Electronic Supplementary Information for Dalton Transactions

Titanocene as a precursor for a cyclopentadienyl-free titanium(III)-manganese(II) clusters: a new approach for nano-size materials

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1.1 Preparation of Compound

General: All reactions were conducted under dinitrogen using standard Schlenk techniques. Manganese (powder, 99.99%) and 2-methoxyethanol (anhydrous liquid, 99.8%) were obtained from Aldrich and used without further purification unless stated otherwise. Bis(cyclopentadienyl)titanium dichloride (Cp_2TiCl_2, powder, 97+%) was obtained from ABCR GmbH & Co. and used without further purification. GC/MS analyses were recorded on a gas chromatograph with a mass detector HP 5971A and an infrared detector HP5965B (Hewlett Packard). Microanalyses were conducted with an ARL Model 3410 + ICP spectrometer (Fisons Instruments) and a VarioEL III CHNS (in-house).

$[Mn_4Ti_4(\mu_2\text{-}Cl)_2Cl_6(\mu_3,\eta^2\text{-}OC_2H_5OMe)_2(\mu_2,\eta^2\text{-}OC_2H_5OMe)_{10}]\cdot 2C_6H_5CH_3$ ($1\cdot 2C_6H_5CH_3$). A Schlenk flask was charged with Cp_2TiCl_2 (1.29 g; 5.18 mmol), metallic Mn (1.32 g; 24.0 mmol), 40 mL of $MeOC_2H_5OH$ (38,6 g; 507 mmol) and toluene $C_6H_5CH_3$ (30 mL). The reaction mixture was stirred for 24 h at 60 ºC. The resulting blue solution was filtered to remove Mn, and the clear solution was reduced in volume to approximately 15 mL. After 72 h blue block crystals were formed. They were filtered off, washed with hexanes (3 × 10 mL) and dried under vacuum (0.8 g, 0.46mmol, 36%). Calcd for $C_{50}H_{100}Cl_8Mn_4O_{24}Ti_4$ (MW, 1780.26): H 5.66 C 33.73 Cl 15.93 Ti 10.76 Mn 12.34. Found: H 5.89 C 34.43 Cl 15.21 Ti 10.46 Mn 12.01. GC/MS: CpH (MW, 66), CpH dimer (traces), 1-methylcyclohexa-1,4-diene (traces), cyclopentene (traces).

1.2 X-Ray Structure Determinations.

Crystal data and refinement details for the title compound are given in Table **S1**. The crystal was mounted on glass fibers and then flash-frozen to 100 K or 160 K (Oxford Cryosystem-Cryostream Cooler). Preliminary examination and intensities data collections were carried out on a Kuma KM4CCD κ-axis diffractometer with graphite-monochromated MoK_α radiation. Data were corrected for Lorentz, polarization and absorption effects. Data reduction and analysis were carried out with the Kuma Diffraction programs[1]. The structure was solved by direct methods and refined by the full-matrix least-squares method on all F^2 data using the SHELXTL software[2]. Carbon bonded hydrogen atoms were included in calculated positions and refined in the riding mode using SHELXTL default parameters. A correction for diffuse effects due to the inclusion of disordered solvent molecules in the crystal structure was made using the SQUEEZE option of *PLATON*.[3] The total potential solvent volume per unit cell was calculated to be 256.00 Å^3 (12.4 % of the cell volume).

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

No CCDC	`671160`
Chemical formula	$C_{36}H_{84}Cl_8Mn_4O_{24}Ti_4 \cdot 2(C_7H_8)$
M_r	1780.26
Cell setting, space group	Triclinic, $P\bar{1}$
Temperature (K)	100 (2)
a, b, c (Å)	10.700(5), 10.787(6), 18.960(6)
α, β, γ (°)	85.12(3), 74.68(3), 77.63(3)
V (Å^3)	2060.7(16)
Z	1
D_x (Mg m^{-3})	1.435
Radiation type	Mo $K\alpha$ radiation
μ (mm^{-1})	1.28
Crystal form, colour	Block, colorless
Crystal size (mm)	0.21 × 0.10 × 0.09
Data collection	
Diffractometer	Kuma KM-4 CCD κ-axis diffractometer
Data collection method	ω scans
Absorption correction	Analytical
$T_{\min}$	0.713
$T_{\max}$	0.831
No. of measured, independent and observed reflections	28065, 9425, 5195
Criterion for observed reflections	$I > 2\sigma(I)$
R_{int}	0.069
$\theta_{\max}$ (°)	29.1
Refinement	
Refinement on	F^2
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.039, 0.075, 0.86
No. of reflections	9425
No. of parameters	413
H-atom treatment	Mixture of independent and constrained refinement
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0398P)^2]$
$(\Delta/\sigma)_{\max}$	0.002
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.42, −0.34

