

# A novel decanuclear Co(II) cluster with adamantane-like metallic skeleton supported by 8-hydroxyquinoline and *in situ* formed $\text{CO}_3^{2-}$ anions†

Lei Wang, Yi Li, Yu Peng, Zhiqiang Liang,\* Jihong Yu and Ruren Xu

Received 16th January 2012, Accepted 21st March 2012

DOI: 10.1039/c2dt30102d

A novel decanuclear Co(II) cluster,  $[\text{Co}_{10}(\text{Q})_{12}(\mu_6\text{-CO}_3)_4]\cdot 2.5\text{DMF}$  (**1**) (Q = 8-hydroxyquinoline), has been synthesized under solvothermal conditions and characterized by powder XRD, TGA and IR spectroscopy. Single-crystal X-ray diffraction analysis shows that **1** represents a new type of decanuclear cobalt cluster with an approximate supertruncated tetrahedral shape coordinated with coexisted Q ligands and *in situ* formed  $\mu_6$ -bridging  $\text{CO}_3^{2-}$  anions. Meanwhile, **1** is the largest aggregate in metal–Q coordination chemistry. Another distinguishing feature of **1** is the adamantane-like metallic skeleton with point symbol  $\{6^3\}_2\{6\}_3$ , which is observed in the polynuclear metal complexes for the first time. Furthermore, it is considered that the *in situ* formed  $\text{CO}_3^{2-}$  anions have a crucial effect on the formation of the resultant unexpected polynuclear structures. The magnetic studies show that antiferromagnetic (AF) interactions exist within **1**.

## Introduction

Polynuclear transition metal (TM) complexes have attracted considerable attention for their complicated electronic structure, magnetic properties as well as potential applications in nanoscale containers and catalysts,<sup>1</sup> information storage devices<sup>2</sup> and molecular magnets.<sup>3</sup> Cobalt has become an ideal candidate to prepare polynuclear metal complexes due to its diverse coordination geometries, larger magnetic anisotropy and higher Curie temperature.<sup>4</sup> Although many polynuclear cobalt complexes with various topologies and sizes have been successfully prepared,<sup>5</sup> few decanuclear cobalt clusters are obtained. Up to now, only four kinds of decanuclear cobalt clusters have been reported, displaying tricapped trigonal prisms,<sup>6</sup> wheel-like shapes,<sup>7</sup> super-tetrahedral shapes<sup>8</sup> and irregular shapes.<sup>9</sup>

The design and synthesis of coordination clusters with predicted aggregate and topology remain a challenging goal. Nowadays, the most practicable strategy for preparing polynuclear TM complexes is to utilize organic molecules containing mono or multi coordination sites as bridged or supported ligands.<sup>10</sup> As a nonconventional method, using those *in situ* formed organic ligands<sup>9e,11</sup> or inorganic anions may yield unexpected novel polynuclear structures. Examples containing both

bridged ligands and *in situ* formed  $\text{CO}_3^{2-}$  anions are some novel polynuclear Ln–TM complexes.<sup>12</sup>

As a multidentate organic ligand, 8-hydroxyquinoline (HQ), as well as its simple derivatives, which possesses the big  $\pi$  electron conjugated structure and strong electron transmission capacity, has been widely used to prepare the electroluminescent materials.<sup>13</sup> Most of the reported polynuclear TM complexes bridged by HQ molecules are mononuclear<sup>14</sup> or tetranuclear,<sup>15</sup> while high-nuclear examples are still rare. Until now, the largest aggregate of polynuclear metal complexes constructed by TM and HQ is the porous ionic/molecular crystal  $[\text{Co}_8(\mu_4\text{-O})\text{Q}_{12}](\text{NO}_3)_2\cdot 16\text{H}_2\text{O}$ , which is composed of discrete triakis tetrahedral  $\text{Co}_8$  clusters with an ideal  $T_d$  symmetry.<sup>16</sup>

In this work, we chose HQ as a bridged ligand and obtained a novel decanuclear cobalt complex,  $[\text{Co}_{10}(\text{Q})_{12}(\mu_6\text{-CO}_3)_4]\cdot 2.5\text{DMF}$  (**1**), which has an approximate supertruncated tetrahedral core and the largest aggregate in metal–Q coordination chemistry. The arrangement of ten cobalt atoms supported by four *in situ* formed  $\mu_6$ -bridging  $\text{CO}_3^{2-}$  anions displays an adamantane topology. To the best of our knowledge, this topology of metallic skeleton has been observed in the polynuclear metal complexes for the first time.

