Supporting Information

Heterobimetallic Complexes with M^{III}-(μ-OH)-M^{II} Cores (M^{III} = Fe, Ga, Mn; M^{II} = Ca, Sr): Structural, Kinetic, and Redox Properties.

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Crystallography

General Methods

Single crystals were mounted on a glass fiber and transferred to a Bruker SMART APEX II diffractometer. The APEX2[1] program package was used to determine the unit-cell parameters and for data collection. The raw frame data was processed using SAINT[2] and SADABS[3] to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL[4] program. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors[5] for neutral atoms were used throughout the analyses. Hydrogen atom H(7) was located from a difference-Fourier map and refined (x,y,z and U_{iso}) with d(O-H) fixed at 0.85Å. The remaining hydrogen atoms were included using a riding model.

Structure of [15-crown-5⊃Ca^{II}-(μ-OH)-Fe^{III}MST]OTf. A yellow crystal of approximate dimensions 0.18 x 0.23 x 0.33 mm was analyzed. There were no systematic absences or any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group *P*-1 was assigned and later determined to be correct. The fluorine atoms, oxygen atoms O(14) and O(15) and carbon atoms C(37), C(38) and C(40) were disordered and included using multiple components and partial site-occupancy-factors. Equivalent anisotropic thermal parameters were used for the fluorine atoms. There was one molecule of dichloromethane solvent present. Least-squares analysis yielded wR2 = 0.1201 and Goof = 1.035 for 733 variables (1 restraint) refined against 13241 data (0.76Å), R1 = 0.0443 for those 11334 data with I > 2.0σ(I).

Structure of [15-crown-5⊃Sr^{II}-(μ-OH)-Fe^{III}MST]OTf.

A yellow crystal of approximate dimensions 0.13 x 0.18 x 0.31 mm was analyzed. The diffraction symmetry was 2/*m* and the systematic absences were consistent with the monoclinic space group $P2_1/c$ that was later determined to be correct. The 15-crown-5 was disordered and included using multiple components, partial site-occupancy-factors and isotropic thermal parameters. There was one molecule of dichloromethane solvent present. At convergence, wR2 = 0.1300 and Goof = 1.035 for 675 variables refined against 12345 data (0.78Å), R1 = 0.0472 for those 10487 data with I > 2.0σ(I).

Structure of [15-crown-5⊃Sr^{II}-(μ-OH)-Mn^{III}MST]OTf. A green crystal of approximate dimensions 0.21 x 0.31 x 0.41 mm was analyzed. There were no systematic absences or any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group *P*-1 was assigned and later determined to be correct. There were two molecules of dichloromethane solvent present. The triflate anion and the solvent chlorine atoms were disordered and included using multiple components and partial site-occupancy-factors. The triflate anion was refined as a rigid group. Isotropic thermal parameters were used for the carbon, fluorine and oxygen atoms associated with the triflate anion and for the chlorine atoms. Least-squares analysis yielded wR2 = 0.1434 and Goof = 1.039 for 674 variables (1 restraint) refined against 12276 data (0.80Å), R1 = 0.0530 for those 11026 data with I > 2.0σ(I).

Structure of [15-crown-5⊃Ca^{II}-(μ-OH)-Ga^{III}MST]. A colorless crystal of approximate dimensions 0.28 x 0.33 x 0.39 mm was analyzed. There were no systematic absences or any diffraction symmetry other than the Friedel condition. The centrosymmetric triclinic space group *P*-1 was assigned and later determined to be correct. The fluorine atoms, carbon C(45) and oxygen atoms O(13), O(14) and O(15) were disordered and included using multiple components and partial site-occupancy-factors. Equivalent isotropic thermal parameters were used for the fluorine atoms and oxygen atoms associated with the triflate anion. There was one molecule of dichloromethane solvent present. Least-squares analysis yielded wR2 = 0.1304 and Goof = 1.059 for 672 variables (1 restraint) refined against 12505 data (0.78Å), R1 = 0.0469 for those 11177 data with I > 2.0σ(I).

