Polish J. Chem., **77**, 829–835 (2003)

Synthesis, Crystal Structure and Magnetic Behavior of a One-Dimensional Cobalt(II) Complex with Mellitic Anion as Bridging Ligand

by M.G. Zhao[1], J.M. Shi[2*], C.Q. Liu[1], W. Xu[2] and Y.Q. Chen[2]

[1]*Department of Chemistry, Xinzhou Normal College, Xinzhou 034000, P.R. China*
[2]*Department of Chemistry, Shandong Normal University, Jinan 250014, P.R. China*

(Received March 10th, 2003)

A one-dimensional complex $\{[Co_3(C_6(COO)_6)(H_2O)_{12}]\}\cdot 6H_2O\}_n$ has been prepared and its crystal structure determined by X-ray crystallography. In the complex mellitic anion provides its six carboxylate groups to coordinate four cobalt(II) ions, in which a seven-membered ring was formed by two ortho-carboxylate groups to coordinate the same cobalt(II) ion. Through the four carboxylate groups bridging two cobalt(II) ions the one-dimensional chain structure was formed. The variable-temperature magnetic susceptibility of the complex was measured in the 4–300 K range and the magnetic data indicate the magnetic interaction between the bridged cobalt(II) ions displays an antiferromagnetic coupling.

Key words: synthesis, crystal structure, cobalt complex, benzene polycarboxylate ligand, magnetism

Much research interest has been focused on the crystal engineering of coordination compounds that may provide new materials with useful properties such as catalytic, microporosity, electrical conductivity, non-linear optical activity and co-operative magnetic behavior. Benzene polycarboxylate anions such as terephthalate [1–7], phthalate [8–11], benzene-1,3,5-tricarboxylate [12–15] and benzene-1,2,4,5-tetracarboxylate [16–19] belong to versatile bridging ligands and many multi-nuclear complexes have been synthesized and some of them display interesting characteristics as regards magnetic property [5,8,10] and structural feature [6,13]. In this polycarboxylate ligands area, there exists another kind of ligand, namely, mellitic anion (benzene-hexacarboxylate anion) and the research dealing with its complexes [20–23] is very limited, as compared with that of the complexes mentioned above. In view of the interest in its novel coordinate function, we prepared the title complex and here we report its synthesis, crystal structure and magnetic behavior.

---

[*] Author to whom all correspondence should be directed.

EXPERIMENTAL

Materials: Mellitic acid was synthesized by oxidation of mellitene using a general method and other chemicals are analytical grade and were used without further purification.

Physical measurements: The IR spectra were recorded on a Shimadzu 408 IR spectrophotometer using KBr discs. C, H, N elemental analysis was carried out on a Perkin-Elmer Elemental analyzer, Model 240. The variable-temperature magnetic susceptibility of measurement was performed using single crystal sample and the magnetic field 5000 G in the 4–300 K range with a SQUID magnetometer.

X-ray crystallography: The determination of the crystal structure was carried out on a Bruker Smart-1000 CCD using graphite-monochromated MoKα radiation (0.71073 Å). Data reduction and structure refinement were performed using the SHELXL-97 program system. Details of crystal parameters and data collection are listed in Table 1. The selected bond lengths and angles are listed in Table 2.

Table 1. Crystallographic data and collection parameters for the complex.

Chemical formula	$C_{12}H_{36}Co_3O_{30}$
Crystal system	orthorhombic
Space group	*Pbca*
a (Å)	17.117(6)
b (Å)	8.516(3)
c (Å)	20.140(7)
V (Å^3)	2935.7(19)
D_{calc} (g · cm^{-3})	1.894
Absorption coefficient (mm^{-1})	1.794
F(000)	1716
Crystal dimension (mm)	0.20×0.16×0.12
θ Range for data collection (°)	2.02–27.10
Limiting indices	$-21 \le h \le 19, -10 \le k \le 10, -22 \le l \le 25$
Reflections collected/unique [R_{int}]	16312/3232 [0.0457]
Data/restraints/parameters	3232/0/277
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0261$, $wR_2 = 0.0417$
R indices (all data)	$R_1 = 0.0511$, $wR_2 = 0.0432$
Goodness-of-fit on F^2	0.703
Largest difference peak and hole (e · Å^{-3})	0.470 and –0.345

Table 2. Selected bond lengths (Å) and angles (°) for the complex.

