

Intermediate Spin Ground State of an Isosceles Triangular $[\text{Mn}^{\text{II}}_3]$ Complex

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SUPPLEMENTARY INFORMATION

Experimental Details:

General procedures: All synthesis steps were performed with strong exclusion of air and external moisture (N_2 atmosphere at a high-vacuum, double-manifold Schlenk line or Ar atmosphere in a glove box). Methanol and THF were dried and freshly distilled prior to use; water was degassed by applying dynamic vacuum (10^{-3} Torr) for several hours. $Ba_2[GeSe_4]$ was prepared as a light yellow, microcrystalline powder in 95% yield by fusing stoichiometric amounts of BaSe, Ge and Se in a sealed quartz ampoule at $900^\circ C$.

Synthesis of $[\{Mn(tmeda)\}_3\{GeSe_3(OMe)\}_2]$ (1). A solution of 0.039 g (0.2 mmol) of $MnCl_2 \cdot 4H_2O$ in MeOH (5 mL) was added dropwise to a solution of 0.070 g (0.1 mmol) of $Na_4[Ge_2Se_6]$ in a mixture of MeOH and H_2O ((4.5:0.5 mL) at room temperature, resulting in the immediate formation of a pale yellow solution and an orange precipitate. Upon stirring for 30 minutes the precipitate filtered off. The filtrate was cooled down to $-40^\circ C$ and layered by 10 mL of TMEDA, whereupon **1** was observed as large, yellow-orange crystals after a few days on the bottom of the flask. Yield: 0.026 g (0.021 mmol, 68% based on Ge). Elemental analysis: observed (calc.) [%]: N: 7.03 (7.04), C: 19.88 (20.11), H: 4.33 (4.56).

Details of the X-ray structural analysis:

Data of the X-ray structural analyses: $T = 193$ K, graphite monochromator, imaging plate detector Stoe IPDS I. The structure was solved by direct methods in SHELXS97 and refined by full-matrix-least-squares refinement against $F2$ in SHELXL97.[1] H atoms bonded to N or C atoms were generated assuming idealized geometry and refined using the riding model (Ueq set at 1.2Ueq (parent atom) for methylene groups and at 1.5Ueq (parent atom) for methyl groups). Displacement ellipsoid diagrams with the labeling scheme for a fragment of the packing of the molecules and the complex itself are provided in Figure S1.

$[C_{20}H_{54}Ge_2Mn_3O_2N_6Se_6]$ (**1**, $M = 1194.45$ g·mol $^{-1}$, orange-red rod, $0.80 \times 0.25 \times 0.25$ mm 3): monoclinic space group $C2/c$, $Z = 4$, $a = 20.257(4)$ pm, $b = 14.013(3)$ pm, $c = 14.277(3)$ pm, $\beta = 106.70(3)$, $V = 3881.9(14) \cdot 10^6$ pm 3 , $\rho(\text{calc.}) = 2.044$ g·cm $^{-3}$, $2\theta = 5.04\text{-}50.00^\circ$, 10628 reflections collected, 3325 independent reflections [$R_{\text{int}} = 0.0519$], 2105 reflections with $I > 2\sigma(I)$; $\mu(\text{MoK}\alpha) = 8.133$ mm $^{-1}$, 182 parameters (refinement of Mn, Ge, Se, O and non-disordered C atomic sites employing anisotropic displacement parameters; two C atoms twofold disordered, according split positions refined using isotropic displacement parameters). Highest/deepest differential peak/hole: $0.711\text{/}-0.577$ e $\cdot 10^{-6}$ pm $^{-3}$. GOF: 0.792. $R_1 = 0.0353$ (for $I > 2\sigma(I)$, based on F), $wR_2 = 0.0619$ (all data, based on F^2).

