Syntheses, crystal structure and magnetocaloric effect of [Gd(PDOA)(NO₃)(H₂O)₂]_n

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Abstract

The coordination polymer [Gd(PDOA)(NO₃)(H₂O)₂]_n (**1**) (PDOA = o-phenylenedioxydiacetato) has been prepared and spectroscopically and structurally characterized. Its crystal structure is formed of a ribbon-like arrangement of Gd(III) atoms linked by bridging carboxylate groups and placed at the cusps of the fused triangles with Gd...Gd distances of about 6.1 Å. The Gd(III) central atoms exhibit decacoordination by oxygen atoms from hexadentate PDOA ligands with chelating and bridging functions, chelating nitrate ligand and two aqua ligands. Intra- and intermolecular hydrogen bonds of the O-H...O and C-H...O types contribute to the stability of the structure. The temperature dependence of the magnetic susceptibility revealed weak magnetic interactions among Gd(III) ions which may be attributed to dipolar coupling. Investigation of the magnetocaloric effect gives an estimate of the maximum value of isothermal change of magnetic entropy $-\Delta S_m \approx 35 \text{ J kg}^{-1} \text{ K}^{-1}$ which suggests, that **1** can be a good material for magnetic cooling at low temperatures.

Keywords: Gd(III) complex; crystal structure; one-dimensional; o-phenylenedioxydiacetato ligand, magnetocaloric effect

1. Introduction

The technological limits of current cooling methods, along with environmental considerations, are driving forces for studying the magnetocaloric effect (MCE) [1]. For enhancing the MCE, a high value of the ground state spin, S and high magnetic density are favorable [2]; as a consequence compounds with a Gd(III) ($S = 7/2$) central atom are good candidates for observation of the MCE [3-6]. It is generally accepted that Gd(III), like other lanthanoids,

prefers coordination by O-donor ligands; this criterion is well fulfilled by the PDOA ligand (PDOA = o-phenylenedioxydiacetato, Scheme 1) with six oxygen atoms, all potential donors. Previously, the PDOA complex $\{[\text{Gd}_2(\text{PDOA})_3(\text{H}_2\text{O})_6] \cdot 2\text{H}_2\text{O}\}_n$ with a ladder-like structure was synthesized and chemically and structurally characterized [7, 8]. As a continuation of our previous study on the Ce(III) complex $[\text{Ce}(\text{PDOA})(\text{NO}_3)(\text{H}_2\text{O})_2]_n$ [9] we have successfully undertaken the preparation and isolation of the Gd(III) analog $[\text{Gd}(\text{PDOA})(\text{NO}_3)(\text{H}_2\text{O})_2]_n$, and here we report its syntheses and spectral and structural characterization along with the results of its magnetic properties with emphasis on its MCE.

Scheme 1. Structure of H_2PDOA

2. Experimental

2.1. Materials

Gadolinium(III) nitrate hexahydrate $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, o-phenylenedioxydiacetic acid (H_2PDOA , $\text{C}_{10}\text{H}_{10}\text{O}_6$), and sodium hydroxide were purchased from commercial sources and used as received.

2.1 Syntheses of $[\text{Gd}(\text{PDOA})(\text{NO}_3)(\text{H}_2\text{O})_2]_n$ (**1**)

The syntheses of the title compound was done by two different procedures. First the microcrystalline material was prepared under reflux conditions as follows:

a mixture of 0.226 g of $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.5 mmol), 0.113 g of H_2PDOA (0.5 mmol), 20 ml of ethanol and 1 ml of 1 M water solution of NaOH were heated during 4 hours under reflux conditions. The separated white microcrystalline powder was filtered and dried on air. Yield: 164 mg; 45 %.

Single crystals were obtained under solvothermal conditions. Into the reaction vessel were put 0.226 g of $\text{Gd}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.5 mmol), 0.113 g of H_2PDOA (0.5 mmol) and 1 ml of 1 M aqueous solution of NaOH along with 1 ml of ethanol. The closed vessel was heated 48

hours at 125 °C and the controlled slow cooling to 30 °C was done during 22 hours. The formed yellowish crystalline material was removed by filtration, Yield: 19 %.