Definitions:

$wR2 = [\Sigma[w(F_o^2-F_c^2)^2] / \Sigma[w(F_o^2)^2]]^{1/2}$

$R1 = \Sigma||F_o|-|F_c|| / \Sigma|F_o|$

$Goof = S = [\Sigma[w(F_o^2-F_c^2)^2] / (n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

References

1. APEX2 Version 2010.3-0, Bruker AXS, Inc.; Madison, WI 2010.
2. SAINT Version 7.68a, Bruker AXS, Inc.; Madison, WI 2009.
3. Sheldrick, G. M. SADABS, Version 2008/1, Bruker AXS, Inc.; Madison, WI 2008.
4. Sheldrick, G. M. SHELXTL, Version 2008/4, Bruker AXS, Inc.; Madison, WI 2008.
5. International Tables for X-Ray Crystallography 1992, Vol. C., Dordrecht: Kluwer Academic Publishers.

Table S1. Crystallographic Data and Structure Refinement Parameters for the M^{II}-(μ-OH)-Fe^{III} Core Complexes

Complex	[15-crown-5⊃Ca^{II}-(μ-OH)-Fe^{III}MST]OTf	[15-crown-5⊃Sr^{II}-(μ-OH)-Fe^{III}MST]OTf
Formula	$C_{44}H_{66}CaF_3FeN_4O_{15}S_4$ •CH_2Cl_2	$C_{45}H_{68}Cl_2F_3Fe\ N_4O_{15}S_4Sr$
Formula weight	1257.10	1304.64
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	14.2376(5)	8.7949(3)
b (Å)	14.5557(5)	28.7099(11)
c (Å)	16.0245(6)	22.4440(9)
α (˚)	112.0349(4)	90
β (˚)	96.1392(4)	98.6131(5)
γ (˚)	107.9824(4)	90
Volume ($Å^3$)	2832.94(17)	5603.2(4)
Z	2	4
δ_{calc} (Mg/m^3)	1.474	1.547
Goodness-of-fit	1.035	1.035
R1	0.0443	0.0472
wR2	0.1145	0.1234

Table S2. Crystallographic Data and Structure Refinement Parameters for the M^{II}-(μ-OH)-M^{III} Core Complexes

Complex	[15-crown-5⊃Sr^{II}-(μ-OH)-Mn^{III}MST]OTf	[15-crown-5⊃Ca^{II}-(μ-OH)-Ga^{III}MST]
Formula	$C_{46}H_{70}Cl_4F_3MnN_4O_{15}S_4Sr$	$C_{45}H_{68}CaCl_2F_3GaN_4O_{15}S_4$
Formula weight	1388.66	1270.97
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	13.9061(7)	14.3885(5)
b (Å)	15.1055(8)	14.7196(5)
c (Å)	16.2620(9)	15.8403(6)
α (°)	68.7445(6)	112.8012(4)
β (°)	75.3429(6)	97.8526(4)
γ (°)	74.3805(6)	106.3846(4)
Volume ($Å^3$)	3019.7(3)	2850.07(18)
Z	2	2
δ_{calc} (Mg/m^3)	1.527	1.481
Goodness-of-fit	1.039	1.059
R1	0.0530	0.0469
wR2	0.1392	0.1264

Table S3. Selected Metrical Parameters for the $[Sr^{II}(OH)\text{-}Mn^{III}]^{+}$ Complex.

	Bond Distances (Å)
Mn1—N1	2.049(3)
Mn1—N2	2.057(3)
Mn1—N3	2.090(3)
Mn1—N4	2.042(3)
Mn1—O7	1.826(2)
O7···O5	2.664(6)
Sr1—O7	2.430(2)
Sr1···O1	2.503(2)
Sr1···O3	2.482(2)
Mn1···Sr1	3.897(2)
Avg Sr1—O_{crown}	2.640(2)
d[Mn–N_{eq}]	0.301
d[M1—O_{crown}]	1.308
	Bond Angles (°)
O7-Mn1-N1	176.02(11)
O7-Mn1-N2	97.68(11)
O7-Mn1-N3	102.74(11)
O7-Mn1-N4	95.43(11)
N1-Mn1-N2	82.76(11)
N1-Mn1-N3	80.84(11)
N1-Mn1-N4	81.18(11)
N2-Mn1-N3	107.40(12)
N3-Mn1-N4	119.87(12)
N2-Mn1-N4	126.32(12)
Mn1-O7-Sr1	132.09(12)
τ value	0.828

