Electronic Supplementary Information

Spin-Crossover Phenomena of Mononuclear Mn^{III} Complex Tuned by Metal Dithiolene Counteranions

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Table S1 Crystal structural data and refinement parameters for **2**.

Complex			**2**		
Chemical formula			$C_{52}H_{52}Br_4Mn_2N_{12}O_4PtS_4$		
Temperature/K	123(2)	296(2)	350(2)	400(2)	473(2)
Fw / g mol^{-1}	1661.91	1661.91	1661.91	1661.91	1661.91
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a/Å	8.1643(19)	8.2697(4)	8.2884(16)	8.3184(11)	8.356(2)
b/Å	10.013(2)	10.0679(5)	10.0517(19)	10.0509(13)	10.057(3)
c/Å	18.323(4)	18.4929(10)	18.518(4)	18.595(2)	18.676(5)
α/°	78.223(3)	78.6030(10)	78.811(3)	78.835(2)	78.942(4)
β/°	79.349(4)	79.1010(10)	79.000(3)	78.768(2)	78.639(4)
γ/°	83.348(4)	84.2880(10)	84.998(3)	85.630(2)	86.212(4)
Unit cell volume/Å^3	1436.3(6)	1479.01(13)	1483.6(5)	1494.8(3)	1509.7(6)
Z	1	1	1	1	1
ρ_{calcd} / mg m^{-3}	1.921	1.866	1.860	1.846	1.828
μ/mm^{-1}	5.846	5.677	5.659	5.617	5.562
Reflections measured	11599	9037	12031	12122	11120
Independent reflections	5576	5784	5759	5813	5249
R_{int}	0.0482	0.0242	0.0348	0.0369	0.0584
R_1 (all data)	0.0572	0.0505	0.0502	0.0685	0.1042
wR_2 (all data)	0.1463	0.0971	0.1369	0.1647	0.1393
GOF on F^2	1.007	1.038	1.001	1.081	1.008

Table S2 Octahedral structural parameters of Mn^{III} for $[Mn(5\text{-Br-sal-N-1,5,8,12})]ClO_4$ and complexes **1**-**3**.

	$[Mn(5\text{-Br-sal-N-1,5,8,12})]ClO_4$				**1(up)** and **2 (down)**					**3**
	100 K		294 K		123 K	296 K	350 K	400K	473 K	296 K
	Mn1	Mn2	Mn1	Mn2	Mn1	Mn1	Mn1	Mn1	Mn1	Mn1
average trigonal distortion angle Φ [°][a]	4.45	2.50	4.37	3.90	1.81 1.95	2.28 2.28	2.52 2.54	2.88 2.95	3.06 3.06	5.69
octahedral distortion parameter Σ [°][b]	66.26	36.99	65.63	59.88	19.5 19.47	24.26 25.87	29.54 30	34.53 37.14	37.64 40.34	83.66

[a] average trigonal distortion angle $\Phi = \Sigma_1^{24}(|60 - \theta_i|)/24$ [$\Phi = 0°$ for an ideal octahedron; θ_i represents the individual trigonal angles of the eight faces of the octahedron][1]
[b] octahedral distortion parameter $\Sigma = \Sigma_1^{12}(|90 - \varphi_i|)$ [$\Sigma = 0°$ for an ideal octahedron; φ_i represents the twelve smallest L–M–L angles][2]

Table S3 Selected bond lengths (Å) and angles (°) for **2**.