## Experimental

### Materials and methods

All chemicals were reagent grade and used as received. Elemental analyses of C, H and N were carried out with a Perkin-Elmer 2400 elemental analyzer. X-ray powder diffraction (XRD) data were collected on a Siemens D5005 diffractometer with Cu  $K\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ). Thermogravimetric analysis (TGA) was carried out on a TG Q500 high-resolution analyzer under air

State Key Lab of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun, 130012, P. R. China. E-mail: liangzq@jlu.edu.cn; Fax: +86-431-85168609; Tel: +86-431-85168609

†Electronic supplementary information (ESI) available: The optical micrographs, experimental polycrystalline and calculated from the single-crystal data X-ray powder diffraction, FTIR spectrum and TG-DTA plot of **1** as well as selected bond lengths and angles for **1**. X-ray crystallographic data for **1** in CIF format. CCDC 855885. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c2dt30102d

atmosphere. The infrared (IR) spectrum was recorded within the 400–4000  $\text{cm}^{-1}$  region on a Bruker-IFS 66V/S spectrometer using KBr pellets. Temperature dependent magnetic susceptibility data were recorded on a Quantum-Design MPMS-XL SQUID magnetometer under an applied field of 1 kOe over the temperature range of 2–300 K. Field-dependent magnetization was measured by Quantum-Design MPMS-XL SQUID magnetometer at 2 K.

## Synthesis

Typical synthesis of compound **1**: HQ (70 mg, 0.48 mmol) was added to the mixture of  $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$  (125 mg, 0.50 mmol) and *N,N*-dimethylformamide (DMF) (5 mL) in a 25 mL glass beaker. After stirring for 30 min, triethylamine (TEA) (30  $\mu\text{L}$ , 0.21 mmol) was added. The mixture became a dark brown solution immediately. After stirring for another 1 h, the mixture was transferred to a Teflon-lined stainless-steel autoclave (23 mL) and kept at 433 K for 3 days and then cooled to room temperature. The red octahedral crystals were recovered by filtration, washed with DMF and dried in air. Anal. Calcd (%) for  $\text{C}_{119.5}\text{H}_{89.5}\text{Co}_{10}\text{N}_{14.5}\text{O}_{26.5}$ : C, 52.35%; H, 3.29%; N, 7.41%. Found: C, 52.16%; H, 3.16%; N, 7.82%. IR (KBr,  $\text{cm}^{-1}$ ): 3043 (w), 1668 (m), 1573 (m), 1492 (s), 1458 (s), 1380 (s), 1278 (m), 1108 (m), 786 (m), 746 (m), 496 (m).

## Structure determination

A suitable single crystal was selected for single-crystal X-ray diffraction analysis. The data were collected on a Bruker AXS SMART APEX II diffractometer ranging from 1.45 to 28.29° at the temperature of 296(2) K using graphite-monochromated Mo- $\text{K}\alpha$  radiation ( $\lambda = 0.71073$  Å). Data processing was accomplished with the SAINT processing program.<sup>17</sup> A total of 159 603 reflections were collected, of which 9156 reflections were unique. The structure was solved by direct method and refined by full matrix least-squares technique with the SHELXTL 97 crystallographic software package.<sup>18</sup> All non-H atoms except the disordered carbon atoms in **1** were located from the difference Fourier map and refined anisotropically. The remaining solvent molecules were disordered and assigned as 20 DMF molecules per unit cell, which were determined by TGA, elemental analysis and SQUEEZE results. The contributions of these disordered solvents to the scattering values have been removed by using the PLATON SQUEEZE program.<sup>19</sup> The C(21)–C(25) atoms of Q ligand are disordered and were split into two equal isotropical positions during the refinement. Two split positions of each C atom were refined with equal thermal displacement parameters by the EADP instructions of SHELXTL97. The H atoms of Q ligands were added geometrically. The crystal data and structure refinement details and selected bond lengths and angles for **1** are given in Table 1 and Table S1, ESI,<sup>†</sup> respectively. Crystallographic data have also been deposited with the CCDC database (CCDC-number 855885).