Bond lengths			
Co(1)–O(1)	2.0638(16)	Co(1)–O(7)	2.094(2)
Co(1)–O(3)	2.1031(16)	Co(2)–O(5)	2.0711(16)
Co(2)–O(8)	2.082(2)	Co(2)–O(11)	2.0965(19)
Co(2)–O(10)	2.101(2)	Co(2)–O(9)	2.103(2)
Co(2)–O(12)	2.159(2)		

Table 2 (continuation)

Bond angles			
O(1A)–Co(1)–O(1)	180.00(9)	O(1)–Co(1)–O(7)	86.03(8)
O(1)–Co(1)–O(7A)	93.97(8)	O(7A)–Co(1)–O(7)	180.00(15)
O(1)–Co(1)–O(3)	89.51(6)	O(1)–Co(1)–O(3A)	90.49(6)
O(7)–Co(1)–O(3)	84.72(8)	O(7)–Co(1)–O(3A)	95.28(8)
O(5)–Co(2)–O(8)	86.69(8)	O(5)–Co(2)–O(11)	94.64(7)
O(8)–Co(2)–O(11)	178.56(9)	O(5)–Co(2)–O(10)	175.86(8)
O(8)–Co(2)–O(10)	90.74(9)	O(11)–Co(2)–O(10)	87.90(8)
O(5)–Co(2)–O(9)	89.52(7)	O(8)–Co(2)–O(9)	86.78(10)
O(11)–Co(2)–O(9)	92.67(9)	O(10)–Co(2)–O(9)	87.09(9)
O(5)–Co(2)–O(12)	92.22(7)	O(8)–Co(2)–O(12)	93.11(9)
O(11)–Co(2)–O(12)	87.39(8)	O(10)–Co(2)–O(12)	91.16(9)
O(9)–Co(2)–O(12)	178.25(8)		

Synthesis of the complex $\{[Co_3(C_6(COO)_6)(H_2O)_{12}]\}\cdot 6H_2O\}_n$: A dilute NaOH solution was added dropwise into a mixture of H_2O and mellitic acid (0.1163 g, 3.40×10^{-4} mol) until the PH value was *ca.* 5. Then the mixture and $Co(ClO_4)_2\cdot 6H_2O$ (0.3781 g, 1.03×10^{-3} mol) were mixed and stirred for a few minutes. The pink single crystals were obtained after the filtered solution (*ca*. 25 cm^3) was allowed to stand at room temperature for a month.

RESULTS AND DISCUSSION

IR spectra: Compared with the peaks of mellitic acid, the characteristic peaks of the carboxylates at 1734, 1624 and 1431 cm^{-1} have shifted to 1575, 1442 and 1340 cm^{-1}, repectively, which indicate that the carboxylates take part in the coordination. In addition, a strong and broad band for the coordinated H_2O molecules and the uncoordinated H_2O molecules appears at *ca.* 3400 cm^{-1}.

