

Electronic Supporting Information

Connecting mononuclear dysprosium single-molecule
magnets to form dinuclear complexes *via in situ* ligand
oxidation

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General Procedures. The reagents dysprosium (III) nitrate hydrate and yttrium (III) nitrate (Strem) were obtained commercially and used as received. Acetonitrile was of reagent grade. The ligand 3,5-di(pyridin-2-yl)-4H-1,2,4,6-thiatriazine (Py₂TTAH) was synthesized according to literature procedures.¹ Melting points were taken using a Mel-Temp apparatus and are uncorrected. NMR spectra were run in CD₃CN solutions at room temperature on a Bruker Avance II 300 MHz spectrometer. IR spectra of solid samples were recorded on an Agilent Technologies Cary 630 FT-IR spectrometer.

Preparation of [Dy₂(1-oxo-Py₂TTA)₂(NO₃)₄(H₂O)₂]·CH₃CN (3a):

Dy(NO₃)₃·6H₂O (85 mg, 0.254 mmol) and Py₂TTAH (66.7 mg, 0.261 mmol) were dissolved in acetonitrile (40 mL) to create a purple solution and was stored at RT. A colourless solution emerged after an hour with crystallization of a white solid. Yield = 60%, dec >260°C, IR ν_{max} = 3332 (br), 3248 (br), 3117 (w), 3100 (w), 1647 (w), 1611 (w), 1600 (w), 1584 (w), 1559 (m), 1498 (s), 1482 (s), 1445 (m), 1407 (m), 1357 (s), 1302 (m), 1281 (s), 1254 (m), 1208 (w), 1162 (w), 1153 (w), 1112 (w) 1102 (w), 1094 (w), 1057 (m), 1036 (s), 1027 (s), 1016 (s), 1008 (s), 977 (w), 912 (w), 901 (w), 815 (m), 809 (m), 787 (m), 759 (s), 751 (s), 748 (s), 736 (m), 724 (s), 709 (m), 697 (m)

Preparation of [Y₂(1-oxo-Py₂TTA)₂(NO₃)₄(H₂O)₂]·CH₃CN (3b): The synthetic procedure followed is the same as that mentioned above using Y(NO₃)₃·6H₂O (68 mg, 0.249 mmol) and Py₂TTAH (64.0 mg, 0.251 mmol). Yield = 65%, dec >260°C, IR ν_{max} = 3335 (br), 3261 (br), 3120 (w), 3103 (w), 1649 (w), 1612 (w), 1600 (w), 1584 (w), 1559 (m), 1502 (s), 1482 (m), 1445 (m), 1407 (m), 1360 (s), 1303 (m), 1285 (s), 1254 (m), 1208 (w), 1162 (w), 1153 (w), 1113 (w), 1102 (w), 1095 (w), 1058 (m), 1038 (s), 1029 (s), 1017 (s), 1009 (s), 977 (w), 912 (w), 901 (w), 815 (m), 810 (m), 788 (m), 759 (s), 753 (s), 749 (s), 736 (m), 725 (s), 709 (w), 697 (m)

Crystallography. Colourless blocks of single crystals of complex **1** and **2** were obtained and collected. Crystallographic data as well as data collection and refinement are summarized in Table S1. Selected bond distances and bond angles are given in Table S2. Single crystal X-ray diffraction data collection was performed at 200 K using a Bruker APEX II CCD detector with a sealed Mo tube source (wavelength 0.71073 Å). Raw data collection and processing were performed with APEX II software package from Bruker AXS. Initial unit cell parameters were determined from 60 data frames with 0.3° ω scan each, collected at the different sections of the Ewald sphere. Semi-empirical absorption corrections based on equivalent reflections were applied.² The structure was solved by direct methods, completed with difference Fourier synthesis, and refined with full-matrix least-squared procedures based on F^2 . All non-hydrogen atoms were refined with anisotropic thermal motion approximation. All hydrogen atom positions were calculated based on the geometry of related non-hydrogen atoms. All hydrogen atoms were treated as idealized contributions during the refinement. All scattering factors are contained in several versions of the SHELXTL program library, with the latest version used being v.6.12.³

Table S1. Crystallographic data and selected data collection parameters for complexes **3a** and **3b**.