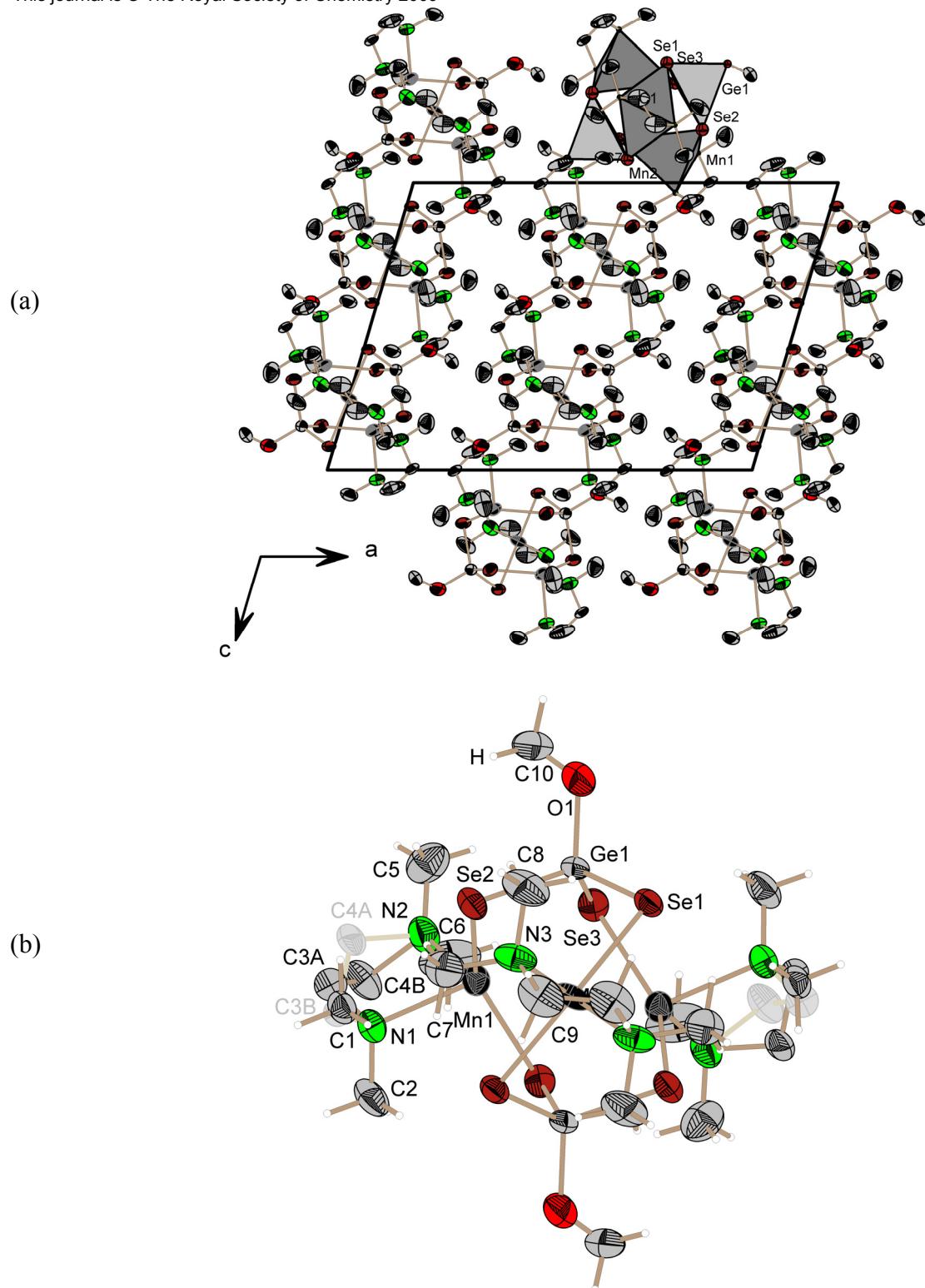


Figure S1. Thermal ellipsoids drawing (50% probability) of (a) the unit cell of **1** and (b) the molecular complex. In (a), one complex is emphasized by polyhedral representation of the coordination environment around Ge (light grey) and Mn (dark grey) and H atoms and disorder (C4, C5) are omitted in (a) for clarity. Selected bond lengths [pm] and angles [$^{\circ}$]: Selected distances /pm and angles / $^{\circ}$: Mn–Se 255.98(11)-258.48(8), Mn–N 227.0(5)-235.8(4), Ge–Se 228.86(9)-234.30(10), Ge–O 183.5(5), O–C 123.3(8); Se–Mn–Se 138.29(4), 149.91(6), N–Mn–N 78.77(17), 79.5(3), Se–Mn–N 98.07(13)- 110.17163), Se–Ge–Se 105.48(3)-115.11(3), O–Ge–Se 106.75(15)-110.61(13), Ge–O–C 121.9(5).