	123K	296K	350K	400K	473K
			Bond Distances (Å)		
Mn(1)-O(1)	1.889(4)	1.883(3)	1.886(3)	1.874(3)	1.891(3)
Mn(1)-O(2)	1.887(4)	1.876(3)	1.880(3)	1.882(3)	1.874(3)
Mn(1)-N(1)	1.975(4)	2.015(4)	2.025(3)	2.071(4)	2.071(4)
Mn(1)-N(2)	2.030(5)	2.069(4)	2.078(4)	2.111(4)	2.115(4)
Mn(1)-N(3)	2.055(4)	2.088(4)	2.102(4)	2.135(5)	2.154(5)
Mn(1)-N(4)	1.978(5)	2.011(4)	2.038(4)	2.054(4)	2.054(4)
Pt(1)-S(1)	2.2865(14)	2.2903(14)	2.2831(13)	2.2859(16)	2.2892(15)
Pt(1)-S(2)	2.2922(14)	2.2992(14)	2.2968(12)	2.2982(14)	2.2922(15)
			Bond Angles (°)		
O(2)-Mn(1)-O(1)	179.60(17)	179.60(15)	178.26(13)	177.64(16)	176.82(16)
O(2)-Mn(1)-N(4)	89.05(18)	88.58(15)	87.63(13)	87.64(15)	87.08(15)
O(1)-Mn(1)-N(4)	90.58(18)	91.20(16)	90.88(14)	90.81(16)	91.01(15)
O(2)-Mn(1)-N(1)	90.93(17)	90.91(15)	91.00(14)	91.16(15)	91.24(15)
O(1)-Mn(1)-N(1)	88.98(17)	88.79(15)	88.35(13)	87.41(15)	86.73(15)
N(4)-Mn(1)-N(1)	95.45(19)	97.75(16)	99.40(15)	101.76(17)	103.31(17)
O(2)-Mn(1)-N(2)	88.56(18)	88.61(16)	89.28(14)	89.48(16)	90.11(16)
O(1)-Mn(1)-N(2)	91.83(18)	91.64(16)	92.32(14)	92.32(17)	92.20(16)
N(4)-Mn(1)-N(2)	173.93(18)	172.58(18)	171.02(15)	170.46(17)	169.71(17)
N(1)-Mn(1)-N(2)	90.17(19)	89.16(17)	89.07(15)	87.38(17)	86.64(17)
O(2)-Mn(1)-N(3)	90.85(18)	91.52(16)	91.62(14)	92.88(16)	92.80(16)
O(1)-Mn(1)-N(3)	89.28(18)	88.81(16)	89.22(14)	88.82(16)	89.63(16)
N(4)-Mn(1)-N(3)	89.71(18)	88.92(17)	87.77(16)	87.13(18)	86.88(18)
N(1)-Mn(1)-N(3)	174.6(2)	172.95(17)	172.46(16)	170.38(18)	169.23(18)
N(2)-Mn(1)-N(3)	84.76(18)	84.28(17)	83.90(16)	83.93(18)	83.37(18)
S(1)- Pt(1)-S(2)	90.05(5)	89.75(5)	89.71(4)	89.55(5)	89.50(5)
S(1)- Pt(1)-S(2A)	89.95(5)	90.25(5)	90.29(5)	90.45(5)	90.50(5)

Symmetry code : 1 − x, 2 − y, 1 − z.