Parameters	3a	3b
Empirical formula	C ₁₄ H ₁₃ DyN ₈ O ₈ S	C ₁₄ H ₁₃ YN ₈ O ₈ S
Formula weight	615.88	542.29
Crystal size, mm	0.110 x 0.070 x 0.050	0.130 x 0.060 x 0.050
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
Z	2	2
a, Å	9.3478(3)	9.347(2)
b, Å	10.5315(4)	10.531(2)
c, Å	11.3151(4)	11.323(2)
α, °	69.422(2)	69.422(5)
β, °	77.825(2)	77.684(5)
γ, °	77.336(2)	77.232(4)
Volume, Å ³	1006.50(6)	1006.3(4)
Calculated density, Mg/m ³	2.032	1.790
Temperature, K	200(2)	200(2)
Absorption coefficient, mm ⁻¹	3.878	3.064
F(000)	598	544
Θ range for data collection, °	2.092 to 28.325	2.092 to 28.479
Limiting indices	h = ± 12, -13 ≤ k ≤ 14, -14 ≤ l ≤ 15	-11 ≤ h ≤ 12, -12 ≤ k ≤ 14, 0 ≤ l ≤ 15
Reflections collected / unique	13612 / 4926	4842 / 4842
R(int)	0.0358	---
Completeness to Θ = 25.242, %	98.8	88.8
Max. and min. transmission	0.7457 and 0.5974	0.7457 and 0.5779
Data / restraints / parameters	4926 / 0 / 290	4440 / 0 / 291
Goodness-of-fit on F ²	1.022	1.016
Final R indices [I > 2σ(I)]	R ₁ = 0.0345; wR ₂ = 0.0825	R ₁ = 0.0715; wR ₂ = 0.1572
R indices (all data)	R ₁ = 0.0428; wR ₂ = 0.0863	R ₁ = 0.1191; wR ₂ = 0.1810
Largest diff. peak/hole, e ⁻ Å ⁻³	1.605 / -1.684	1.294 / -1.437

Table S2. Selected bond lengths (Å) for complexes **3a** and **3b**.

3a	Distance (Å)	3b	Distance (Å)
Dy1-O1	2.293(3)	Y1-O1	2.276(5)
Dy1-O8	2.411(3)	Y1-O8	2.399(5)
Dy1-O6	2.444(3)	Y1-O6	2.434(4)
Dy1-O5	2.452(3)	Y1-O5	2.435(4)
Dy1-N1	2.452(3)	Y1-N1	2.442(5)
Dy1-O3	2.463(3)	Y1-O3	2.456(5)
Dy1-N5	2.478(3)	Y1-N4	2.471(5)
Dy1-N4	2.479(4)	Y1-N5	2.473(5)
Dy1-O2	2.497(3)	Y1-O2	2.490(5)
Dy1-N7	2.851(3)	Y1-N7	2.834(5)
Dy1-N6	2.893(4)	Y1-N6	2.876(7)

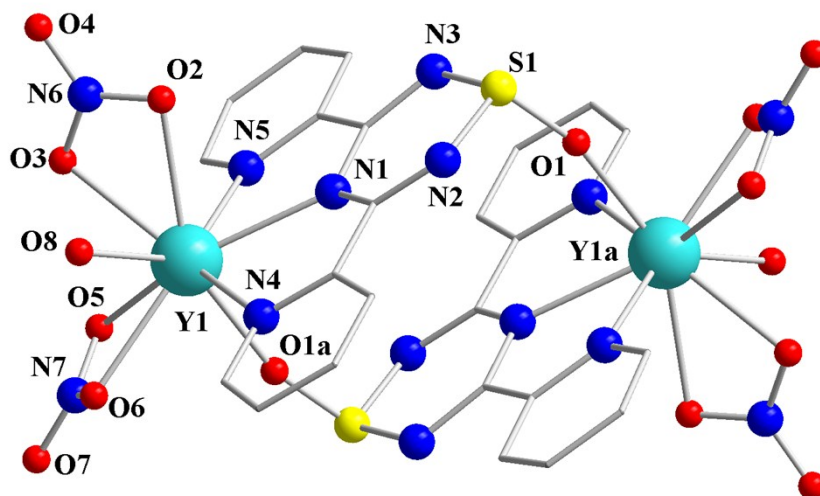


Fig. S1 Partially labelled molecular X-ray structure of the centrosymmetric dinuclear complex **3b**. Hydrogen atoms are omitted for clarity.