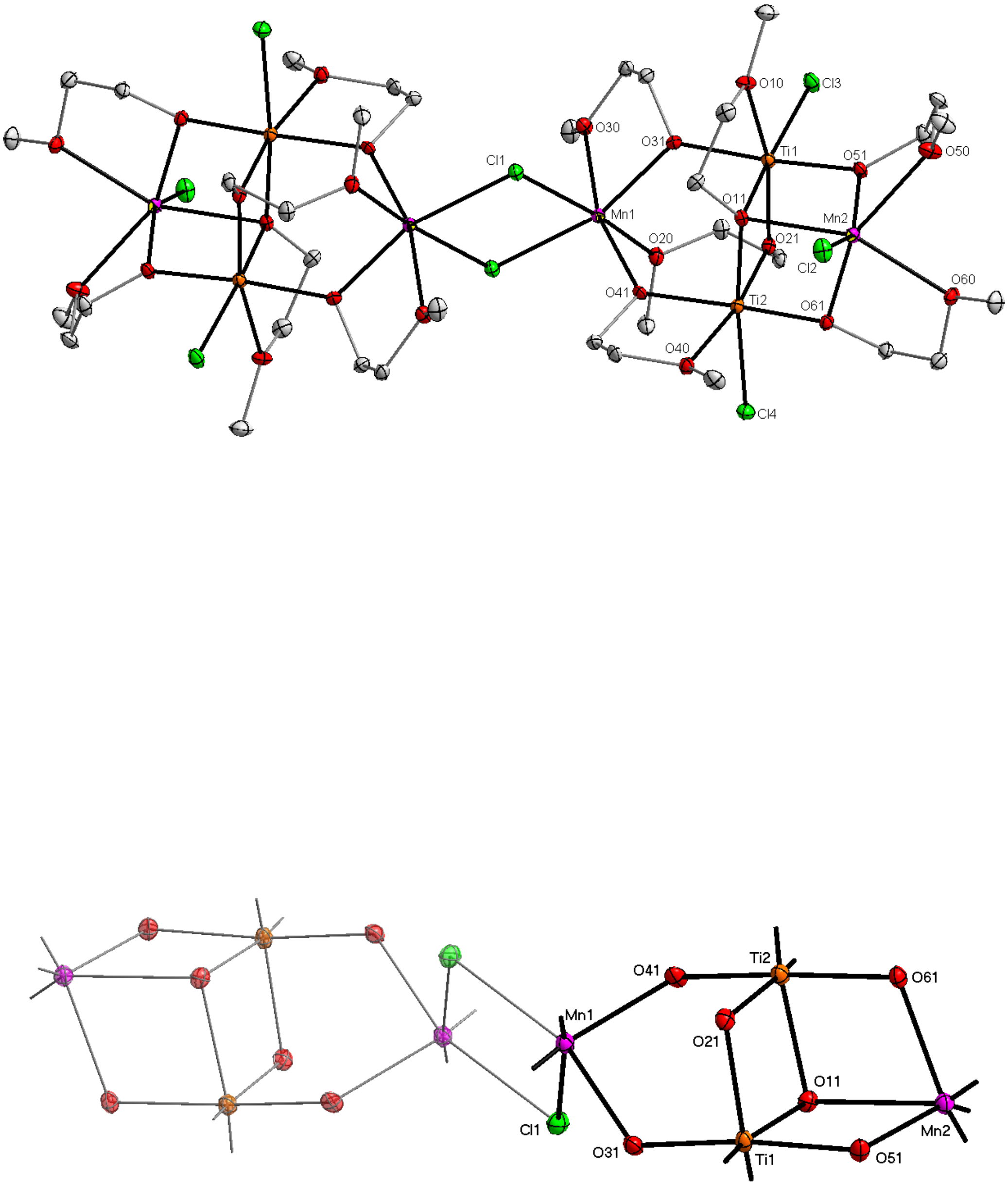


Figure. **S1** The structure of **1** (top); its metal–oxygen core (bottom).
H atoms omitted for clarity.

