

## Bis[ $\mu$ -*N,N'*-bis(3-methylsalicylidene)-propane-1,3-diaminato]dicobalt(II) 0.28-hydrate

Zhong-Lu You

Department of Chemistry and Chemical Engineering, Liaoning Normal University, Dalian 116029, People's Republic of China

Correspondence e-mail: youzhonglu@yahoo.com.cn

Received 5 May 2005

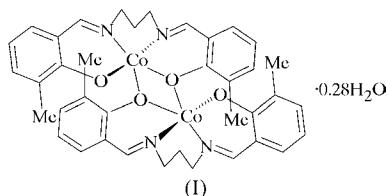
Accepted 16 June 2005

Online 30 June 2005

The title complex, bis[ $\mu$ -6,6-dimethyl-2,2'-[propane-1,3-diyl-bis(nitrilomethylidyne)]diphenolato]dicobalt(II) 0.28-hydrate, [Co<sub>2</sub>(C<sub>19</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>] $\cdot$ 0.28H<sub>2</sub>O, is a dinuclear cobalt(II) complex, which crystallizes in the tetragonal space group *P*<sub>4</sub><sub>1</sub><sub>2</sub><sub>1</sub><sup>2</sup>. The complex molecule is located on a twofold symmetry axis. Each Co<sup>II</sup> ion is five-coordinated by two O and two N atoms from a Schiff base ligand, and by another bridging phenolate O atom from another Schiff base ligand, giving a severely distorted trigonal-bipyramidal coordination environment.

### Comment

Investigation into the magnetic properties of molecule-based materials containing a polymetallic assembly has become a fascinating subject in the field of condensed matter physics and materials chemistry (Dalai *et al.*, 2002; Bhaduri *et al.*, 2003). Much attention has been focused on coordination complexes with novel magnetic properties, which may have potentially useful applications in materials science (Ray *et al.*, 2003). The prime strategy for designing these molecular materials is to use a suitable bridging ligand that determines the nature of the magnetic interactions (Koner *et al.*, 2003).



Our work is aimed at obtaining polymetallic complexes. Based on the above considerations, we have designed and synthesized a flexible tetradentate bridging ligand, namely *N,N'*-bis(3-methylsalicylidene)propane-1,3-diamine (BMPD). The reason we do not use a rigid ligand is that the flexible BMPD ligand can adopt different coordination modes according to the geometric needs of the transition metal ions and the coordination environment (You *et al.*, 2004a). The

phenolate O atoms, acting as bridging ligands, can easily bridge different metal ions, forming polynuclear complexes (You & Zhu, 2004). To the best of our knowledge, Schiff base complexes synthesized under solvothermal conditions have rarely been reported (You *et al.*, 2004b). Furthermore, very few Schiff bases have so far been derived from 3-methylsalicylaldehyde. We report here the title novel dinuclear cobalt(II) complex, (I), formed by the reaction of the BMPD ligand with cobalt(II) acetate under solvothermal conditions.

Complex (I) is a phenolate *O:O*-bridged dinuclear cobalt(II) compound (Fig. 1) which crystallizes in the tetragonal space group *P*<sub>4</sub><sub>1</sub><sub>2</sub><sub>1</sub><sup>2</sup>. The complex molecule is located on a twofold symmetry axis. The structure contains a lattice water molecule, with an occupancy of 0.28. Each cobalt(II) ion in the complex is five-coordinated, by two imine N and two phenolate O atoms from a Schiff base ligand, and by another bridging phenolate O atom from another Schiff base ligand. The Co $\cdots$ Co separation is 3.124 (2) Å. The bond lengths related to the metal ion are comparable with the corresponding values observed in another Schiff base cobalt(II) complex (You *et al.*, 2004c). It is obvious that the Co1–O2 distance [2.100 (2) Å; Table 1] is longer than the Co1–O1 distance [1.932 (2) Å], due to the coordination of atom O2 to both Co1 and Co1<sup>i</sup> [symmetry code: (i) 1 – *y*, 1 – *x*,  $\frac{1}{2}$  – *z*]. The coordination of atom O2 simultaneously to two metal ions weakens the Co–O bond. The bond lengths of C8=N1 [1.285 (3) Å] and C12=N2 [1.282 (3) Å] conform to the value for a double bond, while the bond lengths of C9–N1 [1.475 (3) Å] and C11–N2 [1.473 (3) Å] conform to the value for a single bond.