Crystal structure: Fig. 1 shows the coordination diagram of the complex with the atom numbering scheme. It indicates that all carboxylate groups take part in coordination in monodentate mode and according to the difference of the coordinated spheres, the Co(II) ions are classified into two kinds, which are shown in Co(1) atom and Co(2) atom, respectively. Co(1) atom is coordinated by six oxygen atoms, in which O(1) and O(2) atoms are from two H_2O molecules and other four oxygen atoms are from two benzene-hexacarboxylate anions. It is very interesting that a seven-member chelated ring was formed by the coordination of the two ortho-carboxylate groups to the same cobalt(II) ion, and it occurs rarely in complexes [16]. The Co–O bond distances are 2.0638(16) Å for Co(1)–O(1), 2.131(16) Å for Co(1)–O(3) and 2.049 Å for Co(1)–O(7). When the two Co(1)–O bonds are in *cis*-positions the associated angles range from 84.72(8)° to 95.28(8)°, which means that the coordinate sphere for Co(1) atom is a distorted octahedron. Co(2) atom is also coordinated by six oxygen atoms, in which five oxygen atoms come from five H_2O molecules and another one is from a carboxylate group. The data of the bond distances and the associated angles also indicate that Co(2) atom lies in a distorted octahedron. Obviously, the coordinate mode of the present complex is different from that of other complexes [20–23], in which benzene-hexacarboxylate is used as ligand. The Co(II) ions, the coordinated atoms and the atoms of benzen-hexacarboxylate constitute different planes and some of them are C(1), C(2), C(3), C(1B), C(2B) and C(3B) atoms in plane 1; Co(1), O(1), O(3), O(1A) and O(3A) atoms in plane 2; Co(2), O(5), O(9), O(10) and O(12) atoms in plane 3 closely; O(3), O(4) and C(5) atoms in plane 4; O(1), C(4) and O(2) atoms in plane 5, and O(5), C(6) and O(6) atoms in plane 6. The degrees between the planes are 68.3° for planes 1 and 4; 112.3° for planes 1 and 5; 51.2° for planes 1 and 6; 59.0° for planes 2 and 4; 122.1° for planes 2 and 5; 26.2° for planes 3 and 6. Fig. 2 shows the one-dimensional chain structure and it indicates that the chain consists of the seven-member rings and the benzene-rings. Fig. 3 displays the unit cell and the arrangement of the chains in the crystal. It can be known that the one-dimensional chain lies along *b* axis and the chains are arranged orderly along *c* direction through the hydrogen bonding, which constitute the two-dimensional sheet in *bc* plane and the sheets pile up along *a* direction to form the three-dimensional structure.

Magnetic properties: Fig. 4 shows the relationship of $\chi_M T$ *versus T*, where χ_M is the molar magnetic susceptibility per Co_3 unit. At room temperature, the value of $\chi_M T$ is 5.733 $cm^3 \cdot K \cdot mol^{-1}$, which is close to value expected for isolated three S = 3/2

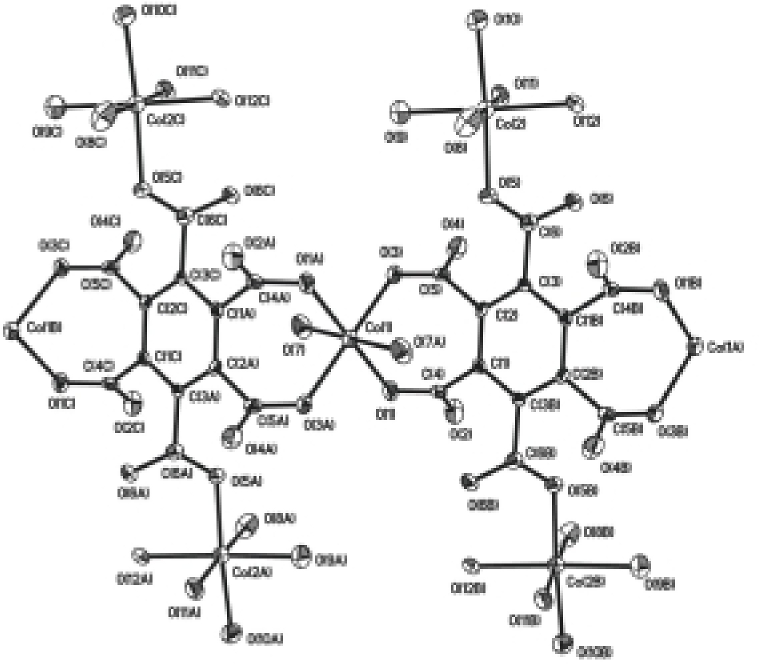

Figure 1. A diagram of the title complex coordination with atom numbering scheme.

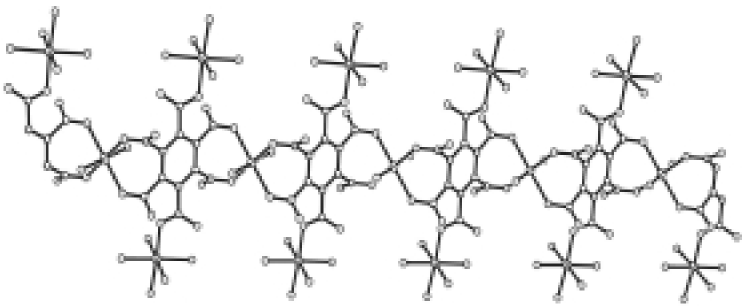

Figure 2. Structure of the one-dimensional chain.

