Electronic Supplementary Material (ESI) for Dalton Transactions.

Understanding the relative binding ability of hydroxyfullerene to divalent and trivalent metals

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Electronic Supplementary Information

Table S1. Observed reactivity between metal salts (500 mM) with fullerenol (4.6 mM).

Metal source	Observation
$AgNO_3$	red-brown precipitate
$Al(NO_3)_3$	red-brown precipitate
$B(OH)_3$	no precipitate
$CaCl_2$	red-brown precipitate
$Cd(NO_3)_2$	red-brown precipitate
$CoCl_2$	red-brown precipitate
$CuCl_2$	red-brown precipitate
KCl	no precipitate
$La(NO_3)_3$	red-brown precipitate
$KMnO_4$	dark solution
$MnCl_2$	red-brown precipitate
NaOH	no precipitate
$Nd(NO_3)_3$	red-brown precipitate
$Ni(NO_3)_2$	red-brown precipitate
$ZnCl_2$	red-brown precipitate

Table S2. Particle size as a function of reaction time as measured by DLS.

$[Fe^{n+}]$ (mM)	[fullerenol] (mM)	Reaction time (min.)	Particle size (μm)
5.0	0.46	12	243-359
0.5	0.046	1	0.25
		1.5	0.80
		2.5	12
0.05	0.0046	14	0.20
		16	2.7

Table S3. Selected bond lengths (Å) and angles (°) for $K_3[Ga(catecholate)_3]\cdot 1.5\ H_2O$ X-ray crystallographic data and *ab initio* calculations.

	Crystallographic data[a]	Gaussian model data[b]
Ga-O	1.969(2) - 2.005(2)	2.013
O1 - C	1.342(3) - 1.355(3)	1.335
$O\text{-}Ga\text{-}O_{chelate}$	83.61(7) - 83.89(7)	82.22 - 82.23
$O\text{-}Ga\text{-}O_{cis}$	89.01(8) - 98.09(8)	91.72 - 94.99
$O\text{-}Ga\text{-}O_{trans}$	170.41(8) - 170.97(8)	171.08 - 171.09
Ga - O1 - C11	109.9(2) - 111.4(2)	112.37 - 112.38
O6 - C22 - C21	117.4 (2)	116.507

[a]B. A Borgias, S. J. Barclay, and K. N. Raymond, *J. Coord. Chem.*, 1986, **15**, 109-123.
[b]B3LYP/3-21G*.

Table S4. Selected calculated bond lengths (Å) and angles (°).

	C-O	O-C-C(O)[a]	O-C-C(H)[b]
Catechol	1.401, 1.382	113.06, 119.24[c]	126.14, 121.44[c]
Catecholate	1.297	120.88	123.42

[a]Carbon atom attached to the second oxygen. [b]Carbon atom attached to hydrogen. [c]Hydrogen bonded OH, see Fig. S9.

Table S5. Selected *ab initio* calculated bond lengths (Å) and angles (°) for $[M(catecholate)_n]^{n-}$.

	M-O	C-O	$O\text{-}M\text{-}O_{chelate}$	$O\text{-}M\text{-}O_{cis}$[a]	$O\text{-}M\text{-}O_{trans}$	O-C-C[b]	O-C-C[c]
$[Zn(catecholate)_2]^{2-}$	1.889	1.343	90.12	119.93	n/a	116.91	124.70
$[Cd(catecholate)_2]^{2-}$	2.190	1.343	79.29	126.36	n/a	119.67	122.43
$[Al(catecholate)_3]^{3-}$	1.932	1.332	83.45	91.35	172.39	114.79	126.36
$[Ga(catecholate)_3]^{3-}$	2.181	1.335	82.23	93.74	171.09	116.51	124.91
$[In(catecholate)_3]^{3-}$	2.181	1.337	77.14	91.72	166.38	118.09	123.69

[a]For tetrahedral complexes this is the non-chelate O-M-O angle. [b]Endo the 5-membered cycle. [b]Exo the 5-membered cycle.