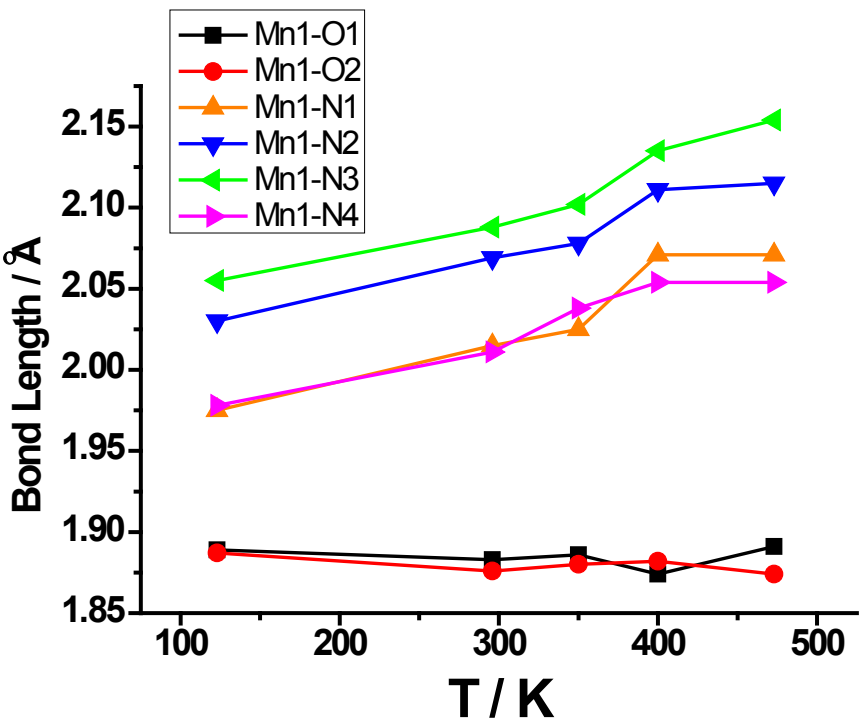

Fig. S1 Comparison of Mn—N and Mn—O bond lengths at five collection temperatures in complex **2**.

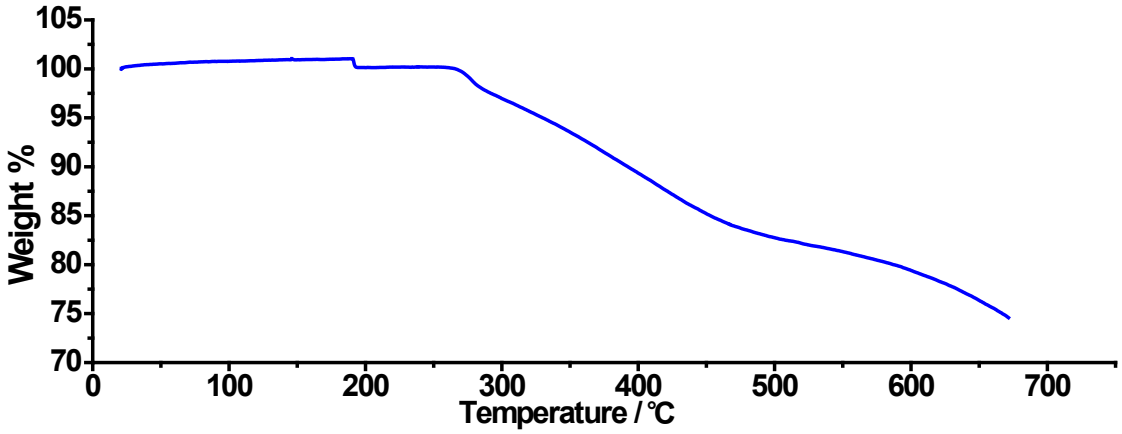

Fig. S2 TG plot of complex **1**.

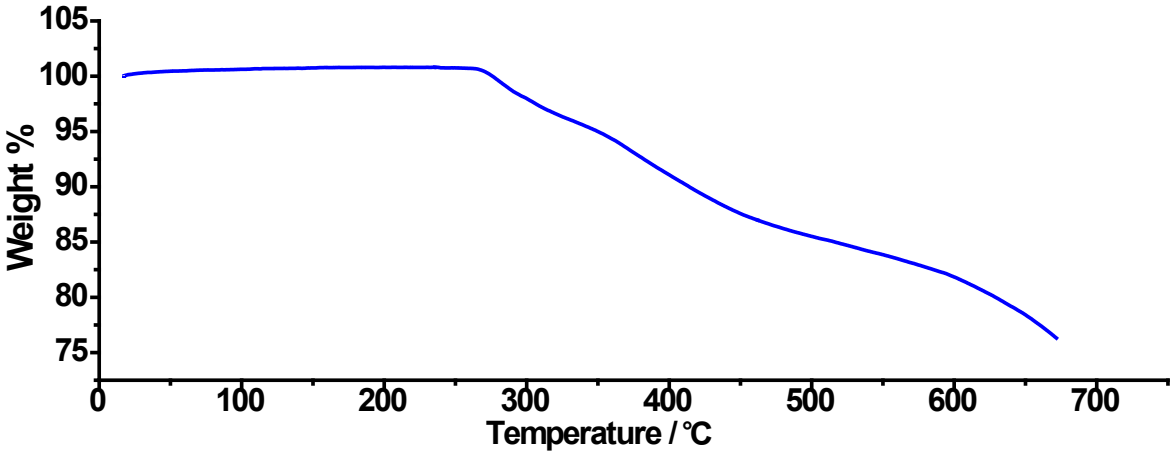

Fig. S3 TG plot of complex **2**.