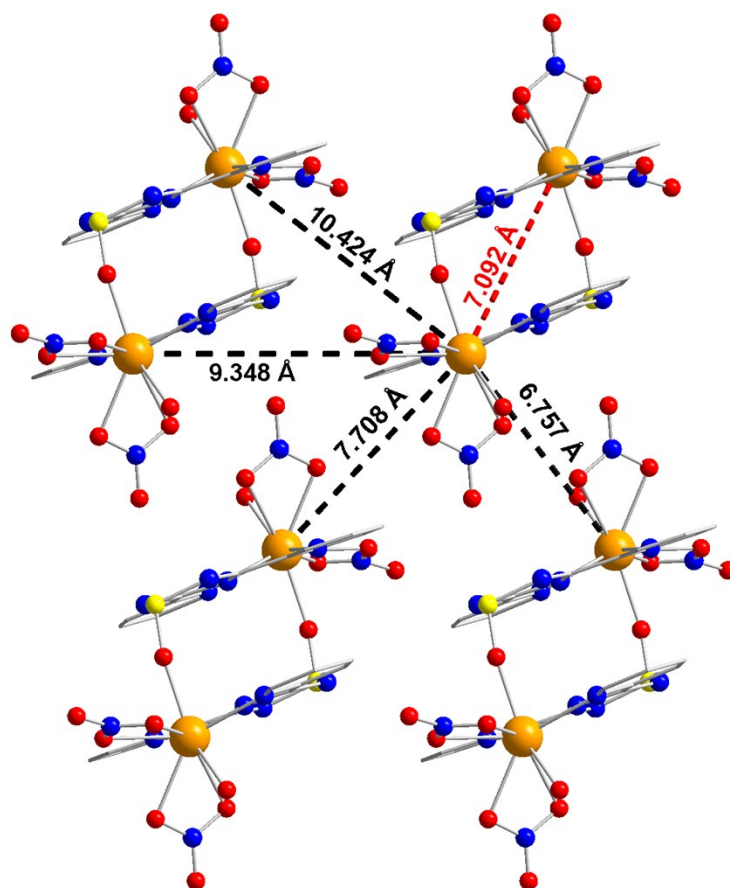


Fig. S2 Packing arrangement for complex **3a** emphasizing Dy-Dy distances with dashed lines (red for intramolecular; black for intermolecular). Hydrogen atoms are omitted for clarity.

Magnetic Measurements. The magnetic susceptibility measurements were obtained using a Quantum Design SQUID magnetometer MPMS-XL7 operating between 1.8 and 300 K. DC measurements were performed on a polycrystalline sample of complex **1** of 16.3 mg. The sample was wrapped in a polyethylene membrane and subjected to fields in a range from -7 to 7 T. The magnetization data was collected at 100 K in order to check for ferromagnetic impurities that were found to be absent in the sample. Diamagnetic corrections were applied to correct for contribution from the sample holder, and the inherent diamagnetism of the sample was estimated with the use of Pascal's constants.