Table S6. Selected *ab initio* calculated bond lengths (Å) and angles (°) for $[M(L_3)_n]^{2-}$ and $[M(L_2)_n]^{2-}$.[a]

	M-O	C-O	$O\text{-}M\text{-}O_{chelate}$	O-M-O[b]
$[Zn(L_3)_2]^{2-}$	1.858, 1.888	1.412, 1.427	90.12	105.04, 105.05, 116.66, 129.01
$[Cd(L_3)_2]^{2-}$	2.144, 2.178	1.415, 1.441	79.29	101.86. 101.86, 122.30, 144.25
$[Zn(L_2)_2]^{2-}$	1.871,1.902	1.410, 1.406	101.59	108.85, 108.85, 113.99, 122.47
$[Cd(L_2)_2]^{2-}$	2.157, 2.197	1.412, 1.415	95.19	108.49, 108.49, 112.90, 136.31

[a]L_3 = *cis*,*cis*-1,3,5-trihydroxycyclohexane, L_2 = *cis*-1,3-dihydroxycyclohexane. [b]Non-chelate angles. [b]Non chelate.

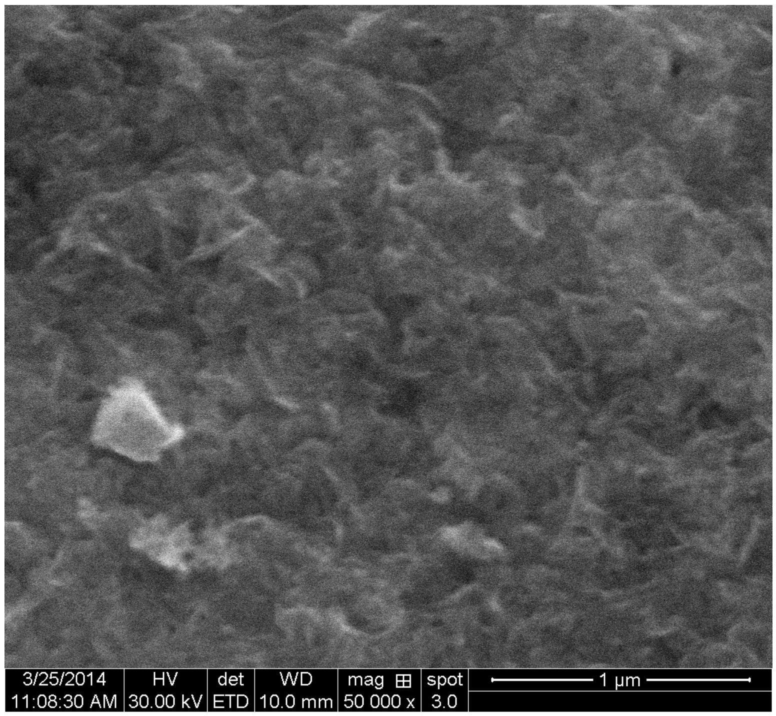

Fig. S1 SEM image of Fe^{3+}/Cd^{2+} cross-linked fullerenol.