**Table 1** Crystallographic data for compound **1**

Compound	<b>1</b>
Empirical formula	$\text{C}_{119.5}\text{H}_{89.5}\text{Co}_{10}\text{N}_{14.5}\text{O}_{26.5}$
Formula weight ( $\text{g mol}^{-1}$ )	2741.86
<i>T</i> (K)	296 (2)
Wavelength (Å)	0.71073
Crystal system, space group	Cubic, $P\bar{a}3$ (No. 205)
<i>a</i> (Å)	28.0546(4)
<i>V</i> (Å <sup>3</sup> )	22 080.7(5)
<i>Z</i> , Calculated density	8, 1.650 $\text{mg m}^{-3}$
Absorption coefficient ( $\mu$ )	1.546 $\text{mm}^{-1}$
<i>F</i> (000)	11 120
Theta range for data collection	1.45 to 28.29°
Limiting indices	$0 \leq h \leq 25, 0 \leq k \leq 26, 2 \leq l \leq 37$
Reflections unique	9156
Refinement method	Full-matrix least-squares on $F^2$
Data/restraints/parameters	9156/0/463
Completeness to $\theta$	28.29°, 100.0%
Goodness-of-fit on $F^2$	1.087
Final <i>R</i> indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0575, wR_2 = 0.1205$
<i>R</i> indices (all data)	$R_1 = 0.1864, wR_2 = 0.1391$
Largest diff. peak and hole	0.701 and $-0.570 \text{ e Å}^{-3}$

$$R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, wR_2 = \{ \sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2] \}^{1/2}.$$

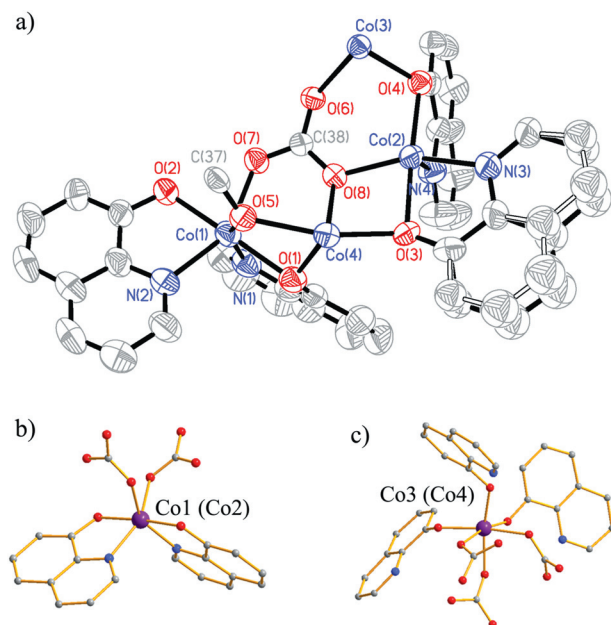
## Results and discussion

### Synthesis

Compound **1** was synthesized under solvothermal conditions in the reaction system with molar composition of 1.0  $\text{Co}(\text{OAc})_2$ : 0.96 HQ: 0.42 TEA: 136.8 DMF at 433 K for 3 days. Many synthesis parameters were found to affect the formation of **1**. The choice of suitable solvent is important for the successful synthesis of compound **1**. When DMF was changed to other solvents, such as *N,N*-dimethylacetamide (DMA), *N,N*-diethylformamide (DEF), EtOH, MeOH and  $\text{H}_2\text{O}$ , compound **1** could not be obtained. The suitable reaction temperatures are ranging from 413 K to 433 K. The suitable amount of TEA was within 0.21–0.84 mmol, while too much TEA ( $>0.84$  mmol) would produce the mixture of **1** and  $\text{Co}_3\text{O}_4$ . Significantly, the anions of cobalt sources are crucial in this synthetic system. The inorganic cobalt salts, such as  $\text{CoCl}_2$ ,  $\text{CoCO}_3$  and  $\text{Co}(\text{NO}_3)_2$  could not produce **1** in DMF. Only  $\text{Co}(\text{acac})_2$  or  $\text{Co}(\text{OAc})_2$  could be used as the cobalt sources to synthesize compound **1**. According to structural determination and IR spectral analysis,  $\text{CO}_3^{2-}$  anions are incorporated in the resultant structure of **1**. We believe that these  $\text{CO}_3^{2-}$  anions might result from the decomposition of a  $\text{Co}(\text{acac})_2$  or  $\text{Co}(\text{OAc})_2$  source but not from  $\text{CoCO}_3$  or DMF. Such a phenomenon has been reported in the literature.<sup>20,21</sup>

### Description of structure

Single-crystal X-ray analysis reveals that compound **1** crystallizes in the cubical space group  $P\bar{a}3$ . As shown in Fig. 1a, the asymmetric unit contains four crystallographically independent Co ions, four Q ligands and two  $\text{CO}_3^{2-}$  anions. Each crystallographically independent Co(3) atom lies on the  $C_3$  axis and is surrounded by the other three Co atoms (Co(1), Co(2) and Co(4)) to form the decanuclear cluster by three-fold symmetry operation. All cobalt ions in **1** are coordinated to Q ligands and  $\text{CO}_3^{2-}$  anions to form an approximate octahedron. Co(1) and