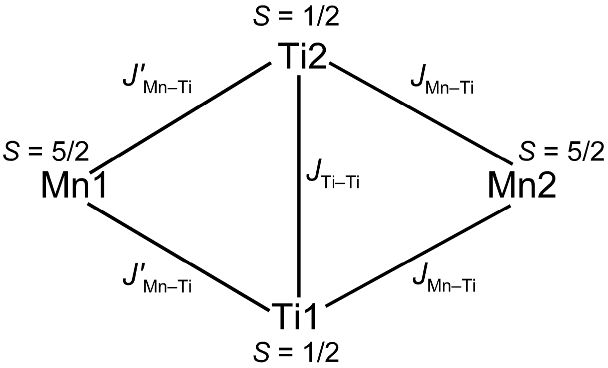
1.3 Magnetic Measurements.

Magnetic susceptibility down to 1.8 K at 500 mT and magnetization up to 5 T at 2.0 K were measured with a Quantum Design SQUID magnetometer. Diamagnetic correction was calculated using Pascal's constants.

Magnetic properties

The experimental data were fit using the Kambe vector coupling method. The exact symmetry of Mn_2Ti_2 cluster is low, but the reasonable simplifying approximation is possible by neglecting Mn(1)···Mn(2) (6.190(2) Å) and taking equal Mn(1)···Ti(1) (3.706(2) Å) and Mn(1)···Ti(2) (3.631(2) Å) as well as Mn(2)···Ti(1) (3.315(2) Å) and Mn(2)···Ti(2) (3.350(2) Å) magnetic interactions (Scheme S1).

Scheme S1



Assuming the wingtip–wingtip interactions to be zero because of the large distance between Mn1 and Mn2 ions (6.190(2) Å), the Heisenberg spin Hamiltonian can be written as:

$$\boldsymbol{H} = -2J_{Mn–Ti}(\mathbf{S}_{Mn2}\cdot\mathbf{S}_{Ti1} + \mathbf{S}_{Mn2}\cdot\mathbf{S}_{Ti2}) - 2J'_{Mn–Ti}(\mathbf{S}_{Mn1}\cdot\mathbf{S}_{Ti1} + \mathbf{S}_{Mn1}\cdot\mathbf{S}_{Ti2}) - 2J_{Ti–Ti}\,\mathbf{S}_{Ti1}\cdot\mathbf{S}_{Ti2}. \quad (1)$$

Unfortunately, the Kambe method can not be used to solve the system with C_s symmetry (Eq. 1). Thus an approximation was introduced, setting $J_{Mn–Ti} = J'_{Mn–Ti}$. Similar assumptions have been usually applied to the analysis of magnetic properties of tetramers.[4–14] The spin Hamiltonian of Eq. 1 simplifies to:

$$\boldsymbol{H} = -2J_{Mn–Ti}(\mathbf{S}_{Mn1}\cdot\mathbf{S}_{Ti1} + \mathbf{S}_{Mn1}\cdot\mathbf{S}_{Ti2} + \mathbf{S}_{Mn2}\cdot\mathbf{S}_{Ti1} + \mathbf{S}_{Mn2}\cdot\mathbf{S}_{Ti2}) - 2J_{Ti–Ti}\,\mathbf{S}_{Ti1}\cdot\mathbf{S}_{Ti2}, \quad (2)$$

with the idealized C_{2v} symmetry. Defining $\mathbf{S}_{Ti} = \mathbf{S}_{Ti1} + \mathbf{S}_{Ti2}$, $\mathbf{S}_{Mn} = \mathbf{S}_{Mn1} + \mathbf{S}_{Mn2}$, and $\mathbf{S}_{\mathbf{T}} = \mathbf{S}_{Ti} + \mathbf{S}_{Mn}$, one obtains 22 coupled spin states, which energies are given by:

$$E(S_T, S_{Ti}, S_{Mn}) = -J_{Ti–Mn}[S_T(S_T + 1) - S_{Ti}(S_{Ti} + 1) - S_{Mn}(S_{Mn} + 1)] - J_{Ti–Ti}[S_{Ti}(S_{Ti} + 1) - 3/2]. \quad (3)$$