Anal. CHNS/O: C₁₀H₁₂Gd₁N₁O₁₁ (M = 462.33 g.mol⁻¹): Found (%): C, 25.53; H, 2.33; N, 2.75; Calc. (%): C, 25.05; H, 2.52; N, 2.89.

IR (in cm⁻¹): 3515(m); 3337(w); 3149(w); 3074(vw), 3026(vw); 2916(vw); 2850(vw); 1612(vs); 1578(s); 1503(s); 1458(msh); 1425(vs); 1336(vs); 1289(m); 1252(s); 1194(s); 1120(s); 1054(msh); 1034(s); 955(m); 829(m); 818(m); 760(s); 696(m); 599(mb); 526(m); 443(wsh).

2.3. Physical measurements

CHN analyses were performed on an Elemental Analyzer vario MICRO instrument. Infrared spectra were recorded on a Nicolet 6700 FT-IR spectrometer using the ATR technique and with Smart Orbit attachment in the range of 4000–400 cm⁻¹. X-ray powder diffraction patterns were recorded on a RIGAKU D-Max/2500 diffractometer with rotating anode and RINT2000 vertical goniometer, in the range 3-50° of 2θ using Cu Kα_{1,2} radiation (λ = 1.5406 Å). The calculated patterns were obtained using the program Mercury CSD 3.1.1 Development [10].

2.4. Magnetic measurements

Temperature dependence of susceptibility and field dependence of magnetization were investigated using a commercial SQUID magnetometer, Quantum Design. For these measurements the powdered sample was placed in a plastic gelcap which was held by a straw. Susceptibility studies were performed in a 100 mT external magnetic field using 14.16 mg sample, the same sample was adopted for magnetization measurements. The contribution of the gelcap itself was subtracted from the total signal.

2.5. Single crystal X-ray crystallography

Single-crystal X-ray data were collected on an Oxford Diffraction Xcalibur diffractometer equipped with a Sapphire3 CCD detector and a graphite monochromator utilizing Mo-Kα radiation (λ = 0.71073 Å). Absorption corrections were based on the multiscan technique using ABSPACK [11]. The structures were solved by the program SIR92 [12] and refined against the F² data using full-matrix least squares methods with the program SHELXL-2014/7 [13]. Anisotropic displacement parameters were refined for all non-hydrogen atoms. The hydrogen atoms bonded to carbon atoms were included at idealized positions and refined as riders with isotropic displacement parameters assigned as 1.2 times the U_{eq} values of the corresponding bonding partners while the hydrogen atoms of the aqua ligands were located in a difference map and refined freely. Five low-angle reflections that fell near the beam stop shadow and two

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

Empirical formula	C ₁₀ H ₁₂ Gd N O ₁₁
Molecular weight	479.46
Crystal system	monoclinic
Space group	P2 ₁ /c
Unit cell dimensions	
<i>a</i> (Å)	15.3506(2)
<i>b</i> (Å)	6.0766(1)
<i>c</i> (Å)	16.5527(2)
β (°)	115.057(2)
<i>V</i> (Å ³)	1398.71(4)
<i>Z</i>	4
<i>D</i> _{calc} (Mg.m ⁻³)	2.227
<i>T</i> (K)	150(2)
μ (mm ⁻¹)	4.804
Crystal dimensions (mm)	0.040x0.069x0.102
Crystal color / form	colorless block (cut)
Index ranges	$-21 \leq h \leq 21$ $-8 \leq k \leq 8$ $-23 \leq l \leq 23$
θ range (°)	4.320,– 30.82
Reflections collected	29105 (<i>R</i> _{int} = 0.0296)
Independent reflections	4169
Observed reflections (<i>I</i> > 2 σ _{<i>I</i>})	3821
Absorption corr. method	multi-scan
<i>T</i> _{min} - <i>T</i> _{max}	0.8573-1.0000
Goodness-of-fit on <i>F</i> ²	1.022
<i>R</i> indices (<i>I</i> > 2 σ _{<i>I</i>})	<i>R</i> ₁ = 0.0168, <i>wR</i> ₂ = 0.0347
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0201, <i>wR</i> ₂ = 0.0358
Diff. peak and hole (e.Å ⁻³)	1.00; -0.59

high-angle reflections that were measured near the corner of the detector were identified as intensity-poor outliers and were excluded from the final refinement. The crystal and experimental data are given in Table 1, and selected geometric parameters are given in Table

