Electronic Supplementary Information (ESI)

First tetrazole-bridged d-f heterometallic MOFs with large magnetic entropy change

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General Materials and Measurements

All raw materials were purchased commercially at analytical grade and used without further purification. C, N and H microanalysis were measured on a Perkin-Elmer elemental analyzer. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku D/Max-2500 diffractometer at room temperature using $Cu_{K\alpha}$ radiation (λ = 1.5406 Å). Inductively Coupled Plasma (ICP) data were collected on a USA Thermo Jarrell-Ash Corp ICP-9000 (N+M) spectrometer. Thermogravimetric analysis (TGA) was performed from a Netzsch TG 209 TG-DTA analyzer in the temperature range of 30-800 ºC with a ramp rate of 10 ºC min^{-1} under N_2 atmosphere. Magnetic properties were measured on PPMS ACMS and Quantum Design SQUID VSM magnetometers.

Synthesis of $\{(H_3O)_3[Gd_3Mn_2(Trz)_4]\cdot 12H_2O\}_n$ (1)

A mixture of $GdCl_3\cdot 6H_2O$ (0.15 mmol, 0.0558 g), $MnCl_2\cdot 4H_2O$ (0.15 mmol, 0.0295 g), KC_4N_3 (0.05 mmol, 0.0065 g), NH_4F (0.3 mmol, 0.0111 g), NaN_3 (0.6 mmol, 0.039 g), H_2O (6 mL) and MeOH (2 mL) were sealed in a 25 mL Teflon-lined bomb and heated in an oven at 145 ºC for three days, and then cooled to room temperature within four days. Colorless polyhedral crystals of **1** were separated by filtration and washed with MeOH. Yield: ca. 20%. Anal. calcd (%) for $Gd_3Mn_2C_{16}N_{48}O_{19}H_{33}$ (1783.37): C, 10.78; N, 37.70; H, 1.86; found (%): C, 10.83; N, 37.62; H, 1.82.

Additionally, for the chemical formula of **1**, due to the high symmetry, it is difficult to determine the assignment of proton. The extra proton may be in the form of H_3O^+, or be attached to tetrazole N atom from the ligand. Therefore, herein one of the chemical formulas is given.

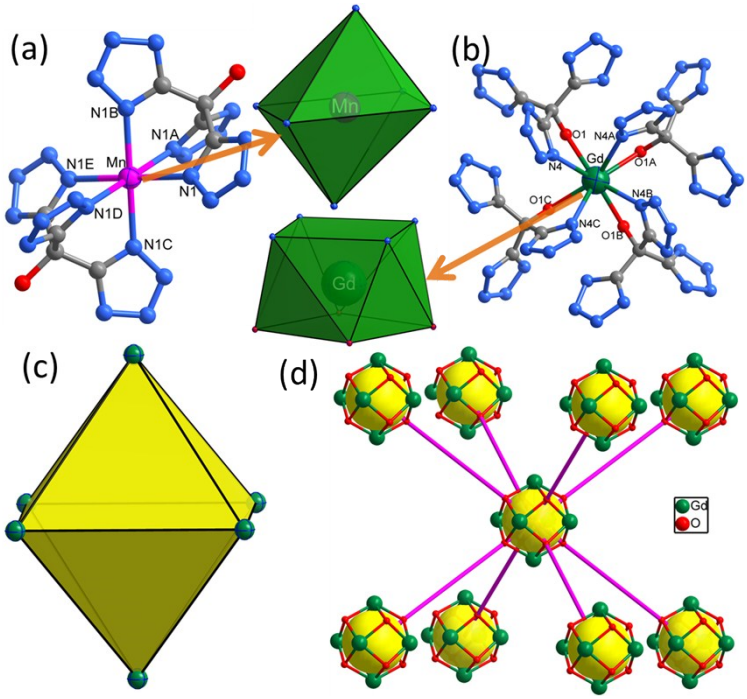

Fig. S1 (a) The coordination environments and geometrical configuration of Mn^{2+} ion and (b) Gd^{3+} ion for compound **1**; (c) Octahedral skeleton for six Gd^{III} ions in each $\{Gd_6O_8\}$ cluster; (d) The $\{Gd_6O_8\}$ cluster represented as an eight-connected node.

