PERGAMON

Available online at www.sciencedirect.com

SCIENCE DIRECT®

Polyhedron 22 (2003) 1917–1920

POLYHEDRON

www.elsevier.com/locate/poly

Hydrothermal synthesis, crystal structure and characterization of a new hexanuclear cobalt(II) complex comprised of octahedral and tetrahedral cobalt ions

Hitoshi Kumagai[a,*], Yoshimi Oka[b,c], Satoshi Kawata[d], Masaaki Ohba[a,e], Katsuya Inoue[b], Mohamedally Kurmoo[f], Hisashi Ōkawa[a,*]

[a] *Department of Chemistry, Kyushu University, Hakozaki 6-10-1 Higashi-ku, Fukuoka 812-8581, Japan*
[b] *Institute for Molecular Science (IMS), Nishigounaka 38, Myoudaiji, Okazaki 444-8585, Japan*
[c] *Japan Department of Structural Molecular Science, The Graduate University for Advanced Studies, Nishigounaka 38, Myoudaiji, Okazaki 444-8585, Japan*
[d] *Department of Chemistry, Shizuoka University, Ohya, Shizuoka 422-8529, Japan*
[e] *PRESTO, JST, Kawaguchi-shi, Japan*
[f] *Institut de Physique et Chimie des Matériaux de Strasbourg, 23 rue du Loess, F-67037 Strasbourg Cedex, France*

Received 6 October 2002; accepted 21 November 2002

Abstract

Reaction of Co(II) with phenylcinnamic acid and sodium hydroxide under hydrothermal conditions yields a new hexanuclear Co(II) complex, $[Co_6(OH)_2(L)_{10}]$ (L = phenylcinnamate). $[Co_6(OH)_2(L)_{10}]$ consists of two edge-sharing octahedral $\{CoO_6\}$ and four tetrahedral $\{CoO_4\}$ units linked through μ-carboxylate ligands and μ-hydroxide ions. The magnetic moment shows a large decrease from 300 to 25 K which amounts to antiferromagnetic coupling between cobalt ions in octahedral and tetrahedral sites leading to an $s = 3$ ground-state at low temperatures.

Keywords: Cobalt cluster; Magnetic properties; Crystal structures; Hydrothermal synthesis; MCD

1. Introduction

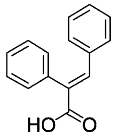
There is considerable interest in metal complex assemblies where the structures present various types of metal–ligand coordination, nuclearity and dimensionality [1–5]. The studies on these assemblies also relate to material science as well as structural chemistry and focus on potential applications to catalysis, sorption, photochemistry and magnetism [6–16]. One of the current challenges is to prepare metal clusters or low-dimensional materials that exhibit unique magnetic and/or optical properties [17–25]. Rational synthesis of these transition metal aggregates is fundamental in understanding nucleation phenomena and developing molecular magnetic materials. Co(II) complexes are of particular interest for developing magnetic and optical materials because of (a) variable coordination geometries (i.e. octahedral, tetrahedral, etc.), (b) significant stability in the air, (c) two different spin states ($s = 3/2$ and 1/2) depending on the ligand field, (d) different electronic structures and color, with a large ε value in tetrahedral geometry and (e) large orbital moment through a spin–orbit coupling in octahedral geometry. One of our objectives is the synthesis and characterization of Co(II) compounds where tetrahedral Co(II) and octahedral Co(II) ions are both present within the structure [26].

We have reported hydrothermal synthesis, structures and magnetic properties of polymeric complexes containing di-carboxylates, tri-carboxylates, and a tetra-carboxylate [15,25,27–35]. The size, shape and charge of the organic ligand all play an important role in the approach to metal complex assemblies. In the present

---

* Corresponding authors. Tel./fax: +81-92-642-2598.
E-mail address: kumagaiscc@mbox.nc.kyushu-u.ac.jp (H. Kumagai).

0277-5387/03/$ - see front matter © 2003 Elsevier Science Ltd. All rights reserved.
doi:10.1016/S0277-5387(03)00139-6



Scheme 1. Structure of phenylcinnamic acid.

study we used phenylcinnamic acid (L) (Scheme 1), a mono-carboxylate in which two benzene rings are connected by π-conjugated ethylene to form a hydrophobic moiety. Hydrothermal techniques have been used for the preparation of crystals of synthetic minerals, metal-organic framework polymers and polyoxometalate clusters [6,36–39]. However, hydrothermal synthesis of Co(II) clusters is much less explored. Here, we report the hydrothermal synthesis, crystal structure, magnetic behavior and spectroscopic properties of a new hexanuclear Co(II) complex, $[Co_6(OH)_2(L)_{10}]$, constructed from tetrahedral Co(II) and octahedral Co(II) units.

