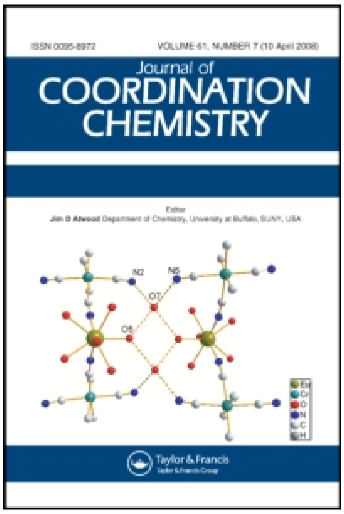

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Syntheses, structure and magnetism of a new linear-chain coordination polymer [[Co(TMA)$_2$(4,4'-bipyridine)$_2$] · H$_2$O]$_{<b><i>n</i>}$ [TMA=Trimesate]

Huan-Ran Xing[a]; Xin-Hua Li[a]; Qian Shi[a]
[a] College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou, Zhejiang 325027, P. R. China

To cite this Article Xing, Huan-Ran , Li, Xin-Hua and Shi, Qian(2008) 'Syntheses, structure and magnetism of a new linear-chain coordination polymer [[Co(TMA)$_2$(4,4'-bipyridine)$_2$] · H$_2$O]$_{<b><i>n</i>}$ [TMA=Trimesate]', Journal of Coordination Chemistry, 61: 4, 499 — 507, First published on: 27 August 2007 (iFirst)

To link to this Article: DOI: 10.1080/00958970701361202

URL: http://dx.doi.org/10.1080/00958970701361202

Journal of Coordination Chemistry
Vol. 61, No. 4, 20 February 2008, 499–507

Taylor & Francis
Taylor & Francis Group

Syntheses, structure and magnetism of a new linear-chain coordination polymer [[Co(TMA)$_2$(4,4′-bipyridine)$_2$] • H$_2$O]$_n$ [TMA = Trimesate]

HUAN-RAN XING, XIN-HUA LI* and QIAN SHI

College of Chemistry and Materials Engineering, Wenzhou University,
Wenzhou, Zhejiang 325027, P. R. China

(*Received 3 February 2007; in final form 24 March 2007*)

A linear-chain one-dimension polymeric complex of Co(II), [[Co(TMA)$_2$(4,4′-bipyridine)$_2$]$\cdot$H$_2$O]$_n$ has been synthesized and characterized. The complex crystallizes in the monoclinic system, space group $P2(1)/c$ with $a = 11.344(3)$ Å, $b = 15.880(4)$ Å, $c = 23.436(5)$ Å, $\beta = 117.831(10)^\circ$, $V = 3733.5(16)$ Å^3 and $D_c = 1.437\ \mathrm{g\,cm^{-3}}$. The effective magnetic moment for this complex indicates that there is almost no ferromagnetic coupling between the Co(II) ions and the magnetic behavior is due to the isolated Co(II).

Keywords: Coordination polymer; Co(II); Linear-chain; Magnetic properties

1. Introduction

The synthesis of organic-inorganic hybrid materials is of great interest because these extended systems play a significant role in the areas of catalysis, chirality, luminescence, magnetism, nonlinear optics, and porosity behavior [1–3]. Among these materials, 1D coordination polymers occupy a large portion of the literature. These compounds have been constructed mainly by combining metals with linear or angular spacer ligands, forming linear chain, zigzag chain, ladder, infinite helix, etc. [4, 5]. In addition, the 1D polymers can further interact through hydrogen bonds to give 2D and 3D hydrogen-bonded coordination polymeric structures [6, 7].

The ligand plays an important role in the design and synthesis of coordination polymers. In this work, we choose two rigid ligands (shown in scheme 1): 4,4′-bipyridine and benzene-1,3,5-tricarboxylic acid. The bidentate 4,4′-bipyridine is a commonly employed spacer ligand for synthesizing metalorganic solids whose structures mimic a number of familiar topologies, including chains, diamondoids, ladders, railroads, grids, brick walls and three dimensional networks [8–17]; Benzene-1,3,5-tricarboxylate has the ability to adopt different bonding modes, unidentate, bidentate, or bridging [18–23]. Herein, we prepared a 1D linear-chain

---

*Corresponding author. Email: lixinhua01@126.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970701361202

(a) (b)

Scheme 1. Structures of 4,4′-bipydinyl (a) and TMA (b) ligands.

polymer of $[[Co(TMA)_2(4,4'\text{-}Bipy)_2] \cdot H_2O]_n$ and report its hydrothermal synthesis, crystal structures and magnetism.