Thermogravimetric Analysis (TGA)

To investigate the thermal stability of compound **1**, thermogravimetric analysis (TGA) curve of **1** were recorded, the 14.2% weight loss in the range of room temperature to 305 ºC may be attributed to the removal of solvent water molecules and restrained water molecules from H_3O^+ ions (calc:15.1 %).

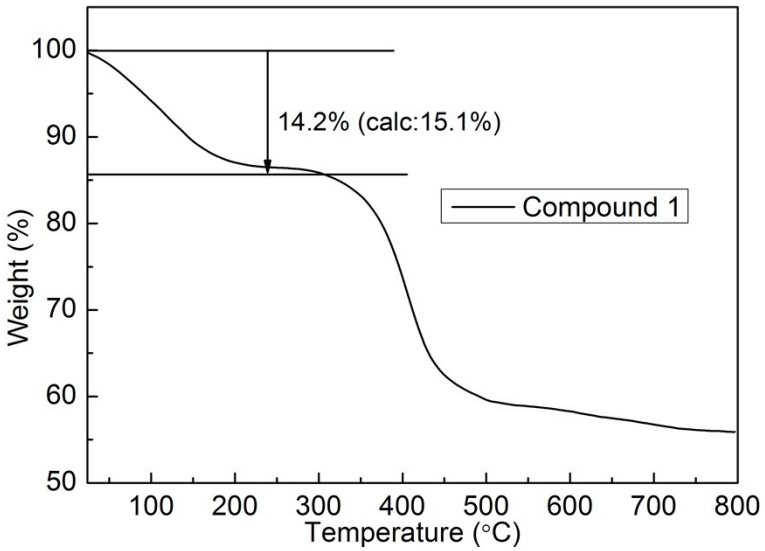

Fig. S2 TGA curve of **1**

Powder X-ray Diffraction (PXRD)

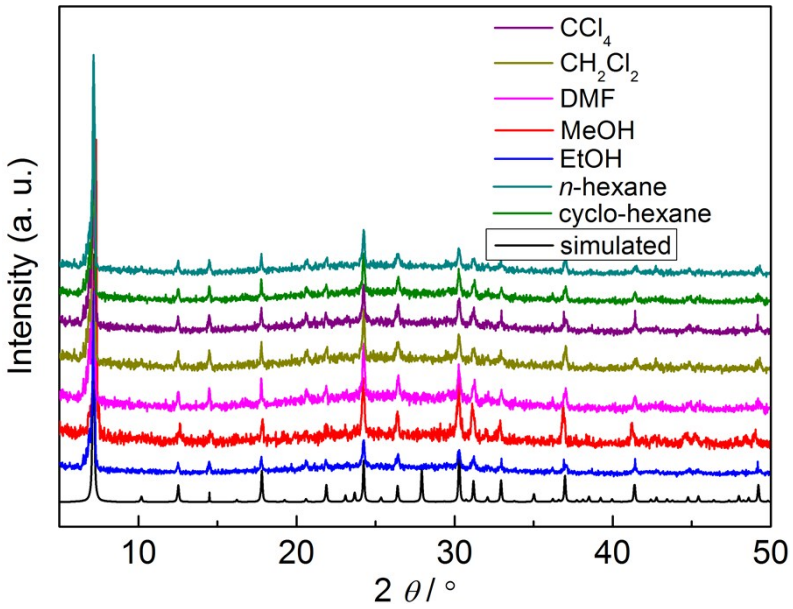

Fig. S3 The power X-ray diffraction patterns of compound **1** in different organic solvents.