Magnetic susceptibility measurements:

The magnetic susceptibility measurements were obtained with the use of a Quantum Design SQUID magnetometer MPMS-XL. This magnetometer works between 1.8 and 400 K for dc applied fields ranging from -7 to 7 T. Measurements were performed on finely ground crystalline samples of 8.5 mg. M vs H measurements have been performed at 100 K to check for the presence of ferromagnetic impurities that has been found systematically absent (Figure S2). The magnetic data were corrected for the sample holder and the diamagnetic contribution from Pascal constants.[2] ac susceptibility measurements have been measured with an oscillating ac field of 3 Oe and ac frequencies ranging from 1 to 1500 Hz, but it is worth noting that no out-of-phase ac signal has been detected.

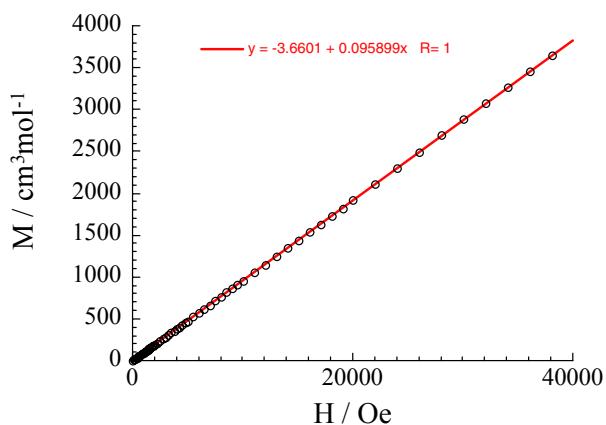


Figure S2. Field dependence of the magnetization of **1** at 100 K.

The susceptibility at 100 K is thus $0.0959 \text{ cm}^3/\text{mol}$, in good agreement with the susceptibility measurements done at 1000 Oe and 1 T. As shown in Figure S3, magnetic susceptibility measurements reveal a paramagnetic behavior in the whole range of temperature studied.

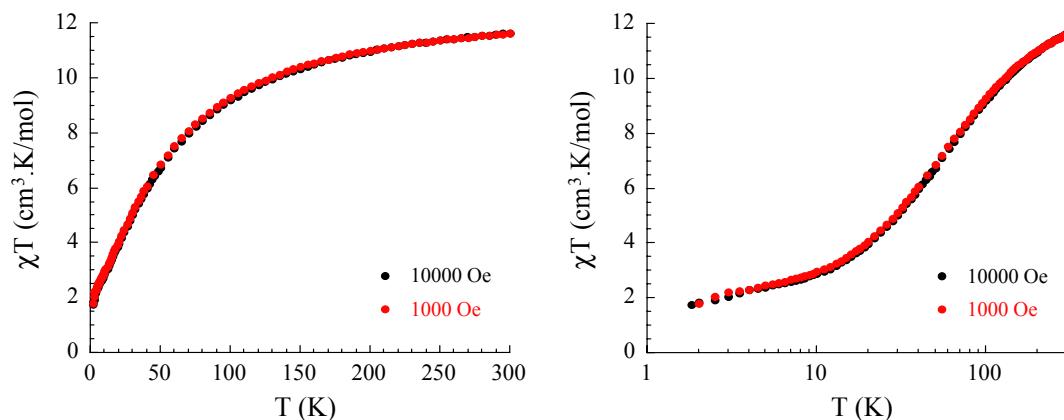


Figure S3. χT versus T plot measured at 1000 and 10000 Oe between 1.8 and 300 K on a polycrystalline sample of **1**. Right hand side: zoom of the graph at low temperatures.

Quantum chemical investigations

DFT [3] investigations were undertaken by means of the program system TURBOMOLE, version 5.10 [4] using the RIDFT program [5] with the Becke-Perdew 86 (BP86) [6], B3LYP [6, 7] or BHLYP [6, 8] functional and the gridsize m3. Basis sets were of def2-TZVP quality (TZVP = triple zeta valence plus polarization). [9] The simultaneous optimizations of geometric and electronic structures were performed without symmetry restrictions, *i.e.* in C_1 symmetry, allowing for convergence into local minima at higher symmetry.

References for the supporting information:

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