absorptions (Table 1) similar to those of **2** and **3**. This suggests the presence of chelating Fe-(sal^{2-}) structural units in these materials. However, the spectra of the steel surface and **1** show an additional strong band at ~1500 and a shift of $\nu_s(CO_2)$ nearer 1380 cm^{-1}. These are also features of the IR spectrum of [Ce(salH)$_3$(H$_2$O)],[12] but not of **2** or **3**. Structures of [Ln(salH)$_3$(H$_2$O)] are polymeric with bridging (bidentate and tridentate) carboxylate groups.[13] Thus it is possible that some structural fragment of the [Ce(salH)$_3$(H$_2$O)]$_n$ polymer is retained in the protective film (and the model compounds **1a**,**b**).

The structures of **2** and **3** establish the importance of chelating Fe^{3+}-(sal^{2-}) units and Ce–OC(R)O–Fe linkages in the corrosion mitigation of steel by Ce(salH)$_3$. In contrast, two Fe^{3+} ions are linked by bridging bidentate carboxylate groups of the commercial inhibitor 3-(4-methylbenzoyl)propionic acid.[14]

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Notes and references

† **1a**: aqueous Na(salH) (2.83 g, 17.7 mmol) added to $CeCl_3{\cdot}7H_2O$ (1.1 g, 3.0 mmol) and $FeCl_3$ (0.48 g, 3.0 mmol) in water (pH ~ 7 with NaOH) gave 1.10 g of a red–brown precipitate. Anal. Found: C 24.6, H 2.5, Ce 24.7, Fe 9.8%. Vis (Nujol): λ_{max} ~470 nm. **1b**: Similarly, Na(salH) (1.72 g, 10.7 mmol), $CeCl_3{\cdot}7H_2O$ (1.0 g, 3.0 mmol) and $FeCl_3$ (0.87 g, 5.7 mmol)) gave 1.24 g of a red–purple precipitate. Anal. Found: C 17.5, H 2.0, Ce 20.2, Fe 19.8%. **2**: $Ce(NO_3)_3{\cdot}6H_2O$ (0.86 g, 2.0 mmol), $Fe(NO_3)_3{\cdot}9H_2O$ (0.81 g, 2.0 mmol), bipy (0.31 g, 2.0 mmol) and salH$_2$ (1.66 g, 12.0 mmol) in water (pH ~ 7 with NaOH) gave red–purple crystals of **2** after recrystallisation of the evaporated residue from EtOH, (0.35 g 28% yield). Anal. Found for $C_{50}H_{44}CeFe_2N_5O_{19}$: C 47.2, H 3.4, N 5.5. Calc.: C 47.3, H 3.5, N 5.5%. ESI-MS(MeOH): *m*/*z* 952 [$CeFe_2(sal)_4(bipy)^+$], 796 [$CeFe_2(sal)_4^+$]. Vis (Nujol): λ_{max} 490 nm. (MeOH): $\lambda_{max}(\varepsilon)$ 500(4170 dm^3 mol^{-1} cm^{-1}) nm. **3**: $CeCl_3{\cdot}7H_2O$ (0.34 g, 0.91 mmol), $FeCl_3$ (0.29 g, 1.8 mmol), bipy (0.28 g, 1.8 mmol) and salH$_2$ (0.50 g, 3.6 mmol) in water (pH ~ 7 with NaOH) similarly gave a few red crystals of **3** from EtOH, sufficient only for identification by single crystal X-ray structure determination and IR spectroscopy.

‡ *Crystal data:* **2**: $C_{50}H_{44}CeFe_2N_5O_{19}$ (1270.72) monoclinic ($P2_1/n$) *a* 12.5989(4), *b* 19.9199(7), *c* 20.6430(8) Å, β 100.614(2)°, *V* 5092(2) Å^3, ρ_{calc}(*Z* = 4) 1.658 g cm^{-3}, μ(MoK$_\alpha$) 1.52 mm^{-1}; 12481 unique (R_{int} 0.116, 5315 $F > 4\sigma(F)$) reflections converged to R_1 = 0.068 ($F > 4\sigma(F)$), wR_2 = 0.138 (all data) (H atoms on water molecules not included). **3**: $C_{112}H_{107}Ce_2Fe_4N_8O_{45}$ (2788.78) triclinic ($P\bar{1}$) *a* 13.8916(3), *b* 19.8401(5), *c* 22.2319(5) Å, α 86.592(1), β 78.871(1), γ 83.810(1)°, *V* 5972(2) Å^3, ρ_{calc} (*Z* = 2) 1.551 g cm^{-3}, μ(MoK$_\alpha$) 1.31 mm^{-1}; 28519 unique (R_{int} 0.098, 11385 $F > 4\sigma(F)$) reflections converged to R_1 = 0.089 ($F > 4\sigma(F)$), wR_2 = 0.264 (all data); all C atoms isotropic, full anisotropic refinement was unsatisfactory possibly due to partial disorder of the bpy groups (oxygen H atoms on water molecules and lattice components not included). (Enraf-Nonius CCD, λ(Mo-Kα) = 0.71073 Å, 123 K).

CCDC 188413 and 188414. See http://www.rsc.org/suppdata/cc/b2/b207722a/ for crystallographic data in CIF or other electronic format.

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