2. Experimental

2.1. *Apparatus and reagents*

All reagents were commercially obtained and used without further purification. Elemental analyses (C, H and N) were carried out on a Carlo-Erba 1112 Elemental Analyzer. The crystal structure was obtained on a Bruker Smart-1000 CCD diffractometer. IR spectra were recorded on an EQUINOX55 (Bruker) spectrophotometer in the range 4000–400 cm^{-1} with KBr disks. Magnetic susceptibility data were carried out at 0.1 T using a Quantum Design MPMS-7 SQUID susceptometer.

2.2. *Synthesis*

The title complex was synthesized with the hydrothermal method from a mixture of $CoSO_4 \cdot 7H_2O$ (0.84 g, 3 mmol), 1,3,5-benzenetricarboxylic acid (trimesate) (0.63 g, 3 mmol), 4,4′-bipyridine (0. 47 g, 3 mmol) and water (20.0 mL) in a 30.0 mL Teflon-lined stainless steel reactor. The solution was heated to 120°C for five days, then slowly cooled to room temperature; pink prisms were collected in 25% yield and washed with distilled water. Anal. Calcd for $C_{38}H_{28}CoN_4O_{13}$ (%) C, 56.47; H, 3.47; N, 6.93. Found: C, 56.43; H, 3.52; N, 6.90. IR (KBr disk, cm^{-1}): 3409w, 3084w, 2502w, 1883w, 1702s, 1610s, 1554s, 1417s, 1372s, 1266s, 1215s, 1105s, 1066s, 1004s, 936s, 810s, 749s, 699s.

2.3. *Crystal structure determination*

All measurements were made on a Bruker Smart-1000 CCD diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.071073$ nm) using the ω-scan technique. Determination of the Laue class, orientation matrix, and cell dimensions were performed according to the established procedures. Lorentz polarization and absorption corrections were applied. Absorption corrections were applied by fitting a pseudo-ellipsoid to the ψ-scan data of selected strong reflections over a wide range of 2θ angles. Most of the non-hydrogen atoms in the crystal structure were located with direct methods, and subsequent Fourier syntheses were used to derive the remaining non-hydrogen atoms. As there are some disordered atoms, the wR_2 is slightly higher than 0.20. All non-hydrogen atoms were refined anisotropically, and all of the hydrogen atoms were held stationary and included in the final stage of full-matrix

Table 1. Crystallographic data and structure refinement summary for **1**.

Compound	$[Co(btc)_2(L^1)_2] \cdot 3H_2O$
Formula	$C_{38}H_{28}CoN_4O_{13}$
Formula wt.	807.57
Crystal system	Monoclinic
Space group	$P2(1)/c$
Unit cell dimens (Å, °)	
a	11.344(3)
b	15.880(4)
c	23.436(5)
β	117.831(10)
V (Å^3), Z	3733.5(16), 4
Calcd density (g cm^{-3})	1.437
Crystal size (mm^3)	$0.24 \times 0.16 \times 0.07$
θ range for data collection (°)	1.62–25.10
Limiting indices	$-13 \le h \le 13$; $-18 \le k \le 18$; $-23 \le l \le 27$
Reflections collections	19438
Independent reflections	6633
Data/restraints/parameters	6633/2/515
Goodness-of-fit on F^2	1.100
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0852$, $wR_2 = 0.2401$
R indices (all data)	$R_1 = 0.0994$, $wR_2 = 0.2513$
Absorption coefficient (mm^{-1})	0.532
$F(000)$	1660

Table 2. Selected bond lengths (Å) and bond angles (°) for **1** at 298 K.

