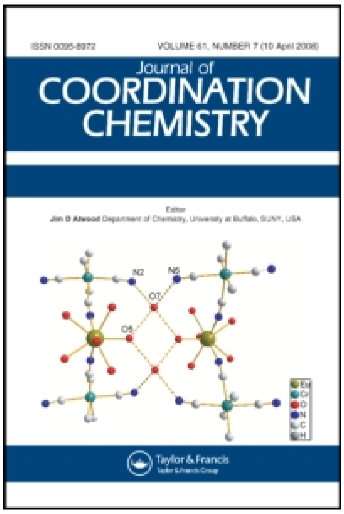

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Hydrothermal synthesis, structure and properties of a heteronuclear Co(III)-Ag(I) complex with the 2,6-pyridine-dicarboxlate

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First published on: 04 September 2007

To cite this Article Sun, Qingjin , Gao, Quanchang , Zhang, Weiping , Song, Yanhong , Xu, Zhanwei , Su, Biyun and Zhao, Jianshe(2008) 'Hydrothermal synthesis, structure and properties of a heteronuclear Co(III)-Ag(I) complex with the 2,6-pyridine-dicarboxlate', Journal of Coordination Chemistry, 61: 5, 669 — 676, First published on: 04 September 2007 (iFirst)
To link to this Article: DOI: 10.1080/00958970701411288
URL: http://dx.doi.org/10.1080/00958970701411288

Journal of Coordination Chemistry
Vol. 61, No. 5, 10 March 2008, 669–676

Hydrothermal synthesis, structure and properties of a heteronuclear Co(III)–Ag(I) complex with the 2,6-pyridine-dicarboxylate

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(*Received 26 March 2007; in final form 21 April 2007*)

A new Ag/Co coordination polymer, [AgCo(PDC)$_2$] (**1**) ($H_2PDC = 2,6$-pyridine-dicarboxylic acid) was synthesized under hydrothermal condition. X-ray crystallographic study reveals that **1** is a 2D network and has a previously unexplored coordination mode. Solid state fluorescence and thermogravimetric analysis (TGA) have been performed.

Keywords: Heteronuclear metal complex; 2,6-Pyridine-dicarboxylic acid; Hydrothermal synthesis; Thermogravimetric analysis

1. Introduction

The design and synthesis of new heteronuclear transition metal complexes [1–7] receive attention due to their interesting structural features, fascinating new topologies and potential applications in catalysis, magnetism and luminescence [8–10]. Recent studies [11–15] show that 2,6-pyridine-dicarboxylic acid (H_2PDC) tends to bind metal centers with nitrogen atoms and carboxylate groups to form extended networks, where carboxylate groups balance the metal charges. The metal centers display different coordination geometries. Inspired by this work, we chose nitrate salts of Ag (I) and Co(II) reacting with H_2PDC and attained a new 2D network structure complex [AgCo(PDC)$_2$] (**1**) under hydrothermal condition. That Co(II) was oxidized to Co(III) was confirmed by thermalgravimetric analysis [16].

Eight coordination modes (scheme 1a) are observed for H_2PDC [17]. In this complex, PDC displays a new coordination mode (see scheme 1b). Ag(I) is coordinated by four oxygen atoms of different [Co(PDC)$_2$] units.

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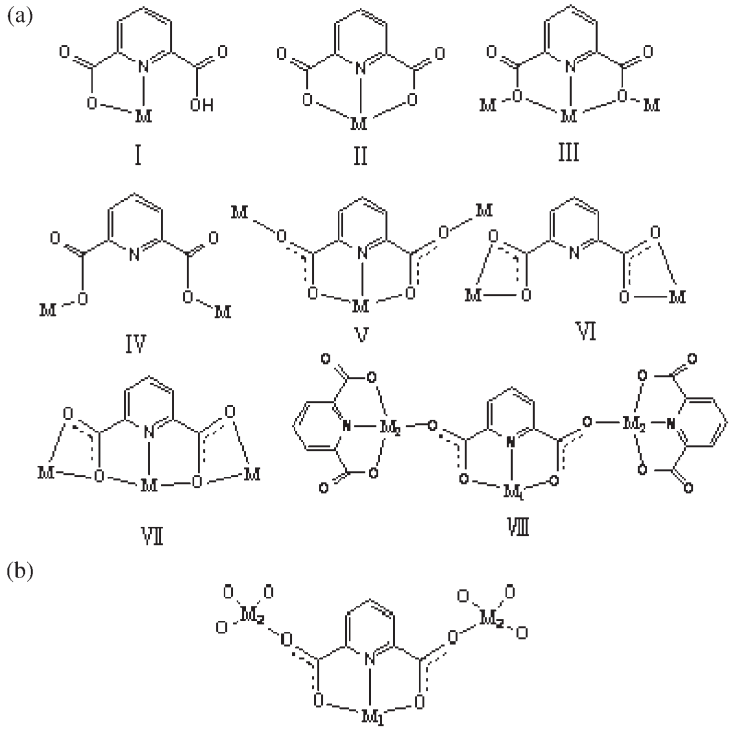
Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970701411288