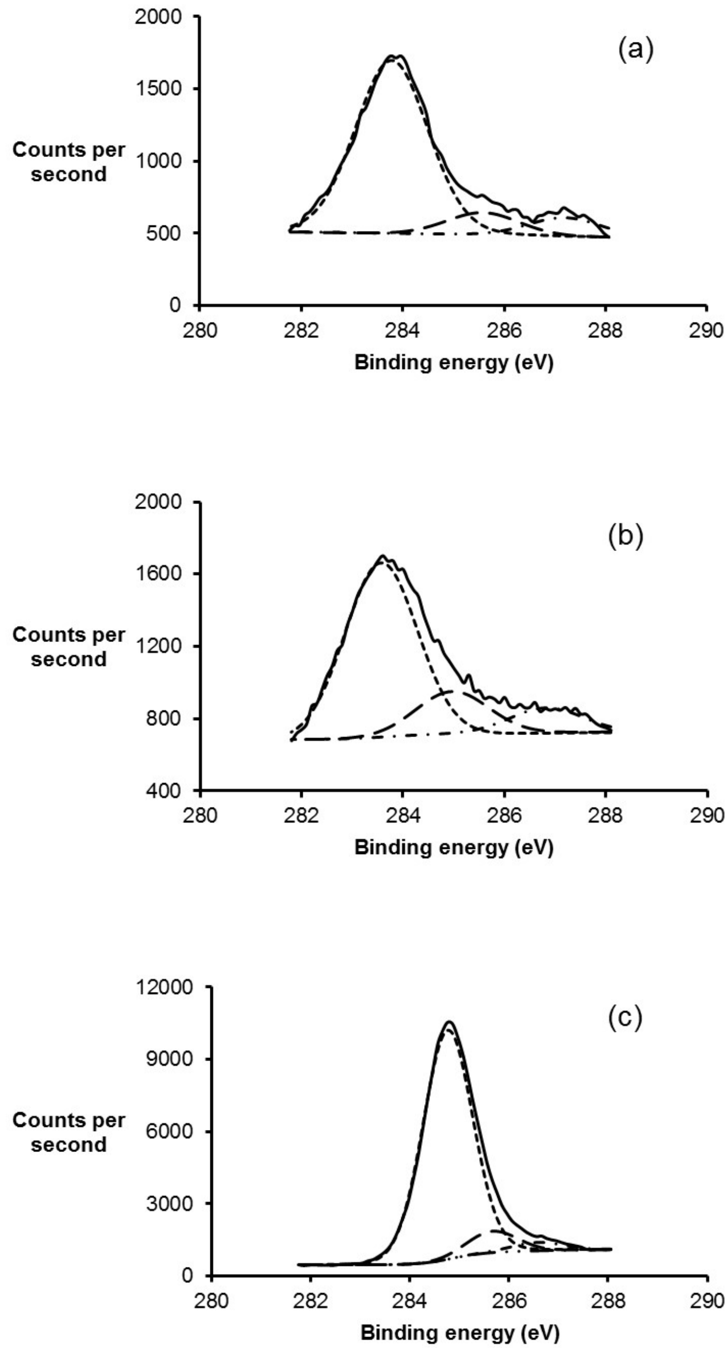

Fig. S2 High resolution C1s XPS data for (a) fullerenol, (b) Fe^{3+} cross-linked fullerenol, and (c) Fe^{3+}/La^{3+} cross-linked fullerenol.

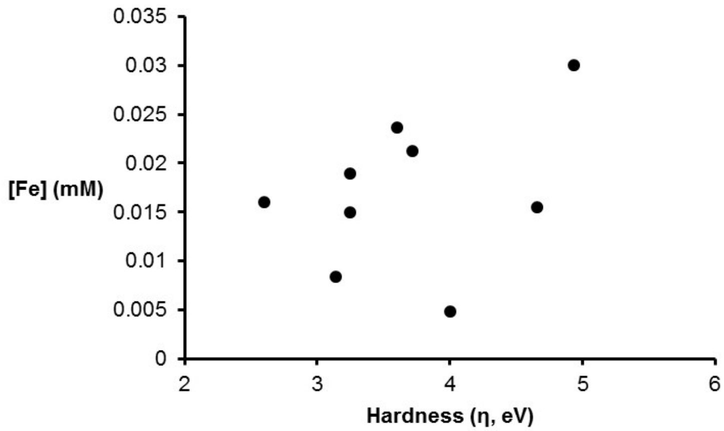

Fig. S3 Plot of [Fe^{3+}] in competitive binding with M^{n+} versus Pearson' absolute hardness (η) of M^{n+}.

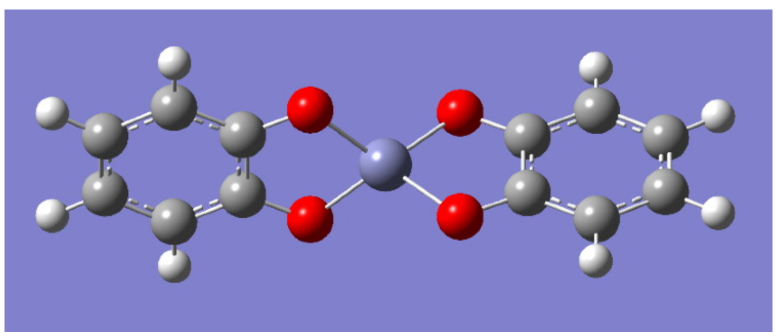

Fig. S4 Calculated structure of [Zn(catecholate)$_2$]$^{2-}$.

