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ISSN: 2414-3146

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IUCrData (2020). **5**, x200796



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Di- μ -aqua-bis[aqua(2,2'-bipyridine)(4-nitrobenzoato)cobalt(II)] bis(4-nitrobenzoate)

Bikshandarkoil R. Srinivasan, Sarvesh S. Harmalkar, Luann R. D'Souza and Sunder N. Dhuri*

School of Chemical Sciences, Goa University, Goa 403206, India. *Correspondence e-mail: sndhuri@unigoa.ac.in

Received 27 May 2020

Accepted 13 June 2020

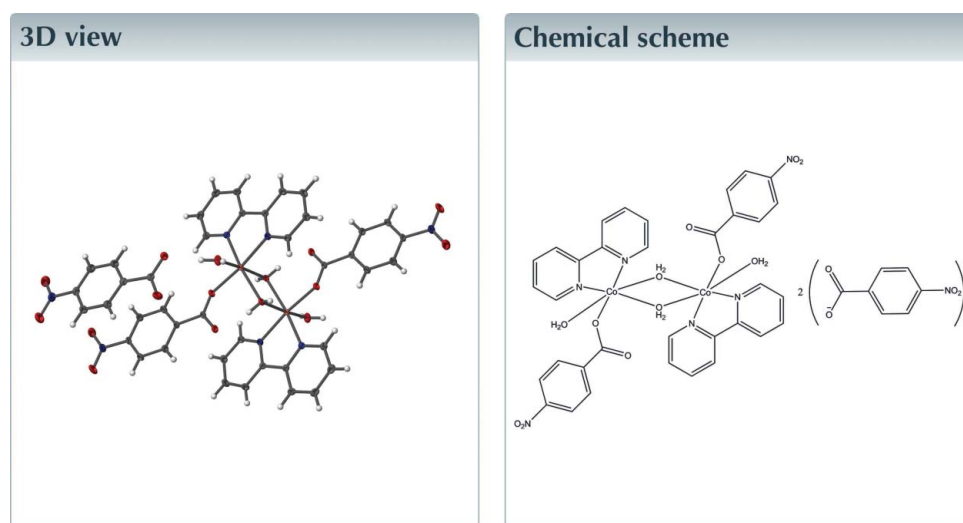
Edited by W. T. A. Harrison, University of Aberdeen, Scotland

Keywords: crystal structure; bimetallic complex; divalent-metal 4-nitrobenzoate; hydrogen bonds.

CCDC reference: 2009578

Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $[\text{Co}_2(\text{C}_7\text{H}_4\text{NO}_4)_2(\text{C}_{10}\text{H}_8\text{N}_2)_2(\text{H}_2\text{O})_4](\text{C}_7\text{H}_4\text{NO}_4)_2$, consists of a centrosymmetric bimetallic complex charge-balanced by free 4-nitrobenzoate anions. The Co^{II} ion exhibits a distorted *cis*- CoN_2O_4 octahedral coordination environment and the $\text{Co}\cdots\text{Co}$ separation is 3.326 (2) Å. In the crystal, the dications and anions are linked by $\text{O}\cdots\text{H}\cdots\text{O}$ and $\text{C}\cdots\text{H}\cdots\text{O}$ hydrogen bonds.



Structure description

As part of an ongoing research program we are investigating the structural aspects of mixed-ligand compounds of divalent-metal 4-nitrobenzoates. Recently we described the structure of $[\text{Co}(\text{H}_2\text{O})_2(\text{DMSO})_2(\text{C}_7\text{H}_4\text{NO}_4)](\text{C}_7\text{H}_4\text{NO}_4)$ **2** (DMSO = dimethylsulfoxide; $\text{C}_7\text{H}_4\text{NO}_4$ = 4-nitrobenzoate) containing a bidentate as well as a free 4-nitrobenzoate anion (Srinivasan *et al.*, 2020). Our attempts to replace the *cis*-aqua ligands of **2** with 2,2'-bipyridine has resulted in the isolation of the diaqua-bridged title dinuclear compound. The Cambridge Structural Database (CSD, version 5.40, update September 2019; Groom *et al.*, 2016) lists the structures of several cobalt 4-nitrobenzoates: of these, more than a dozen are mononuclear cobalt compounds (Srinivasan *et al.*, 2004, 2020; Chakravorty *et al.*, 2011) while only four dinuclear compounds of 4-nitrobenzoate are known to date (Singh *et al.*, 2007; Jung *et al.*, 2009; Yang *et al.*, 2011; Wang & Qi, 2014). The title compound is a new addition to the list of dimeric cobalt 4-nitrobenzoates.