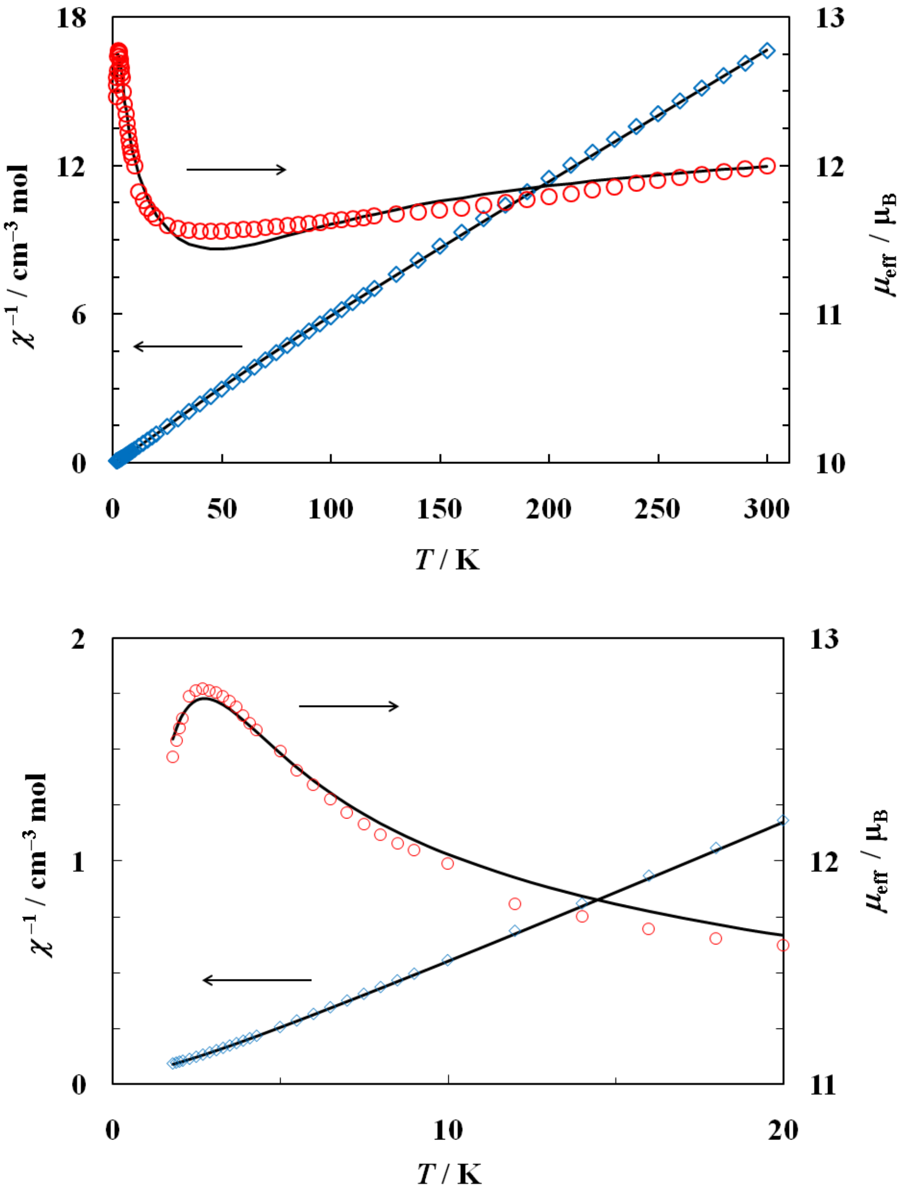


Figure S2. Variation of χ^{-1} (diamonds) and μ_{eff} (triangles) per $\mathrm{Mn^{II}{}_4Ti^{III}{}_4}$ octamer with temperature. The solid lines represent the fit to the Kambe model (see text for details).

Magnetic exchange interactions between the both $\mathrm{Mn_2Ti_2}$ subunits of **1** was estimated in molecular field approximation,[15] and the expression for the magnetic susceptibility was $\chi_{\mathrm{mf}} = \chi / (1 - 2zJ'\chi / Ng^2\beta^2)$, where χ is the susceptibility of $\mathrm{Mn_2Ti_2}$ tetramer.

