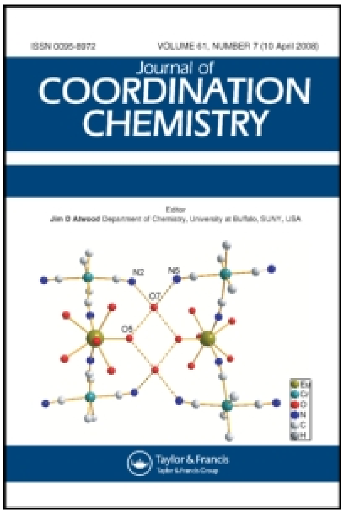

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Strongly decussated π-stacking in a Ag(I)-Co(III) complex containing a Ag_2Co_2 4^4 square tile motif

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Strongly decussated π-stacking in a Ag(I)–Co(III) complex containing a Ag_2Co_2 4^4 square tile motif

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A mixed Co–Ag complex with 2,6-dicarboxypyridine (H_2PDC), $AgCo(PDC)_2$, was synthesized under hydrothermal conditions. The complex adopts a 2D layer structure formed by intramolecular π-stacking. Each Co(III) ion is chelated by two 2,6-dicarboxypyridine anions to give the $[Co(PDC)_2]^-$ anion that is further extended by Ag^+ to form 4^4 square grids.

Keywords: Cobalt; Silver; 2,6-Dicarboxypyridine; Crystal structure; π-Stacking; Decussated structural motif

1. Introduction

The synthesis and characterization of infinite two- and three-dimensional networks has been an area of rapid growth in recent years [1–3]. Self-assembly of molecular building blocks containing organic ligands and metal ions provides an efficient and reliable approach for the design and synthesis of such organic-inorganic hybrid materials [4, 5]. The control of network topologies and structural motifs results in many different molecular and crystal architectures. Many examples of 2D metal–organic frameworks with topologies such as 4^4 squares, 6^3 hexagons or 3^6 triangles have been reported [6–8]. In this context, we introduced a 2D framework with 4^4 tile motifs based on 2,6-dicarboxypyridine (H_2PDC). H_2PDC has the facility to form multi-dimensional networks with 4f or 3d metals with variable coordination modes under hydrothermal conditions [9]. However, to our knowledge, there is no example of a 2D 4^4 square topology. The structure reported below is based on the $[Co(PDC)_2]^-$ anion (figure 1b)) linked by Ag^+ cations to form planar frameworks with a 4^4 tile motif (figure 1a).

2. Experimental

2.1. *Physical measurements*

Elemental analyses (C, H, N) were carried out with an Elementar Vario EL instrument. Infrared spectra (KBr pellets) were measured on a Magna-IR 560 FTIR spectrophotometer in the 400–4000 cm^{-1} range.

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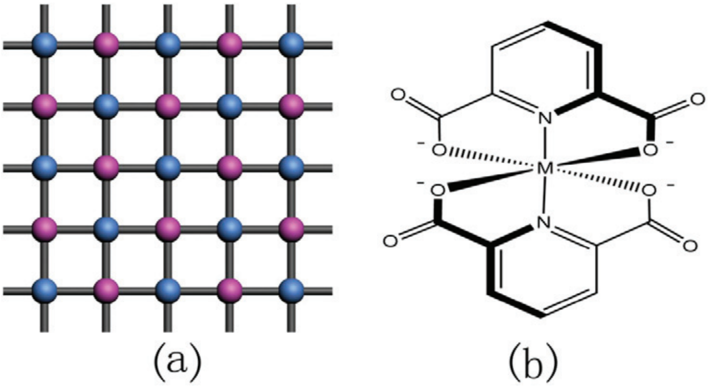

Figure 1. (a) The 2D network with 4^4 topology; (b) the $[Co(PDC)_2]^-$ building block.

2.2. *Synthesis*

$AgCo(PDC)_2$ was synthesized by mixing 2,6-dicarboxypyridine (0.33 g, 2 mmol), $Co(NO_3)_2 \cdot 6H_2O$ (0.29 g, 1 mmol), $AgNO_3$ (0.17 g, 1 mmol) and 5 cm^3 of H_2O. The mixture was heated in a 25 cm^3 acid-digestion bomb at 160°C for 7 days. Dark red crystals (30% yield) suitable for X-ray investigation were obtained. Anal. Calcd for $AgCo(PDC)_2$ (%): C, 33.83; H, 1.22; N, 5.64. Found: C, 33.16; H, 1.51; N, 5.52.