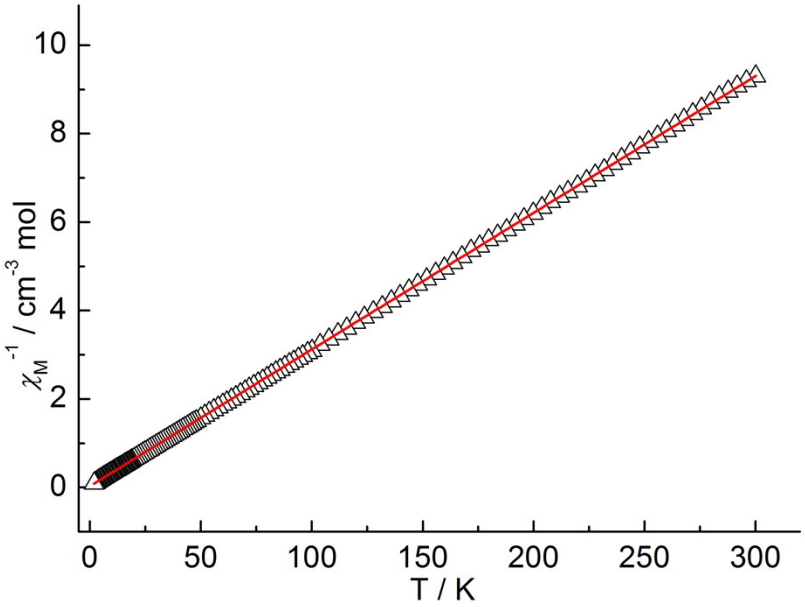

Fig. S4 Temperature dependence of χ_M^{-1} for compound **1** in applied field of 1000 Oe from 2 to 300K. The solid line is the best fit according to the Curie-Weiss law.

Crystallography Information

Table S1 Crystal data and structure refinement for **1**

Empirical formula	$Gd_3Mn_2C_{16}N_{48}O_{19}H_{33}$
Formula weight	1783.37
Temperature/K	130.80(14)
Crystal system	cubic
Space group	Pn-3n
a/Å	17.1065(12)
b/Å	17.1065(12)
c/Å	17.1065(12)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/Å^3	5005.9(6)
Z	4
ρ_{calc} mg/mm^3	2.291
m/mm^{-1}	4.523
F(000)	3304.0
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection	5.84 to 50°
Index ranges	-12 ≤ h ≤ 7, -10 ≤ k ≤ 20, -19 ≤ l ≤ 12
Reflections collected	4051
Independent reflections	753 [R_{int} = 0.0864, R_{sigma} = 0.0761]
Goodness-of-fit on F^2	1.070
Final R indexes [I>=2σ (I)]	R_1 = 0.0550, wR_2 = 0.1571
Final R indexes [all data]	R_1 = 0.0937, wR_2 = 0.1824
$^aR_1 = \sum\|\|F_O\| - \|F_C\|\| / \sum\|F_O\|$	$^bwR_2 = \left[\sum w\left(F_O^2 - F_C^2\right)^2 / \sum wF_O^4\right]^{1/2}$

Table S2 Inductively Coupled Plasma (ICP) analyses for Na^+ and K^+ in **1** and blank, respectively.

sample	Na^+ (mg/L)	K^+ (mg/L)
blank	1.01	0.22
1	1.05	0.26

Blank: The solution of 10 mL water and 200 uL hydrochloric acid.

1: 5 mg sample **1** was dissolved in 200 uL hydrochloric acid, and then 10 mL water was added to form the solution.

Table S3 Summary of the value of $-\Delta S_m$ for more than 60 reported 3d-4f molecule-based magnetic coolants