Co–O(7)	2.011(4)	Co-N(1)	2.142(5)
Co–N(2)	2.143(4)	Co–N(4)#1	2.167(4)
Co–O(2)	2.167(4)	Co–O(1)	2.182(4)
O(7)–Co–N(1)	91.68(17)	O(7)–Co–N(2)	93.85(17)
N(1)–Co–N(2)	96.19(17)	O(7)–Co–N(4)#1	87.17(17)
N(1)–Co–N(4)#1	175.21(17)	N(2)–Co–N(4)#1	88.53(18)
O(7)–Co–O(2)	172.11(15)	N(1)–Co–O(2)	88.31(17)
N(2)–Co–O(2)	94.00(16)	N(4)#1–Co–O(2)	92.19(17)
O(7)–Co–O(1)	111.97(14)	N(1)–Co–O(1)	89.67(16)
N(2)–Co–O(1)	153.38(16)	N(4)#1–Co–O(1)	86.46(16)
O(2)–Co–O(1)	60.14(13)		

Symmetry transformations used to generate equivalent atoms: #1 = $x - 1$, y, z.

Table 3. Hydrogen bonds for **1** (Å and °).

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
O(13)–H(13B)···O(1)	0.86(3)	2.00(5)	2.818(6)	157(9)
O(13)–H(13A)···O(10)#1	0.82(3)	1.90(3)	2.715(7)	171(9)
O(11)–H(11)···O(13)#2	0.82	1.90	2.613(7)	145.1
O(9)–H(9A)···O(8)#1	0.82	1.98	2.551(6)	126.4
O(5)–H(5)···O(6)#3	0.82	1.83	2.638(6)	167.7
O(3)–H(3)···N(3)#4	0.82	1.85	2.636(6)	160.0

Symmetry transformations used to generate equivalent atoms: #1 = $-x$, $-y$, $-z$, #2 = $x - 1$, $-y + 1/2$, $z - 1/2$, #3 = $-x + 1$, $-y$, $-z + 1$, #4 = $x + 1$, $-y + 3/2$, $z + 1/2$.

least-squares refinement based on F^2 using the SHELXS-97 and SHELXL-97 program package [24–25]. The water H atoms were refined subject to the restraint O–H = 0.82(1) Å. The other H atoms were positioned geometrically and allowed to ride on their parent atoms at distances of C–H = 0.93 Å and U_{iso} (H) = $1.2U_{\mathrm{eq}}$(C), and O–H = 0.82 Å and U_{iso}(H) = $1.5U_{\mathrm{eq}}$(O). Data collection, structure refinement parameters and crystallographic data for the complex are given in table 1, selected bond distances and angles in table 2, and hydrogen-bonding geometry in table 3.

3. Results and discussion

3.1. *Crystal structure descriptions*

The single crystal X-ray diffraction analysis reveals that the complex has a one-dimensional linear-chain structure, which is bridged by 4,4′-bipyridine coordinated with cobalt. The fundamental unit is shown in figure 1.