2. Experimental

All chemicals were obtained from Aldrich, Tokyo Kasei or Fluka, and used without purification. The syntheses were carried out in home-built teflon-lined cylindrical stainless steel pressure bombs with maximum capacity of 120 ml. The measurements of temperature and field dependence of the magnetization of the complex were performed on a Quantum Design MPMS-XL SQUID operating in the temperature range 2–300 K and an applied field up to 5 T. Solid-state MCD spectra were measured on a KBr pellet, using a JASCO J-820 spectropolarimeter in the temperature range of 5–100 K and an applied field up to 1.5 T. UV–Vis spectra were recorded on a Shimazu UV-3100PC spectrometer.

3. Preparation of $[Co_6(OH)_2(L)_{10}]$

Cobalt(II) nitrate hexahydrate (1 g), phenylcinnamic acid (1.91 g) and NaOH (0.34 g) were dissolved in distilled water (30 ml). The mixture was placed in the Teflon liner of autoclave, sealed and heated to 170 °C for 1 day. It was allowed to cool to room temperature in a water bath. $[Co_6(OH)_2(L)_{10}]$ was obtained as violet crystals, which were washed with water and acetone and dried in air (yield ≈ 60%).

4. X-ray crystal structure analysis

A single crystal was glued on the top of a glass fiber. Data were collected at room temperature on a Brucker SMART APEX CCD area detector with ω scan mode. The diffractometer employs graphite monochromated Mo Kα radiation (0.7107 Å). The data were corrected for Lorentz and polarization effects. The absorption correction was based on symmetry equivalent reflections using the SADABS programs. The structure was solved by direct methods and expanded using Fourier techniques [40]. All non-hydrogen atoms were refined anisotropically. The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters and converged (large parameter shift was σ times its e.s.d.) with unweighted and weighted agreement factors of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. No extinction corrections have been applied. Data for $[Co_6(OH)_2(L)_{10}]$; Empirical Formula, $Co_3O_{11}C_{75}H_{56}$, Formula Weight, 1310.06, Crystal System, triclinic, Space Group, $P\bar{1}$, $a = 14.329(1)$ Å, $b = 15.615(1)$ Å, $c = 18.045(2)$ Å, $\alpha = 65.328(1)°$, $\beta = 72.580(2)°$, $\gamma = 63.474(1)°$, $V = 3250.8(5)$ Å^3, $Z = 2$, $D_c = 1.338$ g cm^{-3}, μ (Mo Kα) = 8.18 cm^{-1}, R (R_w) (all data), 0.114 (0.190), R ($I > 2\sigma(I)$), 0.062.

5. Results and discussion

The X-ray structure analysis of $[Co_6(OH)_2(L)_{10}]$ reveals the formation of a hexanuclear cluster made up of two octahedral and four tetrahedral Co(II). The asymmetric unit consists of an octahedral Co(II), two tetrahedral Co(II), five phenylcinnamate ligands and a bridging hydroxide. Fig. 1 shows the structure of the hexanuclear core. Crystallographic inversion centre sits on the middle of Co(1)···Co(1′). Co(1) exhibits a slightly distorted octahedral geometry with five oxygen atoms of phenylcinnamate ligands and one oxygen atom of bridging hydroxide. The O–Co–O bond angles in the distorted $\{CoO_6\}$ octahedral site range from 80.3(1) to 98.2(1)° and bond distances range from 2.043(3) to 2.180(3) Å (av. 2.10 Å). The Co(1)–O(11′) bond distance is the longest in the $\{CoO_6\}$ octahedral site since O(11) bridges Co(1) and Co(1′) in a μ_2-mode. The octahedron of Co(1) and that of Co(1′) share the O(11)···O(11′) edge and the Co(1)···Co(1′) separation is 3.30 Å and the Co(1)–O(11)–Co(1′) bond angle is 99.7(1)°. On the other hand, Co(2) and Co(3) show a distorted tetrahedral geometry comprising of three oxygen atoms of phenylcinnamate ligands and one oxygen atom of bridging hydroxide. The O–Co–O bond angles in the distorted $\{CoO_4\}$ tetrahedral sites range from 100.4(1) to 124.9(1)° and bond distances range from 1.924(3) to 1.997(3) Å (av. 1.96 Å). These values are similar to those found in a one-dimensional chain complex made up from octahedral and tetrahedral Co(II) [26]. Co(2) and Co(3) are bridged by a hydroxide (O(1)) and by a phenylcinnamate ligand in *syn–syn* mode. The distance between Co(2) and Co(3) is 3.17 Å. Octahedral Co(1)