The magnetization of complex **1** was calculated in magnetic field of 500 mT using the method described by Belorizky.[16,17] Least-squares fitting of the data gave $J_{\mathrm{Ti-Ti}} = -28(1)$ cm^{-1}, $J_{\mathrm{Ti-Mn}} = -5.2(2)$ cm^{-1}, $g = 1.982(2)$, and $zJ' = 0.0166(4)$ cm^{-1}. Temperature independent paramagnetism (TIP) was set at $130 \cdot 10^{-6}$ emu·mole^{-1} for Ti(III) and 0 for Mn(II) ions.[18] No paramagnetic impurity was needed for the simulation. The agreement factor $R = \Sigma[(\chi T)_{\mathrm{exp}} - (\chi T)_{\mathrm{calc}}]^2 / \Sigma[(\chi T)_{\mathrm{exp}}]^2$ was $8.7 \cdot 10^{-5}$ (68 points). The ground state was found to be $|S_{\mathrm{T}}, S_{\mathrm{Ti}}, S_{\mathrm{Mn}}>$

= |4, 1, 5> with the sixfold degenerate |*n*, 0, *n*> state (n = 0–5) at 7.3 cm^{-1} above the ground state.

To make sure if the global minimum had been obtained in the fitting procedure, the relative error surface diagram[4,6,11,13] was calculated (Figure S3). The error surface was generated as a function of $J_{\mathrm{Ti–Ti}}$ and $J_{\mathrm{Ti–Mn}}$ with g and zJ' parameters changing freely (g = 1.97–2.00 and zJ' = 0.014–0.028 cm^{-1} for the fits comprised in the Figure). The minimum achieved on the error surface is rather swallow and only a little worse fit is obtained for $J_{\mathrm{Ti–Ti}}$ ranging from –20 to –40 cm^{-1} and $J_{\mathrm{Ti–Mn}}$ from –4 to –7 cm^{-1}. However, all results gave the |4, 1, 5> ground state and the |*n*, 0 *n*> sextet as the first excited state.

Magnetic interactions between Mn_2Ti_2 clusters are weak. $J_{\mathrm{Mn–Mn}}$ between the bridging Mn$^{\mathrm{II}}$ ions may be estimated from zJ' employing the relation:[19] $J_{\mathrm{Mn–Mn}}\,S_{\mathrm{Mn}}^{2} = zJ'\,S_{\mathrm{T}}^{2}$, with S_{Mn} = 5/2 and S_{T} = 4. The value of $J_{\mathrm{Mn–Mn}}$ = 0.02 cm^{-1} supports the assumption that both halves of the Mn_4Ti_4 cluster may be treated independently.

The low-temperature magnetization of **1** is almost saturated at 5 T at a value of *ca* 17 μ_{B} (Figure S4). It is a little more then the value of 16 μ_{B} expected for weakly interacting S = 4 dimer but below 20 μ_{B} for S = 5 dimer (g = 2.00 in both cases). The experimental magnetization may be simulated using the exchange parameters obtained from fitting $\mu_{\mathrm{eff}}(T)$ data, but with g value equal to 2.13. A source of that discrepancy is not clear, but the lowest-temperature magnetization may be influenced by ZFS and other anisotropic effects. Assuming that only the ground state is populated (a first excited level at 7.3 cm^{-1}), we have tried to calculate magnetization by the full matrix diagonalization of the spin Hamiltonian:

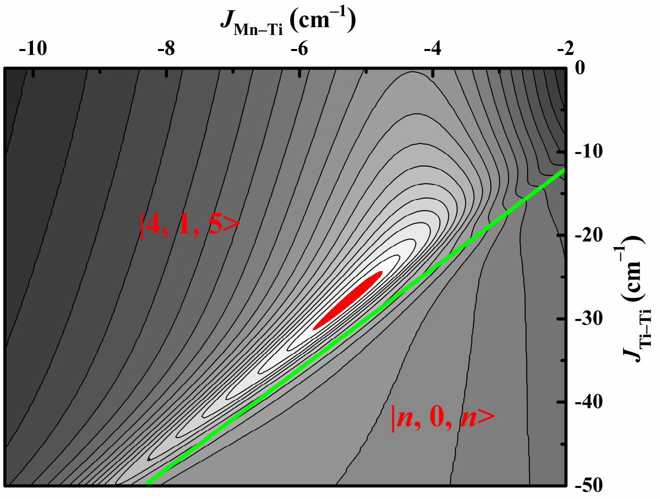


Figure S3. Contour projection of the error surface of the magnetic susceptibility fit. The green line separates the parts of {$J_{\mathrm{Mn–Ti}}$, $J_{\mathrm{Ti–Ti}}$} space with different ground states.

$$\boldsymbol{H} = \mu_B \boldsymbol{B}\cdot\boldsymbol{g}\cdot\boldsymbol{S} + D[\boldsymbol{S}_z^2 - 1/3\cdot S(S+1)] + E(\boldsymbol{S}_x^2 - \boldsymbol{S}_y^2), \quad (4)$$

where $S = 4$, D and E are the second order ZFS parameters. Good fit was obtained for $D = -0.12$ cm^{-1}, $E = 0$, but $g = 2.16$ was still too large.