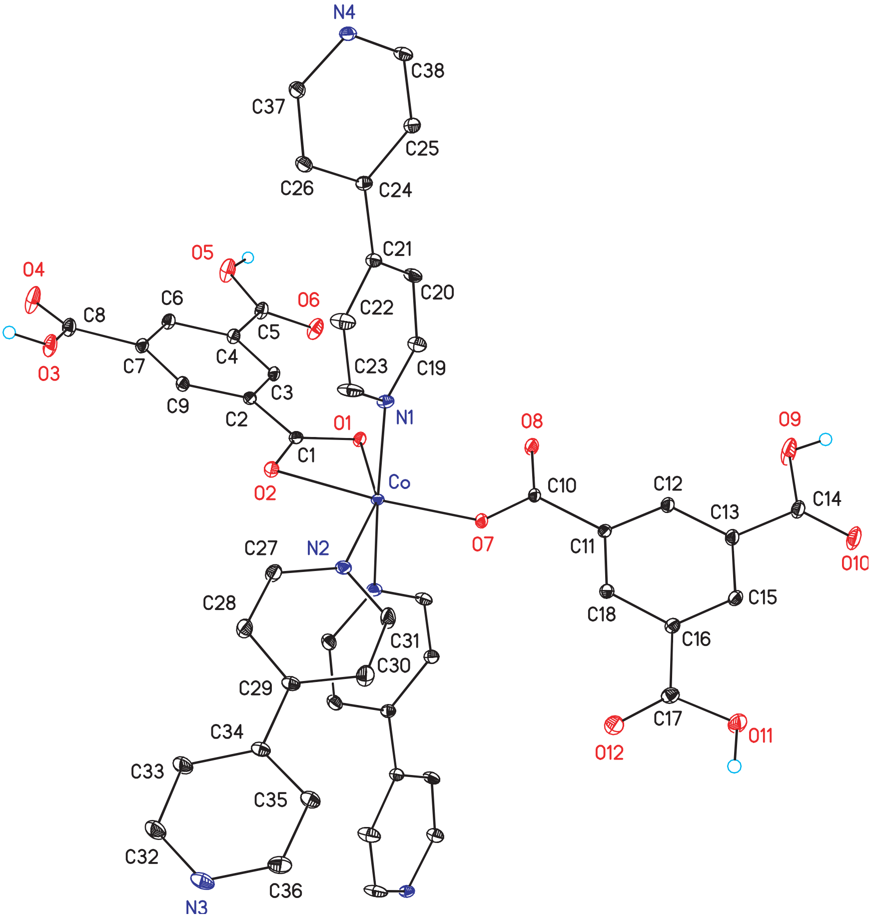

Figure 1. ORTEP drawing of the coordination geometry of $[[\mathrm{Co(TMA)_2(4,4'\text{-}Bipy)_2]\cdot H_2O}]_n$. Some hydrogen atoms and all solvent molecules are omitted for clarity.

In **1**, Co is six coordinate to three 4,4′-Bipy ligands and to two TMA ligands. One water molecule is outside the coordination sphere. The Co center coordinates to two oxygen atoms of one chelating bidentate TMA ligand, one oxygen atom from unidentate TMA ligand, one nitrogen atom from unidentate 4,4′-Bipy ligand and two nitrogen atoms which occupy the axial position from two different bridging 4,4′-Bipy ligands. Then, the whole unit looks like a fan, in which the bridging ligands are the immobilizing axes. Therefore, in the complex, the Co has a distorted octahedral geometry.

As shown in figure 2, the two distorted octahedra are connected to form a linear-chain Co polymer. The Co ⋯ Co separation across the 4,4′-bipyridine is 11.344 Å.

The 1D chains of $[[Co(TMA)_2(4,4'\text{-bipyridine})_2] \cdot H_2O]_n$ are linked by intermolecular hydrogen bonding to form a 3D network in the crystal lattice (figure 3). The types

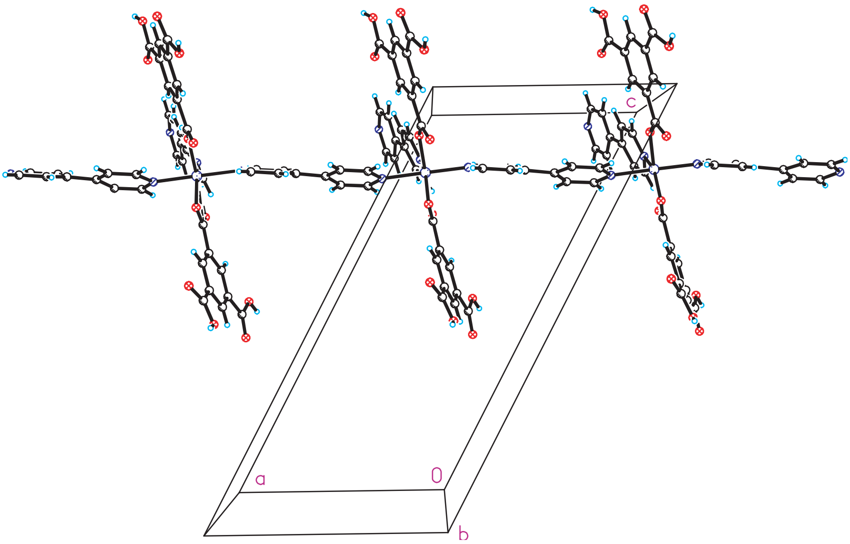

Figure 2. A portion of the linear 1D coordination polymeric structure of $[[Co(TMA)_2(4,4'\text{-Bipy})_2] \cdot H_2O]_n$.