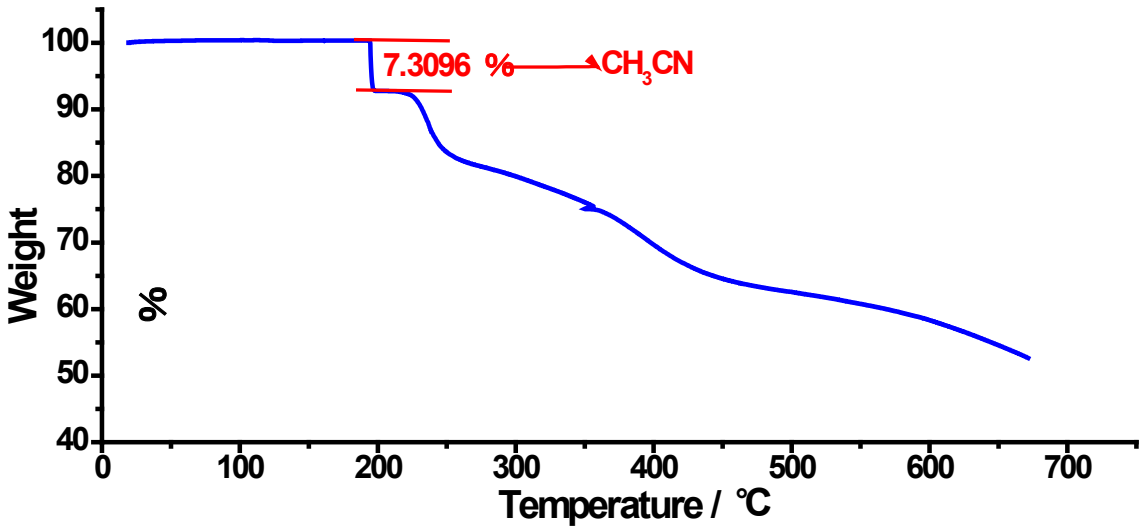

Fig. S4 TG plot of complex **3**.

Table S4 Calculated atomic spin population for the tetranuclear model in complex **3**.

Br1 -0.000009	C11 -0.002410	C21 0.004757	O31 -0.001408	C41 0.002892
Br2 0.000255	C12 0.000009	C22 0.001684	Br32 -0.000024	C42 -0.002434
C3 0.010531	C13 0.002727	C23 0.000960	Br33 0.000252	C43 0.000005
C4 -0.002199	C14 0.003601	C24 0.005654	C34 0.010805	C44 0.002719
C5 0.003807	C15 0.000509	Mn25 3.890469	C35 -0.002482	C45 0.003621
C6 -0.000694	C16 0.001801	N26 -0.025517	C36 0.004082	C46 0.000506
C7 0.004286	C17 0.000935	N27 0.026463	C37 -0.001044	C47 0.001816
C8 -0.002992	C18 0.023297	N28 0.016463	C38 0.004600	C48 0.000906
C9 0.019913	C19 0.000080	N29 -0.006923	C39 -0.003300	C49 0.023315
C10 0.002877	C20 -0.001650	O30 -0.005456	C40 0.020179	C50 0.000041

C51 -0.001650	O61 -0.005538	S71 -0.160345	C81 -0.031354	S91 -0.048771
C52 0.004873	O62 -0.001675	S72 0.003450	C82 -0.000099	S92 -0.152802
C53 0.001511	C63 -0.041083	S73 0.005636	C83 -0.033074	S93 -0.153376
C54 0.001121	C64 -0.031299	S74 -0.048545	C84 -0.034130	S94 0.004288
C55 0.005539	C65 -0.000046	S75 -0.152831	C85 -0.000584	S95 0.004719
Mn56 3.891053	C66 -0.032905	S76 -0.153748	Ni86 -0.161884	S96 -0.043318
N57 -0.025817	C67 -0.034435	S77 0.004325	S87 -0.150640	
N58 0.026460	C68 -0.000561	S78 0.004675	S88 -0.160766	
N59 0.016363	Ni69 -0.162180	S79 -0.043342	S89 0.003495	
N60 -0.006885	S70 -0.150713	C80 -0.041317	S90 0.005682	