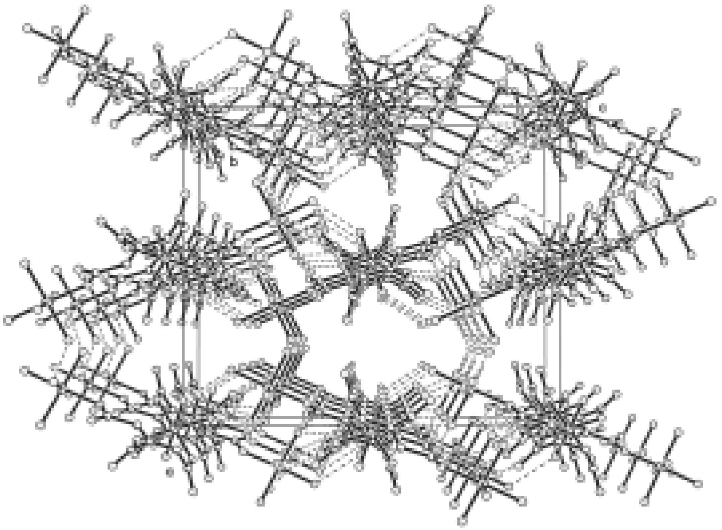

Figure 3. Packing plot of the complex viewed along *b* axis of the unit cell.

spins (5.627 for $g_{Co} = 2$). The $\chi_M T$ values decrease gradually with the decreasing temperature, from 5.733 $cm^3 \cdot K \cdot mol^{-1}$ at 300 K reach 3.283 $cm^3 \cdot K \cdot mol^{-1}$ at 4.92 K. Viewed from the crystal structure, the major magnetic interaction of the present complex deals with Co(1) and Co(1A) ions, Co(1) and Co(1B) ions, Co(1) and Co(2) ions, and Co(1) and Co(2B) ions. Obviously, it is not a uniform chain structure and up to now there is no appropriate theoretic model to be used in the structure. We use the Curie-Weiss law to analyze the magnetic data tentatively and the values of magnetic susceptibility obey this law with a negative Weiss constant $\theta = -10.644$ K. The θ value suggests that there exists a weak antiferromagnetic coupling between the Co(II) ions. Generally, one of the factors that affect the magnetic exchange interaction is whether

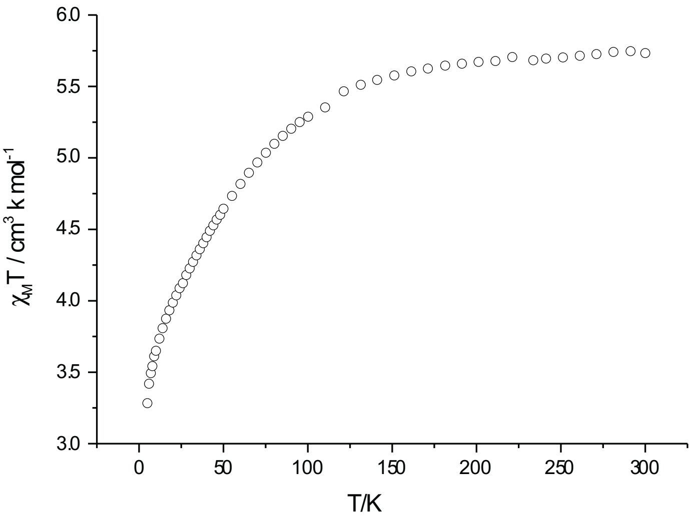

Figure 4. The relationship of $\chi_M T$ *versus T.*

there exists a delocalized π orbital between the bridging parametallic ions [24–25]. In the present complex the values of the angles between the planes, as mentioned above, indicate that there exist no delocalized π orbitals between Co(1) ion and Co(1A) ion, or between Co(1) ion and Co(2) ion, which constitutes one of the factors that limit the magnetic exchange interaction effectively and leads to the weak coupling between the cobalt(II) ions.

Supplemental material: The X-ray crystallographic file, in CIF format, has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 198792 for the crystal. Copy of this information may be obtained free of charge from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail:deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk/conts/retrieving.html

Acknowledgments

This project was supported by the National Nature Science Foundation of China (No. 20271043) and the Natural Science Foundation of Shandong Province, China (No. Y2002B10).