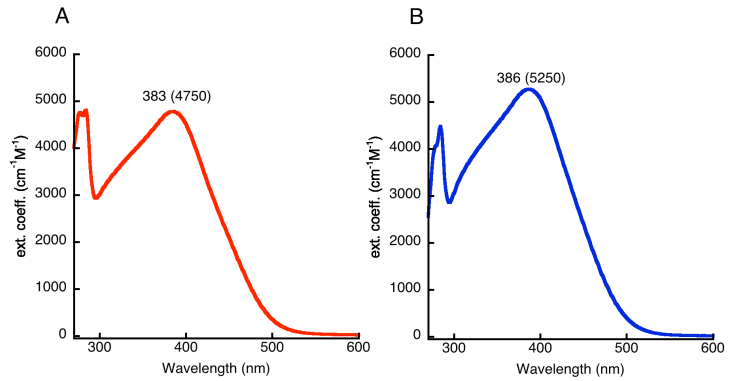

Figure S1. UV/Vis spectra for A: [15-crown-5⊃Ca^{II}-(μ-OH)-Fe^{III}MST]$^{+}$ and B: [15-crown-5⊃Sr^{II}-(μ-OH)-Fe^{III}MST]$^{+}$. The measurements were done in DCM at room temperature.

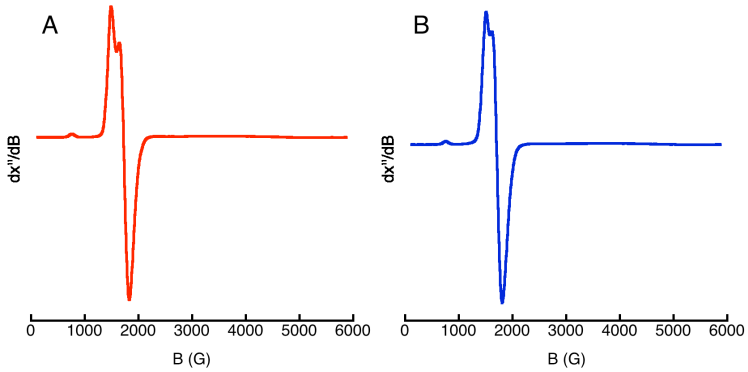

Figure S2. EPR spectra for A: [15-crown-5⊃Ca^{II}-(μ-OH)-Fe^{III}MST]$^{+}$ and B: [15-crown-5⊃Sr^{II}-(μ-OH)-Fe^{III}MST]$^{+}$. The measurements were done in DCM at 4K.

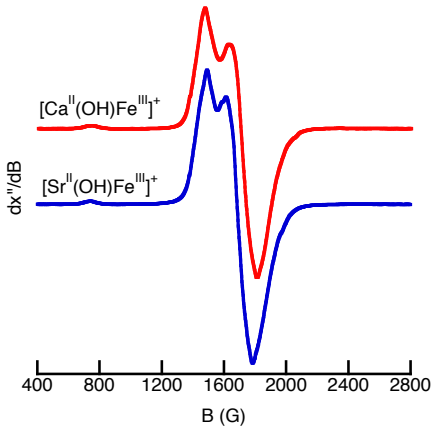

Figure S3. Stack plot of EPR spectra for [15-crown-5⊃Ca^{II}-(μ-OH)-Fe^{III}MST]$^+$ and [15-crown-5⊃Sr^{II}-(μ-OH)-Fe^{III}MST]$^+$.

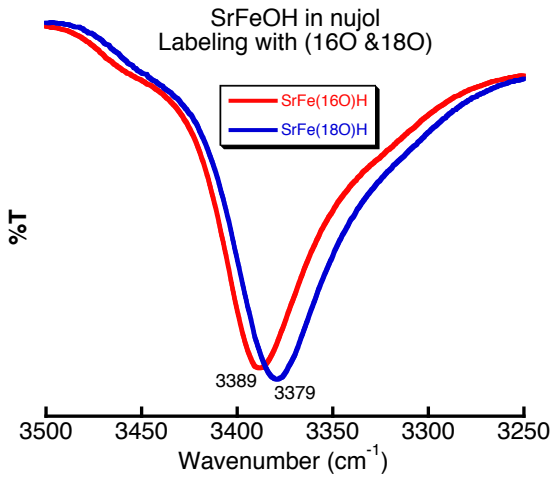

Figure S4. FTIR spectra of [15-crown-5⊃Sr^{II}-(μ-^{16}OH)-Fe^{III}MST]$^+$ (red) and [15-crown-5⊃Sr^{II}-(μ-^{18}OH)-Fe^{III}MST]$^+$ (blue) in Nujol.