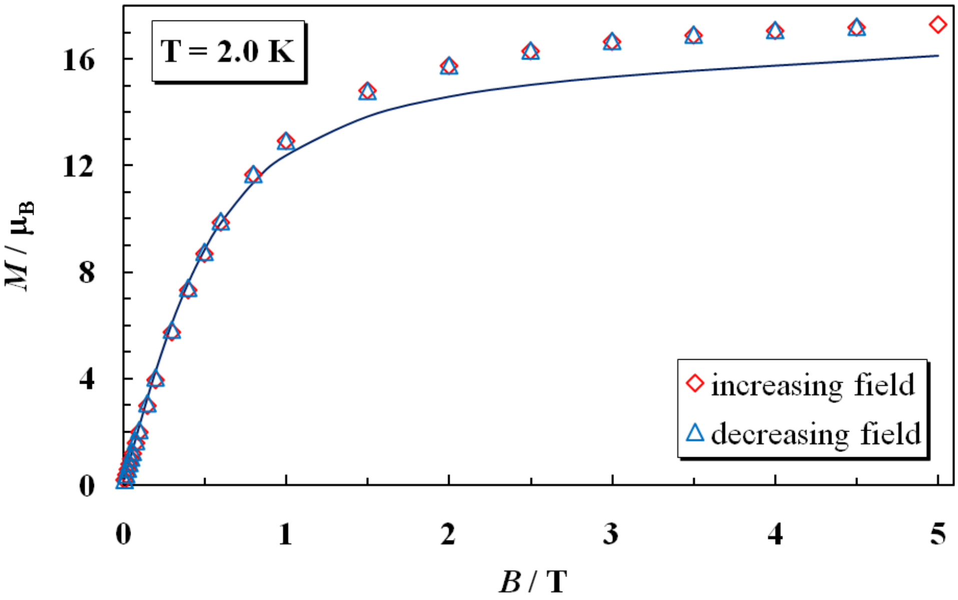


Figure S4. Field dependence of magnetization for **1**. The solid curve is calculated with the parameters obtained from fitting the susceptibility data.

Compounds contained magnetically coupled d^1–d^5 system are very rare. We have found only one example of manganese(II)–titanium(III) compound, $[(Cp)_2TiCl]_2MnCl_2$.[18] It is a trimer containing the $Ti^{III}(\mu\text{–}Cl)_2Mn^{II}(\mu\text{–}Cl)_2Ti^{III}$ core. The magnetic parameters were estimated from fitting the magnetic susceptibility: $J_{Ti–Mn} = -8.24$ cm^{-1}, $g = 2.00$ and $J_{Ti–Ti} \approx 0$. d^1–d^5 magnetic exchange was also observed in vanadium(IV)–manganese(II) compounds. Oxalate-bridged $[MnVO(ox)_2(phen)_2]\cdot H_2O$ (phen = 1,10-phenantroline) contains antiferromagnetically coupled Mn^{II}–$V^{IV}O$ pairs and the fitting of the susceptibility data gave $J = -30.9$ cm^{-1}, $g_{Mn} = 2.01$, $g_{VO} = 2.06$.[20] The magnetic behavior of $[(VO)LMn(m\text{–}OAc)(H_2O)](ClO_4)\cdot H_2O$, where L is a symmetric tetraaminodiphenol macrocyclic ligand, is characteristic of an antiferromagnetically coupled system with $J = -14.2$ cm^{-1}, $g_{Mn} = 2.00$, $g_{VO} = 1.86$.[21] Tetranuclear compound $\{[(Tp^*)V(O)(CN)_2]_2[Mn(bipy)_2]_2[OTf]_2\}\cdot MeCN$ (Tp* = hydridotris(3,5-dimethylpyrazol-1-yl)borate, OTf = trifluoromethanesulfonate, bipy = 2,2’-bipyridine) includes rectangular, cyanido-bridged $Mn^{II}_2V^{IV}_2$ clusters.[22] Antiferromagnetic exchange between the Mn^{II} and $V^{IV}O$ magnetic centers has been characterized by $J_{V–Mn}$ (sides) = -7.85 cm^{-1}, $J_{V–V}$ (diagonal) = -0.010 cm^{-1}, $g = 2.07$ ($S = 4$ ground state). On the contrary to the above-mentioned Mn^{II}–V^{IV} compounds, $[LV(\mu\text{–}O)(\mu\text{–}OAc)_2MnL]$ (L = hydridotris(pyrazolyl)borate) contains V═O…Mn bridge and exhibits ferromagnetic behavior ($J = +22.8$ cm^{-1}, $g = 1.979$, $S = 3$ ground state).[23]