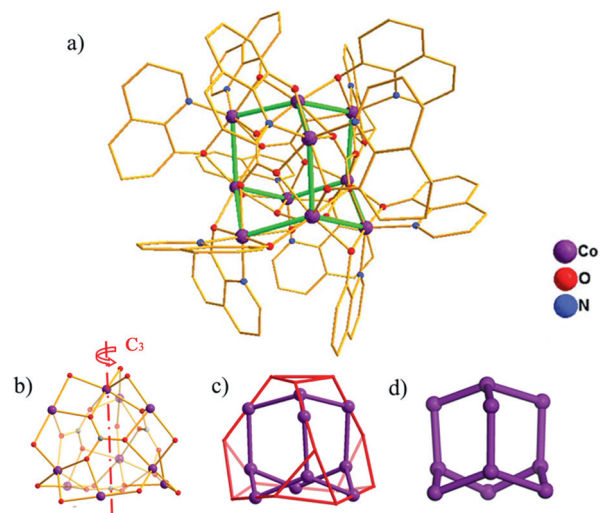


**Fig. 1** (a) Asymmetric unit of the decanuclear cobalt cluster showing the atomic labeling scheme. Thermal ellipsoids are at the 50% probability level. (b) and (c) The coordination environments of two types of cobalt ions.

Co(2) are coordinated to two  $\mu_2$ -O atoms from  $\text{CO}_3^{2-}$  anions, two N atoms and two  $\mu_2$ -O atoms from chelated Q molecules (Fig. 1b). Another type of cobalt sites (Co(3) and Co(4)) is coordinated to three  $\mu_2$ -O atoms from Q and three  $\mu_2$ -O atoms from  $\text{CO}_3^{2-}$  anions (Fig. 1c). The Co–O bond lengths are ranged from 2.049(3) Å to 2.188(3) Å (Table S1†). The Co–N bond lengths are from 2.083(3) Å to 2.116(3) Å. The Co– $\mu_2$ -O–Co angles ( $96.64(13)^\circ$ – $99.59(14)^\circ$ ) are larger than the Co– $\mu_3$ -O–Co angles ranging from  $94.03(12)^\circ$  to  $97.74(13)^\circ$ . The bond valence sums (BVS) calculations<sup>22</sup> indicate that the four crystallographic independent Co atoms are in +2 valence state.

The decanuclear cobalt cluster has the largest aggregate in metal–Q coordination chemistry and represents a new geometrical shape. We believe that the *in situ* formed  $\text{CO}_3^{2-}$  anions in the synthetic system are crucial for the formation of the unexpected  $\text{Co}_{10}$  cluster, which can supply high bridging sites to increase the size of the cluster. As shown in Fig. 2a, the  $\text{Co}_{10}$  cluster is enveloped by twelve Q ligands to form a sphere-like  $[\text{Co}_{10}(\text{Q})_{12}(\mu_6\text{-CO}_3)_4]$  molecule with the diameter *ca.* 1.5 nm. The twelve oxygen atoms of Q ligands are connected with the ten Co atoms supported by four  $\mu_6\text{-CO}_3$  anions forming an approximate supertruncated tetrahedral cluster  $[\text{Co}_{10}\text{O}_{12}(\mu_6\text{-CO}_3)_4]$  with  $C_3$  symmetry. The Co(3) and the C(37) of carbonate lie on the three-fold axis. The ideal truncated tetrahedron belongs to the  $T_d$  group and consists of four hexagons and four triangles. In compound **1**, the distortion of the Co coordination environment leads to the final compound with  $C_3$  symmetry.

The metallic skeleton (Fig. 2d) in **1** consists of ten Co ions, which are supported by four well-documented  $\mu_6$ -bridging carbonate<sup>23</sup> to form the adamantane topology as two nodal (2, 3) cage with point symbol  $\{6^3\}_2\{6\}_3$ . Each  $\mu_6$ -bridging carbonate connects to six cobalt atoms, the arrangement of which