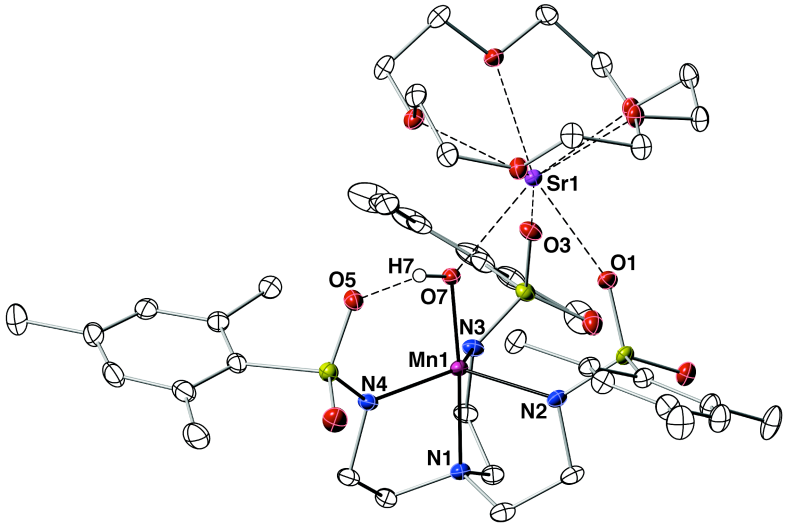

Figure S5. Thermal ellipsoid diagram depicting the molecular structure of $[Sr^{II}(OH)Mn^{III}]^{+}$. Ellipsoids are drawn at the 50% probability level and only the hydroxo hydrogen atom is shown for clarity.