Compounds	$-\Delta S_m$ (J kg^{-1} K^{-1})	ΔH (T)	T(K)	Ref.
$[Mn(H_2O)_6][MnGd(oda)_3]_2\cdot 6H_2O$	50.1	7	1.8	1
$[Gd_{42}Co_9^{II}Co^{III}(\mu_3\text{-}OH)_{68}(CO_3)_{12}(CH_3COO)_{30}(H_2O)_{70}]\cdot (ClO_4)_{25}\cdot (CH_3CH_2OH)_n\cdot 70H_2O$	41.3	7	2	2
$\{(H_3O)_3[Gd_3Mn_2(Trz)_4]\cdot 12H_2O\}_n$ (this work)	**40.3**	**7**	**2**	
$[\{CrF_3(Me_3tacn)\}_2Gd_3F_2(NO_3)_7(H_2O)(CH_3CN)]\cdot 4CH_3CN$	38.3	7	2	3
$[Gd_{42}Ni^{II}_{10}(\mu_3\text{-}OH)_{68}(CO_3)_{12}(CH_3COO)_{30}(H_2O)_{70}]\cdot(ClO_4)_{24}\cdot 80H_2O$	38.2	7	2	2
$[Gd_{36}Ni_{12}(CH_3COO)_{18}(\mu_3\text{-}OH)_{84}(\mu_4\text{-}O)_6(H_2O)_{54}(NO_3)Cl_2](NO_3)_6Cl_9\cdot 30H_2O$	36.3	7	3	4
$[Cu^{II}_2Gd^{III}_7(OH)_{10}(teaH)_2(teaH_3)_2(O_2CPh)_6(MeOH)_3(H_2O)_3](Cl)_5\cdot 6H_2O$	34.6	9	2.7	5
$[Ni_2Gd_2(hmp)_4(OAc)_6]$	34.4	7	4.5	6
$[Mn^{II}_4Gd^{III}_6(O_3PCH_2Ph)_6(HO_2C^tBu)_{13}(O_2CMe)(HO_2C^tBu)(OH_2)_2(MeCN)_2](MeCN)_3$	33.7	7	3	7
$[\{FeF_3(Me_3tacn)\}_2Gd_3F_2(NO_3)_7(H_2O)(CH_3CN)]\cdot 4CH_3CN$	33.1	7	4.2	3
$[Co^{II}_6Gd^{III}_8(\mu_3\text{-}OH)_8(O_3PtBu)_6(O_2C^tBu)_{16}(H_2O)_2](MeCN)_2$	33.0	14	4	8
$[Cu^{II}_4Gd^{III}_{12}(OH)_{20}(teaH)_2(teaH_2)_4(O_2CPh\text{-}2\text{-}Ph)_8(H_2O)_6Cl_2](Cl)_6\cdot 2MeOH\cdot 4H_2O$	33.0	9	2.9	5
$[Co_4Gd_{10}(O_2C^tBu)_{12}(O_3PC_6H_{10}NH_2)_8(PO_4)_2(O_2CMe)_2(O_3PC_6H_{10}NH_3)_2]$	32.6	7	2	9
$[Ni_6Gd_6(\mu_3\text{-}OH)_2(\mu_2\text{-}OAc)_2(O_3PR)_6(O_2C^tBu)_{16}]$	32.0	7	3	10
$[Gd^{III}_3Fe^{III}_2(\mu_5\text{-}O)L_2(NO_3)_5(H_2O)(MeOH)]\cdot 0.5MeOH$	31.7	7	3	11
$[Cu^{II}_5Gd^{III}_4O_2(OMe)_4(teaH)_4(O_2CC(CH_3)_3)_2(NO_3)_4]\cdot 2MeOH\cdot 2Et_2O$	31.0	9	3	12
$\{[Gd_5Zn(BPDC)_3(H_2O)_{10}(\mu_3\text{-}OH)_6](CO_3)_{0.5}(NO_3)_4\cdot 12H_2O\}_n$	30.7	7	3	13
$[\{CrF_3(Me_3tame)\}_2Gd_3(hfac)_6(\mu\text{-}F)_3]\cdot 7CH_3CN$	28.7	9	2.2	14
$[Co^{II}_6Gd^{III}_8(\mu_3\text{-}OH)_8(O_3PtBu)_6(O_2C^tBu)_{16}(H_2O)_2](MeCN)_2$	28.6	7	3	8
$[Mn^{II}_9Gd^{III}_9(O_3PMe)_{12}(O_2C^tBu)_{18}(L)]$	28.0	7	3	7
$[Ni^{II}_6Gd^{III}_6(OH)_2(O_3PCH_2Ph)_6(O_2CtBu)_{16}(MeCO_2H)_2](MeCN)_4$	26.5	7	3	15
$[Co_{16}Ln_{24}(OH)_{50}(pyacac)_{16}(NO_3)_{18}(H_2O)_{12}][Gd(H_2O)_8]_2(NO_3)_{16}(OH)_{10}\cdot 20MeOH\cdot 60H_2O$	26.0	7	3.8	16
$[Gd^{III}_2Cu^{II}_2(OH)_2(NO_3)_{2.5}(OAc)_{3.5}(L^1)_2]_n$	25.7	7	2.4	17
$[CuGd(pta)_2(Hpta)(4,4'\text{-}bipy)_{0.5}(H_2O)]_n$	24.8	7	3	18
$[Co^{II}_4Gd^{III}_6(O_3PCH_2Ph)_6(O_2C^tBu)_{14}(MeCN)_2]$	23.6	7	3	8
$[\{(HL)(L)(DMF)Cu^{II}Gd^{III}(DMF)(H_2O)\}_6]\cdot 6DMF$	23.5	7	2	19
$[Mn(CH_3OH)(\mu\text{-}L)Gd(NO_3)_3]$	23.5	7	2.7	20
$[Cu_{15}Gd_7(OH)_6(CO_3)_4(O_2CPh)_{19}(pdm)_9(pdmH_2)_3(H_2O)_2]$	22.2	7	2.5	21
$[Gd^{III}_4Ni^{II}_8(OH)_8(L)_8(O_2CR)_8](ClO_4)_4$	22.0	7	3.6	22
$[Gd_5Ni_{12}(Gly)_{12}(IDA)_6(\mu_3\text{-}OH)_9(H_2O)_3](ClO_4)_6\cdot 11H_2O$	21.8	7	4	23