2. Possible hydrogen bonds are gathered in Table 3. The structural figures were drawn using Diamond [14].

3. Results and Discussion

3.1 Preparation and identification of $[\text{Gd}(\text{PDOA})(\text{NO}_3)(\text{H}_2\text{O})_2]_n$ (**1**)

Complex **1** was prepared by two different methods. While the bulk microcrystalline sample was formed under reflux conditions with ethanol as solvent, single crystals suitable for X-ray study were formed under solvothermal conditions. The phase purity and identity of the bulk sample of **1** was checked by comparison of the experimental X-ray powder diffraction pattern with the one calculated on the basis of the known crystal structure (see Fig. 1).

Fig. 1. Comparison of the experimental and calculated powder diffraction patterns for **1**.

The IR spectrum of **1** is very similar to that of the analogous Ce(III) complex [9] (Fig. 2). The positions of the observed absorption bands are gathered in the experimental part for identification purposes. The characteristic absorption bands at 1612 and 1334 cm^{-1} can be attributed to the asymmetric and symmetric $\nu(\text{COO}^-)$ vibrations. The presence of the aqua ligands is confirmed by medium absorption bands observed at 3461 and 3335 cm^{-1} . Very weak but easily identifiable are the absorption bands found at 3074, 3026 cm^{-1} as well as at 2944 which may arise from $\nu(\text{C}_{\text{ar}}-\text{H})$ and $\nu(\text{C}_{\text{al}}-\text{H})$ stretching vibrations, respectively. The assignment was done with respect to the literature values [8, 15].

Fig. 2. IR spectrum of the title complex **1**.

3.2 Crystal structure

The title complex $[\text{Gd}(\text{PDOA})(\text{NO}_3)(\text{H}_2\text{O})_2]_n$ (**1**) (Fig. 3,4) is isostructural to the recently reported analogous Ce(III) complex [9]. Its crystal structure is built up of ribbons parallel to the *b*-axis, formed by fused triangles with Gd(III) atoms placed at the vertices. Within the ribbons the Gd(III) atoms are linked by *syn-anti* bridging carboxylate groups from the PDOA ligands (Fig. 4); the Gd(III)⋯Gd(III) distances lie in the narrow range of 6.052–6.077 Å.

The Gd(III) atom is decacoordinated by ten oxygen atoms; six are from three crystallographically independent PDOA ligands (O1, O3, O4, O5, O2, O6), two from the chelating nitrato ligand (O7, O8) and two from aqua ligands (O10W, O11W) (Fig. 3). Using the program SHAPE [16] it was found that the coordination polyhedron can be viewed as a deformed square antiprism with two additional pyramidal caps (O3 and O8, see Fig. 3).

Fig. 3. View of the molecular structure of $[\text{Gd}(\text{PDOA})(\text{NO}_3)(\text{H}_2\text{O})_2]_n$ (left) and coordination polyhedron of the Gd(III) atom (right). The thermal ellipsoids are drawn at 50 % probability level. Symmetry codes: i: $x, y-1, z$; ii: $-x, 0.5+y, 0.5-z$

The hexadentate PDOA ligand is both bridging and chelating; the four inner oxygen atoms form parts of three 5-membered metallocycles while the two oxygen atoms from the carboxylate groups link the Gd(III) central atom to the neighboring Gd(III) atoms. The same coordination mode of the PDOA ligand was observed in the isostructural $[\text{Ce}(\text{PDOA})(\text{NO}_3)(\text{H}_2\text{O})_2]_n$ [9], as well as in $\{[\text{Na}_2\text{Ca}(\text{PDOA})_2(\text{H}_2\text{O})_5] \cdot 2\text{H}_2\text{O}\}_n$ [17].

Fig. 4. Simplified view of the ribbon-like polymeric structure of **1**. The distances between the Gd(III) atoms within the ribbon (dotted line) are given in the figure.