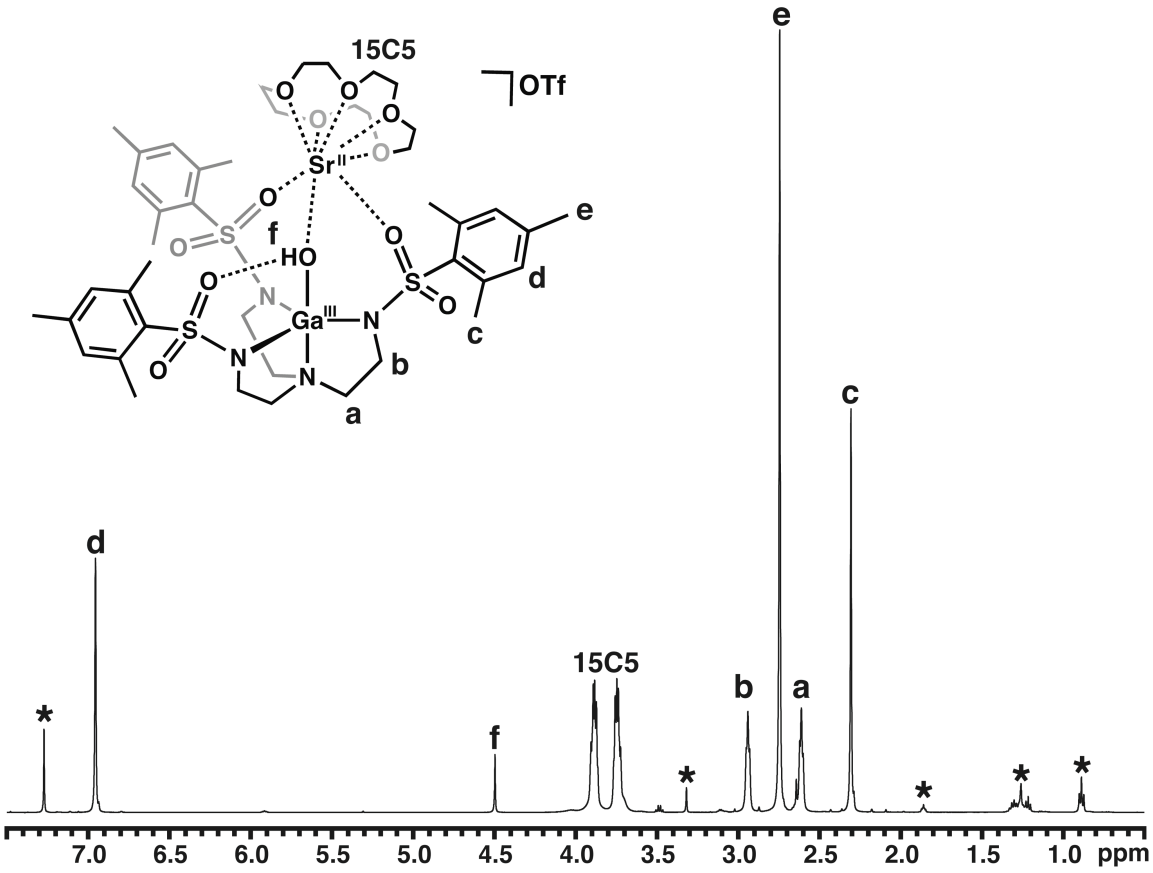

Figure S6. ^{1}H NMR spectrum of $[Sr^{II}(OH)Ga^{III}]^{+}$ in $CDCl_3$ at 298 K. Asterisks denote residual solvent peaks.

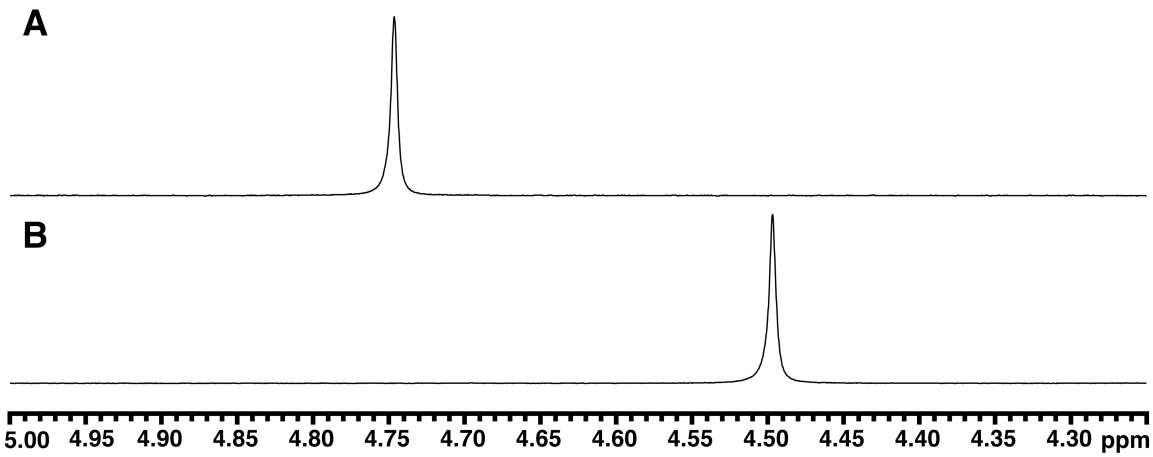

Figure S7. Overlay of ^{1}H NMR spectra of $[Ca^{II}(OH)Ga^{III}]^{+}$ (A) and $[Sr^{II}(OH)Ga^{III}]^{+}$ (B) in $CDCl_3$ at 298 K.

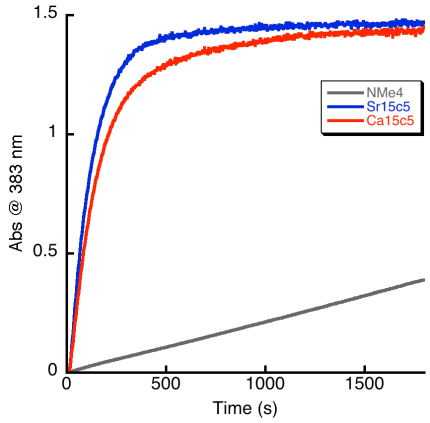

Figure S8. Time-course profiles for the reaction of $[Fe^{II}MST]^{-}$ and O_2 in the presence of $[NMe_4]^{+}$, 3 equiv of $Sr(OTf)_2$/15-crown-5, and 3 equiv of $Ca(OTf)_2$/15-crown-5. Reactions were done in CH_2Cl_2 at 20˚C.

