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SUPPLEMENTARY MATERIAL

Allan White and Solvento/Aqua Complexes: Sc^{III} Solvation

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A. Figures S1 and S2 (Hirshfeld surface diagrams)

B. Tables S1 - S4

Part A

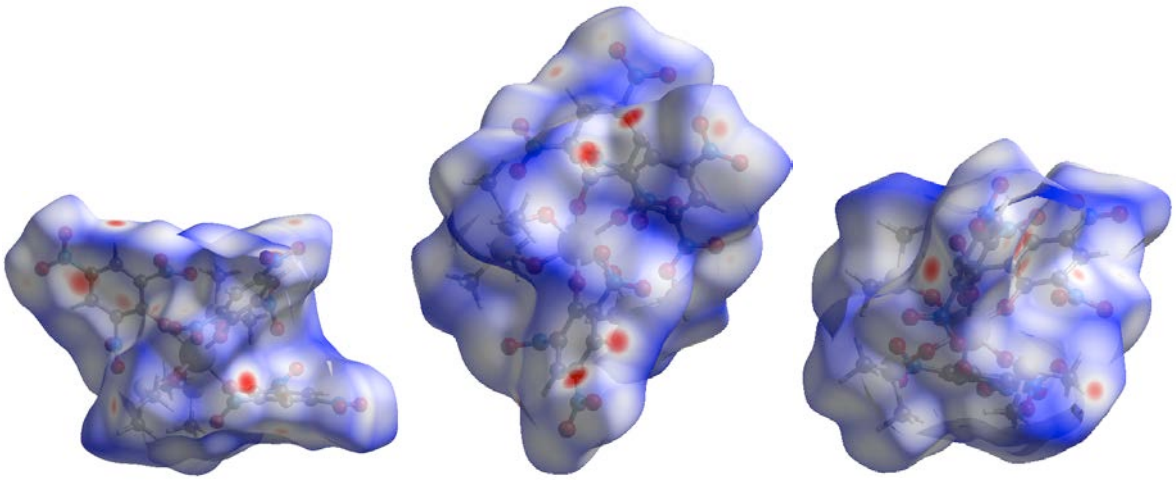

Figure S1(a) Views of the Hirshfeld surface obtained using CrystalExplorer for $[Sc(pic\text{-}O)_3(dmso)_3]$ down the *a*, *b* and *c* crystallographic axes, respectively. Red regions on the surface indicate points where interactions with external species exceed dispersion.

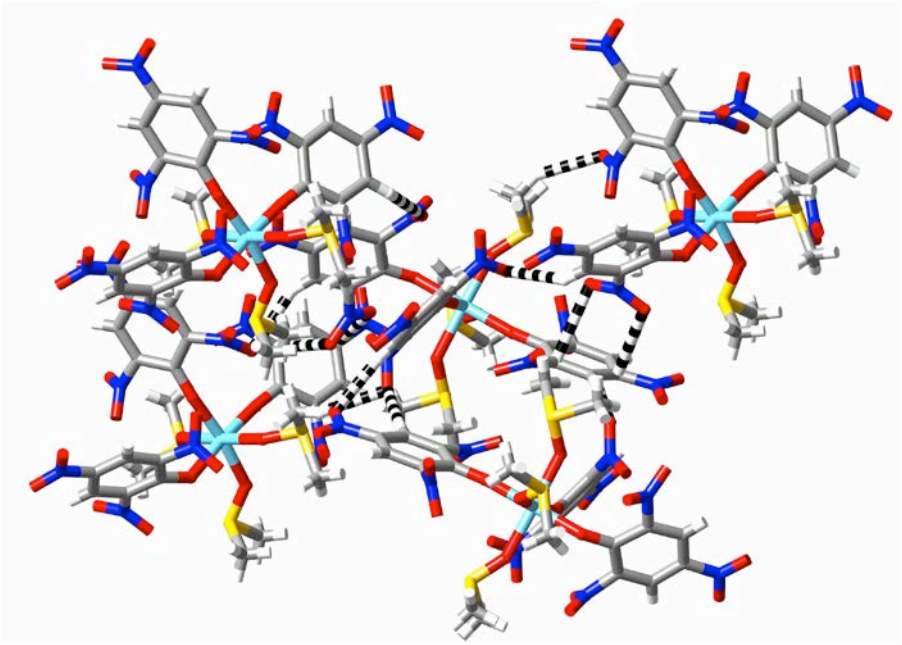

Figure S1(b) Interactions (black and white dashed lines) of one $[Sc(pic\text{-}O)_3(dmso)_3]$ with 4 neighbouring molecules as deduced from the Hirshfeld surface. To simplify the view, stick representation is used.