2.3. *X-ray crystallography*

Intensity data were collected with a Bruker SMART 1000 CCD diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293(2) K. The structure was solved by direct methods and refined with full-matrix least-squares techniques using the SHELXS-97 and SHELXL-97 programs [10]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms and hydrogen atoms were set in calculated positions. The weighting scheme used was $w = 1/[\sigma^2(F_o^2) + (0.0297P)^2 + 1.2736P]$ where $P = (F_o^2 + 2F_o^2)/3$. Crystallographic data are summarized in table 1 and selected bond lengths and angles are listed in table 2.

3. Result and discussion

IR spectra showed two intense peaks in the carboxyl region at 1634 (antisymmetric) and 1341 cm^{-1} (symmetric). The large difference (293 cm^{-1}) indicates the existence of unidentate coordinated carboxylate groups [11]. Two medium intensity peaks at 3083 and 3049 cm^{-1} are due to C–H stretching.

X-ray structural analysis reveals that the asymmetric unit consists of one Ag(I) ion, one Co(III) ion and two PDC^{2-} ligands. The complex crystallizes in the high symmetry space group $I4_1/a$. Co(III) has a distorted octahedral environment, with four *anti*-O(2) atoms of two PDC^{2-} ligands in the equatorial plane and two N atoms in axial

Table 1. Crystallographic data for the complex.

Formula	$AgCoC_{14}H_6N_2O_8$
Formula weight	497.01
Crystal systerm	Tetragonal
Space group	$I4_1/a$
a (Å)	6.7810(7)
b (Å)	6.7810(7)
c (Å)	28.622(6)
V (Å^3)	1316.1(3)
Z	4
D_c (g cm^{-3})	2.508
μ (mm^{-1})	2.807
Crystal size (mm^3)	$0.24 \times 0.20 \times 0.16$
θ range (°)	$2.85 < \theta < 26.36$
Reflections measured	3012
Independent reflections (R_{int})	673 (0.0298)
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0209$, $wR_2 = 0.0526$
R indices (all data)	$R_1 = 0.0279$, $wR_2 = 0.0564$
Goodness-of-fit	1.021

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

Ag(1)–O(1)	2.4679(16)	O(2)–C(1)	1.298(2)
Co(1)–N(1)	1.837(2)	N(1)–C(2)	1.333(2)
Co(1)–O(2)	1.9114(15)	O(1)–C(1)	1.221(3)
O(1)#1–Ag(1)–O(1)	87.77(7)	N(1)–Co(1)–O(2)#5	96.21(4)
O(1)–Ag(1)–O(1)#2	121.30(4)	N(1)#3–Co(1)–O(2)#5	83.79(4)
N(1)–Co(1)–N(1)#3	180	O(2)–Co(1)–O(2)#5	90.670(9)
N(1)–Co(1)–O(2)	83.79(4)	O(2)#3–Co(1)–O(2)#5	167.57(8)
O(2)#4–Co(1)–O(2)	167.58(8)	O(1)–C(1)–O(2)	124.01(19)
O(2)–Co(1)–O(2)#3	90.672(9)		

Symmetry transformations used are #1: $-x+0$, $-y+1/2$, $z+0$; #2: $y-1/4$, $-x+1/4$, $-z+5/4$; #3: $y-1/4$, $-x+5/4$, $-z+5/4$; #4: $-x+1$, $-y+3/2$, $z+0$; #5: $-y+5/4$, $x+1/4$, $-z+5/4$.

positions (figure 2). The two PDC^{2-} ligands are perpendicular to each other. The four *syn*-O(1) atoms of PDC are bonded at a distance of 2.4679(16) Å to Ag(I) to form an AgO_4 tetrahedron. All Co(III) and Ag(I) ions lie in a plane with a shortest Co $\cdots$ Ag contact of 4.795 Å. A search of the Cambridge Structural Database (version 5.26 [12]) reveals that the $[M(PDC)_2]^{n-}$ building block has been reported many times, but in those structures units are extended by interactions such as hydrogen bonding and π-stacking [13]. The present structure is the first example of 2D sheet structure with 4^4 topology. Each carboxylate group associated with two $[Co(PDC)_2]^-$ ions links two Ag(I) ions to give a 4^4 tessellated 2D net of Co_2Ag_2 groups with a Co $\cdots$ Ag separation of 4.975 Å (figure 3).

Significant π-stacking involving pyridine rings is evident between the layers. The stacking propagates along the a and b axes in a decussated fashion (figure 4). This places pyridyl rings of neighbouring layers on top of one another with a separation of 3.10 Å (centroid–centroid = 3.50 Å, slippage angle = 27.5°). The rest of the layer contents stack by filling alternate bumps and hollows in adjacent layers.