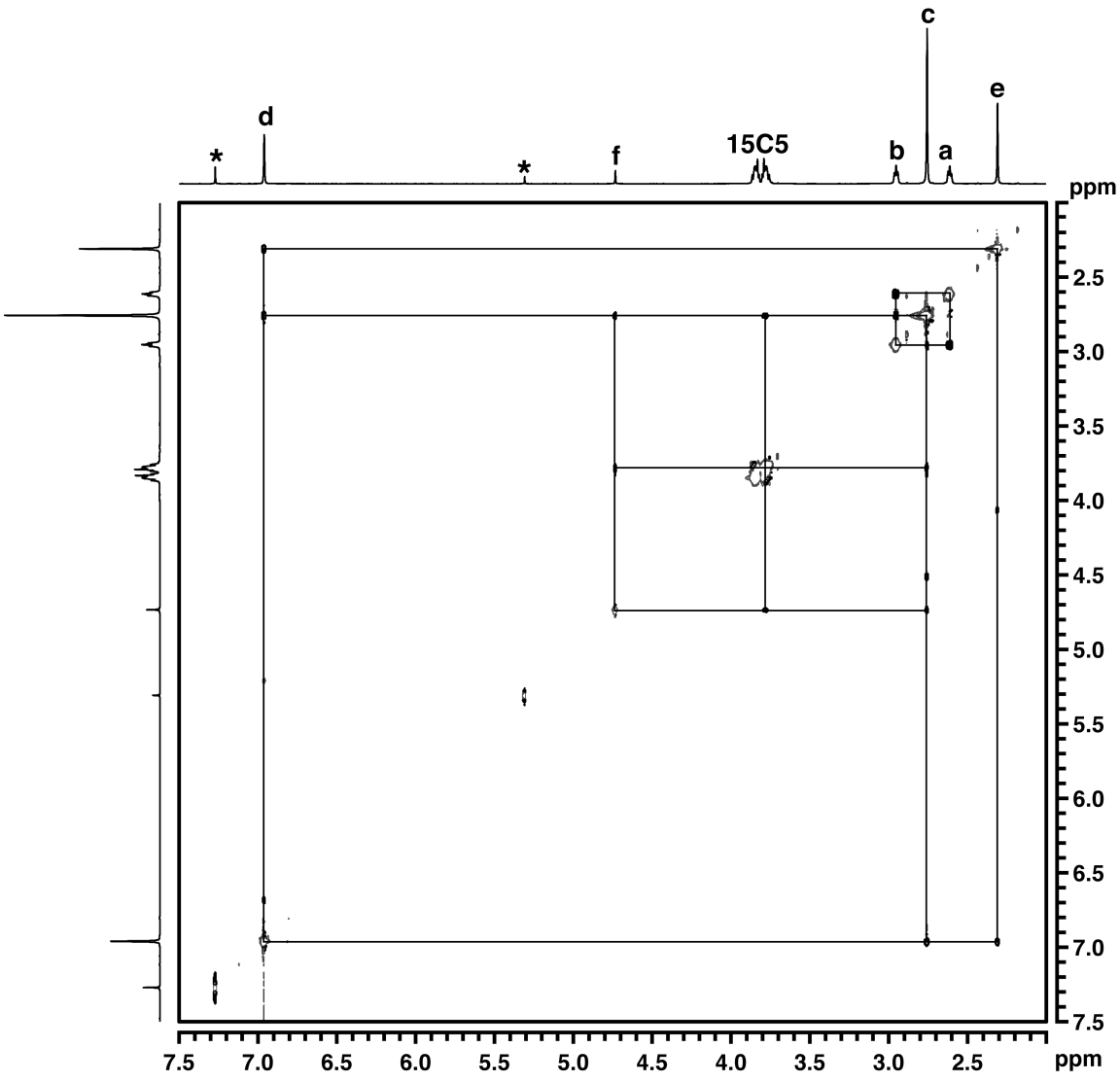

Figure S9. Full ^{1}H NOESY NMR spectrum of $[Ca^{II}(OH)Ga^{III}]^{+}$ in $CDCl_3$ at 298 K. Asterisks denote residual solvent peaks, and the drawn lines indicate NOE interactions.