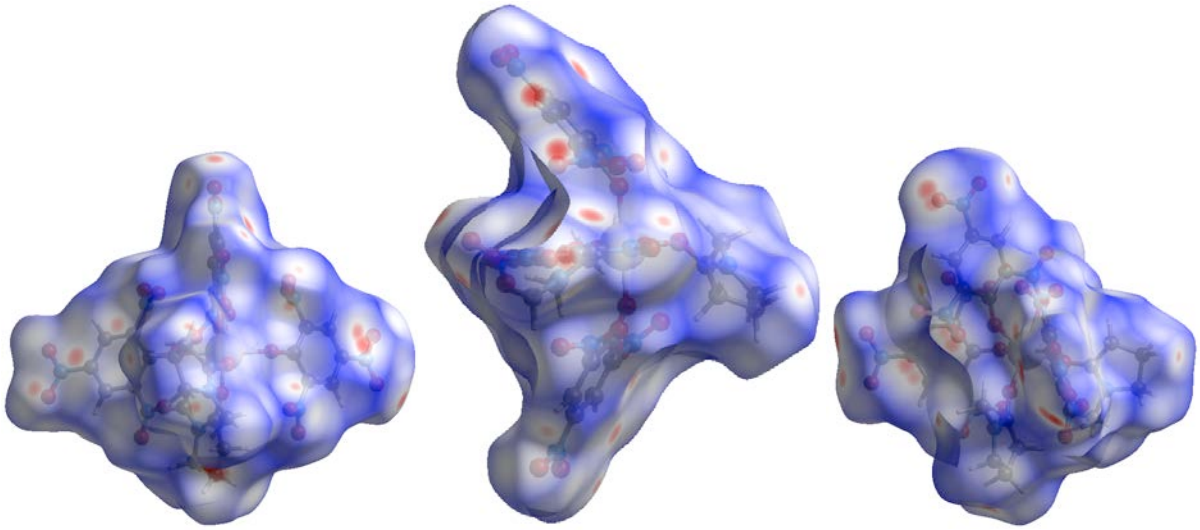

Figure S2 Views of the Hirshfeld surface obtained using CrystalExplorer for [Sc(pic-O)$_2$(pic-O,O')(nmp)$_2$] down the *a*, *b* and *c* crystallographic axes, respectively. Red regions on the surface indicate points where interactions with external species exceed dispersion.

Part B

Table S1

Scandium environments: *mer*-[Sc(dmso-*O*)$_3$(pic-*O*)$_3$] (300 K, **170 K**) (Å, degrees)

Atom	*r*	O(21)	O(31)	O(01)	O(02)	O(03)	Sc-O-C,S
O(11)	2.037(2)	97.21(9)	87.17(9)	93.02(9)	88.81(9)	173.02(9)	163.7(2)[a]
	2.0423(9)	**97.80(4)**	**87.79(4)**	**92.18(4)**	**87.11(4)**	**172.25(4)**	**162.58(9)**
O(21)	2.034(2)		175.61(9)	89.75(1)	88.01(11)	88.23(10)	172.8(2)
	2.0246(9)		**174.41(4)**	**90.11(4)**	**88.70(4)**	**87.03(4)**	**173.18(9)**
O(31)	2.074(2)			90.36(9)	91.75(9)	87.38(9)	141.0(2)
	2.0787(9)			**89.77(4)**	**91.49(4)**	**87.40(4)**	**138.12(8)**
O(01)	2.074(2)				177.27(10)	91.37(11)	151.9(2)
	2.0698(10)				**178.52(5)**	**93.87(4)**	**151.30(7)**
O(02)	2.103(2)					87.10(11)	133.6(2)
	2.1114(10)					**86.95(4)**	**133.38(6)**
O(03)	2.092(3)						133.7(2)
	2.0976(9)						**132.27(6)**

[a] The value for the second component of O/S(03) (300K only) is 162.4(2)°.

Sc lies 0.418(3), 0.313(3), 1.351(3) Å out of the three OC_6N_3 planes for the 300K and 0.417(1), 0.286(2), 1.456(1) Å for the 170K structure. The dihedral angles(°) of the OC_6N_3 to CNO_2 planes n2, n4, n6 are: 44.6(1), –4.3(1), 58.1(1) (pic1); –73.3(2), –6.5(2), –40.9(2); (pic2); 41.3(2), 5.8(2), –58.1(2) (pic3) (300K) and 45.17(6), 4.13(5), 57.53(5) (pic1); –64.90(6), –8.42(5), –41.39(5) (pic2); 40.03(8), 5.91(6), –58.88(6) (pic3) (170 K), positive or negative values corresponding to a clock- or anticlock-wise rotation of the nitro group for a standard 'Newman' projection oriented with the nitro group toward the viewer. (For non-chiral structures (as is the case here) these are only useful for defining internal relativities within each complex component.)