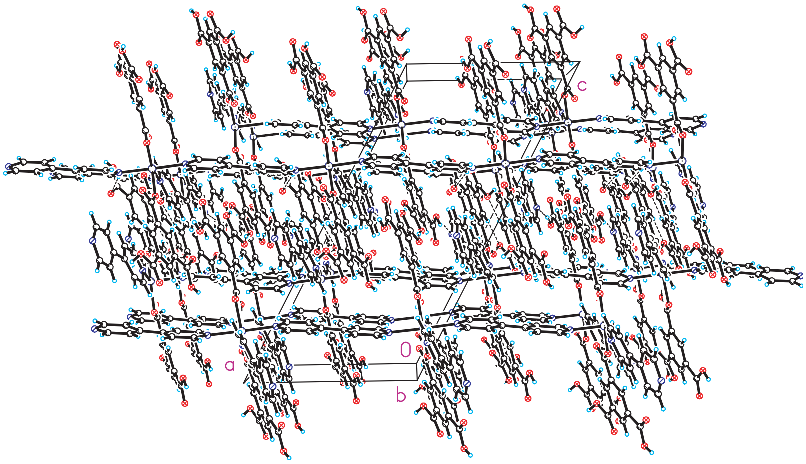

Figure 3. A perspective view of the molecular packing of the title compound along the *b* axis.

of H bonding are O–H···O and O–H···N. Water acts as both donor and acceptor of hydrogen atoms.

3.2. *IR spectroscopy*

The IR spectrum of **1** shows characteristic bands of the TMA ligand at 1610 and $1554\,\mathrm{cm}^{-1}$ for the asymmetric vibrations and at 1417 and $1372\,\mathrm{cm}^{-1}$ for the symmetric vibrations, and the broad bands of water at $3409\,\mathrm{cm}^{-1}$. The Δ values, which represent the separation between ν_{asym}(–COO) and ν_{sym}(–COO), are 193 and $182\,\mathrm{m}^{-1}$, respectively. The splitting of ν_{asym}(–COO) in **1** confirms that the carboxylate groups have different coordination modes [26], in agreement with the crystal structure. The existence of the expected characteristic bands at $1702\,\mathrm{m}^{-1}$ attributed to the protonated carboxylate groups indicates incomplete deprotonation of trimesate in the reaction with Co [20].

3.3. *Magnetic properties*

The temperature dependence of the magnetic susceptibility (χ_{M}) for **1** at 2 kOe in the temperature range 1.79–305 K is shown in figure 4.

To probe magnetic interactions, the Curie-Weiss law was applied between 50 K and 300 K, affording $C = 3.1\,\mathrm{cm}^3\,\mathrm{K\,mol}^{-1}$ and $\theta = -7.93\,\mathrm{K}$. The Curie constant is in the usual range of octahedral high-spin Co(II) ions (2.8–$3.4\,\mathrm{cm}^3\,\mathrm{K\,mol}^{-1}$) [27–29]. The negative θ value indicated that there may be anti-ferromagnetic interactions in the compound.

From the structure information, we know that Co(II) ions are well separated, so we can treat the magnetic data by considering a mononuclear Co(II) with a spin-orbit coupling parameter $\lambda(H = -\lambda LS)$ in a molecular-field approximation.

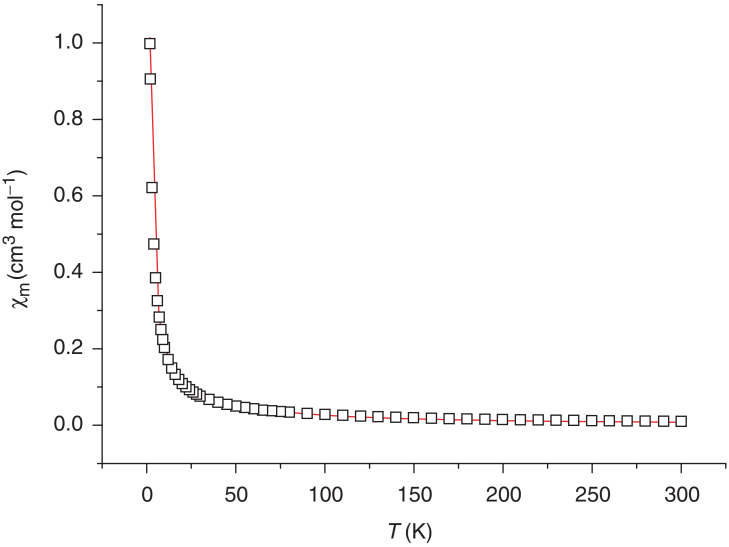

Figure 4. χ_{M} *vs.* T curve for the title compound, the red line represents the best theoretical fit.