The question arises as to whether the coordination polyhedron around each cobalt(II) ion can be described as a distorted square pyramid or a distorted trigonal bipyramid. Further information can be obtained by determining the structural index  $\tau$  which represents the relative amount of trigonality (square pyramid,  $\tau = 0$ ; trigonal bipyramid,  $\tau = 1$ ; Addison *et al.*, 1984).  $\tau = (\beta - \alpha)/60^\circ$ ,  $\alpha$  and  $\beta$  being the two largest angles around the central atom. The value of  $\tau$  for each Co<sup>II</sup> ion in (I) is 0.629, indicating the coordination geometry of

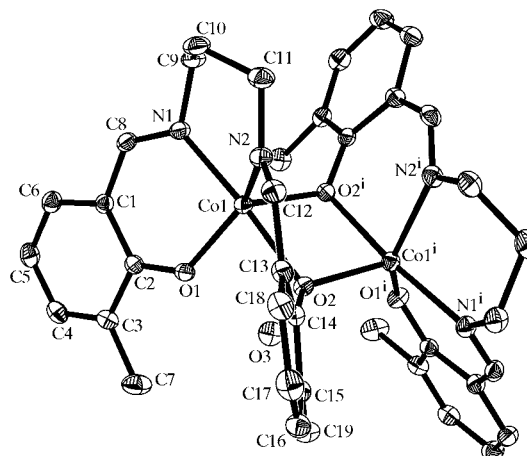


Figure 1

The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. All H atoms have been omitted for clarity. [Symmetry code: (i) 1 – *y*, 1 – *x*,  $\frac{1}{2}$  – *z*.]

each Co<sup>II</sup> ion is a severely distorted trigonal bipyramid. Atoms O1, N2 and O2<sup>i</sup> act as the basal plane of the trigonal bipyramid, while the apical positions are occupied by atoms N1 and O2. Atom O2<sup>i</sup> acts as a basal donor for the Co1 moiety and as an axial donor atom for the Co1<sup>i</sup> moiety. The deviation of atom Co1 from the least-squares plane defined by atoms N2, O1 and O2<sup>i</sup> towards N1 is 0.202 (2) Å.

The O2—Co1—O2<sup>i</sup> bond angle [79.91 (7) °] is much smaller than the N1—Co1—O2<sup>i</sup> angle [106.27 (7) °], due to the strain created by the four-membered bridging ring Co1/O2/Co1<sup>i</sup>/O2<sup>i</sup>. This ring is not planar but slightly roof-shaped. The chelate ring formed by atoms Co1/N1/C9—C11/N2 has a chair conformation. The diagonally positioned atoms Co1 and C10 are displaced from the least-squares plane defined by atoms N1/N2/C9/C11 by -0.724 (2) and 0.702 (5) Å, respectively. The dihedral angle [61.2 (2)°] between the two benzene rings, C1—C6 and C13—C18, is bigger than the corresponding value of 52.7 (3)° observed in another Schiff base cobalt(II) complex, viz. [N,N'-bis(2-hydroxynaphthylmethylene)propane-1,3-diaminato]cobalt(II) (You *et al.*, 2004d), which is probably due to the coordination of O2 to Co1<sup>i</sup> and O2<sup>i</sup> to Co1.

Experimental

3-Methylsalicylaldehyde (0.2 mmol, 26.8 mg) and propane-1,3-diamine (0.1 mmol, 7.4 mg) were dissolved in MeOH (5 ml). The mixture was stirred at room temperature for 10 min to give a yellow mixture, to which was added an MeOH solution (3 ml) of Co(CH<sub>3</sub>-COO)<sub>2</sub>·4H<sub>2</sub>O (0.1 mmol, 25.1 mg). The mixture was stirred for another 10 min at room temperature and then transferred to a stainless steel bomb, which was sealed, heated at 423 K for 12 h, and cooled gradually to room temperature, whereupon brown block-shaped crystals of (I) formed.

Crystal data

[Co<sub>2</sub>(C<sub>19</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>)<sub>2</sub>].0.28H<sub>2</sub>O Mo Kα radiation  
M<sub>r</sub> = 739.08 Cell parameters from 9201 reflections  
Tetragonal, P4<sub>1</sub>2<sub>1</sub>2 reflections  
a = 10.381 (2) Å θ = 2.3–24.6°  
c = 32.513 (1) Å μ = 0.99 mm<sup>-1</sup>  
V = 3503.8 (10) Å<sup>3</sup> T = 298 (2) K  
Z = 4 Block, brown  
D<sub>x</sub> = 1.393 Mg m<sup>-3</sup> 0.30 × 0.18 × 0.18 mm

Table 1

Selected geometric parameters (Å, °).