**Fig. 2** (a) Molecular structure of **1** and its metallic skeleton with adamantane topology highlighted by the thick green line. For clarity, hydrogen atoms and carbon atoms in HQ molecules have been omitted. (b) The ball and stick representation of  $[\text{Co}_{10}\text{O}_{12}(\mu_6\text{-CO}_3)_4]$  core with  $C_3$  symmetry in **1**. (c) The supertruncated tetrahedral core of  $[\text{Co}_{10}\text{O}_{12}(\mu_6\text{-CO}_3)_4]$  core with the metallic skeleton in it. (d) The metallic skeleton of **1**.

constructs the six-numbered ring of the adamantane cage. The distances of adjacent Co atoms range from 3.126 Å to 3.181 Å. The second nearest distance of Co–Co within the intra-cluster is about 5 Å. Although the adamantane cage is an ordinary geometrical configuration found in many organic, inorganic<sup>24</sup> and metal–organic compounds,<sup>25</sup> this topology is first found in polynuclear complexes.

Fig. 3 shows the crystal structure and stacking way of **1** viewed down the *c*-axis. The  $[\text{Co}_{10}\text{O}_{12}(\mu_6\text{-CO}_3)_4]$  cores build up a very dense structure stacking in an ABAB sequence and separate each other by disordered DMF molecules. Unlike the reported  $\text{Co}_8$  cluster,<sup>16</sup> no intermolecular  $\pi$ – $\pi$  interactions are found between the Q ligands from adjacent clusters in our present case. The nearest distance of Co–Co\* between two neighboring clusters is approximate 7.985 Å.

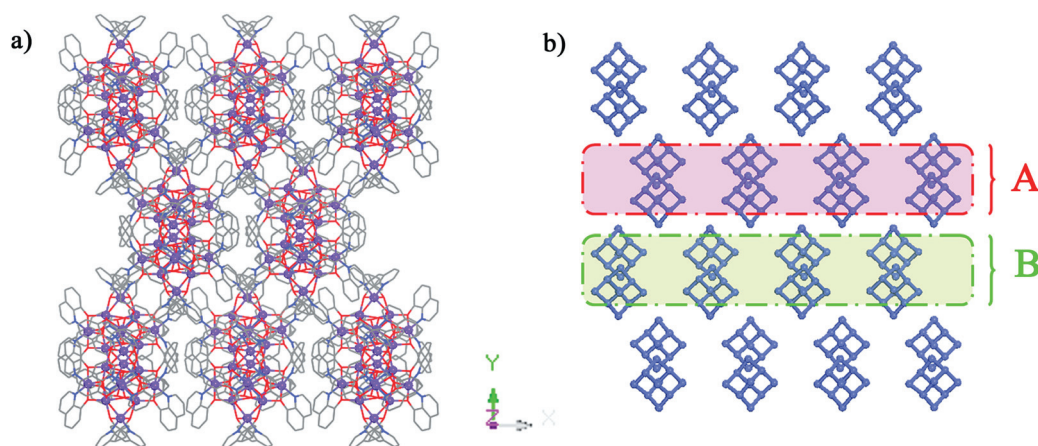
## IR analysis

The IR spectrum of **1** was recorded within the 400–4000  $\text{cm}^{-1}$  (Fig. S3, ESI†). There is a strong band at 1492  $\text{cm}^{-1}$  assigned to the characteristic absorption of carbonate groups.<sup>26</sup> The band at 1668  $\text{cm}^{-1}$  belongs to the C=O vibration of DMF molecules. The bands at 1573, 1458, 1380, 1278 and 1108  $\text{cm}^{-1}$  are assigned to the stretching and bending vibrations of Q ligands.<sup>27</sup>

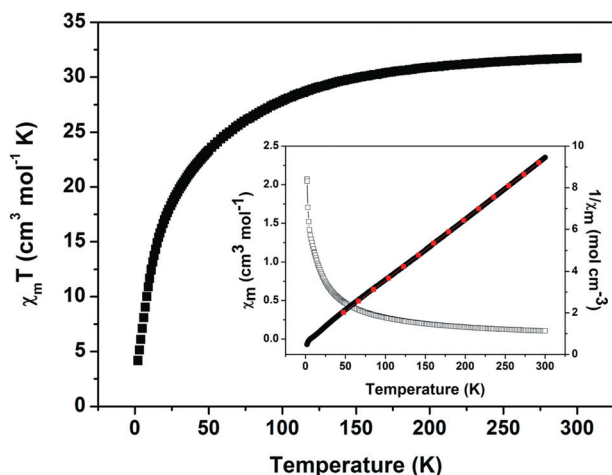
## TG analysis

The thermogravimetric analysis was carried out on a TG Q500 high-resolution analyzer under air atmosphere in the temperature range from 30 to 886 °C (Fig. S4, ESI†). The first weight loss of 6.24% from 30 to 300 °C corresponds to the loss of DMF molecules (calc. 6.66%). The second weight loss of 60.63% from 300 to 400 °C is assigned to the decomposition of





**Fig. 3** (a) View of the crystal structure of **1** along the *c*-axis. (b) The AB stacking diagram of **1** along the *b*-axis. The Co<sub>10</sub> is shown in the metallic skeleton for clarity.