The χ_{mono} for mononuclear Co(II) in an octahedral environment can be calculated from equation (1), [30]

$$\chi_{\text{mono}} = \frac{1}{T} \times \frac{\begin{array}{l}\left(7(3-A)^2/5\right) + \left(12(2+A)^2/25A\right) + \\ \left\{\left(2(11-2A)^2/45\right) + \left(176(2+A)^2/675A\right)\right\}\exp(-5Ax/2) + \\ \left\{\left((5+A)^2x/9\right) - \left(20(2+A)^2/27A\right)\right\}\exp(-4Ax)\end{array}}{8x/3\left\{3 + 2\exp(-5Ax/2) + \exp(-4Ax)\right\}} \tag{1}$$

with $x = \lambda/k_{\text{B}}T$. The parameter A gives a measure of the crystal field strength relative to the interelectronic repulsions and is equal to 1.5 for a weak crystal field, 1.32 for a free ion, and 1.0 for a strong field. Considering the molecular-field approach with zJ as the total exchange coupling between Co(II) ions, we can fit our experimental data with equation (2): [28]

$$\chi = \frac{\chi_{\text{mono}}}{1 - (2zJ/Ng^2\beta^2)\chi_{\text{mono}}} \tag{2}$$

In equations (1) and (2), N, g, β, k_{B} and T have their usual meanings. The best fitting of the susceptibility data in the temperature range of 1.79 to 300 K gives $\lambda = -34.8\,\text{cm}^{-1}$, $A = 1.005$, and $zJ = 0.75\,\text{cm}^{-1}$ with $R = \left(\sum_i (\chi_i^{\text{obs}}\chi_i^{\text{Calcd}})/\sum_i (\chi_i^{\text{obs}})\right)^2 = 8.0 \times 10^{-5}$. The very small positive zJ value indicates almost no ferromagnetic coupling between the Co(II) ions.

By using the equation $\mu_{\text{eff}} = (8\chi_{\text{M}}T)^{1/2}$, at 300 K the effective magnetic moment per cobalt atom of this compound is consistent with the expected spin only value of $5.00\mu_{\text{B}}$ ($S = 2$, $g = 2.0$, shown in figure 5), which is larger than expected for the spin-only case ($\mu_{\text{eff}} = 3.87\mu_{\text{B}}$, $S = 2$, $g = 2.0$), also indicating that an orbital-spin contribution is involved [31–32]. During the temperature decrease, the effective

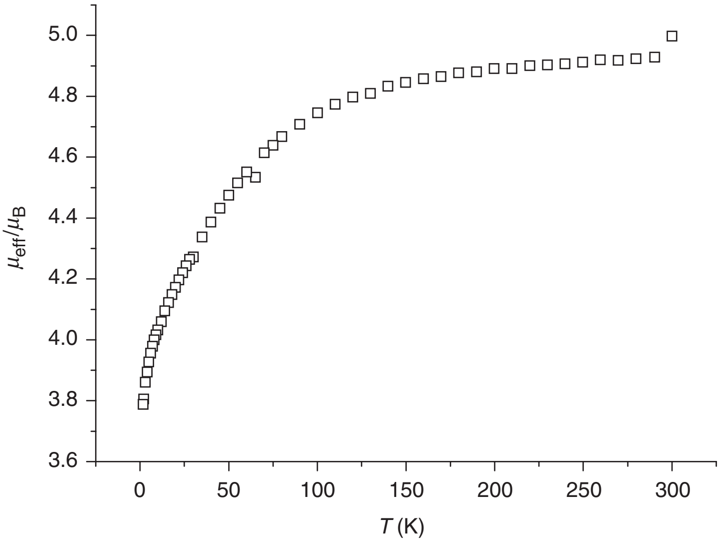

Figure 5. μ_{eff} *vs.* T curve for the title compound.

magnetic moment stays constant down to 100 K ($4.75\mu_B$) and then decreases more rapidly to $3.78\mu_B$ at 1.79 K. So the magnetic behavior is due to isolated Co(II) ions.