The structure of the title compound, **1**, consists of a crystallographically unique cobaltous ion and a 2,2'-bipyridine molecule, two crystallographically independent 4-nitrobenzoate ions and two unique aqua ligands (one terminal, one bridging). The Co^{II} ion, one 4-nitrobenzoate ion, one 2,2'-bipyridine molecule and each of a terminal and bridging water molecule build up one half of a dimeric dicationic species



Table 1
Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O2 <i>W</i> —H2 <i>B</i> ···O5 ⁱ	0.84 (2)	1.67 (2)	2.5101 (13)	173 (2)
O2 <i>W</i> —H2 <i>A</i> ···O3	0.79 (2)	1.88 (2)	2.6483 (13)	164 (2)
O1 <i>W</i> —H1 <i>B</i> ···O3 ⁱⁱ	0.82 (2)	2.04 (2)	2.8477 (14)	174 (2)
O1 <i>W</i> —H1 <i>A</i> ···O6 ⁱⁱⁱ	0.81 (2)	1.88 (2)	2.6803 (14)	171 (2)
C21—H21···O2 ^{iv}	0.93	2.48	3.2219 (17)	137
C17—H17···O5 ⁱ	0.93	2.24	3.1679 (16)	172
C16—H16···O2 ^v	0.93	2.57	3.4644 (17)	160
C14—H14···O6 ^{vi}	0.93	2.41	3.3126 (16)	164
C9—H9···O7 ^{vii}	0.93	2.64	3.5467 (18)	164

Symmetry codes: (i) $x - 1, y, z$; (ii) $-x, -y + 1, -z + 1$; (iii) $-x + 1, -y + 1, -z + 1$; (iv) $x + 1, y, z - 1$; (v) $x, y, z - 1$; (vi) $x, y + 1, z$; (vii) $x, y + 1, z + 1$.

[Co₂(H₂O)₂(C₁₀H₈N₂)₂(C₇H₄NO₄)₂(μ₂-H₂O)₂]²⁺, the other half being generated by inversion symmetry (Fig. 1). The crystallographic inversion centre is situated at the midpoint of the line connecting the Co^{II} atoms in the dimer. A charge-balancing 4-nitrobenzoate ion completes the structure.

In the centrosymmetric dimer, each Co^{II} ion exhibits a distorted octahedral environment and is bonded to a terminal aqua ligand, a monodentate 4-nitrobenzoate ligand disposed *cis* to the terminal aqua ligand and a bidentate 2,2'-bipyridine molecule. A pair of *cis*-aqua ligands bridges the metal centres

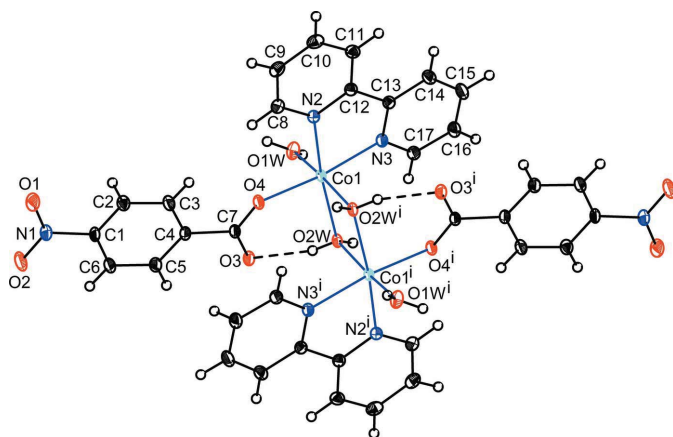


Figure 1
The dinuclear dication in **1** with displacement ellipsoids drawn at the 50% probability level. Intramolecular hydrogen bonds are shown as broken lines [Symmetry code: (i) $1 - x, 1 - y, 1 - z$].

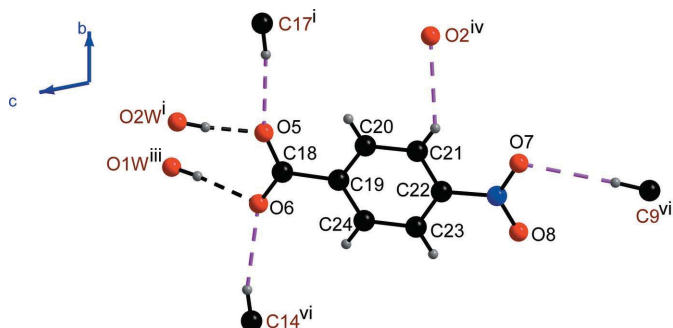


Figure 2
The hydrogen-bonding scheme around the 4-nitrobenzoate anion showing the O—H···O and C—H···O hydrogen bonds as dashed lines. For symmetry codes see Table 1.

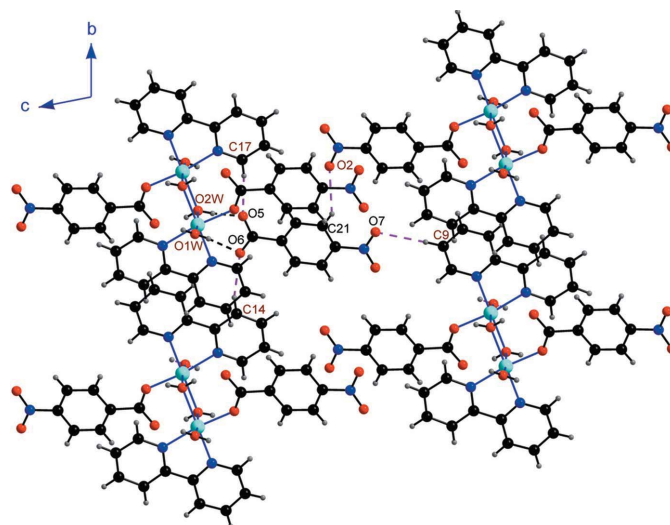


Figure 3
Environment of the anion, showing its hydrogen bonds to four symmetrically related dicationic units *via* O—H···O and C—H···O bonds.