There exist a lot of magnetically coupled compounds with Ti^{III}–Ti^{III} core, most of them are variations of $[Cp_2Ti(\mu\text{–}X)_2TiCp_2]$ system (Cp = cyclopentadienyl or its derivative). The halogeno-bridged complexes exhibit strong antiferromagnetic behavior with exchange integrals –100÷–160 cm^{-1}.[24,25] Stronger antiferromagnetic interactions were found in dimers containing $(\mu\text{–}Cl)_3$ bridges: $J = -171$ cm^{-1} for $[NEt_4]_3[Ti_2Cl_9]$ (with unusually low g value 1.61 and $N\alpha = 880 \cdot 10^{-6}$ cm^{-1}),[26] $J = -262$ cm^{-1} for $[PPh_4][Ti_2(\mu\text{–}Cl)_3Cl_4(PEt_3)_2] \cdot CH_2Cl_2$.[27]

Oxo-bridged titanium(III) dimers are more diversified. Linear or nearly linear molecules are weakly antiferromagnetic or even ferromagnetic: $J = -7.8$ cm^{-1} in the linear $[L_2Ti_2(NCO)_4(\mu\text{–}O)]$ (L = 1,4,7-trimethyl-1,4,7-triazacyclononane)[28] and $J = +11$ cm^{-1} in $[(Cp_2Ti)_2(\mu\text{–}O)]$[29] (Ti–O–Ti angle equal to 170.9°); both values of exchange constants were corroborated with theoretical calculations.[30,31] Strong antiferromagnetic coupling was discovered in metoxo-bridged $[Cp_2Ti(\mu\text{–}OCH_3)]_2$. The Ti–O–Ti bond angles are equal to 108.8° and the exchange constant J, determined from the temperature dependence of the EPR intensity, is equal to –268 cm^{-1}.[24]

Small Ti-O-Ti bond angles in **1** (90.87° and 95.60°) and, consequently, very short Ti-Ti distance of 2.967 Å, could facilitate direct metal-metal antiferromagnetic exchange. As pointed out by Kahn,[32] an indirect Ti-O–Ti exchange is strongly antiferromagnetic for the bond angle much larger than 90° (assuming titanium(III) magnetic orbitals of x^2–y^2 type), but an accidental orthogonality of the orbitals (and ferromagnetism) may takes place for bridging angle close to 90°. The low symmetry of the $[Ti_2O_2]$ moiety excludes pure ferromagnetic behavior of **1**, but the exchange constant $J_{Ti\text{–}Ti}$ is relatively small.

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[1] Oxford Diffraction. *CrysAlis CCD* and *CrysAlis RED*. Versions 1.171.31. **2006**, Oxford Diffraction Poland, Wroclaw, Poland.

[2] Bruker. *SHELXTL*. Version 6.14. **2003**, Bruker AXS Inc., Madison, Wisconsin, USA.

[3] A. L. Spek, *J. Appl. Cryst.*, 2003, **36**, 7–13.

[4] M. W. Wemple, H.-L. Tsai, W. E. Streib, D. N. Hendrickson, G. Christou, *J. Chem. Soc., Chem. Commun.*, 1994, 1031-1033.

[5] J. B. Vincent, C. Christmas, H.-R. Chang, Q. Li, P. D. W. Boyd, J. C. Huffman, D. N. Hendrickson, G. Christou, *J. Am. Chem. Soc.*, 1989, **111**, 2086-2097.

[6] E. Libby, J.K. McCusker, E.A. Schmitt, K. Folting, D.N. Hendrickson, G. Christou, *Inorg. Chem.*, 1991, **30**, 3486-3495.

[7] J. Yoo, E. K. Brechin, A. Yamaguchi, M. Nakano, J. C. Huffman, A. L. Maniero, L.-C. Brunel, K. Awaga, H. Ishimoto, G. Christou, D. N. Hendrickson, *Inorg. Chem.*, 2000, **39**, 3615-3623.

[8] B. Albela, M.S. El Fallah, J. Ribas, K. Folting, G. Christou, D.N. Hendrickson, *Inorg. Chem.*, 2001, **40**, 1037-1044.