Table S2

Scandium environments, *cis*-[Sc(L-*O*)$_2$(pic-*O*)$_2$(pic-*O*,*O*')](·nS)

L	tmp	hmpa1[a]	hmpa2[a](1)	hmpa2[a](2)	dma	nmp
Distances (Å)						
Sc-O(11)	2.036(2)	2.0618(11)	2.069(3)	2.078(3)	2.0811(11)	2.015(3)
Sc-O(121)	2.199(2)	2.2622(11)	2.241(3)	2.233(2)	2.2060(11)	2.222(3)
Sc-O(21)	2.018(2)	2.0703(11)	2.049(3)	2.043(3)	2.0212(11)	2.091(3)
Sc-O(31)	2.037(2)	2.0743(11)	2.067(3)	2.067(3)	2.0449(11)	2.086(3)
Sc-O(L1)	2.049(2)	2.0337(11)	2.022(3)	2.029(3)	2.0465(11)	2.009(2)
Sc-O(L2)	2.052(2)	2.0115(11)	2.018(3)	2.013(3)	2.0468(11)	2.021(3)
Angles (°)						
O(11)-Sc-O(121)	78.13(7)	76.11(4)	76.10(11)	76.38(10)	76.95(4)	75.8(1)
O(11)-Sc-O(21)	90.82(8)	89.16(5)	92.31(12)	93.38(12)	90.60(5)	87.98(11)
O(11)-Sc-O(31)	88.77(8)	88.66(5)	85.49(12)	86.68(12)	87.63(5)	90.74(11)
O(11)-Sc-O(L1)	163.18(7)	156.45(5)	158.14(12)	156.57(11)	158.95(5)	161.53(11)
O(11)-Sc-O(L2)	91.02(7)	91.21(4)	92.21(11)	91.46(11)	98.22(5)	96.39(11)
O(121)-Sc-O(21)	85.23(7)	84.46(5)	84.41(12)	86.26(12)	92.23(5)	89.97(10)
O(121)-Sc-O(31)	90.17(8)	89.48(5)	90.45(12)	91.12(12)	89.83(5)	89.92(10)
O(121)-Sc-O(L1)	85.05(7)	80.38(4)	83.22(11)	80.72(11)	82.48(4)	85.65(10)
O(121)-Sc-O(L2)	169.10(7)	167.28(4)	167.72(11)	167.68(11)	174.70(5)	171.95(11)
O(21)-Sc-O(31)	175.38(8)	173.90(5)	174.77(12)	177.29(12)	176.92(5)	178.65(11)
O(21)-Sc-O(L1)	89.96(8)	89.84(5)	92.66(12)	89.98(12)	94.66(5)	91.24(11)
O(21)-Sc-O(L2)	93.55(8)	96.44(5)	92.45(12)	92.58(12)	89.97(5)	87.43(12)
O(31)-Sc-O(L1)	89.11(8)	89.88(5)	87.70(12)	88.90(12)	87.88(4)	90.09(10)
O(31)-Sc-O(L2)	91.06(8)	89.31(5)	92.37(11)	90.13(12)	87.78(5)	92.50(12)
O(L1)-Sc-O(L2)	105.80(8)	112.28(5)	108.82(12)	111.56(11)	102.15(5)	102.01(11)
Sc-O(11)-C(11)	137.32(15)	138.16(10)	138.7(3)	138.7(3)	137.56(10)	138.7(3)
Sc-O(121)-N(12)	136.31(15)	137.58(9)	137.2(3)	136.8(3)	137.45(10)	138.3(2)
Sc-O(21)-C(21)	176. 0(2)	155.07(10)	169.2(3)	170.2(3)	153.33(11)	152.7(2)
Sc-O(31)-C(31)	164.0(2)	162.55(11)	149.1(3)	152.1(3)	141.93(10)	145.9(4)
Sc-O(L1)-C,P	172.5(1)	165.87(8)	163.3(2)	160.7(2)	136.24(15)	135.2(2)
Sc-O(L2)-C,P	158.1(2)	175.09(7)	158.6(2)	157.0(2)	146.92(13)	164.0(3)
Inter-planar dihedral angles (°)						
$OC_6H_2N_3$(1)/NO_2(12)	–9.05(10)	–4.43(5)	7.1(2)	–10.2(2)	8.80(6)	–1.81(13)
$OC_6H_2N_3$(1)/NO_2(14)	4.61(11)	–3.58(7)	–1.8(2)	–5.7(3)	2.50(9)	5.6(2)
$OC_6H_2N_3$(1)/NO_2(16)	–29.40(10)	60.85(7)	–29.0(2)	–38.4(2)	–36.83(8)	–47.2(2)
$OC_6H_2N_3$(2)/NO_2(22)	16.1(3)	25.20(7)	37.8(2)	–33.7(2)	–33.28(6)	–29.25(13)
$OC_6H_2N_3$(2)/NO_2(24)	–6.82(13)	–19.22(7)	–4.6(2)	3.4(2)	–8.23(8)	–3.63(14)
$OC_6H_2N_3$(2)/NO_2(26)	2.6(2)	45.27(9)	–43.7(2)	–39.8(2)	40.47(7)	41.7(2)
$OC_6H_2N_3$(3)/NO_2(32)	17.66(11)	27.62(7)	–37.6(2)	35.3(2)	26.68(6)	36.29(14)
$OC_6H_2N_3$(3)/NO_2(34)	–1.27(10)	7.59(8)	–4.0(2)	–9.0(2)	–4.24(6)	2.79(13)
$OC_6H_2N_3$(3)/NO_2(36)	–45.34(10)	–46.16(3)	–38.8(2)	–43.9(2)	–41.23(5)	–43.75(13)
Out-of-plane deviations (δSc, Å)						
$OC_6H_2N_3$(1)	0.283(3)	0.148(2)	0.316(4)	0.234(5)	0.133(2)	0.047(4)
$OC_6H_2N_3$(2)	0.007(3)	0.562(2)	0.357(5)	0.290(5)	1.007(2)	1.095(3)
$OC_6H_2N_3$(3)	0.764(3)	0.724(2)	1.355(5)	1.161(5)	1.468(2)	1.287(3)