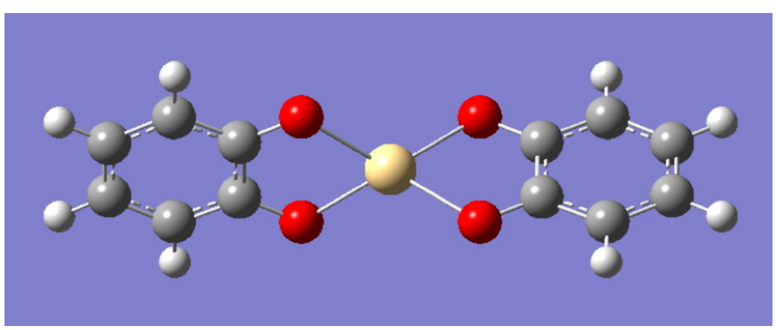

Fig. S5 Calculated structure of [Cd(catecholate)$_2$]$^{2-}$.

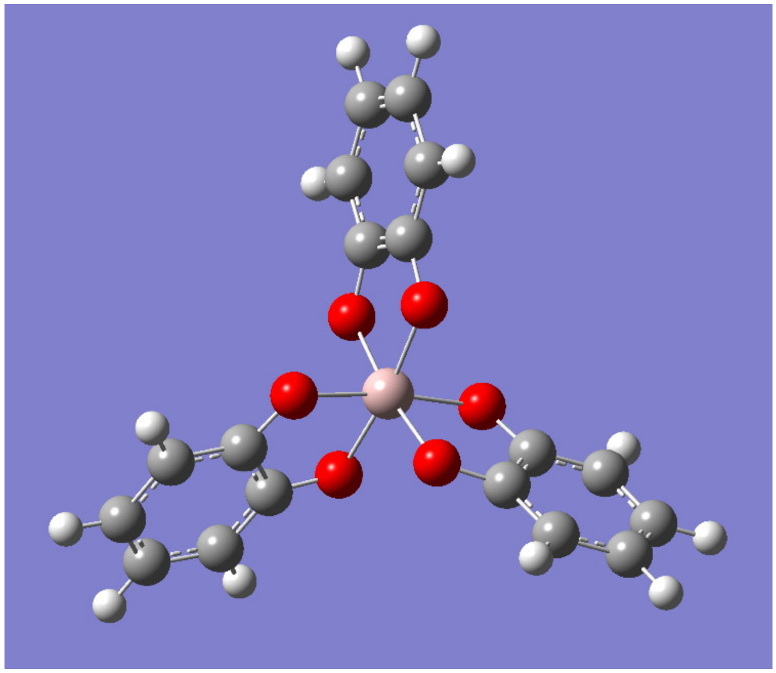

Fig. S6 Calculated structure of $[Al(catecholate)_3]^{3-}$.

