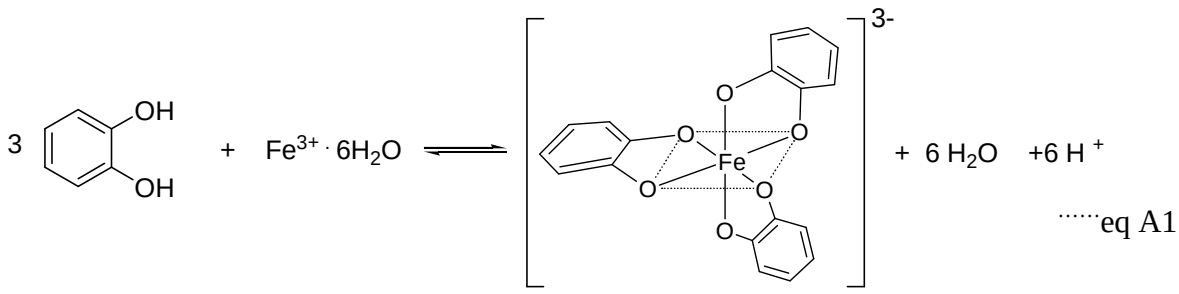
Appendix 2

Metal ion selectivity of the catechol group

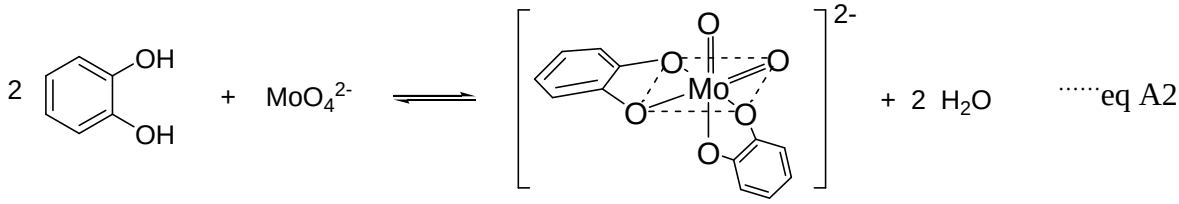
The interaction between catechol and tri-basic metal cations usually involves the displacement of 6 protons (eq A.1). High spin iron(III) with a radius of 0.64Å has an optimum fit for a cation in an octahedral field generated by 3 catechol functions. Tri-basic cations with smaller (Al(III)) and larger radii (In(III)) bind to catechol less tightly (Table A.1). Dibasic cations bind less tightly by virtue of the much reduced charge density on the coordinated cation, see for instance copper(II) (Table A.1).

Molybdenum, vanadium and tungsten can also react with catechol. These metals each possess a range of oxidation states and in cells often adopt the highest oxidation state forming oxyanions. Thus vanadium(V) is favoured in the vanadate anion $[VO_4]^{3-}$, molybdenum (VI) forms molybdates $[MoO_4]^{2-}$, and tungsten(VI) favours tungstates $[WO_4]^{2-}$. In principle these three metals can react with catechol in 2 different ways; in the normal 3:1 mode or in a 2:1 mode with the remainder of the coordination sphere being occupied with one or two oxygen atoms. With molybdenum(VI) a *cis* dioxo structure is favoured [1,2], which is stable in aqueous solutions at pH 7.4 and possesses a net charge of 2^- (eq A.2). Under these conditions, the molybdenum ion has as effective radius of 0.59Å and an effective charge of the 3.6^{+} [3]. Consequently it fits the catechol "bite distance" well. Tungsten is similar to molybdenum, but due to its larger size accommodates three catechols more readily and forms the normal 3:1 complex [4]. Like molybdenum, vanadium can also form two complex types with catechol containing ligands, the normal 3:1 complex and a 2:1 complex with an additional oxygen atom coordinating the vanadium cation. In aqueous media the 3:1 complex is favoured with a vanadium oxidation state of (III)[5] and so the vanadium(III) catechol complex is very similar to that of iron(III).

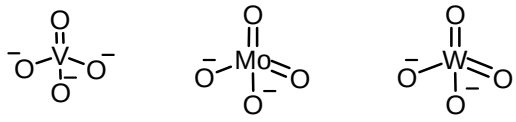
Thus catechol – containing siderophores will bind all of the metals listed in Table A1 and indeed may have a role in the absorption of molybdenum [6] and vanadium [7].



.....eq A1



.....eq A2



Vanadate Molybdate Tungstate

Appendix 2 References:

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		Ionic radius (Å)	number of catechols in complex	log K_1	Reference
Indium	In^{3+}	0.80	3	16.5	8
Iron	Fe^{3+}	0.64	3	20.5	9
Gallium	Ga^{3+}	0.62	3	18.9	10
Chromium	Cr^{3+}	0.61	3	-	10
Aluminium	Al^{3+}	0.53	3	16.3	10
Zinc	Zn^{2+}	0.74	2	9.9	10
Copper	Cu^{2+}	0.73	2	13.9	10
Manganese	Mn^{2+}	0.67	2	7.7	10
Vanadium	V^{3+}	0.64	3	18.3	10
Molybdenum	$Mo^{VI}O_2^{2+}$	0.59	2	-	

Table A1