Table 2. Selected geometric parameters for **1** [Å, °]

Gd1-O1	2.3634(13)	Gd1-O11W	2.4324(14)
Gd1-O2	2.4151(12)	O7-N1	1.2629(19)
Gd1-O3	2.7484(13)	O8-N1	1.259(2)
Gd1-O4	2.5766(12)	O9-N1	1.234(2)
Gd1-O5	2.4001(13)	O1-Gd1-O3	59.10(4)
Gd1-O6	2.4193(13)	O3-Gd1-O4	57.61(4)
Gd1-O7	2.5035(14)	O4-Gd1-O5	63.66(4)
Gd1-O8	2.6481(13)	O7-Gd1-O8	49.34(4)
Gd1-O10W	2.4257(14)	O10W-Gd1-O11W	140.16(5)

Selected geometric parameters are gathered in Table 2. The Gd-O bonds range from 2.3634(13) to 2.7484(13) Å; this range is somewhat shorter than the corresponding range of 2.442(2) – 2.791(2) Å in the isostructural [Ce(PDOA)(NO₃)(H₂O)₂]_n but falls within the range of Gd-O bond lengths of 2.297(2)-2.642(2) Å in the complex {[Gd₂(PDOA)₃(H₂O)₆]·2H₂O}_n containing the same PDOA ligand [7, 8].

The stability of the ribbons is reinforced by intramolecular hydrogen bonds (HBs) between the aqua ligands and carboxylate oxygen atoms (O10W-H110...O5ⁱⁱⁱ and O11W-H111...O1^v; for symmetry codes see the footnote to Table 3). The individual ribbons are linked in the *c* axis direction by intermolecular hydrogen bonds of the O-H...O type (Table 3, Fig. 5). In addition, the resulting supramolecular layers are interlinked by weaker C6^{vii}-H6^{vii}...O7 HBs with distances H6^{vii}...O7: 2.40 Å, C6^{vii}...O7: 3.2261(1) Å and angle C6^{vii}-H6^{vii}-O7: 145° (vii: 1-x, 2-y, 1-z; Fig. 5).

Table 3. Possible hydrogen bonds in **1** [Å, °].

D-H...A	D-H	H...A	D...A	DHA
O10W-H110...O5 ⁱⁱⁱ	0.82	1.97	2.7297(1)	153
O10W-H210...O8 ^{iv}	0.81	2.07	2.8751(1)	176
O11W-H111...O1 ^v	0.80	1.85	2.6119(1)	160
O11W-H211...O9 ^{vi}	0.87	1.90	2.7515(1)	164

Symmetry codes: iii: x, 1+y, z; iv: -x, 2-y, 1-z; v: -x, -0.5-y, 0.5-z; vi: x, 1.5-y, -0.5+z

Fig. 5. Hydrogen bonding system in **1**. Only Gd(III) atoms and atoms participating in HBs are shown for clarity. Gd(III) atoms within the ribbons are linked by thin lines. Symmetry codes: ii: $-x, 0.5+y, 0.5-z$; iii: $x, 1+y, z$; iv: $-x, 2-y, 1-z$; v: $-x, -0.5-y, 0.5-z$; vi: $x, 1.5-y, -0.5+z$; vii: $1-x, 2-y, 1-z$.

3.3 Magnetic properties of **1**

Temperature dependence of susceptibility was studied from 2 K to 300 K in a magnetic field of 100 mT and the results are presented in Fig. 6. The data are characterized by monotonic increase with decreasing temperature; no sign of long-range ordering was indicated in the studied temperature range. The inverse susceptibility was analyzed using the Curie–Weiss law,

Fig. 6. Temperature dependence of the magnetic susceptibility of **1**. The solid line represents the fit of the data using the Curie–Weiss law.

$\chi = C/(T - \theta)$, the fit yielded $C = 8.2 \pm 0.11$ emu.K/mol corresponding to the value of the g – factor, $g = 2.04$, and $\theta = -0.13 \pm 0.01$ K. The obtained value of the g – factor confirms a small orbital contribution to the magnetic moment, confirming the S state of the Gd(III) ion. Since for these ions crystal field effects represent a second–order perturbation, the deviation from Curie–law behavior may be attributed predominantly to magnetic interactions, presumably of dipolar origin.