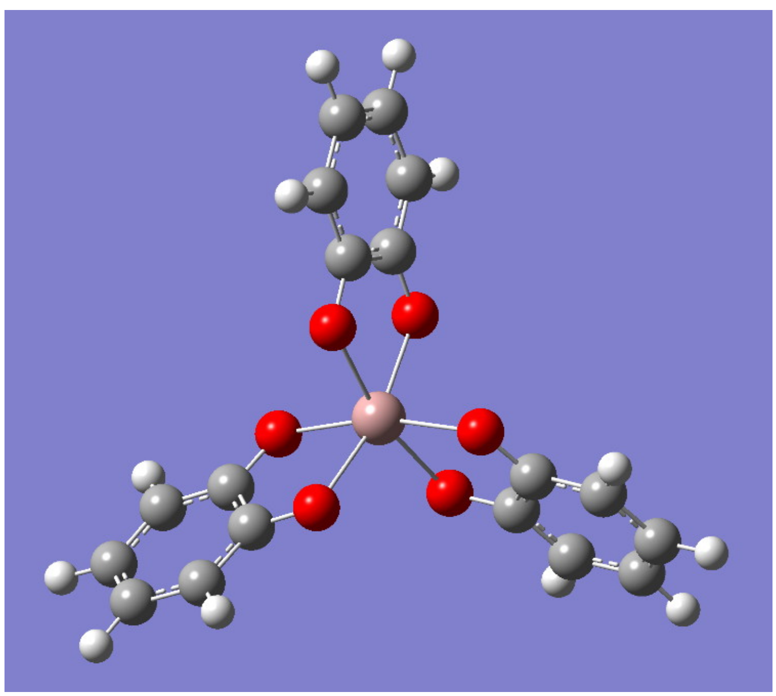

Fig. S7 Calculated structure of $[Ga(catecholate)_3]^{3-}$.

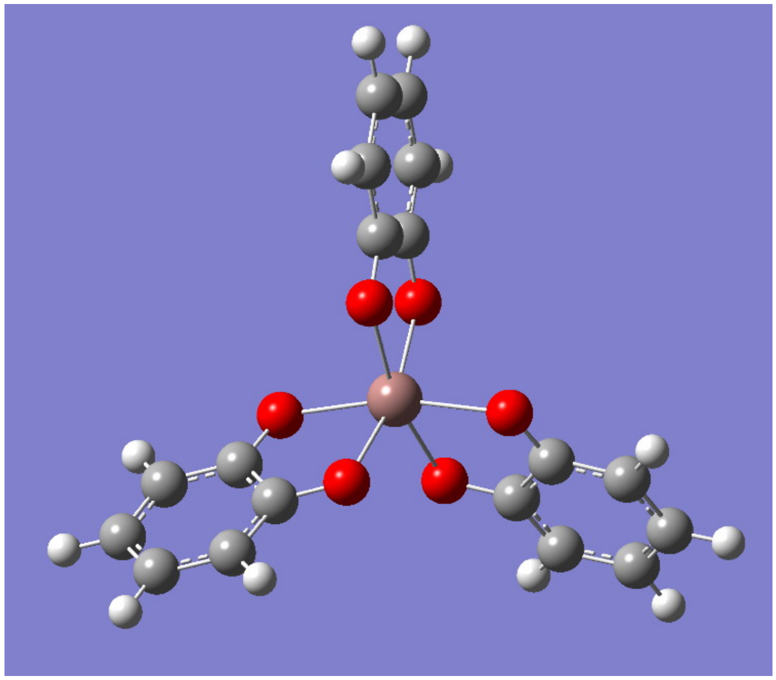

Fig. S8 Calculated structure of $[In(catecholate)_3]^{3-}$.

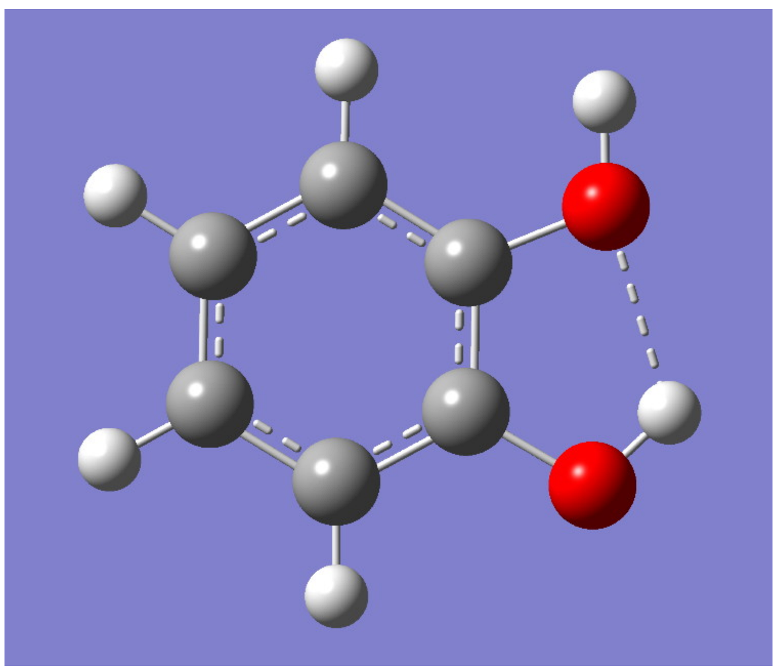

Fig. S9 Calculated structure of catechol.

