Synthesis and characterization of dithiooxamidate-bridged polynuclear Ni complexes

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Supplementary Materials

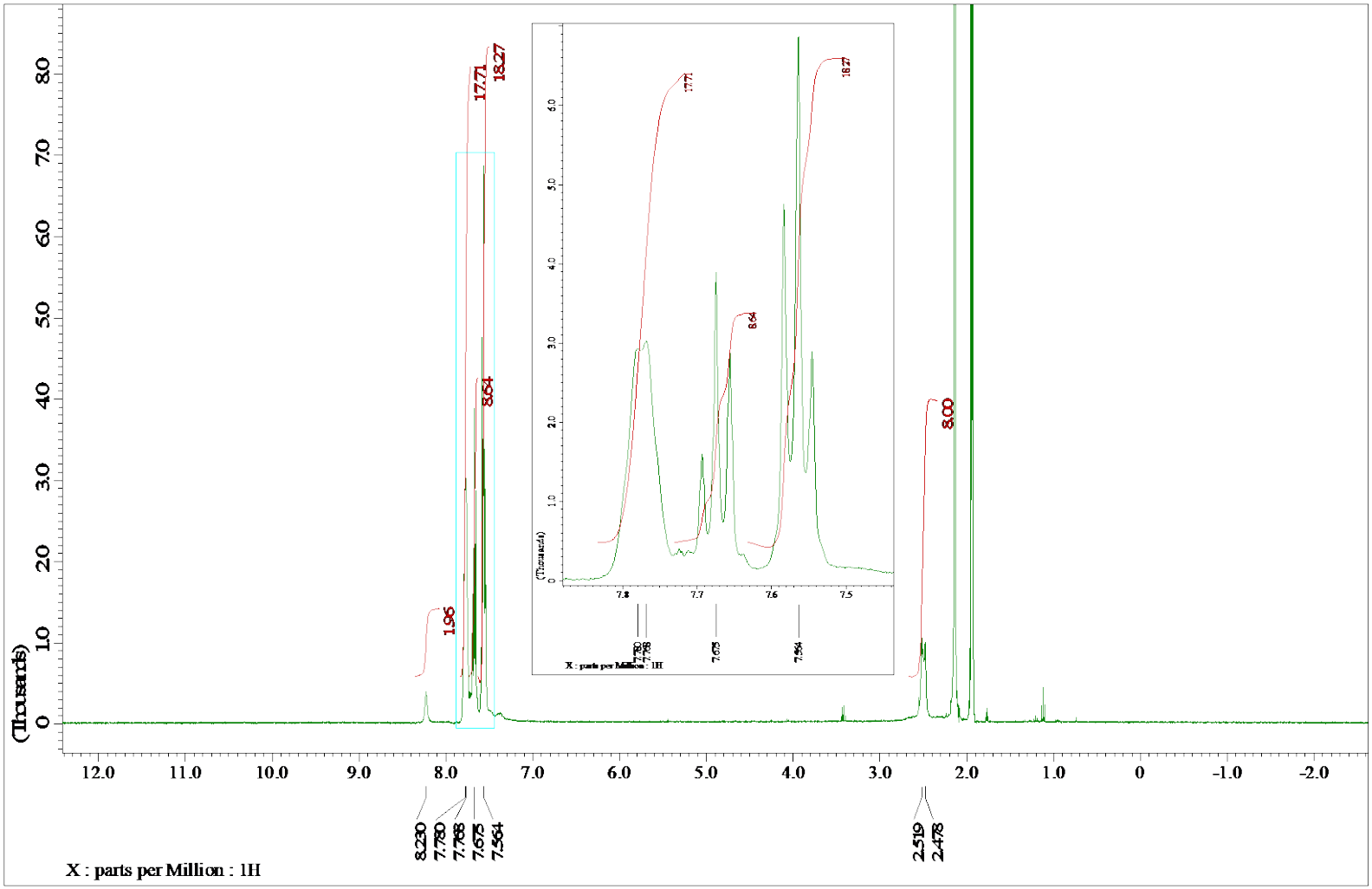

Figure S1 ^{1}H NMR spectrum of complex **1** in CD_3CN

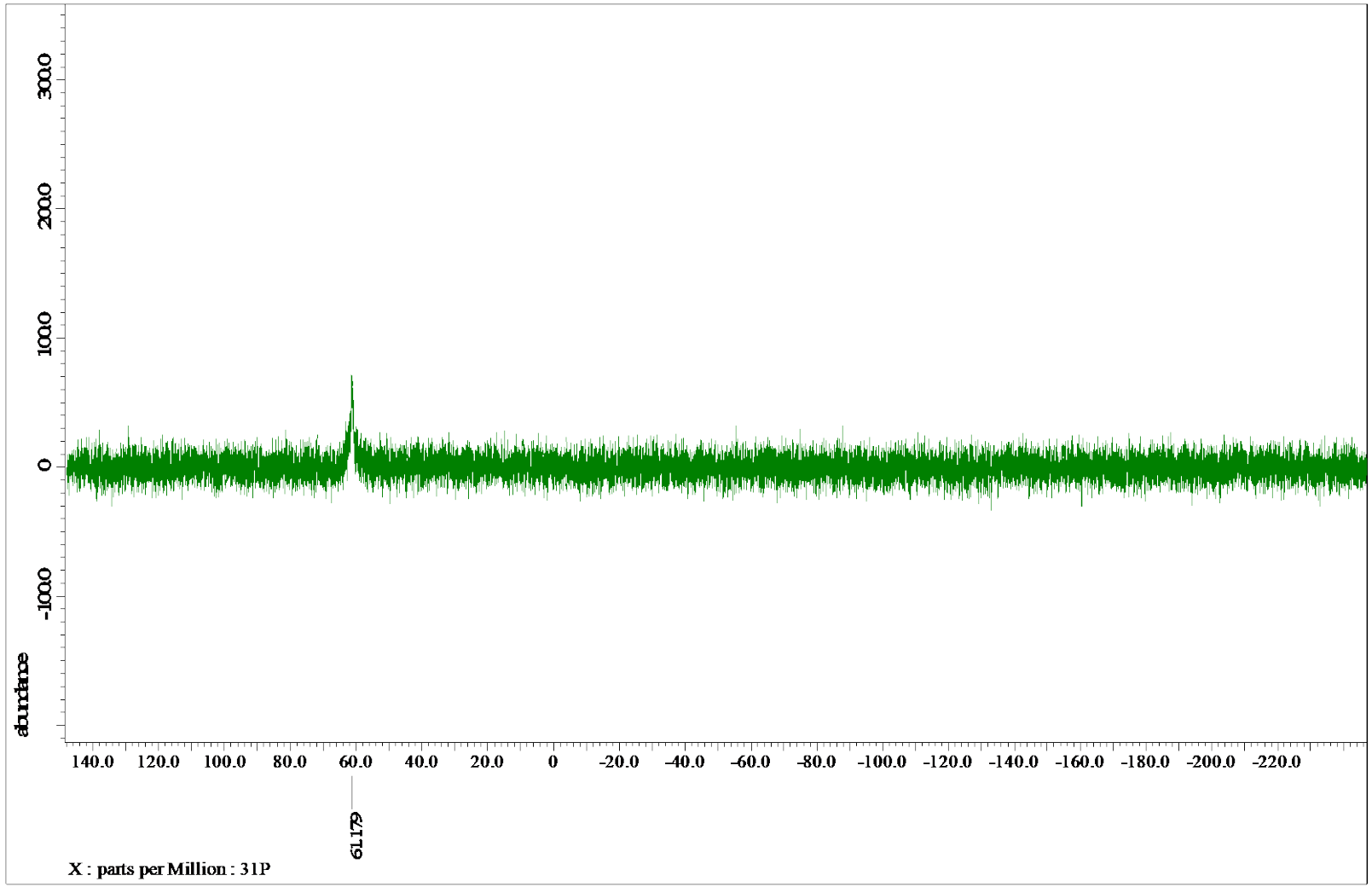

Figure S2 ^{31}P NMR spectrum of complex **2** in CD_3CN (85% H_3PO_4 aq. shows a singlet peak at δ −1.458 ppm)

Table S1 Crystallographic data

	complex **1**	complex **1a**	complex **2a**	complex **3a**
Formula	C84H84B2F8N4Ni2O4P6S2	C56H54B2F8N2Ni2O0P4S2	C93.28H97.85B2F8N7Ni3O2P6S4	C105H120B2F8N6Ni4O6P6S6
Formula weight	1754.53	1234.05	2012.82	2348.70
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P*-1	*P*-1	*P*-1	*P*-1
a/Å	12.6917(5)	12.9801(10)	15.3755(5)	17.3068(5)
b/Å	13.3422(5)	15.7005(13)	16.7251(5)	18.1122(4)