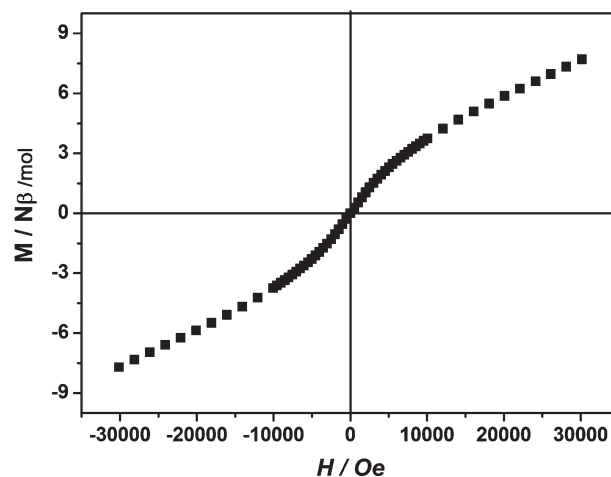


**Fig. 4** The variable temperature magnetic susceptibility plot for **1** at 1000 Oe. The insert figure is variable-temperature magnetic susceptibility  $\chi_m$  (○) and  $1/\chi_m$  (●), the simulated  $1/\chi_m$  line shown in red.

Q ligands (calc. 59.58%). The overall weight loss (%) of **1** is 66.87% (calc. 66.24%).

### Magnetic measurements

The variable temperature magnetic susceptibility data of **1**, collected using a polycrystalline sample on an applied field of 1000 Oe, is plotted as the  $\chi_m T$  versus *T* (where  $\chi_m$  is the molar magnetic susceptibility) shown in Fig. 4. The room temperature  $\chi_m T$  value of 31.73 cm<sup>3</sup> K mol<sup>−1</sup> is larger than the expected value for ten non-interacting  $S = 3/2$  Co<sup>2+</sup> ions (18.7 cm<sup>3</sup> K mol<sup>−1</sup> for  $g = 2$ ). This may be attributed to the significant orbital contribution of Co(II) ions in an octahedral field.<sup>28</sup> As the temperature decreases from 300 K to 2 K, the  $\chi_m T$  value decreases very slowly and reaches the lowest value of 4.15 cm<sup>3</sup> K mol<sup>−1</sup> until 2 K. This magnetic behavior indicates that there exists an AF interaction within the cobalt centers. The plot of  $1/\chi_m$  vs. *T* (insert in Fig. 4) in the range of 50–300 K obeys the Curie–Weiss law with Curie constant  $C = 34.05$  cm<sup>3</sup> K mol<sup>−1</sup> and



**Fig. 5** Field dependence of magnetization at 2.0 K.

Weiss constant  $\theta = -21.15$  K. And this negative  $\theta$  value further confirms the weak AF exchange interactions within this decanuclear cobalt cluster.

A field-dependent magnetization measurement at 2 K is shown in Fig. 5. The *M*–*H* plot increases gradually to reach the transition point at *ca.* 3.73 Nβ at 10 KOe and then linearly goes up with the continual magnetic field. This value is lower than the saturation value of ten Co ions. No hysteresis loop is observed.

### Conclusions

In summary, we have successfully synthesized a novel decanuclear cobalt(II) complex, [Co<sub>10</sub>(Q)<sub>12</sub>(μ<sub>6</sub>-CO<sub>3</sub>)<sub>4</sub>]·2.5DMF (**1**) with an approximate supertruncated tetrahedral geometrical shape and the largest aggregate in metal–Q coordination chemistry to the best of our knowledge. Those *in situ* formed CO<sub>3</sub><sup>2−</sup> anions play a crucial role in the formation of this decanuclear cobalt(II) cluster. The metallic skeleton in **1** has the adamantane topology as two nodal (2,3) with point symbol {6<sup>3</sup>}<sub>2</sub>{6<sup>3</sup>}<sub>3</sub>, which is first observed in the polynuclear complexes. The magnetic study

shows that there exists an AF interaction within **1**. Meanwhile, utilizing the multidentate organic molecules and *in situ* formed small molecules as coexisted ligands may be a feasible route to synthesize “unexpected” polynuclear metal complexes, which could not be obtained by the conventional method.