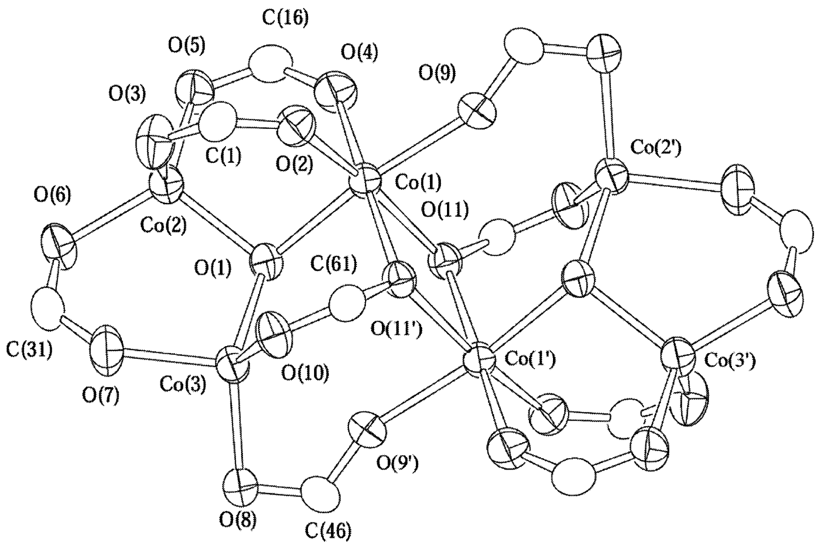


Fig. 1. ORTEP drawing of hexanuclear core with 50% probability level. Phenyl groups are omitted for clarity.

and tetrahedral Co(2) and Co(3) share the vertex (O(1)) and are further connected by four phenylcinnamate ion to yield an overall hexanuclear complex, $[Co_6(OH)_2(L)_{10}]$. The Co(1)···Co(2) and Co(1)···Co(3) separations are 3.16 and 3.53 Å, respectively.

Temperature-dependence of magnetic susceptibility is shown in Fig. 2. The effective magnetic moment of $[Co_6(OH)_2(L)_{10}]$ at 300 K is $11.56\mu_B$, which is larger than the spin-only value of $9.48\mu_B$ for six high-spin Co(II) ions. This value is indicative of an appreciable orbital contribution to the magnetic moment of the high-spin Co(II) in octahedral surrounding [41]. The χ-value increases gradually with decreasing temperature down to 25 K and increases rapidly below 25 K. Isothermal magnetization measurements on the polycrystalline sample at 2 K exhibit a gradual increase with increasing magnetic field and approach to value of approximately $6\mu_B$ at 50 kOe. The saturation magnetization value suggests that a ferromagnetic interaction operates between at least two Co(II).

UV–Vis spectrum of a DMF solution exhibits three absorption around 570 ($\varepsilon = 1094$) and 530 (shoulder, $\varepsilon = 970$ M^{-1} cm^{-1}) nm. The absorption bands corresponding to the transition $^4A_2 \rightarrow {}^4T_1(P)$ of tetrahedral Co(II) generally occur in the 550–770 nm region with molar extinction coefficients of the order of 100–1000 M^{-1} cm^{-1} [42]. Both the reflectance spectrum of solid sample and UV–Vis spectrum in DMF show a marked similarity. Reflectance spectrum and MCD spectrum of solid sample are shown in Fig. 3. The MCD spectrum

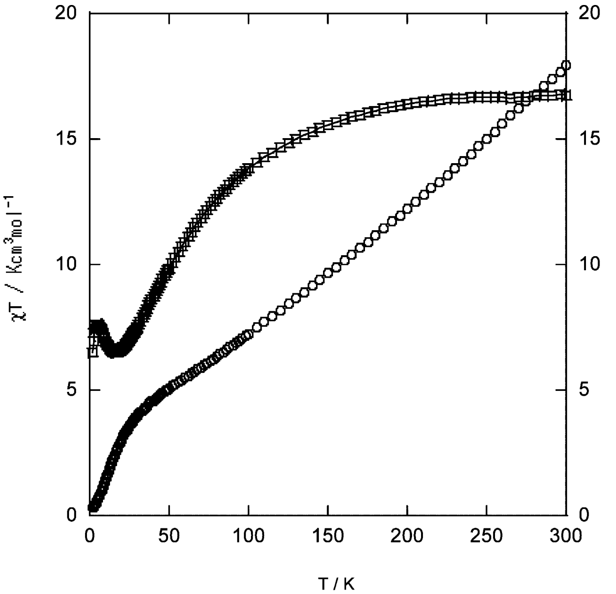


Fig. 2. Temperature-dependence of magnetic susceptibility.