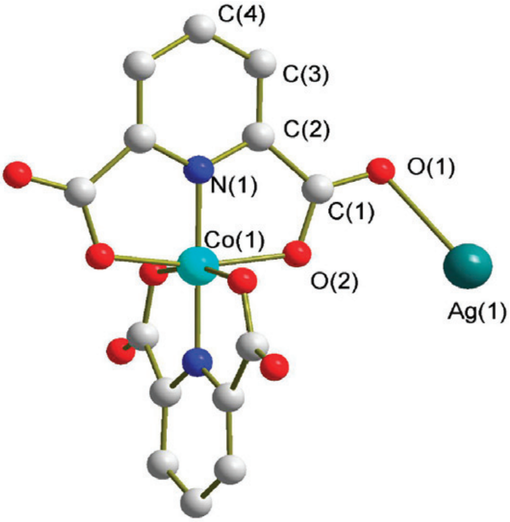

Figure 2. Molecular structure of $CoAg(PDC)_2$ showing the atom numbering scheme.

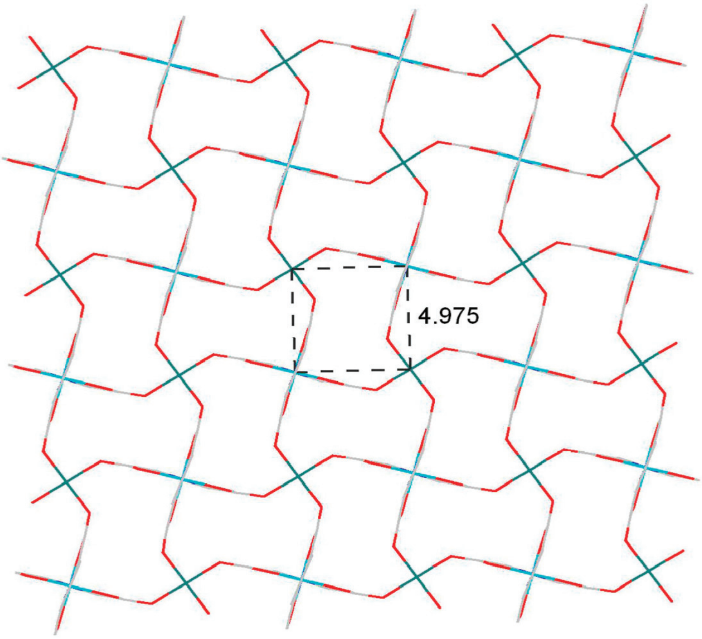

Figure 3. 2D sheet structure perpendicular to the *c* axis.

Although the π-stacking exhibits an offset face-to-face motif, the short separation distance indicates a strong π–π interaction [14]. It is expected that use of different metals or ramification of the ligand will provide a strategy to deliberately design novel related 2D or 3D architectures.

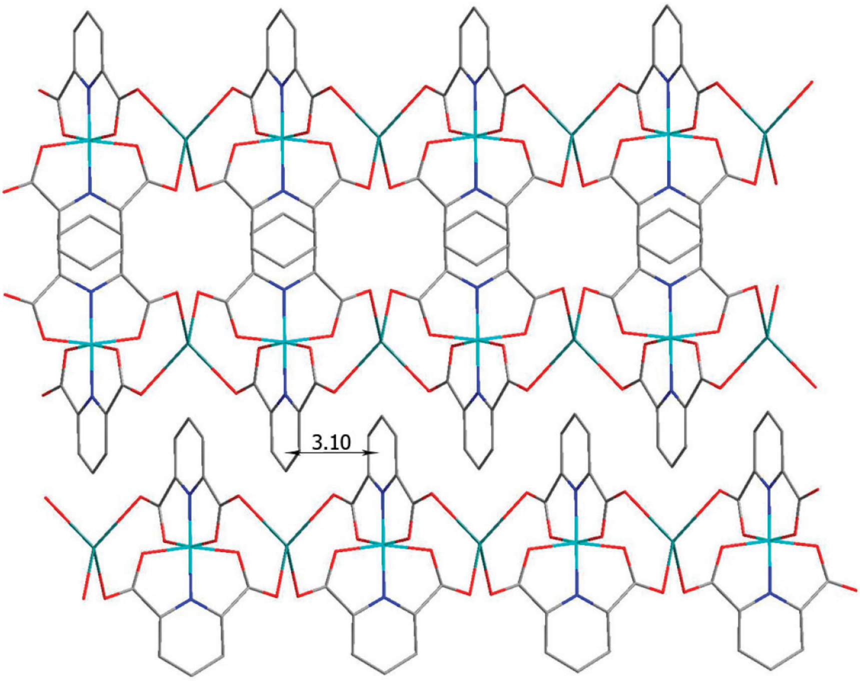

Figure 4. π-Stacking perpendicular to the *a* axis (along *b* the same arrangement is found).

Supplementary material

Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC-292757). These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or Email: deposit@ccdc.cam.ac.uk.

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