Co1—O1	1.930 (2)	N1—C8	1.285 (3)
Co1—O2 <sup>i</sup>	1.994 (2)	N1—C9	1.475 (3)
Co1—N1	2.044 (2)	N2—C12	1.282 (3)
Co1—N2	2.074 (2)	N2—C11	1.473 (3)
Co1—O2	2.100 (2)		
O1—Co1—O2 <sup>i</sup>	114.31 (7)	N1—Co1—N2	92.54 (8)
O1—Co1—N1	91.38 (7)	O1—Co1—O2	86.74 (7)
O2 <sup>i</sup> —Co1—N1	106.27 (7)	O2 <sup>i</sup> —Co1—O2	79.91 (7)
O1—Co1—N2	136.01 (8)	N1—Co1—O2	173.77 (7)
O2 <sup>i</sup> —Co1—N2	106.47 (7)	N2—Co1—O2	84.73 (7)

Symmetry code: (i) -y + 1, -x + 1, -z + ½.

Data collection

Bruker SMART CCD area-detector 4024 independent reflections  
diffractometer 3729 reflections with I > 2σ(I)  
ω scans R<sub>int</sub> = 0.040  
Absorption correction: multi-scan θ<sub>max</sub> = 27.5°  
(SADABS; Sheldrick, 1996) h = -13 → 13  
T<sub>min</sub> = 0.755, T<sub>max</sub> = 0.842 k = -13 → 13  
30177 measured reflections l = -42 → 42

Refinement

Refinement on F<sup>2</sup> w = 1/[σ<sup>2</sup>(F<sub>o</sub><sup>2</sup>) + (0.0334P)<sup>2</sup>  
R[F<sup>2</sup> > 2σ(F<sup>2</sup>)] = 0.033 + 0.8675P]  
wR(F<sup>2</sup>) = 0.078 where P = (F<sub>o</sub><sup>2</sup> + 2F<sub>c</sub><sup>2</sup>)/3  
S = 1.09 (Δ/σ)<sub>max</sub> < 0.001  
4024 reflections Δρ<sub>max</sub> = 0.39 e Å<sup>-3</sup>  
221 parameters Δρ<sub>min</sub> = -0.17 e Å<sup>-3</sup>  
H-atom parameters constrained Absolute structure: Flack (1983)  
Flack parameter: 0.006 (16)

All H atoms were placed in geometrically idealized positions and allowed to ride on their parent atoms, with C—H distances in the range 0.93–0.97 Å and with U<sub>iso</sub>(H) = 1.2 or 1.5U<sub>eq</sub>(C). The structure contains a lattice water molecule, with an occupancy of 0.28. There are 1606 Friedel pairs.

Data collection: SMART (Bruker, 1998); cell refinement: SMART; data reduction: SAINT (Bruker, 1998); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a); molecular graphics: SHELXTL (Sheldrick, 1997b); software used to prepare material for publication: SHELXTL.

The author thanks Liaoning Normal University, People's Republic of China, for funding this study.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1247). Services for accessing these data are described at the back of the journal.

References

Addison, A. W., Rao, T. N., Reedijk, J., van Rijn, J. & Verschoor, G. C. (1984). *J. Chem. Soc. Dalton Trans.* pp. 1349–1356.  
Bhaduri, S., Tasiopoulos, A. J., Bolcar, M. A., Abboud, K. A., Streib, W. E. & Christou, G. (2003). *Inorg. Chem.* **42**, 1483–1492.  
Bruker (1998). SMART (Version 5.628) and SAINT (Version 6.02). Bruker AXS Inc., Madison, Wisconsin, USA.  
Dalai, S., Mukherjee, P. S., Drew, M. G. B., Lu, T.-H. & Chaudhuri, N. R. (2002). *Inorg. Chim. Acta*, **335**, 85–90.  
Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.  
Koner, S., Saha, S., Okamoto, K.-I. & Tuchagues, J.-P. (2003). *Inorg. Chem.* **42**, 4668–4672.  
Ray, M. S., Mukhopadhyay, G., Drew, M. G. B., Lu, T.-H., Chaudhuri, S. & Ghosh, A. (2003). *Inorg. Chem. Commun.* **6**, 961–965.  
Sheldrick, G. M. (1996). SADABS. University of Göttingen, Germany.  
Sheldrick, G. M. (1997a). SHELXS97 and SHELXL97. University of Göttingen, Germany.  
Sheldrick, G. M. (1997b). SHELXTL. Version 5.10. Bruker AXS Inc., Madison, Wisconsin, USA.  
You, Z.-L. & Zhu, H.-L. (2004). *Acta Cryst.* **C60**, m445–m446.  
You, Z.-L., Zhu, H.-L. & Liu, W.-S. (2004a). *Acta Cryst.* **E60**, m805–m807.  
You, Z.-L., Zhu, H.-L. & Liu, W.-S. (2004b). *Z. Anorg. Allg. Chem.* **630**, 1617–1622.  
You, Z.-L., Zhu, H.-L. & Liu, W.-S. (2004c). *Acta Cryst.* **E60**, m1900–m1902.  
You, Z.-L., Zhu, H.-L. & Liu, W.-S. (2004d). *Acta Cryst.* **E60**, m654–m656.