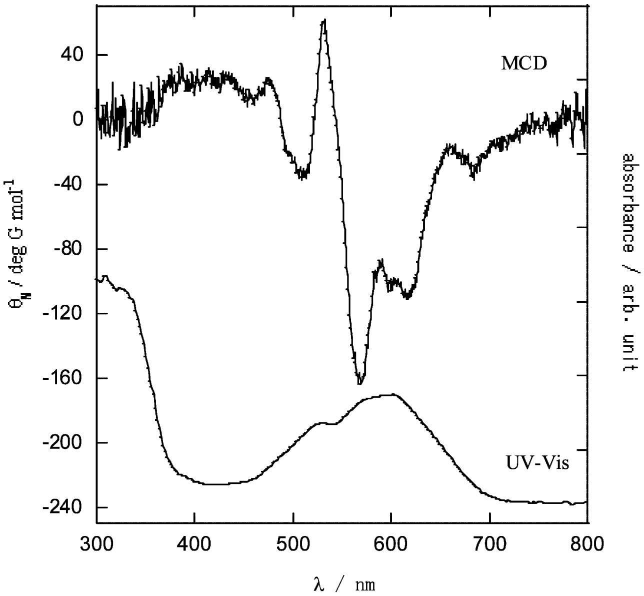


Fig. 3. Reflectance spectrum and MCD spectrum.

shows three major bands corresponding to similar bands in the UV–Vis absorption spectrum. Complete assignment is not made at this stage. However, it must be mentioned that the MCD spectrum of the complex is similar to those of tetrahedral Co(II) complexes, $Co(Ph_3PO)_4^{2+}$ and $Co(TBPO)_4^{2+}$ (TBPO = tri-*n*-butylphosphine oxide). The main feature of MCD of $Co(Ph_3PO_4)^{2+}$ and $Co(TBPO)_4^{2+}$ arises from the spin–orbit splitting of the upper state $^4T_1(P)$ in the tetrahedral field, and the major MCD at room temperature comes from the temperature-dependent *C* term whose origin lies in Zeeman splitting of the ground-state $^4A_2$ [42].

In conclusion, the present results show that the combination of the hydrothermal synthesis and hydrophobic carboxylate, phenylcinnamate, affords a hydroxide-bridged cluster, $[Co_6(OH)_2(L)_{10}]$. Hydrothermal synthesis of Co(II) clusters is still rare and $[Co_6(OH)_2(L)_{10}]$ is a new example of a structurally characterized hexanuclear cluster comprising of both tetrahedral Co(II) and octahedral Co(II) ions.

6. Supplementary material

Crystallographic data have been deposited at Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-194470. Copies of this informationmay be obtained free of charge from The Director, 12 unio Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was founded by a Grant-in-Aid for scientific research (No. 13640561) and COE research 'Design and Control of Advanced Molecular Assembly System' (No. 08CE2005) from Ministry of Education, Science, Sports and Culture, Japan.