Scheme 1. (a) Reported coordination modes of H_2PDC ligand; (b) coordination mode of complex **1** ($M_1 = Co$ and $M_2 = Ag$).

2. Experimental

2.1. *Main reagents and apparatus*

All reagents and solvents were of analytical or reagent grade, purchased commercially and used without further purification.

The C, H and N analyses were taken with a Perkin Elmer model 2400 element analyzer. IR spectra were recorded on an EQUINOX 55 IR spectrophotometer with KBr pellets. TGA measurements were carried out from room temperature to 850°C in a flowing nitrogen atmosphere using a Seiko Exstar 6000 TG/DTA6300 instrument with a heating rate of $10^{\circ}\,min^{-1}$. The photoluminescence spectra were performed on a Perkin–Elmer LS55 spectrofluorometer.

2.2. *Synthesis of the complex [AgCo(PDC)$_2$] (1)*

A mixture of $AgNO_3$ (85 mg, 0.5 mmol), $Co(NO_3)_2 \cdot 6H_2O$ (174.6 mg, 0.5 mmol) and H_2PDC (167.1 mg, 1.0 mmol) in the molar ratio of 1 : 1 : 2 and 5 mL 1 : 1 water : ethanol were sealed in a 10 mL stainless steel reactor with Teflon liner, and heated directly to 180°C. After keeping at 180°C for 120 h, it was cooled slowly to 30°C at a rate for $10^{\circ}C\,h^{-1}$. Purple crystals were obtained in 50% yield. Anal. Calcd for $AgCoC_{14}H_6N_2O_8$ (%): C, 33.83; H, 1.22; N, 5.64. Found: C, 33.78; H, 1.26; N, 5.70.

Table 1. Crystal data of **1**.

Empirical formula	$AgCo(C_7H_3NO_4)_2$
Formula weight	497.01
Temperature (K)	295(2)
Crystal system	Tetragonal
Space group	$I4_1/a$
a (Å)	6.8021(6)
b (Å)	6.8021
c (Å)	28.712(3)
α (°)	90.00
β (°)	90.00
γ (°)	90.00
V (Å^3)	1328.5(2)
Z	4
D_{calc} (Kg m^{-3})	2.485
μ (Mo-Kα) (mm^{-1})	2.780
Crystal size (mm^3)	0.33 × 0.26 × 0.19
F(000)	968
θ range for data collection (°)	2.8–27.5
Reflections collected	5703
Independent reflections (R_{int})	772(0.016)
Goodness-of-fit on F^2	1.11
Final R indices	$R_1 = 0.023$, $wR_2 = 0.060$
R indices (all data)	$R_1 = 0.026$, $wR_2 = 0.063$
Largest difference in peak and hole (e Å^3)	0.42 and −0.92

FT-IR (KBr, cm^{-1}): 3424 (w), 3081 (w), 2361 (w), 1628 (s), 1471 (w), 1337 (s), 1191 (w), 1004 (w), 859 (w), 824 (w), 781 (m), 754 (m), 677 (w), 492 (s), 452 (w).

2.3. *Crystal structure measurement*

The data of **1** were collected on a Bruker Smart-1000CCD diffractometer using graphite-monochromated Mo-Kα radiaton ($\lambda = 0.71073$ Å). Intensity measurements were performed using graphite monochromated Mo-Kα radiation from a sealed tube and a monocapillary collimator. SMART was used for preliminary determination of the cell constants and data collection control. The determination of integral intensities and global cell refinement were performed with the Bruker SAINT software package using a narrow-frame integrative algorithm. The structure was solved by direct methods (SHELXTL-97) and refined by the full-matrix least-squares method on F^2. The final refinement included anisotropic displacement parameters for all atoms and a secondary extinction parameter. Some crystallographic details are listed in table 1. Selected bond lengths and bond angles of **1** are listed in table 2.