c/Å	13.3579(5)	17.4317(13)	20.9172(6)	20.3566(5)
α/ °	115.314(8)	109.039(8)	91.506(6)	107.072(2)
β / °	91.395(6)	98.793(7)	110.803(8)	108.790(2)
γ / °	97.129(7)	94.153(7)	106.440(7)	95.823(2)
V/Å^3	2021.39(18)	3290.1(5)	4774.3(4)	5637.7(3)
Z	1	2	2	2
T/K	100(2)	100(2)	120(2)	130(2)
D_{calc}/g cm^{-3}	1.441	1.246	1.400	1.384
μ / mm^{-1}	0.708	0.789	0.840	0.921
F(000)	908	1268	2085	2440
Crystal size/mm^3	0.25 × 0.06 × 0.06	0.30 × 0.18 × 0.07	0.32 × 0.23 × 0.10	0.79 × 0.31 × 0.18
Reflections collected	32589	52221	76421	97896
Independent reflections	9251	15046	21849	32501
R_{int}	0.0735	0.1196	0.0423	0.0549
Completeness	0.998	0.998	0.998	0.999
Goodness-of-fit on F^2	1.054	0.948	1.070	1.054
R_1, wR_2 ($I > 2\sigma(I)$)*	0.0648, 0.1326	0.0773, 0.1648	0.0543, 0.1335	0.0920, 0.2470
R_1, wR_2 (all data)*	0.1007, 0.1456	0.1372, 0.1916	0.0715, 0.1422	0.1301, 0.2853