REFERENCES

1. Verdaguer M., Gouteron J., Jeannin S., Jeannin Y. and Kahn O., *Inorg. Chem.*, **23**, 4291 (1984).
2. Bakalbassis E.G., Bozopoulos A.P., Mrozinski J., Rentzeperis P.J. and Tsipis C.A.,*Inorg. Chem*., **27**, 529 (1988).
3. Deng Z.L., Shi J., Jiang Z.H., Liao D.Z., Yan S.P., Wang G.L., Wang H.G. and Wang R.J., *Polyhedron*, **11**, 885 (1992).
4. Xanthopoulos C.E., Sigalas M.P., Katsoulos G.A., Tsipis C.A., Terzis A., Mentzafos M. and Hountas A., *Inorg. Chem.*, **32**, 5433 (1993).

5. Bakalbassis E., Bergerat P., Kahn O., Jeannin S., Jeannin Y., Dromzee Y. and Guillot M., *Inorg. Chem.*, **31**, 625 (1992).
6. Choi H.J. and Suh M.P., *Inorg. Chem.*, **38**, 6309 (1999).
7. Sun D.F., Cao R., Liang Y.C., Shi Q., Su W.P. and Hong M.C.,*J. Chem. Soc., Dalton Trans*., 2335 (2001).
8. Shakhatreh S.K., Bakalbassis E.G., Brudgam I., Hartl H., Mrozinski J. and Tsipis C.A.,*Inorg. Chem*., **30**, 2801 (1991).
9. Bakalbassis E.G. and Terzis A., *Inorg. Chim. Acta*, **218**, 167 (1994).
10. Jiang Z.H., Ma S.L., Liao D.Z., Yan S.P., Wang G.L., Yao X.K. and Wang R.J., *Science in China, Series B*, **37**, 923 (1994).
11. Bakalbassis E.G., Paschalidis D.G., Raptopoulou C.P. and Tangoulis V., *Inorg. Chem.*, **37**, 4735 (1998).
12. Smith G., Reddy A.N., Byriel K.A. and Kennard C.H.L., *J. Chem. Soc., Dalton Trans*., 3565 (1995).
13. Chui S.S.Y., Lo S.M.F., Charmant J.P., Orpen A.G. and Williams L.D., *Science*, **283**, 1148 (1999).
14. Prior T.J. and Rosseinsky M.J., *J. Chem. Soc., Chem. Commun.*, 1222 (2001).
15. Plater M.J., Foreman M.R.St.J., Howie R.A., Skakle J.M.S., Coronado E., Gomez-Garcia C.J., Gelbrich T. and Hursthouse M.B., *Inorg. Chim. Acta*, **319**, 159 (2001).
16. Chaudhuri P., Oder K., Wieghardt K., Gehring S., Haase W., Nuber B. and Werss J., *J. Am. Chem. Soc*., **110**, 3657 (1988).
17. Shi Q., Cao R., Sun D.F., Hong M.C. and Liang Y.C., *Polyhedron*, **20**, 3287 (2001).
18. Rochon F.D. and Massarweh G., *Inorg. Chim. Acta*, **314**, 163 (2001).
19. Plater M.J., Foreman M.R.St.J., Howie R.A., Skakle J.M.S. and Slawin A.M.Z., *Inorg. Chim. Acta*, **315**, 126 (2001).
20. Tamura H., Ogawa K. and Mori W., *J. Crystall. Spectro. Research*., **19**, 203 (1989).
21. Wu L.P., Yamamoto M., Kuroda-Sowa T., Maekawa M., Fukui J. and Munakata M., *Inorg. Chim. Acta*, **239**, 165 (1995).
22. Wu L.P., Munakata M., Kuroda-Sowa T., Maekawa M. and Suenaga Y., *Inorg. Chim. Acta*, **249**, 183 (1996).
23. Zhao M.G., Liu C.Q., Shi J.M. and Xu W., *Trans. Met. Chem*., in press.
24. Kahn O., *Angew. Chem. Int. Ed. Engl*., **24**, 834 (1985).
25. Shi J.M., Xu W., Xu W. and Wu C.J., *Trans. Met. Chem.*, **28**, 308 (2003).