Systematic studies of magnetic field dependence of magnetization were conducted in magnetic fields up to 5 T in the temperature range 2 K – 20 K; the results are presented in Fig. 7. The magnetization increases with increasing magnetic field for each temperature and for $T = 2$ K and $B = 5$ T tends to reach the saturation value per Gd(III) ion $M_{sat} = 7.15 \mu_B$. The estimated value of M_{sat} agrees reasonably with the value $7 \mu_B$ anticipated for an isolated Gd(III) ion with $S = 7/2$, $L = 0$ and $g = 2.0$. The large magnetic moment of Gd(III) together with the density of Gd(III) ions in the structure of **1** indicates that the studied material may be considered as a potential magnetic refrigerant at low temperatures.

Fig. 7. Magnetic field dependence of the magnetization for **1** studied at various temperatures (open and closed symbols). The solid line represents magnetization calculated using Brillouin function with $g = 2.04$ and spin $S = 7/2$ at $T = 2$ K.

The study of the magnetocaloric effect is usually based on the analysis of ΔS_m , the isothermal change of magnetic entropy with (de)magnetization of the refrigerant. The quantity ΔS_m can be evaluated using the Maxwell relation:

$$\Delta S_m(T) = \int \left(\frac{\partial M(T, H)}{\partial T} \right)_H dH \quad (1)$$

Since discrete values of both temperature and magnetization are obtained in a real experiment, Eq. (1) should be approximated in the form:

$$\Delta S_m \left(\frac{T_n + T_{n+1}}{2}, H \right) = \sum_n \frac{(M_{n+1} - M_n)_H}{T_{n+1} - T_n} \Delta H \quad (2)$$

where M_n and M_{n+1} are the magnetization values measured in magnetic field H at temperatures T_n and T_{n+1} , respectively. Generally, the $-\Delta S_m$ tends to grow gradually upon reducing temperature and becomes more pronounced when applying higher magnetic fields, see Fig. 8. The most pronounced entropy change can be found below 5 K; however, no indication of saturation is observed in the range of temperatures and magnetic fields used. It should be noted, that discretization of Maxwell relation introduces an error in the calculation of ΔS_m . Since the magnetization closely follows Brillouin function, the error can be estimated by comparison of ΔS_m calculated from fitting the magnetization data at various temperatures using Brillouin function and ΔS_m obtained from Eq (2).

Fig. 8. Temperature dependence of isothermal entropy ΔS_m for **1** studied at various temperatures. The error bars are presented only for data at 2 K for clarity.

Nevertheless, the maximum value of $-\Delta S_m$ can be estimated from the available data as lower than nominally $35 \text{ J kg}^{-1} \text{ K}^{-1}$. This value is still considerable, yet somewhat smaller than those obtained from other Gd-based magnetic salts *e.g.*, $[\text{Gd}(\text{HCOO})(\text{OAc})_2(\text{H}_2\text{O})_2]_n$ (OAc = acetato) ($45.9 \text{ J kg}^{-1} \text{ K}^{-1}$) [18], $[\text{Gd}(\text{OAc})_3(\text{H}_2\text{O})_{0.5}]_n$ ($47.7 \text{ J kg}^{-1} \text{ K}^{-1}$) [19]. The lower value of $-\Delta S_m$ found for **1** in comparison with that reported for other Gd-based compounds [18 Lorusso, 2012; 19 Guo, 2012) appears to be due to the higher molecular weight of **1** resulting from the presence

of the PDOA ligand in the structure. On the other hand, a theoretical estimation of the maximum $-\Delta S_m$ per mole can be obtained by summing the contribution of uncoupled Gd(III) ions which yields:

$$|\Delta S_m^{theor}| = R \ln(2S + 1) \quad (3)$$

which gives the upper limit of $-\Delta S_m = 36.06 \text{ J kg}^{-1} \text{ K}^{-1}$ for $[\text{Gd}(\text{PDOA})(\text{NO}_3)(\text{H}_2\text{O})_2]_n$. The upper limit is slightly higher than the value estimated from the experimental data. The difference may be attributed to the weak magnetic interactions between Gd(III) ions. From this point of view, compound **1** represents a good refrigerant for magnetic cooling at low temperatures.