* $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, w$R_2 = ((\Sigma(w(F_o^2-F_c^2)^2))/\Sigma(wF_o^4))$

Table S2 Selected bond lengths (Å) and angles (°)

complex **1**		complex **1a**		complex **2a**		complex **3a**	
Ni1–S1	2.205(1)	Ni1–S1a	2.286(5)	Ni1–S1	2.2086(8)	Ni1–S1	2.196(1)
		Ni1–S2b$	2.263(4)	Ni1–S2	2.2251(8)	Ni1–S2	2.183(1)
		Ni2–S3a	2.25(1)	Ni2–S3	2.2082(9)	Ni2–S3	2.185(1)
		Ni2–S4b%	2.238(3)	Ni2–S4	2.2030(8)	Ni2–S4	2.174(1)
						Ni3–S5	2.179(1)
						Ni3–S6	2.174(1)
Ni1–N1#	1.932(3)	Ni1–N1a$	1.83(2)	Ni3–N1	1.873(2)	Ni4–N1	2.104(4)
		Ni1–N2b	1.86(1)	Ni3–N2	1.870(2)	Ni4–N2	2.064(4)
		Ni2–N3a%	1.89(2)	Ni3–N3	1.861(2)	Ni4–N3	2.099(4)
		Ni2–N4b	1.89(2)	Ni3–N4	1.870(2)	Ni4–N4	2.080(4)
						Ni4–N5	2.085(4)
						Ni4–N6	2.054(4)
Ni1–P1	2.186(1)	Ni1–P1	2.180(1)	Ni1–P1	2.1958(8)	Ni1–P1	2.193(1)
Ni1–P2	2.180(1)	Ni1–P2	2.176(1)	Ni1–P2	2.2069(9)	Ni1–P2	2.187(1)
		Ni2–P3	2.184(1)	Ni2–P3	2.2027(9)	Ni2–P3	2.191(1)
		Ni2–P4	2.179(1)	Ni2–P4	2.1954(9)	Ni2–P4	2.190(1)
						Ni3–P5	2.197(1)
						Ni3–P6	2.176(2)
S1–C27	1.723(4)	S1a–C28	1.587(7)	S1–C28	1.708(3)	S1–C84	1.718(4)
		S2b–C28	1.589(7)	S2–C29	1.717(3)	S2–C85	1.723(4)
		S3a–C56	1.55(1)	S3–C57	1.714(3)	S3–C88	1.726(4)
		S4b–C56	1.639(6)	S4–C58	1.720(3)	S4–C89	1.729(5)
						S5–C86	1.736(5)
						S6–C87	1.715(4)
N1–C27	1.313(5)	N1a–C28	1.44(2)	N1–C29	1.290(4)	N1–C84	1.291(6)
		N2b–C28	1.38(1)	N2–C28	1.298(4)	N2–C85	1.286(6)
		N3a–C56	1.36(2)	N3–C57	1.287(4)	N3–C88	1.286(6)
		N4b–C56	1.37(2)	N4–C58	1.287(4)	N4–C89	1.270(6)
						N5–C86	1.290(6)
						N6–C87	1.294(6)
C27–C27#	1.496(7)	C28–C28$	1.459(9)	C28–C29	1.493(4)	C84–C85	1.507(6)
		C56–C56%	1.472(9)	C57–C58	1.487(4)	C86–C87	1.500(6)
						C88–C89	1.500(6)
N1#–Ni1–S1	89.07(9)	N1a$–Ni1–S1a	86.6(6)				
		N2b–Ni1–S2b$	85.0(3)				
		N3a%–Ni2–S3a	83.3(6)				
		N4b–Ni2–S4b%	87.0(5)				
				S1–Ni1–S2	91.70(3)	S2–Ni1–S1	91.93(5)
				S4–Ni2–S3	92.85(3)	S4–Ni2–S3	92.31(5)
						S6–Ni3–S5	92.36(5)
				N2–Ni3–N1	83.4(1)	N2–Ni4–N1	77.9(1)
				N3–Ni3–N4	83.3(1)	N4–Ni4–N3	77.8(1)
						N6–Ni4–N5	78.4(2)
P2–Ni1–P1	85.93(4)	P2–Ni1–P1	93.36(5)	P1–Ni1–P2	91.13(3)	P2–Ni1–P1	91.08(5)
		P4–Ni2–P3	91.61(5)	P4–Ni2–P3	90.32(3)	P4–Ni2–P3	90.88(5)
						P6–Ni3–P5	90.80(5)

The subscripts #, $ and % indicate the equivalent atoms generated by the symmetry operators (1−x, 1−y, −z), (2−x, −y, 1−z) and (1−x, 1−y , 2−z), respectively.