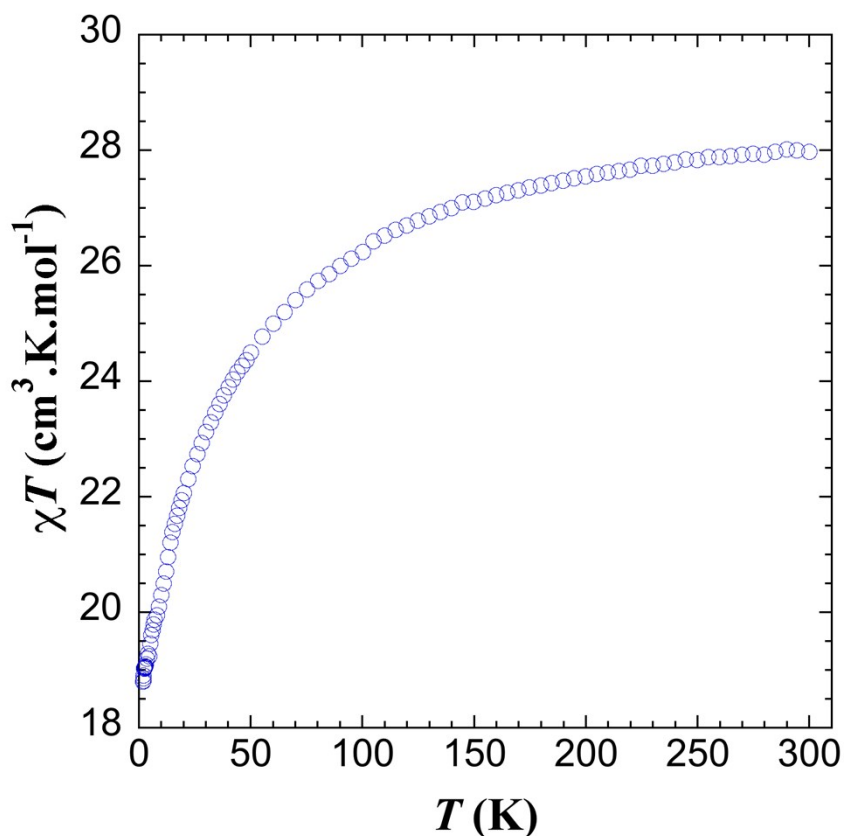


Fig. S3 Temperature dependence of the χT product at 1000 Oe for **3a** with χ being the molar magnetic susceptibility equal to M/H per mole of the compound.

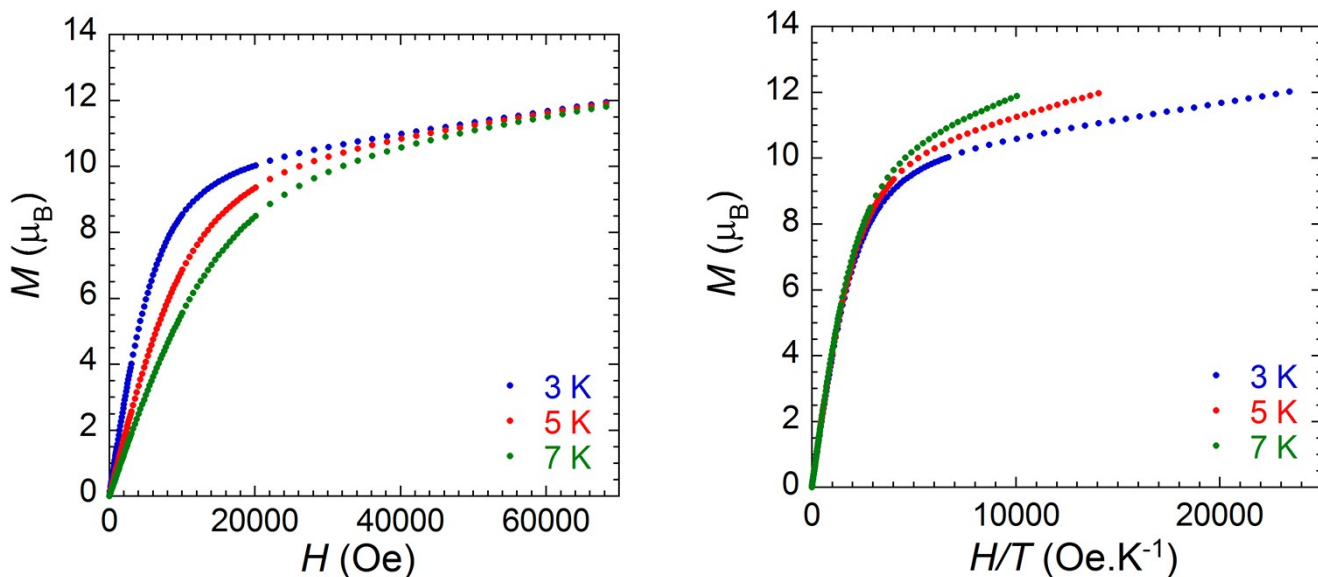


Fig. S4 Field dependence of the magnetization, M , at the indicated temperatures (left) for **3a** illustrating the non-saturation. M vs. H/T plot (right) showing non-superposition of the magnetization curves at different temperatures.