[9] J. Yoo, A. Yamaguchi, M. Nakano, J. Krzystek, W. E. Streib, L.-C. Brunel, H. Ishimoto, G. Christou, D. N. Hendrickson, *Inorg. Chem.*, 2001, **40**, 4604-4616.

[10] E. C. Sañudo, V. A. Grillo, J. Yoo, J. C. Huffman, J. C. Bollinger, D. N. Hendrickson, G. Christou *Polyhedron*, 2001, **20**, 1269-1272.

[11] C. Cañada-Vilalta, J. C. Huffman, G. Christou, *Polyhedron*, 2001, **20**, 1785-1793.

[12] E. C. Sañudo, V. A. Grillo, M. J. Knapp, J. C. Bollinger, J. C. Huffman, D. N. Hendrickson, G. Christou, *Inorg. Chem.*, 2002, **41**, 2441-2450.

[13] G. Aromí, S. Bhaduri, P. Artús, J. C. Huffman, D. N. Hendrickson, G. Christou, *Polyhedron*, 2002, **21**, 1779-1786.

[14] I. S. Tidmarsh, E. Scales, P. R. Brearley, J. Wolowska, L. Sorace, A. Caneschi, R. H. Laye, E. J. L. McInnes, *Inorg. Chem.*, 2007, **46**, 9743-9753.

[15] A. P. Ginsberg, R. L. Martin, R. W. Brookes, R. C. Sherwood, *Inorg. Chem.*, 1972, **11**, 2284-2285.

[16] E. Belorizky, P. H. Fries, E. Gojon, J.-M. Latour, *Mol. Phys.*, 1987, **61**, 661-668.

[17] E. Belorizky, *J. Phys. I France*, 1993, **3**, 423-445.

[18] D. Sekutowski, R. Jungst, G. D. Stucky, *Inorg. Chem.*, 1978, **17**, 1848-1855.

[19] L. Lecren, O. Roubeau, C. Coulon, Y-G. Li, X.-F. Le Goff, W. Wernsdorfer, H. Miyasaka, R. Clérac, *J. Am. Chem. Soc.*, 2005, **127**, 17353-17363.

[20] X.-R. Sun, M.-M. Miao, P. Cheng, D.-Z. Liao, Z.-H. Jiang, G.-L. Wang, *Polyhedron*, 1996, **15**, 2927-2930.

[21] S. Mohanta, K. K. Nanda, L. K. Thompson, U. Flörke, K. Nag, *Inorg. Chem.*, 1998, **37**, 1465-1472.

[22] D. Li, S. Parkin, G. Wang, G. T. Yee, S. M. Holmes, *Inorg. Chem.*, 2006, **45**, 2773-2775.

[23] N. S. Dean, N. S. Cooper, J. K. Czernuszewicz, R. S. Ji, D. Carrano, *Inorg. Chem.*, 1997, **36**, 2760-2764.

[24] E. Samuel, J. F. Harrod, D. Gourier, Y. Dromzee, F. Robert, Y. Jeannin, *Inorg. Chem.*, 1992, **31**, 3252-3259.

[25] R. Jungst, D. Sekutowski, J. Davis, M. Luly, G. Stucky, *Inorg. Chem.*, 1977, **16**, 1645-1655.

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[26] S. L. Castro, W. E. Streib, J. C. Huffman, G. Christou, *J. Chem. Soc., Chem. Commun.*, 1996, 2177-2178.

[27] L. Chen, F. A. Cotton, K. R. Dunbar, X. Feng, R. A. Heintz, C. Uzelmeir *Inorg. Chem.*, 1996, **35**, 7358-7363.

[28] P. Jeske, K. Wieghardt, B. Nuber, *Inorg. Chem.*, 1994, **33**, 47-53.

[29] W. W. Jr. Lukens, R. A. Andersen, *Inorg. Chem.*, 1995, **34**, 3440-3443.

[30] K. Fink, R. Fink, V. Staemmler, *Inorg. Chem.*, 1994, **33**, 6219-6229.

[31] Q. Ren, Z. Chen, J. Ren, H. Wei, W. Feng, L. Zhang, *J. Phys. Chem. A*, 2002, **106**, 6161-6166.

[32] O. Kahn, J. Galy, Y. Journaux, J. Jaud, I.Morgenstern-Badarau, *J. Am. Chem. Soc.*, 1982, **104**, 2165-2176.