## Acknowledgements

We thank the National Natural Science Foundation of China and the State Basic Research Project of China (Grants: 2011CB808703) for support of this work.

## References

- (a) J. G. McAlpin, T. A. Stich, C. A. Ohlin, Y. Surendranath, D. G. Nocera, W. H. Casey and R. D. Britt, *J. Am. Chem. Soc.*, 2011, **133**, 15444; (b) J. L. Atwood, E. K. Brechin, S. J. Dalgarno, R. Inglis, L. F. Jones, A. Mossine, M. J. Paterson, N. P. Power and S. J. Teat, *Chem. Commun.*, 2010, **46**, 3484.
- M. Cavallini, J. Gomez-Segura, D. Ruiz-Molina, M. Massi, C. Albonetti, C. Rovira, J. Veciana and F. Biscarini, *Angew. Chem., Int. Ed.*, 2005, **44**, 888.
- (a) D. Gatteschi and R. Sessoli, *Angew. Chem., Int. Ed.*, 2003, **42**, 268; (b) M. Murrie, *Chem. Soc. Rev.*, 2010, **39**, 1986.
- J. M. D. Coey, *Magnetism and Magnetic Materials*, Cambridge University Press, New York, 2010.
- (a) A. Tsohos, S. Dionyssopoulou, C. P. Raptopoulou, A. Terzis, E. G. Bakalbassis and S. P. Perlepes, *Angew. Chem., Int. Ed.*, 1999, **38**, 983; (b) G. S. Papaefstathiou, S. P. Perlepes, A. Escuer, R. Vicente, M. Font-Bardia and X. Solans, *Angew. Chem., Int. Ed.*, 2001, **40**, 884; (c) E. K. Brechin, O. Cador, A. Caneschi, C. Cadiou, S. G. Harris, S. Parsons, M. Vooni and R. E. P. Winpenny, *Chem. Commun.*, 2002, 1860; (d) T. A. Hudson, K. J. Berry, B. Moubarak, K. S. Murray and R. Robson, *Inorg. Chem.*, 2006, **45**, 3549; (e) Y.-Z. Zhang, W. Wernsdorfer, F. Pan, Z.-M. Wang and S. Gao, *Chem. Commun.*, 2006, 3302; (f) M.-H. Zeng, M.-X. Yao, H. Liang, W.-X. Zhang and X.-M. Chen, *Angew. Chem., Int. Ed.*, 2007, **46**, 1832; (g) G. N. Newton, G. J. T. Cooper, P. Kögerler, D.-L. Long and L. Cronin, *J. Am. Chem. Soc.*, 2008, **130**, 790; (h) P. Alborés and E. Rentschler, *Angew. Chem., Int. Ed.*, 2009, **48**, 9366; (i) F. Klöwer, Y. Lan, J. Nehr Korn, O. Waldmann, C. E. Anson and A. K. Powell, *Chem.–Eur. J.*, 2009, **15**, 7413.
- A. Graham, S. Meier, S. Parsons and R. E. P. Winpenny, *Chem. Commun.*, 2000, 811.
- H. N. Miras, I. Chakraborty and R. G. Raptis, *Chem. Commun.*, 2010, **46**, 2569.
- L. Lisnard, F. Tuna, A. Candini, M. Affronte, R. E. P. Winpenny and E. J. L. McInnes, *Angew. Chem., Int. Ed.*, 2008, **47**, 9695.
- (a) E. K. Brechin, S. Parsons and R. E. P. Winpenny, *J. Chem. Soc., Dalton Trans.*, 1996, 3745; (b) C. Benelli, A. J. Blake, E. K. Brechin, S. J. Coles, A. Graham, S. G. Harris, S. Meier, A. Parkin, S. Parsons, A. M. Seddon and R. E. P. Winpenny, *Chem.–Eur. J.*, 2000, **6**, 883; (c) C. Cadiou, M. Helliwell and R. E. P. Winpenny, *C. R. Chim.*, 2003, **6**, 241; (d) E. Fursova, O. Kuznetsova, V. Ovcharenko, G. Romanenko, V. Ikorskii, I. Eremenko and A. Sidorov, *Polyhedron*, 2007, **26**, 2079; (e) Y. Bi, W. Liao, G. Xu, R. Deng, M. Wang, Z. Wu, S. Gao and H. Zhang, *Inorg. Chem.*, 2010, **49**, 7735.