$[Co^{II}_8Ln^{III}_8(\mu_3\text{-}OH)_4(NO_3)_4(O_3P^tBu)_8(O_2C^tBu)_{16}]$	21.4	7	3	8
$[Gd^{III}_9Cu^{II}_8(NO_3)_2(OH)_{10}(L^3)_4(OAc)_{18}(H_2O)_4](NO_3)_2(OH)_3\cdot 22H_2O\cdot 4MeOH$	21.4	7	2.7	17
$[Co^{II}_8Gd^{III}_4\ (O_3P^tBu)_6(O_2C^tBu)_{16}]$	21.1	7	3	8
$[Gd_{24}Cu_{36}(OH)_{72}(NO_3)_6(O_2CPh)_{60}(MeOH)_6(H_2O)_{12}](NO_3)_6\cdot 39H_2O\cdot 8MeOH\cdot 18MeCN$	21.0	7	2.1	24
$[Gd^{III}_4Co^{II}(\mu_3\text{-}O)(dipp)_6(DMSO)_6(MeOH)_2]\cdot H_2O$	20.3	7	3	25
$[Co^{II}_4Gd^{III}_2(O_3PtBu)_2(O_2C^tBu)_{10}(MeCN)_2](MeCN)_2$	20.0	7	3	8
$[Na_2Co_6Gd_4(\mu_3\text{-}OH)_2(O_2C^tBu)_{12}(O_3PC_6H_{10}NH_2)_6(MeCN)_2]$	19.7	7	2	9
$[Mn^{III}_4Gd^{III}_4(OH)_4(L)_4(NO_3)_2(dmf)_6(H_2O)_6](OH)_2$	19.0	7	4	26
$[Ln_6Cu_{24}(Ala)_{12}(FA)_8(\mu_3\text{-}OH)_{30}(\mu_2\text{-}OH)_6(H_2O)_{18}](ClO_4)_{10}\cdot 64H_2O$	18.8	5	2	27
$[Gd_2Ni_2(NO_3)_6(H_2O)_{1.5}(CH_3CN)_2(L)_2]\cdot CH_3CN$	18.5	5	3	28
$[Ni_3Gd(hmp)_4(OAc)_5]\cdot H_2O\cdot CH_2Cl_2$	18.3	7	5.5	29
$[Gd^{III}_4Zn^{II}_8(OH)_8(L)_8(O_2CR)_8](ClO_4)_4$	18.0	7	2	22
$[Et_4N][Gd_2Ni_6(val)_{12}(MeCN)_6(H_2O)_3][Gd(NO_3)_5](ClO_4)_5$	17.6	5	3	30
$[Gd_6Mn_{12}O_7(OH)_{10}(OAc)_{14}(mpea)_8]\cdot 13H_2O\cdot 6MeOH$	17.0	7	7	31
$[Gd_6Mn_{12}O_9(OH)_8(OAc)_{10}(mpea)_8(mp)_2(MeOH)_2(H_2O)_2]\cdot 17H_2O\cdot 12MeOH$	15.8	7	6	31
$[Gd^{III}_4Cu^{II}_8(OH)_8(L)_8(O_2CR)_8](ClO_4)_4$	14.6	7	5.6	22
$[Gd^{III}_6Cu^{II}_{12}(OH)_{12}(L^3)_6(NO_3)_7(OAc)_3(H_2O)_{12}](OH)_8\cdot 19H_2O\cdot MeCN$	14.0	7	4.5	32
$[Ni_2Gd(L^-)_6](NO_3)$	13.7	7	4	33
$[Gd^{III}_4Cu^{II}_8(OH)_8(Me_3CCOO)_8(L^1)_8](NO_3)_2(OH)_2\cdot 15H_2O\cdot 3MeCN$	13.5	7	4.5	17
$[Ni_3Tb(hmp)_4(OAc)_5]\cdot H_2O\cdot CH_2Cl_2$	13.5	7	4.5	29
$[Mn^{II}_6Dy^{III}_6(\mu_3\text{-}OH)_2(O_3PCH_2Ph)_6(O_2C^tBu)_{16}(MeCN)_5$	13.0	7	3	7
$[Ln_2Cu_8(\mu_2\text{-}OH)_2(\mu_3\text{-}OH)_2(ClO_4)_2(HTMHSA)_4(H_2O)_{10}]\cdot 15H_2O$	12.8	7	3	34
$[Co_3Dy(hmp)_4(OAc)_5H_2O]$	12.6	7	5.5	35