References

[1] P. Day, J. Chem. Soc., Dalton Trans. (2000) 3483.
[2] O. Kahn, Molecular Magnetism, VCH, New York, 1993.
[3] O. Kahn, Acc. Chem. Res. 33 (2000) 647.
[4] D. O'Hare, D.W. Bruce, Inorganic Materials, Wiley, Chichester, 1992.
[5] J.-M. Lehn, Supramolecular Chemistry, VCH, Weinheim, 1995.
[6] A.K. Cheetham, G. Ferey, T. Loiseau, Angew. Chem., Int. Ed. 38 (1999) 3268.
[7] E. Coronado, J.R. Galan-Mascaros, V. Laukhin, Nature 408 (2000) 447.
[8] E. Coronado, J.-R. Galan-Mascaros, C.-J. Goemez-Garcia, J. Ensling, P. Gütlich, Chem. Eur. J. 6 (2000) 552.
[9] M. Eddaoudi, H. Li, O.M. Yaghi, J. Am. Chem. Soc. 122 (2000) 1391.
[10] T.J. Barton, L.M. Bull, W.G. Klemperer, D.A. Loy, B. McEnaney, M. Misono, P.A. Monson, G. Pez, G.W. Scherer, J.C. Vartuli, O.M. Yaghi, Chem. Mater. 11 (1999) 2633.
[11] S. Kitagawa, M. Kondo, Bull. Chem. Soc. Jpn 71 (1998) 1739.
[12] S. Kawata, S. Kitagawa, H. Kumagai, T. Ishiyma, K. Honda, H. Tobita, K. Adachi, M. Katada, Chem. Mater. 10 (1998) 3902.
[13] P.G. Lacroix, R. Clement, K. Nakatani, J. Zyss, I. Ledoux, Science 263 (1994) 658.
[14] H. Akutsu, A.A. Sato, S.S. Turner, D. Le Pevelen, P. Day, V. Laukhin, A.-A. Klehe, J. Singleton, D.A. Tocher, M.R. Probert, J.A.K. Howard, J. Am. Chem. Soc. 124 (2002) 12430.
[15] A. Rujiwatra, C.J. Kepert, J.B. Claridge, M.J. Rosseinsky, H. Kumagai, M. Kurmoo, J. Am. Chem. Soc. 123 (2001) 10584.
[16] M. Kurmoo, A.W. Graham, P. Day, S.J. Coles, M.B. Hursthouse, J.L. Caulfield, J. Singleton, J.P. Francis, W. Hayes, L. Ducasse, P. Guionneau, J. Am. Chem. Soc. 117 (1995) 12209.
[17] A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio, R. Sessoli, J. Chem. Soc., Dalton Trans. (2000) 3907.
[18] D. Gatteschi, R. Sessori, A. Cornia, Chem. Commun. (2000) 725.
[19] A. Caneschi, D. Gatteschi, N. Lalioti, C. Sangregorio, R. Sessoli, G. Venturi, A. Vindigni, A. Rettori, M.G. Pini, M.A. Novak, Angew. Chem., Int. Ed. 40 (2001) 760.
[20] S.M. Aubin, M.W. Wemple, D.M. Adams, H.L. Tsai, G. Christou, D.N. Hendrickson, J. Am. Chem. Soc. 118 (1996) 7746.
[21] S.L. Castro, Z.M. Sun, C.M. Grant, J.C. Bollinger, D.N. Hendrickson, G. Christou, J. Am. Chem. Soc. 120 (1998) 2365.
[22] M. Kurmoo, H. Kumagai, M.A. Green, B.W. Lovett, S.J. Blundell, A. Ardavan, J. Solid State Chem. 159 (2001) 343.
[23] M. Kurmoo, Phil. Trans. A 357 (1999) 3041.
[24] M. Kurmoo, J. Mater. Chem. 9 (1999) 2595.
[25] M. Kurmoo, P. Day, A. Derory, C. Estournes, R. Poinsot, M.J. Stead, C.J. Kepert, J. Solid State Chem. 145 (1999) 452.
[26] H. Kumagai, Y. Oka, M. Ohba, K. Inoue, H. Okawa, Chem. Lett. (2002) 1006.
[27] M. Kurmoo, C.J. Kepert, New J. Chem. (1998) 1515.
[28] C.J. Kepert, M.J. Rosseinsky, Chem. Commun. (1999) 375.
[29] C.J. Kepert, T.J. Prior, M.J. Rosseinsky, J. Am. Chem. Soc. 122 (2000) 5158.
[30] H. Kumagai, C.J. Kepert, M. Kurmoo, Inorg. Chem. 41 (2002) 3410.
[31] C.J. Kepert, M.J. Rosseinsky, Chem. Commun. (1998) 31.
[32] H. Kumagai, K. Inoue, M. Kurmoo, Bull. Chem. Soc. Jpn 75 (2002) 1283.
[33] H. Kumagai, M. Akita-Tanaka, K. Inoue, M. Kurmoo, J. Mater. Chem. 11 (2001) 2146.
[34] H. Kumagai, Y. Oka, M.-A. Tanaka, K. Inoue, Inorg. Chim. Acta 332 (2002) 176.
[35] H. Kumagai, Y. Oka, K. Inoue, M. Kurmoo, J. Chem. Soc., Dalton Trans. (2002) 3442.
[36] D.J. Price, A.K. Powell, P.T. Wood, J. Chem. Soc., Dalton Trans. (2000) 3566.
[37] M.T. Pope, A. Müller, Angew. Chem., Int. Ed. Engl. 30 (1991) 34.
[38] M.I. Khan, Y.-S. Lee, C.J. O'Connor, J. Zubieta, J. Am. Chem. Soc. 116 (1994) 5001.
[39] L.A. Gerrard, P.T. Wood, Chem. Commun. (2000) 2107.
[40] G.M. Sheldrick, Crystallographic Computing, Oxford University Press, 1985.
[41] R.L. Carlin, Magnetochemistry, Springer, New York, 1986.
[42] H. Kato, K. Akimoto, J. Am. Chem. Soc. 96 (1974) 1351.