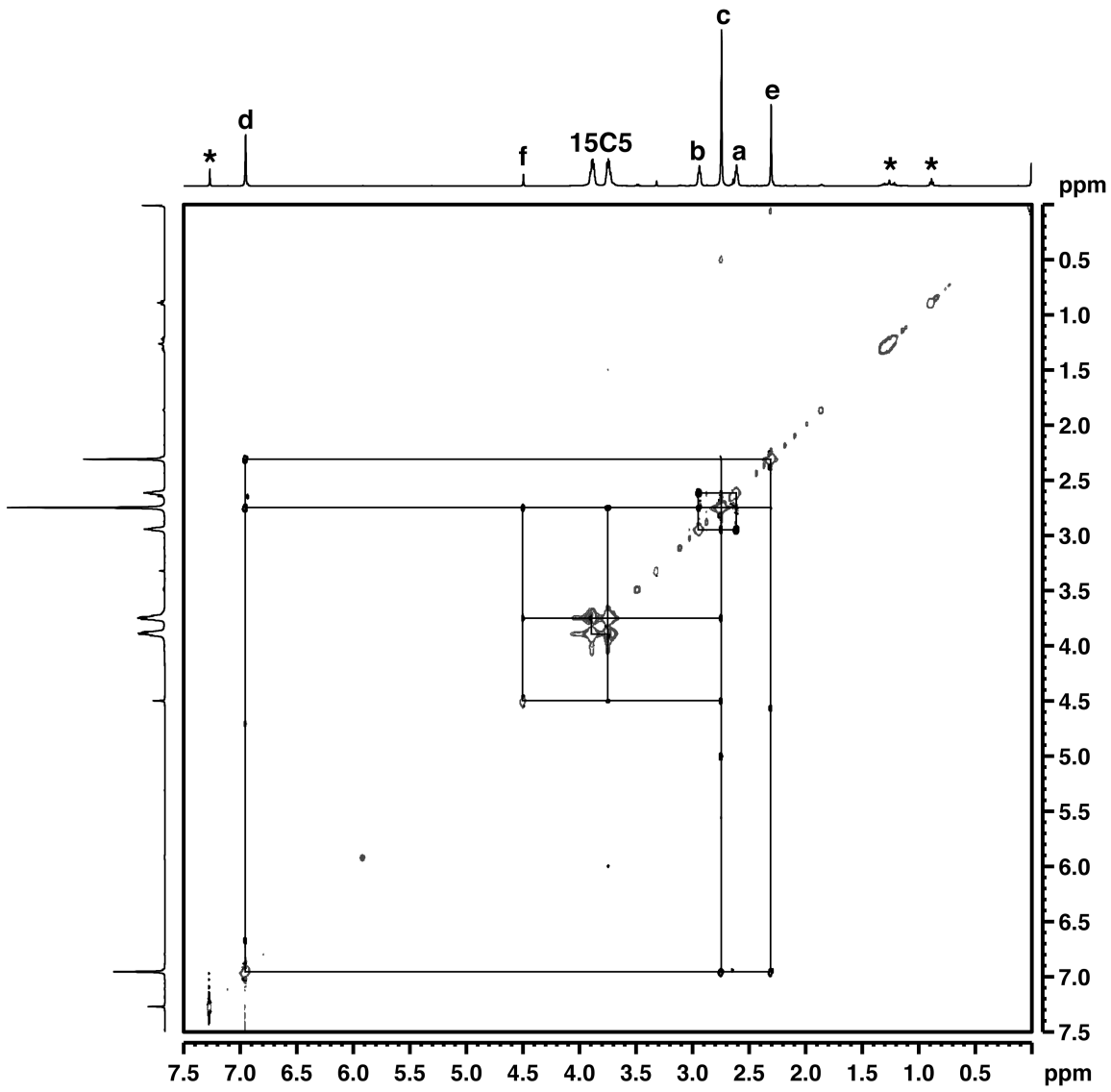

Figure S10. ^{1}H NOESY NMR spectrum of $[Sr^{II}(OH)Ga^{III}]^{+}$ in $CDCl_3$ at 298 K. Asterisks denote residual solvent peaks, and the drawn lines indicate NOE interactions.