4. Conclusions

In conclusion, we have successfully prepared and chemically and spectroscopically characterized the novel coordination polymer $[\text{Gd}(\text{PDOA})(\text{NO}_3)(\text{H}_2\text{O})_2]_n$ (**1**) (PDOA = o-phenylenedioxydiacetato). The polymeric crystal structure of **1** is built-up of a ribbon-like arrangement of Gd(III) atoms linked by bridging carboxylate groups from PDOA ligands. The chromophore $\text{GdO}_6\text{O}_2\text{O}_2$ is composed of hexadentate PDOA ligands, a chelating nitrato ligand and two aqua ligands. The investigation of magnetic properties revealed only a weak magnetic coupling between the Gd(III) atoms. A pronounced magnetocaloric effect was found for complex **1**, which may be considered as a good magnetic refrigerant.

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Supplementary data

CCDC 1519503 (complex **1**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>,

or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

- [1] V. K. Pecharsky, K.A. Gschneidner Jr., *Int. J. Refrig.*, 29 (2006) 1239-1249.
- [2] J.-Z. Qiu, Y.-C. Chen, L.-F. Wang, Q.-W. Li, M. Orendáč, M.-L. Tong, *Inorg. Chem. Front.*, 3 (2016) 150-156.
- [3] J. W. Sharples, D. Collison, *Polyhedron*, 66 (2013) 15-27.
- [4] Y. C. Chen, F. S. Guo, J. L. Liu, J. D. Leng, P. Vrabel, M. Orendáč, J. Prokleska, V. Sechovský, M. L. Tong, *Chem. Eur. J.*, 20 (2014) 3029-3025.
- [5] Z.-M. Zhang, K.H. Zangana, A.K. Kostopoulos, M.-L. Tong, R.E.P. Winpenny, *Dalton Trans.*, 45 (2016) 9041-9044.
- [6] O. Blacque, A. Amjad, A. Caneschi, L. Sorace, P.-E. Car, *New J. Chem.*, 40 (2016) 3571-3577.
- [7] P. Gawryszewska, Z. Ciunik. *J. Photochem. Photobiol. A: Chem.*, 202 (2009) 1-9.
- [8] M. Stolárová, J. Černák, M. Tomás, I. Ara, L.R. Falvello, R. Boča, J. Titiš, *J. Coord. Chem.*, 67 (2014) 1046-1060.
- [9] M. Stolárová, J. Černák, M. Tomás, I. Ara, M. Orendáč, L. R. Falvello, *Polyhedron*, 88 (2015) 149–155.
- [10] C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Cryst.*, 41 (2008) 466-470,.
- [11] R. H. Blessing, *Acta Crystallogr.*, B51 (1995) 816-823; R. H. Blessing, *J. Appl. Crystallogr.*, 30 (1997) 421-426.
- [12] A. Altomare, G. Cascarano, C. Giacovazzo, A. Gualardi, *J. Appl. Crystallogr.*, 26 (1993) 343-350.
- [13] G. M. Sheldrick, *Acta Crystallogr.*, C71 (2015) 3-8.
- [14] K. Brandenburg, H. Putz. *Crystal Impact Diamond*, Crystal and Molecular Structure Visualization, GbR, Postfach 1251, D-53002 Bonn, Germany (2008).
- [15] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Part B: Applications in Coordination, Organometallic, and Bioinorganic Chemistry, Wiley, New York, 1997.
- [16] M. Llunell, D. Casanova, J. Cirera, P. Alemany, S. Alvarez,: *SHAPE - Program for the Stereochemical Analysis of Molecular Fragments by Means of Continuous Shape*

Measures and Associated Tools, Version 2.1, University of Barcelona, Spain, March 2013.

- [17] G. Smith, R. C. Bott, D. S. Sagatys, C. H. L. Kennard, *Polyhedron*, 10 (1991) 1565-1568.
- [18] G. Lorusso, M. A. Palacios, G. S. Nichol, E. K. Brechin, O. Roubeau, M. Evangelisti, *Chem. Commun.*, 48 (2012) 7592-7594.
- [19] F.-S. Guo, J. D. Leng, J.-L. Liu, Z.-S. Meng, M.-L. Tong, *Inorg. Chem.* 51 (2012) 405-413.