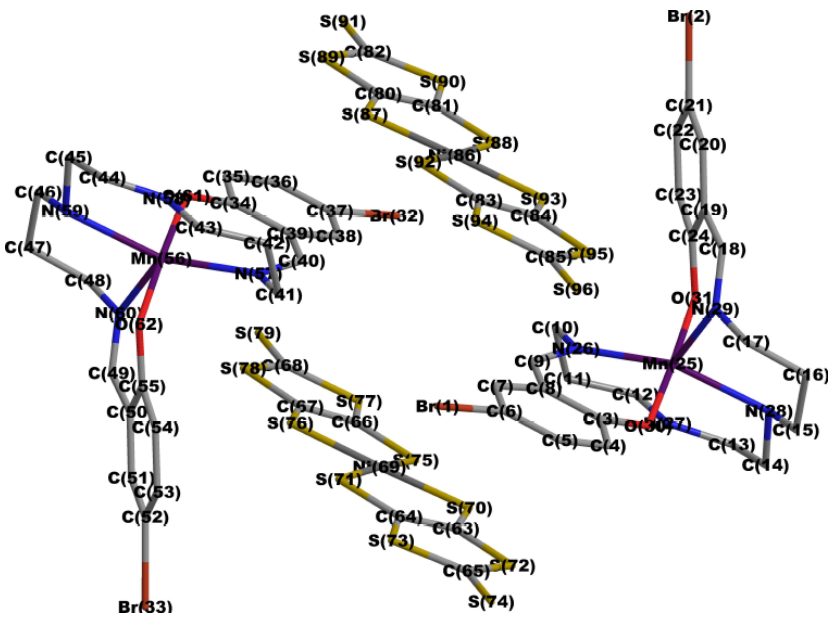

Fig. S5 The corresponding model for calculated atomic spin population for complex **3**.

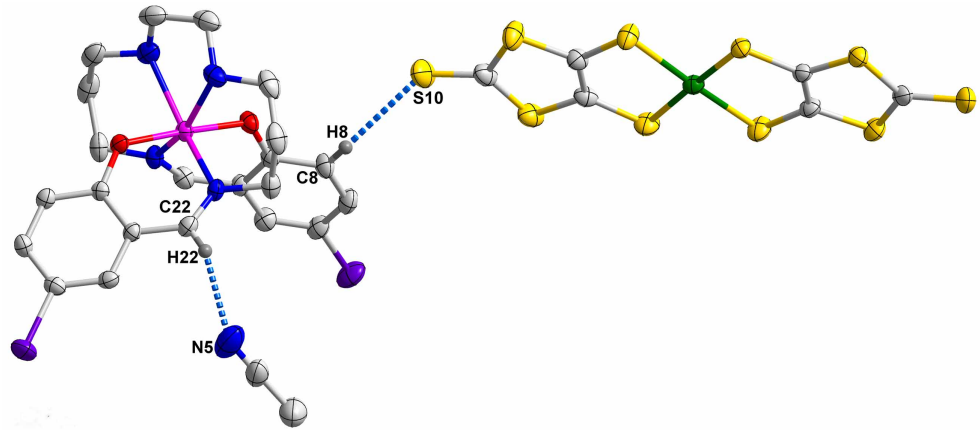

Fig. S6 Details of hydrogen bonds for complex **3** (A majority of hydrogen atoms are omitted for clarity).