- (a) W. Schmitt, M. Murugesu, J. Goodwin, J. Hill, A. Mandel, R. Bhalla, C. Anson, S. Heath and A. Powell, *Polyhedron*, 2001, **20**, 1687; (b) G. Ambrosi, M. Formica, V. Fusi, L. Giorgi and M. Micheloni, *Coord. Chem. Rev.*, 2008, **252**, 1121; (c) A. J. Tasiopoulos and S. P. Perlepes, *Dalton Trans.*, 2008, 5537; (d) T. Glaser, *Chem. Commun.*, 2011, **47**, 116.
- (a) Q. Chen, M.-H. Zeng, L.-Q. Wei and M. Kurmoo, *Chem. Mater.*, 2010, **22**, 4328; (b) Q. Chen, M.-H. Zeng, Y.-L. Zhou, H.-H. Zou and M. Kurmoo, *Chem. Mater.*, 2010, **22**, 2114.
- (a) X.-J. Kong, Y.-P. Ren, L.-S. Long, Z. Zheng, R.-B. Huang and L.-S. Zheng, *J. Am. Chem. Soc.*, 2007, **129**, 7016; (b) X.-J. Kong, Y.-P. Ren, W.-X. Chen, L.-S. Long, Z. Zheng, R.-B. Huang and L.-S. Zheng, *Angew. Chem., Int. Ed.*, 2008, **47**, 2398; (c) X.-J. Kong, Y.-P. Ren, L.-S. Long, Z. Zheng, G. Nichol, R.-B. Huang and L. S. Zheng, *Inorg. Chem.*, 2008, **47**, 2728.
- C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, 1987, **15**, 913.
- Cambridge Crystallographic Data Centre: <http://www.ccdc.cam.ac.uk/>
- S. G. Telfer, R. Kuroda, J. Lefebvre and D. B. Leznoff, *Inorg. Chem.*, 2006, **45**, 4592.
- X.-N. Cheng, W. Xue, J.-B. Lin and X.-M. Chen, *Chem. Commun.*, 2010, **46**, 246.
- SMART and SAINT software package, Siemens Analytical X-ray Instruments Inc., Madison, WI, 1996.
- G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **64**, 112.
- (a) A. L. Spek, *J. Appl. Crystallogr.*, 2003, **36**, 7; (b) A. L. Spek, *Acta Crystallogr., Sect. D: Biol. Crystallogr.*, 2009, **65**, 148.
- (a) T. M. Mccollom and J. S. Seewald, *Geochim. Cosmochim. Acta*, 2003, **67**, 3645; (b) Z. Jia, Y. Tang, L. Luo and B. Li, *Cryst. Growth Des.*, 2008, **8**, 2116; (c) L. Tian, J. L. Zhu, L. Chen, B. An, Q. Q. Liu and K. L. Huang, *J. Nanopart. Res.*, 2011, **13**, 3483.
- J. Guzman, B. G. Anderson, C. P. Vinod, K. Ramesh, J. W. Niemantsverdriet and B. C. Gates, *Langmuir*, 2005, **21**, 3675.
- I. D. Brown and D. Altermatt, *Acta Crystallogr., Sect. B: Struct. Sci.*, 1985, **41**, 244.
- G. J. T. Cooper, G. N. Newton, P. Kögerler, D.-L. Long, L. Engelhardt, M. Luban and L. Cronin, *Angew. Chem., Int. Ed.*, 2007, **46**, 1340.
- G. C. Hampson and A. J. Stosick, *J. Am. Chem. Soc.*, 1938, **60**, 1814.
- (a) M. L. Miller, S. A. Ibrahim, M. L. Golden and M. Y. Darensbourg, *Inorg. Chem.*, 2003, **42**, 2999; (b) T. Shiga, G. N. Newton, J. S. Mathieson, T. Tetsuka, M. Nihei, L. Cronin and H. Oshio, *Dalton Trans.*, 2010, **39**, 4730.
- S. I. Swamy, J. Bacsa, J. T. A. Jones, K. C. Stylianou, A. Steiner, L. K. Ritchie, T. Hasell, J. A. Gould, A. Laybourn, Y. Z. Khimyak, D. J. Adams, M. J. Rosseinsky and A. I. Cooper, *J. Am. Chem. Soc.*, 2010, **132**, 12773.
- M. Cölle, S. Forero-Lenger, J. Gmeiner and W. Brütting, *Phys. Chem. Chem. Phys.*, 2003, **5**, 2958.
- O. Kahn, *Molecular Magnetism*, VCH, New York, 1993.