and completes the hexa-coordination around the metal ions resulting in a Co···Co($1 - x, 1 - y, 1 - z$) separation of 3.326 (2) Å. It is interesting to note that in three of the four known dinuclear cobalt compounds (Singh *et al.*, 2007; Yang *et al.*, 2011; Wang & Qi, 2014), the 4-nitrobenzoate anion functions as a monodentate ligand as in the title compound. One example each of a dinuclear (Jung *et al.*, 2009) and a tetranuclear cobalt compound (Dimitrou *et al.*, 2001) is known where the 4-nitrobenzoate ion functions as a symmetric bridging ligand.

The geometric parameters of **1** are in their normal ranges and are in agreement with reported data (Srinivasan *et al.*, 2020). The Co—O_w (*w* = water) bonds [2.0743 (10) and 2.1617 (9) Å] are elongated as compared to the Co—O_c (*c* = carboxylate) distance, which is the shortest at 2.0494 (9) Å. The *cis*-O—Co—O and N—Co—N bond angles range between 77.97 (4) and 100.02 (4)°, while the *trans* bond angles deviate from ideal values, indicating a distortion of the {CoN₂O₄} octahedron.

All of the H atoms attached to the aqua ligands, and five of the other H atoms *viz.* H9, H14, H16, H17 and H21 bonded to C9, C14, C16, C17 and C21, respectively, function as hydrogen-bond donors, while the oxygen atoms O2, O3, O5, O6 and O7 of the 4-nitrobenzoate ions function as acceptors, resulting in a

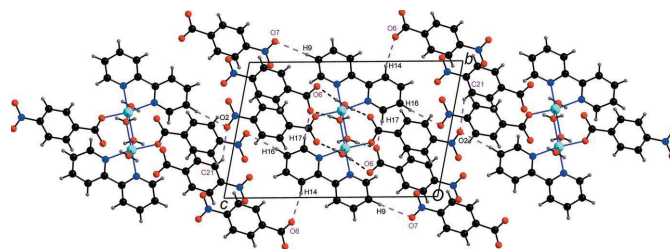


Figure 4
The hydrogen-bonding scheme around the dication showing its linking with eight anions and two cations *via* O—H···O and C—H···O hydrogen bonds.

total of four O—H···O and five C—H···O hydrogen bonds (Table 1). Each free 4-nitrobenzoate anion is linked with four symmetry-related dications with the aid of two O—H···O hydrogen bonds and four C—H···O hydrogen bonds (Figs. 2 and 3). Each of the dinuclear dicobalt dicationic species is linked with two symmetry-related dications and eight symmetry-generated anions (Fig. 4), resulting in a three-dimensional supramolecular network.

Synthesis and crystallization

Crystals of **2** (0.0292 g, 0.05 mmol) were taken in DMSO (3 ml) to obtain a purple solution. 2,2'-Bipyridine (0.0078 g, 0.05 mmol) was dissolved in DMSO (3 ml) in a separate beaker and then was added dropwise to the cobalt solution with continuous swirling. The pale-orange solution thus obtained was left undisturbed at room temperature. After to days, dark-orange blocks of **1** started forming in the solution, which were isolated by filtration and air dried. Yield 60%.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Funding information

We thank Council of Scientific and Industrial Research (CSIR) New Delhi, for financial support.

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Table 2

Experimental details.

Crystal data	
Chemical formula	[Co ₂ (C ₇ H ₄ NO ₄) ₂ (C ₁₀ H ₈ N ₂) ₂ ·(H ₂ O) ₄](C ₇ H ₄ NO ₄) ₂
<i>M</i> _r	1166.74
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	7.2747 (5), 10.4927 (8), 16.3560 (12)
α , β , γ (°)	97.735 (2), 102.840 (2), 102.607 (2)
<i>V</i> (Å ³)	1165.70 (15)
<i>Z</i>	1
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	0.81
Crystal size (mm)	0.45 × 0.32 × 0.21
Data collection	
Diffractometer	Bruker D8 Quest eco
Absorption correction	Multi-scan (<i>SADABS</i> ; Krause <i>et al.</i> , 2015)
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	26747, 5763, 5312
<i>R</i> _{int}	0.025
($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.666
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.025, 0.064, 1.05
No. of reflections	5763
No. of parameters	368
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.36, -0.31

Computer programs: *APEX3* and *SAINT* (Bruker, 2019), *SHELXT2014/5* (Sheldrick, 20015a), *SHELXL2018* (Sheldrick, 2015b), *DIAMOND* (Brandenburg, 1999) and *shelXle* (Hübschle *et al.*, 2011).

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