This compound bridged by 4,4′-bipyridine has almost no magnetic interactions because of the long distance between two metal ions. Similar results could be observed in polymeric chains connected by 4,4′-bipyridine [33], 4,4′-methylenebis(3,5-dimethyl-pyrazole) [34] and dicyanamide [35]. The C–C bond connecting the two pyridine rings in 4,4′-bipyridine has single bond character, which breaks the conjugation of the 4,4′-bipyridine. In addition, the expected magnetic behavior **1** could also be attributed to the unfavorable *p*-type exchange pathway as well as the long π-type exchange pathway for 4,4′-bipyridine bridging ligand.

Supporting material

CCDC-634013 contains the supplementary crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Center, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk].

Acknowledgements

This work was supported by the Zhejiang Provincial Natural Science Foundation of China (grant No. Y404294), "151" distinguished person foundation of Zhejiang Province and the Nation Natural Science Foundation of China (grant No. 20601021).

References

[1] P.J. Hagrman, D. Hagrman, J. Zubieta. *Angew. Chem., Int. Ed.*, **38**, 2639 (1999).
[2] (a) H.R. Allcock. *AdV. Mater.*, **6**, 106 (1994); (b) H.R. Allcock. *Inorg. Chem.*, **44**, 2060 (2005).
[3] C. Janiak. *Dalton Trans.*, 2781 (2003).
[4] B. Moulton, M.J. Zaworotko. *Chem. Rev.*, **101**, 1629 (2001).
[5] (a) A.F. Wells. *Three-Dimensional Nets and Polyhedron*, Willey-Interscience, New York (1977); (b) A.F. Wells. *Structural Inorganic Chemistry*, 5th Edn, Oxford University Press, Oxford (1984).
[6] (a) C.B. Aakeröy. *Acta Cryst.*, **B53**, 569 (1997); (b) C.B. Aakeröy, A.M. Beatty. *Aust. J. Chem.*, **54**, 409 (2001); (c) A.M. Beatty. *Cryst. Eng. Commun.*, **51**, 1 (2001).
[7] (a) D. Braga. *J. Chem. Soc., Dalton Trans.*, 3705 (2000); (b) S.L. James. *Chem. Soc. Rev.*, **32**, 276 (2003).
[8] L. Carlucci, G. Ciani, D.M. Proserpio, A. Sironi. *J. Chem. Soc., Dalton Trans.*, 1801 (1997).
[9] R.H. Groeneman, L.H. MacGillivray, J.L. Atwood. *Inorg. Chem.*, **38**, 208 (1999).
[10] M.J. Zaworotko. *Chem. Soc. Rev.*, **24**, 283 (1994).
[11] B.D. Wagner, G.J. McManus, B. Moulton, M.J. Zaworotko. *Chem. Commun.*, **18**, 2176 (2002).
[12] O.M. Yaghi, H. Li, T.L. Groy. *Inorg. Chem.*, **36**, 4292 (1997).
[13] M. Fujita, Y.J. Kwon, S. Washizu, K. Ogura. *J. Am. Chem. Soc.*, **116**, 1151 (1994).
[14] M.-L. Tong, S.-L. Zheng, X.-M. Chen. *Polyhedron*, **19**, 1809 (2000).
[15] R.W. Gable, B.F. Hoskins, R. Robson. *J. Chem. Soc., Chem. Commun.*, **23**, 1677 (1990).
[16] T. Soma, H. Yuge, T. Iwamoto. *Angew. Chem., Int. Ed. Engl.*, **33**, 1655 (1994).
[17] S. Subramanian, M.J. Zaworotko. *Angew. Chem., Int. Ed. Engl.*, **34**, 2127 (1995).
[18] C. Volkringer, T. Loiseau. *Mater. Res. Bull.*, **41**, 948 (2006).
[19] D. Cheng, M.A. Khan, R.P. Houser. *Crystal Growth & Des.*, **4**, 600 (2004).