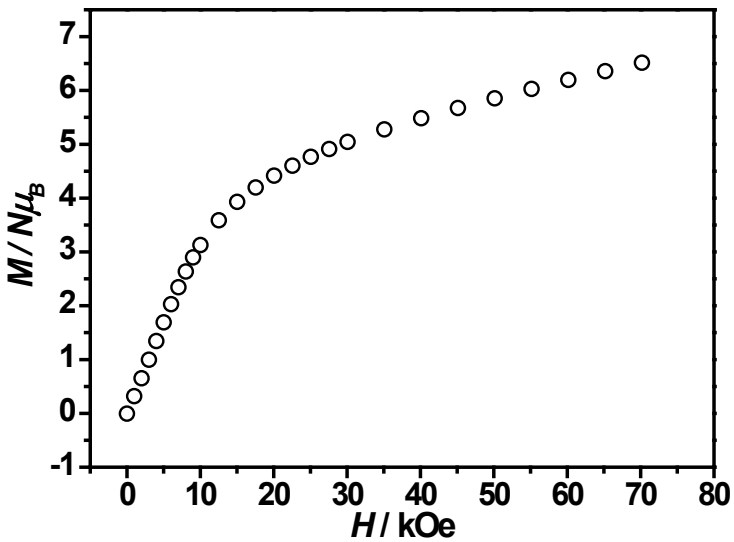

Fig. S7 Field dependence of magnetization at 1.8 K for complex **3**.

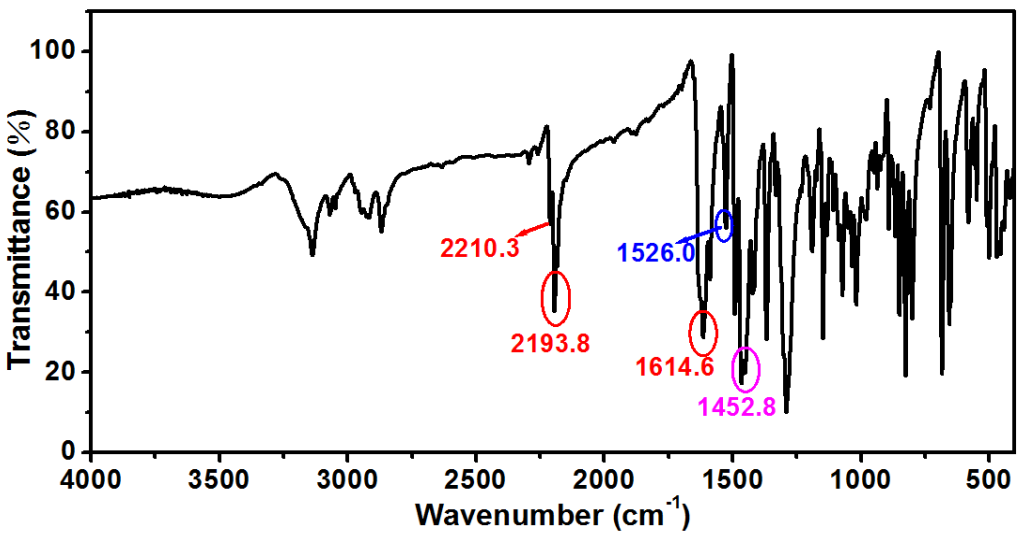

Fig. S8 IR spectrum of complex **1**.