3. Discussion

3.1. *Description of the crystal structure*

Complex **1** was analyzed by single crystal X-ray crystallography. The molecular structure consists of heteronuclear $[AgCo(PDC)_2]$ units, as shown in figure 1.

In each unit, two PDC ligands bind to one cobalt ion as a tridentate ligand in the same coordination mode. Co1 is octahedrally coordinated by four carboxylate oxygens (O1, O1, O1 and O1) and two pyridyl nitrogens (N1 and N1) from two PDC ligands. The bond lengths of cobalt with these oxygen atoms are all the same (1.919(2) Å). The dihedral angle between two PDC rings is 88.59° which is indicative that the planes of two PDC rings are almost orthogonal and N1–Co1–N1 bond angle is 180.00°. The coordination sphere of each silver (I) atom is a distorted tetrahedron and the Ag–O bond lengths are 2.474(2) Å. The O–Ag1–O bond angles are 87.8(1)° (O2–Ag1–O2, O2–Ag1–O2) and 121.3(1)° (O2–Ag1–O2, O2–Ag1–O2, O2–Ag1–O2 and O2–Ag1–O2). Compared to previously reported mixed metal PDC complexes [17], **1** displays a new coordination mode that each $[Co(PDC)_2]$ unit is connected to the silver(I) by another O atom of carboxyl to generate a 2D network structure. The 3D supramolecular

Table 2. Selected bond lengths ($\times 10^{-1}$ nm) and bond angles (°) of **1**.

Co(1)–O(1)	1.919(2)	Co(1)–N(1)	1.838(2)
Ag(1)–O(2)	2.473(2)	O(1)–C(1)	1.298(2)
O(2)–C(1)	1.229(2)	N(1)–C(2)	1.337(2)
O(1)–Co(1)–O(1)$^{\#1}$	167.6(1)	O(1)–Co(1)–O(1)$^{\#2}$	90.7(1)
O(1)–Co(1)–O(1)$^{\#3}$	90.7(1)	O(1)–Co(1)–N(1)	83.8(1)
O(1)–Co(1)–N(1)$^{\#2}$	96.2(1)	N(1)$^{\#2}$–Co(1)–N(1)	180
O(2)–Ag(1)–O(2)$^{\#4}$	87.8(1)	O(2)–Ag(1)–O(2)$^{\#5}$	121.3(1)
(2)–Ag(1)–O(2)$^{\#6}$	121.3(1)	O(2)$^{\#4}$–Ag(1)–O(2)$^{\#5}$	121.3(1)
O(2)$^{\#4}$–Ag(1)–O(2)$^{\#6}$	121.3(1)	O(2)$^{\#5}$–Ag(1)–O(2)$^{\#6}$	87.8(1)

Symmetry codes used are: #1 $= -x, -y-1/2, z$; #2 $= y+1/4, -x-1/4, -z+3/4$; #3 $= -y-1/4, x-1/4, -z+3/4$; #4 $= -x+1, -y+1/2, z$; #5 $= y+1/4, -x+3/4, -z+3/4$; #6 $= -y+3/4, x-1/4, -z+3/4$.

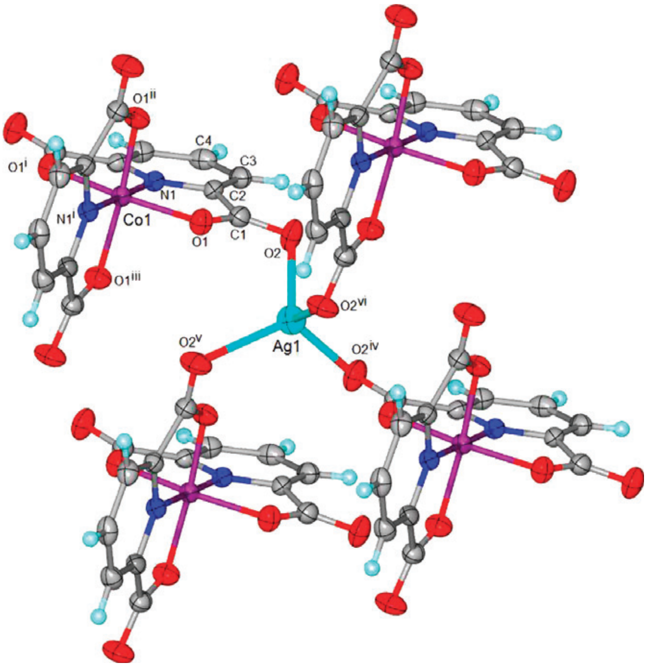


Figure 1. Molecular structure of **1** with 30% thermal ellipsoid probability.

structure is formed via π–π interactions of the pyridine rings of PDC ligands (figure 2) with face-to-face distance of 3.450 Å.