[a] Lattice solvent (nS) is $CHCl_3$ ('hmpa1'), CH_2Cl_2 ('hmpa2').

Table S3

Scandium environment, *cis*-[Sc(ompa-*O*,*O*′)$_2$(pic-*O*)$_2$](pic)

Atom	*r*	O(21)	O(101)	O(102)	O(201)	O(202)	θ
O(11)	2.043(2)	95.21(8)	86.55(7)	167.10(8)	89.14(7)	95.71(7)	145.5(2)
O(21)	2.030(2)		92.55(8)	92.08(8)	170.00(7)	88.53(7)	171.9(2)
O(101)	2.097(2)			82.50(7)	96.70(7)	177.40(7)	139.18(11)
O(102)	2.132(2)				85.40(7)	95.10(7)	136.30(10)
O(201)	2.118(2)					82.07(6)	135.98(10)
O(202)	2.100(2)						139.04(11)

Sc lies 1.222(2), 0.101(2) Å out of the two coordinated OC_6N_3 planes; the dihedral angles of the latter to CNO_2 planes n2, n4, n6 are : –37.36(10), 6.07(15), –48.4(5)/19(1)° (pic1); –29.98(10), 14.38(12), –61.00(12)° (pic2).

Table S4

Selected picrate and ligand parameters

L/mol.	dmso[a]	tmp	hmpa1	hmpa2 (1)	hmpa2 (2)	dma	nmp	ompa
Phenoxide distances (Å)								
O(11)-C(11)	1.273(2)	1.267(4)	1.278(2)	1.265(4)	1.270(4)	1.279(2)	1.265(5)	1.282(3)
O(21)-C(21)	1.270(2)	1.272(3)	1.270(2)	1.277(5)	1.272(5)	1.285(2)	1.315(6)	1.280(3)
O(31)-C(31)	1.281(2)	1.274(4)	1.269(2)	1.275(5)	1.263(5)	1.280(2)	1.267(4)	1.244(3)
C_6 (phenyl) Interplanar dihedral angles (°)								
1/2	64.78(4)	86.87(10)	69.22(5)	78.3(2)	71.1(2)	57.82(6)	58.0(2)	39.84(9)
1/3	49.31(4)	71.00(9)	67.92(6)	52.1(2)	48.4(2)	47.20(6)	52.8(2)	82.69(9)
2/3	69.48(4)	16.73(10)	8.24(6)	27.1(2)	23.1(2)	75.02(6)	69.82(15)	48.80(9)
Inter-centroid distances (Å)								
1/2	6.84_2	6.90_9	7.02_3	6.56_2	7.00_1	6.12_9	6.11_0	6.22_7
1/3	5.29_4	6.07_0	6.24_1	6.09_1	5.94_7	6.01_7	5.92_1	7.36_8
2/3	9.10_7	9.42_6	9.43_9	9.29_7	9.34_8	8.49_9	8.80_9	5.06_2
Ligand sulfoxide, carbonyl and phosphoryl distances (Å)								
O(m1)-C,P,S(m1)	1.512(1)	1.472(2)	1.504(1)	1.500(3)	1.500(3)	1.294(3)	1.243(4)	1.499(2)
O(m2)-C,P,S(m2)	1.528(1)	1.418(4)	1.503(1)	1.510(3)	1.509(2)	1.283(2)	1.270(6)	1.504(2)

Lattice solvents are $CHCl_3$ (hmpa1), CH_2Cl_2 (hmpa2).

[a] Values presented are for the 170K structure. The value for the sulfoxide distance O(33)-S(33) is 1.529(1) Å.