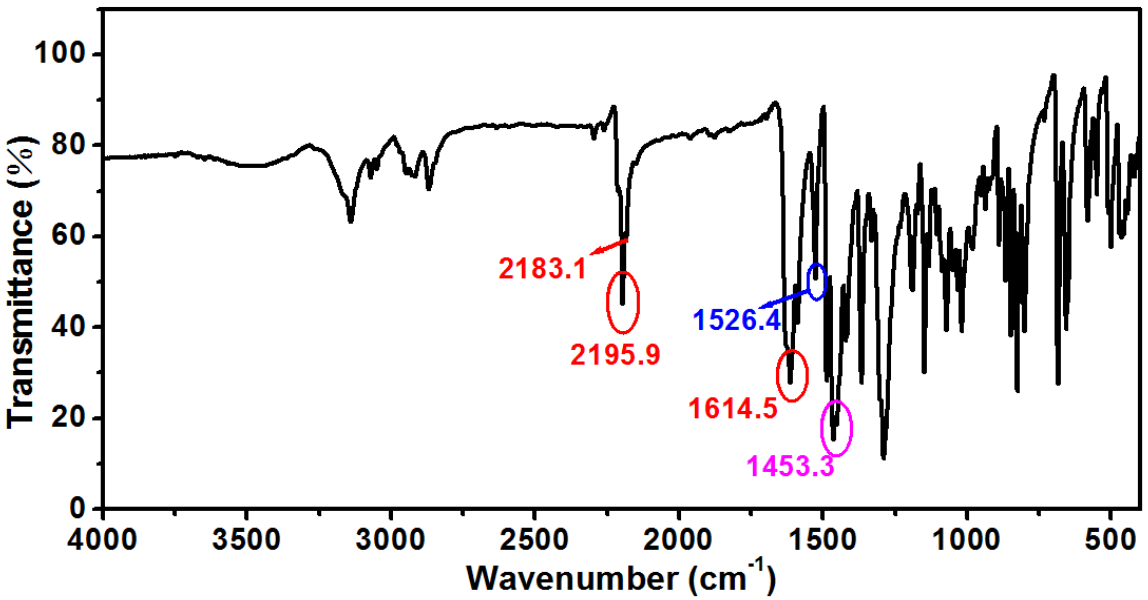

Fig. S9 IR spectrum of complex **2**.

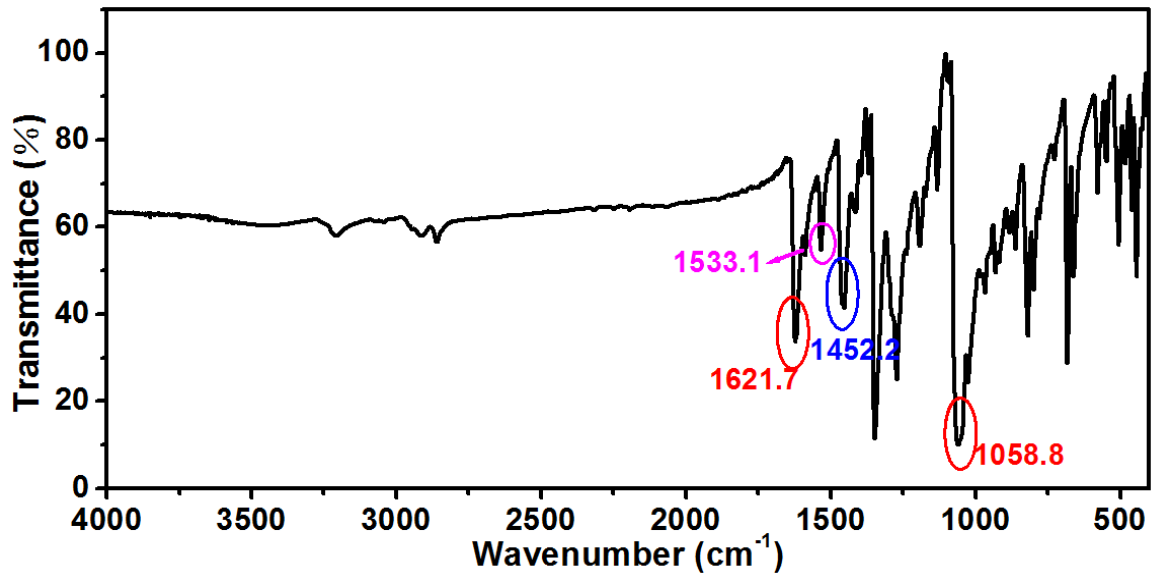

Fig. S10 IR spectrum of complex **3**.

References

1. N. Ortega-Villar, A. L. Thompson, M. C. Muñoz, V. M. Ugalde-Saldívar, A. E. Goeta, R. Moreno-Esparza and J. A. Real, *Chem. Eur. J.*, 2005, **11**, 5721-5734.

2. J. Klingele, D. Kaase, M. H. Klingele, J. Lach and S. Demeshko, *Dalton Transactions*, 2010, **39**, 1689.