In this 2D network structure, in one layer, all metal atoms are in the same plane along the crystallographic *c*-axis (figure 3). Interestingly, four Co atoms around one Ag atom

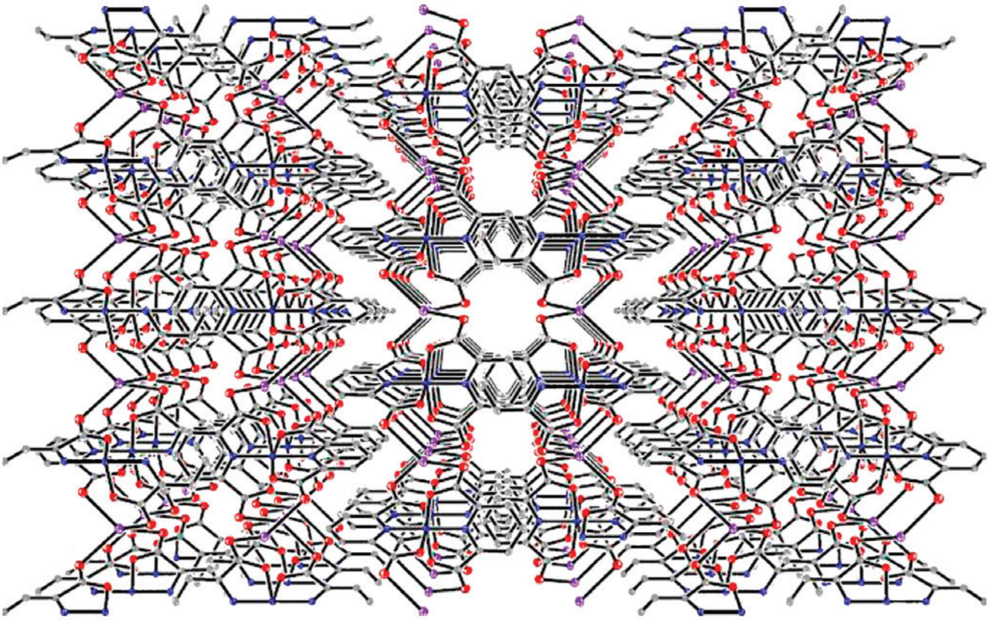


Figure 2. Packing diagram of **1** along the *b*-axis.

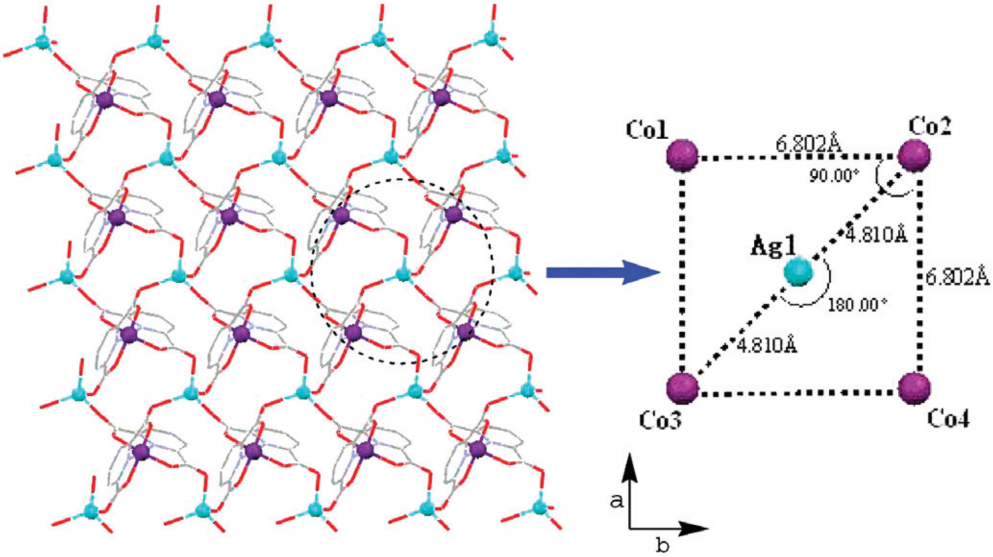


Figure 3. All metal atoms are in the *ab* plane and each Ag (or Co) atom is located in the center of the square formed by four Co (or Ag) atoms.