$[Ni^{II}_6Dy^{III}_6(OH)_2(O_3PCH_2Ph)_6(O_2CtBu)_{16}(MeCO_2H)_2](MeCN)_4$	12.2	7	3	15
$[Cu_6Gd_2(L^{3-})_4(NO_3)_3(OAc)(CH_3OH)_6]\cdot NO_3\cdot OAc\cdot 3CH_3OH\cdot 2H_2O$	11.9	7	2	36
$[Ni_2Gd(LH_3)_4]\cdot 3NO_3\cdot 3MeOH\cdot H_2O\cdot CH_3CN$	11.8	5	4	37
$[Co^{II}_8Gd^{III}_2\ (\mu_3\text{-}OH)_2(O_3PCH_2Ph)_4(O_2C^tBu)_{12}(HO_2CMe)_2](MeCN)_6$	11.8	7	3	8
$[Ni_3Dy(hmp)_4(OAc)_5]\cdot H_2O\cdot CH_2Cl_2$	11.8	7	4.5	29
$[Cr_2Gd_2(\mu\text{-}F)_4F_2(py)_6(hfac)_6]$	11.4	9	4.1	38
$\{[Dy_5Zn(BPDC)_3(H_2O)_{10}(\mu_3\text{-}OH)_6](CO_3)_{0.5}(NO_3)_4\cdot 10H_2O\}_n$	10.8	7	4	13
$[Ni_3Y(hmp)_4(OAc)_5]\cdot H_2O\cdot CH_2Cl_2$	10.8	7	4.5	24
$[Ni_2Gd_4(hfac)_8(pao)_6(CH_3COO)_2(MeOH)]\cdot H_2O\cdot MeOH$	10.2	5	4	39
$[Dy^{III}_3Fe^{III}_2(\mu_5\text{-}O)L_2(NO_3)_5(H_2O)(MeOH)]\cdot 0.5MeOH$	9.8	7	4	11
$Mn^{III}_3Mn^{IV}O_3Gd_3(OH)(piv)_6(EtO)_3(EtOH)_3(Et\text{-}sao)_3$	7.4	5	6	40
$[Ni_3Ho(hmp)_4(OAc)_5]\cdot H_2O\cdot CH_2Cl_2$	7.3	7	4.5	29
$[Gd_2Cu_6(Gly)_6(FA)_3(\mu_3\text{-}OH)_3(\mu_3\text{-}OH_2)_3(H_2O)_9](ClO_4)_6\cdot 15H_2O$	6.0	5	2	27

$[Gd_2Cu_6(Gly)_6(FA)_3(\mu_3\text{-}OH)_3(\mu_3\text{-}OH_2)_3(H_2O)_8](ClO_4)_6\cdot 10H_2O$	5.8	5	2	27
$[Ni^{II}_6Y^{III}_6(OH)_2(O_3PCH_2Ph)_6(O_2C\textit{t}Bu)_{16}(MeCO_2H)_2](MeCN)_4$	5.6	7	3	15
$Mn^{III}_3Mn^{IV}O_3Dy_3(OH)(piv)_6(EtO)_3(EtOH)_3(Et\text{-}sao)_3$	3.7	5	6	40

Crystal Data Collection and Structure Determination

Suitable single crystal of **1** was mounted on a SuperNova diffractometer equipped with a graphite monochromator Mo-Kα radiation source (λ = 0.71073 Å). The structure was solved using direct methods by SHELXS-97 and refined by full matrix least-squares on F^2 using SHELTL-97 in conjunction with the OLEX2 graphical user interface. [41,42] The anisotropic thermal parameters were refined for all non-hydrogen atoms, and hydrogen atoms were calculated and refined with a riding model.

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