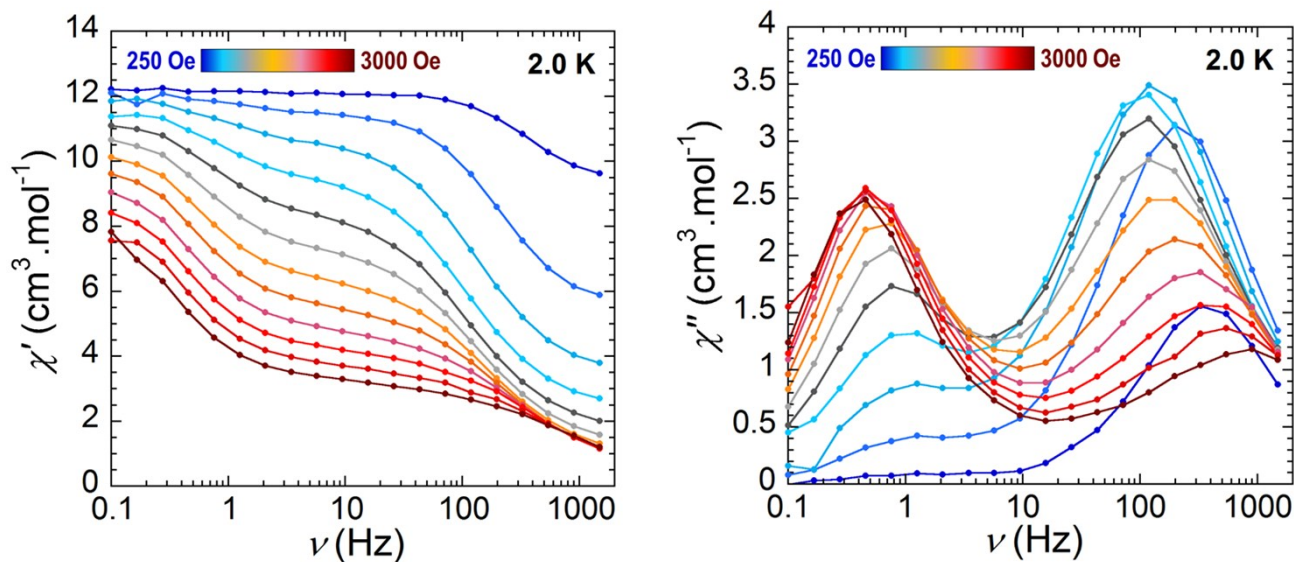


Fig. S5 Frequency dependence of the in-phase χ' (left) and out-of- phase χ'' (right) ac susceptibility signals under various dc fields for **3a** at 2K.

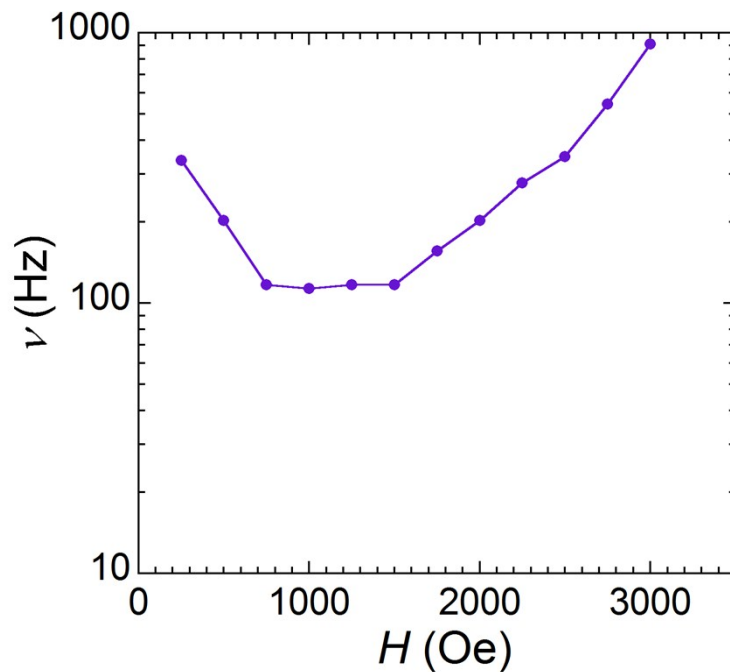


Fig. S6 Field dependence of the characteristic frequency as a function of the applied dc field for **3a** at 2 K.