[20] J.-X. Chen, S.-X. Liu, E.-Q. Gao. *Polyhedron*, **23**, 1877 (2004).

[21] Y.-F. Zhou, B.-Y. Lou, D.-Q. Yuan, Y.-Q. Xu, F.-L. Jiang, M.-C. Hong. *Inorg. Chim. Acta*, **358**, 3057 (2005).

[22] E.Y. Choi, Y.-U. Kwon. *Inorg. Chem. Commun.*, **7**, 942 (2004).

[23] T.J. Prior, D. Bradshaw, S.J. Teat, M.J. Rosseinsky. *Chem. Commun.*, 500 (2003).

[24] G.M. Sheldrick. *SHELXTL Version 5, Siemens*, Industrial Automation Inc., Madison, Wisconsin, USA (1995).

[25] G.B. Deacon, R. Philips. *Coord. Chem. Rev.*, **88**, 227 (1980).

[26] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, New York (1986).

[27] R.L. Carlin. *Magnetochemistry*, Springer-Verlag, Berlin (1986).

[28] O. Kahn. *Molecular Magnetism*, VCH, New York (1993).

[29] (a) J.-M. Rueff, N. Masciocchi, P. Rabu, A. Sironi, A. Skoulios. *Eur. J. Inorg. Chem.*, **11**, 2843 (2001); (b) J.-M. Rueff, N. Masciocchi, P. Rabu, A. Sironi, A. Skoulios. *Chem. Eur. J.*, **8**, 1813 (2002).

[30] (a) B.N. Figgis, M. Gerloch, J. Lewis, F.E. Mabbs, G.A. Webb. *J. Chem. Soc. A*, 2086 (1968); (b) H.L. Sun, Z.M. Wang, S. Gao. *Inorg. Chem.*, **44**, 2169 (2005); (c) S. Konar, P.S. Mukherjee, M.G.B. Drew, J. Ribas, N.R. Chaudhuri. *Inorg. Chem.*, **42**, 2545 (2003).

[31] R.L. Carlin. *Magnetochemistry*, Springer-Verlag, New York (1986).

[32] F.E. Mabbs, D.J. Machin. *Magnetism and Transition Metal Complexes*, Oxford University Press, Oxford (1973).

[33] (a) M.P. Gupta, R.D. Sahu, R. Ram, P.R. Maulik. *Z. Kristallogr.*, **163**, 155 (1983); (b) Y.Q. Zheng, J.L. Lin. *Z. Kristallogr.*, **215**, 159 (2000); (c) Y.Q. Zheng, J.L. Lin. *Z. Kristallogr.*, **215**, 157 (2000); (d) Y.Q. Zheng, J.L. Lin, J. Sun, H.L. Zhang. *Z. Kristallogr.*, **215**, 163 (2000); (e) E. Suresh, M.M. Bhadbhade, K. Venkatasubramanian. *Polyhedron*, **18**, 657 (1999); (f) D. Sun, R. Cao, Y. Liang, Q. Shi, W. Su, M. Hong. *J. Chem. Soc., Dalton Trans.*, 2335 (2001).

[34] H. Kumagai, Y. Oka, K. Inoue, M. Kurmoo. *J. Chem. Soc., Dalton Trans.*, 3442 (2002).

[35] (a) Y.Q. Zheng, J.L. Lin, J. Sun, A.Y. Pan. *Z. Kristallogr.*, **215**, 161 (2000); (b) Y.Q. Zheng, J.L. Lin, A.Y. Pan. *Z. Anorg. Allg. Chem.*, **626**, 1718 (2000); (c) L. Pan, C. Ching, X. Huang, J. Li. *Inorg. Chem.*, **39**, 5333 (2000); (d) L. Pan, B.S. Finkel, X. Huang, J. Li. *Chem. Commun.*, 105 (2001); (e) Y.J. Kim, D.-Y. Jung. *Inorg. Chem.*, **39**, 1470 (2000); (f) Y.J. Kim, E.W. Lee, D.-Y. Jung. *Chem. Mater.*, **13**, 2684 (2001); (g) K.O. Kongshaug, H. Fjellvåg. *Solid State Sci.*, **4**, 443 (2002).