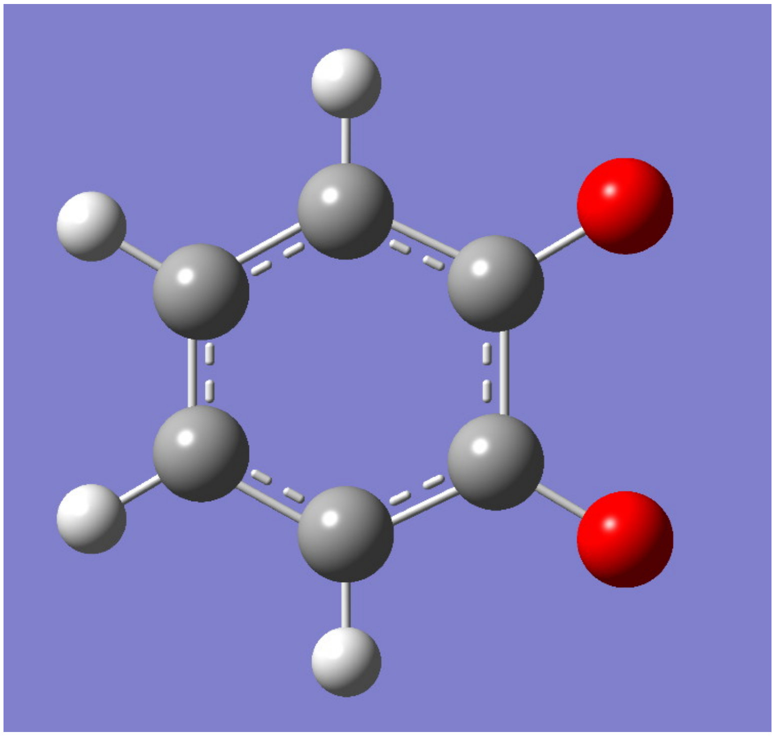

Fig. S10 Calculated structure of [catecholate]$^{-}$.

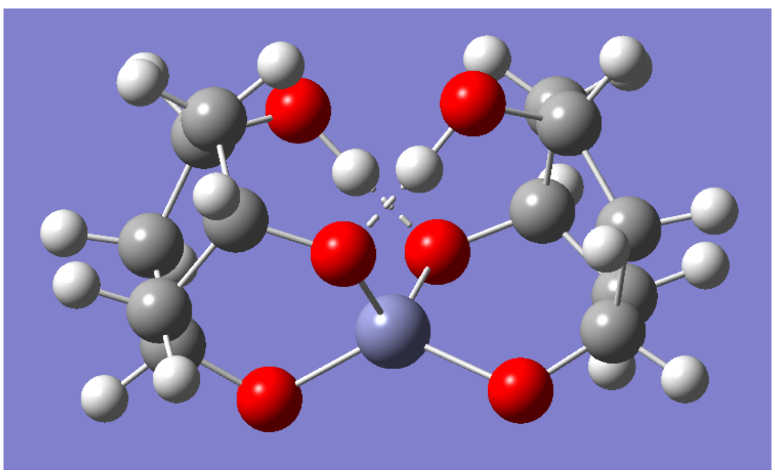

Fig. S11 Calculated structure of $[Zn(L_3)_2]^{2-}$.