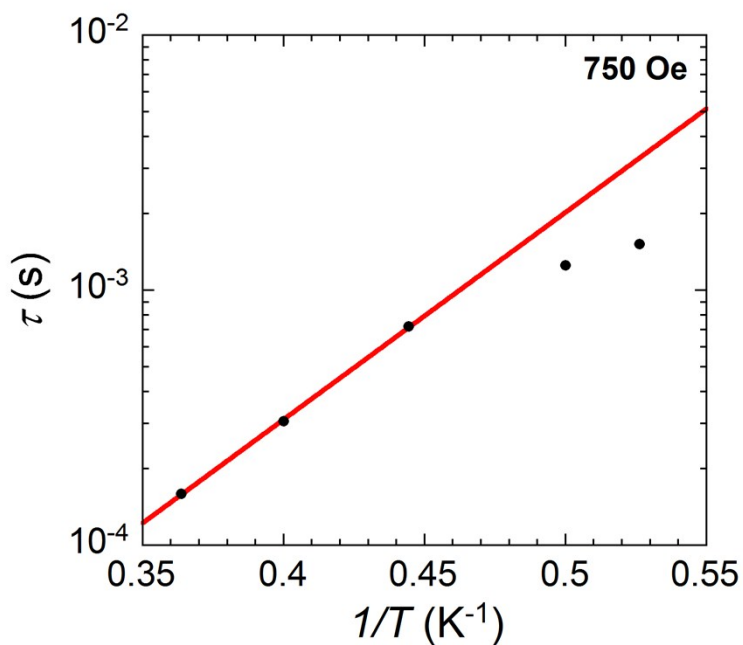


Fig. S7 Magnetization relaxation time (τ) versus $1/T$ plot for **3a** under the optimum field of 750 Oe. The solid red line corresponds to the Arrhenius law.

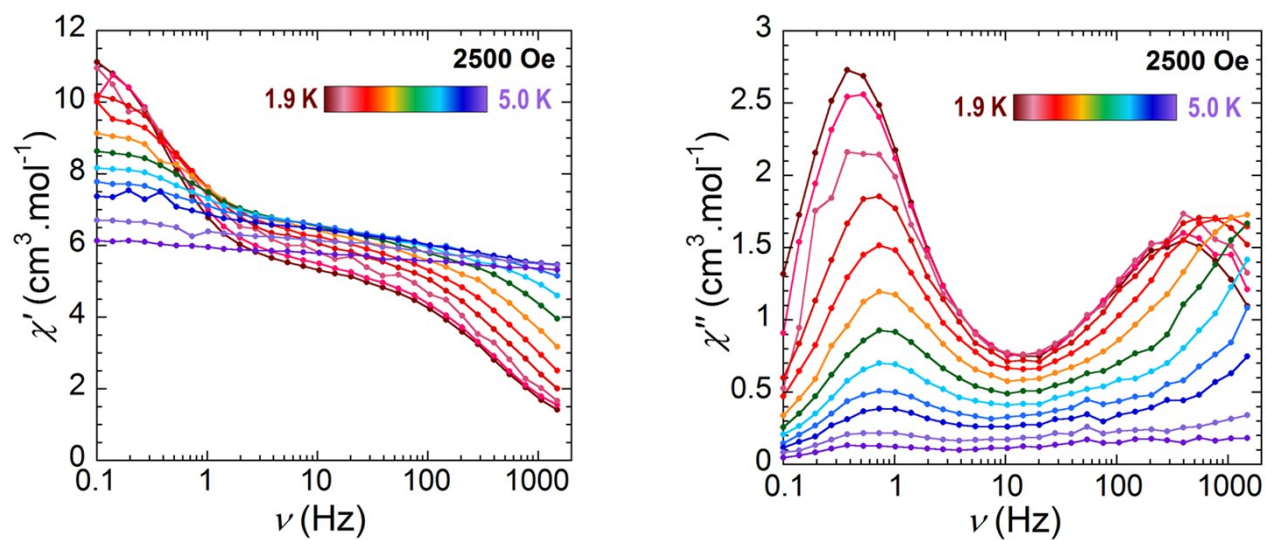


Fig. S8 Frequency dependence of the in-phase χ' (left) and out-of-phase χ'' (right) ac susceptibility signals under 2500 Oe dc field for **3a** at indicated temperatures.

References

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