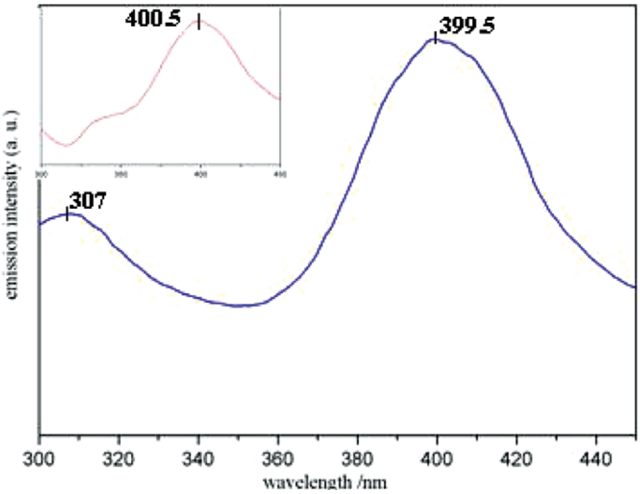


Figure 4. Emission spectrum of **1** (blue) and H_2PDC (red) ligand in solid state at room temperature.

form a square and the Ag atom is located in the center of the square. Consequently, each Co atom is the center of ambient four Ag atoms (Co···Co (or Ag···Ag) distance is 6.802 Å, Co···Ag distance is 4. 810 Å).

3.2. *Luminescent properties*

The luminescence of **1** and free pyridine-2,6-dicarboxylic acid ligand have been investigated in the solid state at room temperature (figure 4). Complex **1** exhibits a shoulder at 307 nm and a main peak at 399.5 nm. The emission observed at 307 nm may be due to a metal-to-ligand charge-transfer transition [18–19]. The studies clearly indicate that the emission at 399.5 nm can be assigned to the intraligand π–π^* transition process of H_2PDC (H_2PDC, 400.5 nm) [20–22].

3.3. *Thermogravimetric analysis*

In order to get more information about the thermal stability of **1**, thermogravimetric analysis (TGA) was been performed at 25–800°C under N_2 (figure 5). The TGA curve of the sample exhibits one weight loss stage in the temperature range 313–527°C, corresponding to release of 2,6-PDC groups [23]. The residue is Ag and Co_2O_3. The whole weight loss (67.83%) is in agreement with the calculated (67.42%).

4. Conclusion

A heteronuclear complex, **1**, constructed by PDC ligand has been synthesized under hydrothermal condition and characterized by single-crystal X-ray diffraction. Complex **1** displays a new coordination mode in which silver(I) and cobalt(III) are

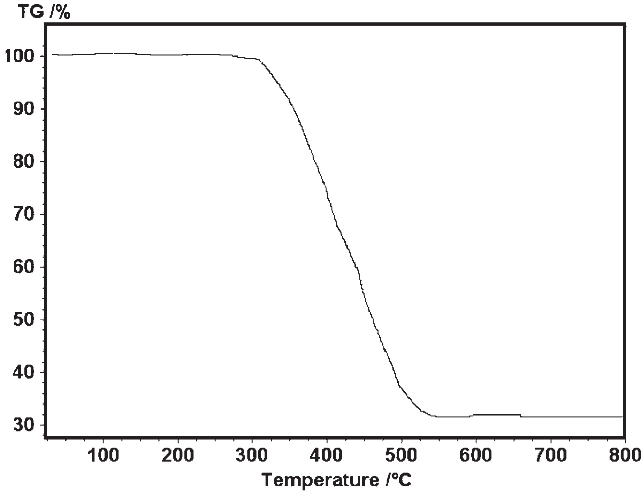


Figure 5. TGA curve of **1**.

linked by PDC to form a 2D supramolecular framework. In one layer, all metal atoms are in the same plane. The adjacent 2D layers are parallel with each other and construct a 3D framework via π–π interactions.

Supplementary data

Crystallographic data for the complex **1** have been deposited at the Cambridge Crystallographic Data Center as supplementary publication (CCDC-631269). These data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; Email: deposit@ccdc.cam.ac.uk).

Acknowledgements

We are grateful to the Natural Science Foundation of China (No. 20671076), the National Basic Research Program (the 973 Program, No. 2003CB214600), the Program for Changjiang Scholars and Innovative Research Team in University, PCSIRT (IRT0559), the Key Laboratory Research and Establishment Program of Shaanxi Education Section (No. 03JS006) for financial support.

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