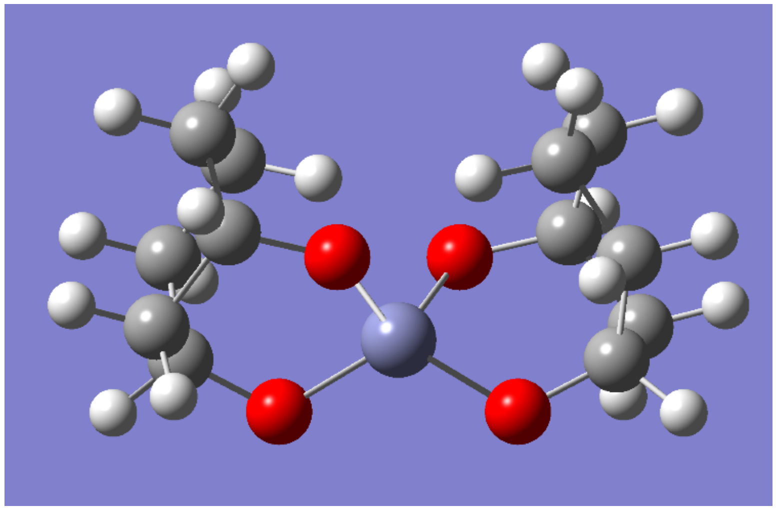

Fig. S12 Calculated structure of $[Zn(L_2)_2]^{2-}$.

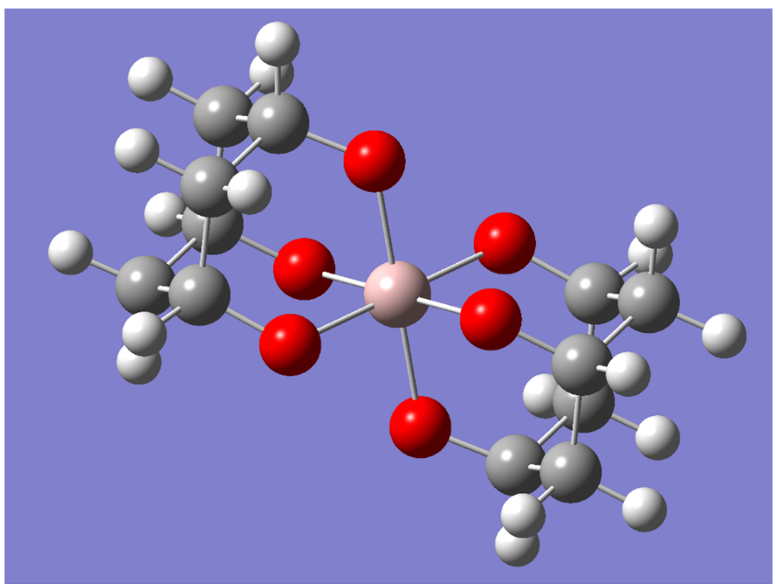

Fig. S13 Calculated structure of $[Al(L_3)_2]^{3-}$.

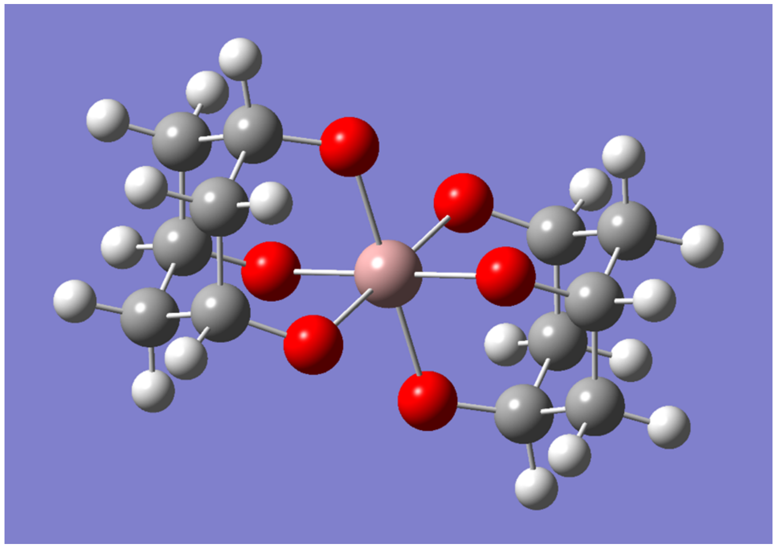

Fig. S14 Calculated structure of $[Ga(L_3)_2]^{3-}$.