Crystal structure of Co(II)/Zn(II) coordination polymers supported by 1,3-bis(4-pyridyl)propane, $\{[Co(ClO_4)_2(C_{13}H_{14}N_2)_2] \cdot 2C_6H_6\}_n$ and $\{[Zn(ClO_4)_2(C_{13}H_{14}N_2)_2] \cdot 2C_6H_6\}_n$

T. M. Bujici[I], X.-T. Wang*[,I], S.-J. Li[II] and C. Zheng[II]

[I] University of Colorado at Denver, Department of Chemistry, Campus Box 194, P. O. Box 173364, Denver CO 80204, USA
[II] Northern Illinois University, Department of Chemistry and Biochemistry, DeKalb, IL 60115, USA

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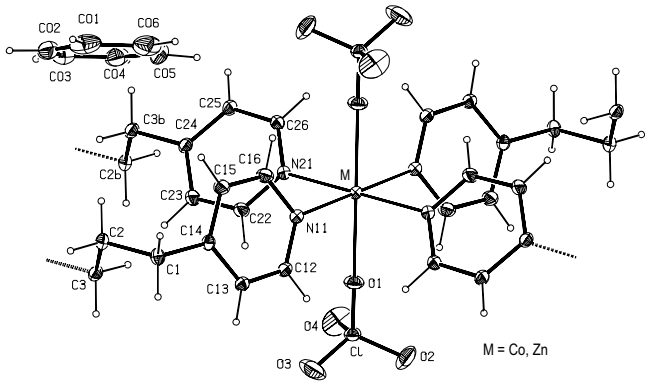

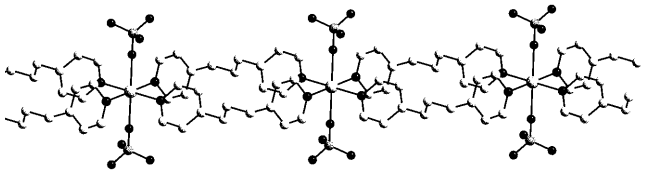

Abstract

$C_{38}H_{40}Cl_2CoN_4O_8$ (**1**), triclinic, $P\bar{1}$ (No. 2), a = 9.142(2) Å, b = 10.582(3) Å, c = 11.491(3) Å, α = 110.216(4)°, β = 90.116(4)°, γ = 110.499(4)°, V = 967.5 Å^3, Z = 1, $R_{gt}(F)$ = 0.057, $wR_{ref}(F^2)$ = 0.158, T = 293 K.

$C_{38}H_{40}Cl_2N_4O_8Zn$ (**2**), triclinic, $P\bar{1}$ (No. 2), a = 9.160(3) Å, b = 10.587(4) Å, c = 11.457(4) Å, α = 69.381(6)°, β = 89.914(7)°, γ = 69.338(7)°, V = 963.4 Å^3, Z = 1, $R_{gt}(F)$ = 0.061, $wR_{ref}(F^2)$ = 0.127, T = 293 K.

Source of material

A methanol solution (4 mL) of $Co(ClO_4)_2$ (47.6 mg, 0.13 mmol) was layered over a benzene solution (4 mL) of bpp (25 mg, 0.13 mmol). Rod-like pink crystals of **1** were formed after 12 h. A similar procedure was used to prepare the Zn(II) coordination polymer (**2**) and colorless crystals were obtained.

Experimental details

H atoms were introduced at calculated positions as riding atoms. Their isotropic displacement parameters were refined.

Discussion

We have studied the spacer dipyridyl ligand 1,3-bis(4-pyridyl)-propane (= bpp or $C_{13}H_{14}N_2$) to the end of supporting novel coordination polymers. Our work has led to the report of the structures of $\{[Ag(C_{13}H_{14}N_2)]ClO_4\}_n$ and $\{[Ag(C13H14N_2)]PF_6\}_n$ [1], as well as $\{[M(NO_3)_2(C_{13}H_{14}N_2)_2] \cdot 2C_6H_6\}_n$ (M = Co, Cd) [2]. In the present work, the use of $Co(ClO_4)_2$ and $Zn(ClO_4)_2$ has resulted in $\{[Co(ClO_4)_2(C_{13}H_{14}N_2)_2] \cdot 2C_6H_6\}_n$ (**1**) and $\{[Zn(ClO_4)_2(C13H14N_2)_2] \cdot 2C_6H_6\}_n$ (**2**), two isostructures that display a 1D charge-neutral coordination network similar to that of $\{[M(NO_3)_2(C_{13}H_{14}N_2)_2] \cdot 2C_6H_6\}_n$. Since **1** and **2** are isostructural, we will describe here only the structure of **1** in detail. The figure shows the metal coordination environment and the asymmetric unit. The Co(II) ion is coordinated equatorially by four pyridyl N atoms of different bpp units, as well as axially by two perchlorate O atoms. The Co—N11 and Co—N21 bond lengths are 2.174(4) Å and 2.144(3) Å, respectively, which are essentially identical with the lengths of the Co—N bonds in $\{[Co(NO_3)_2(C_{13}H_{14}N_2)_2] \cdot 2C_6H_6\}_n$. But the Co—O($ClO_4$) bond [2.201(3) Å] in **1** is somewhat longer than the Co—O(NO_3) bond [2.163(3) Å] in $\{[Co(NO_3)_2(C_{13}H_{14}N_2)_2] \cdot 2C_6H_6\}_n$; this agrees with the fact that perchlorate is less coordinating than nitrate. In the 1D network structure (lower figure), two adjacent Co(II) ions are bridge by two bpp units, forming a double stranded chain of loops extending in the crystallographic *c* direction. Each bpp molecule in the loop adopts a *trans-gauche* conformation. The size of the loop is measured by the Co···Co separation (11.49 Å) and the distance between the middle C atoms of the two diametrically opposing trimethyle spacers (8.46 Å). It is interesting to note that the number of lattice benzene molecules in **1** is half that in $\{[M(NO_3)_2(C_{13}H_{14}N_2)_2] \cdot 2C_6H_6\}_n$. This could be understood with reference to the sizes of perchlorate and nitrate. As compared with nitrate in $\{[M(NO_3)_2(C_{13}H_{14}N_2)_2] \cdot 2C_6H_6\}_n$, the bulkier perchlorate ions occupy more interchain space in **1**, which leaves less room for benzene molecules.

1. $\{[Co(ClO_4)_2(C_{13}H_{14}N_2)_2] \cdot 2C_6H_6\}_n$

Table 1. Data collection and handling.

Crystal:	pink fragment, size 0.08 × 0.08 × 0.14 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	6.37 cm^{-1}
Diffractometer, scan mode:	Siemens SMART CCD, ω
$2\theta_{max}$:	46.56°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4106, 2693
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2108
$N(param)_{refined}$:	262
Programs:	SIR97 [3], SHELXTL [4], SADABS [5]

* Correspondence author (e-mail: xwang@carbon.cudenver.edu)

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(01)	2*i*	0.6247	–0.0212	0.8661	0.14(3)
H(02)	2*i*	0.6995	0.1456	1.0650	0.31(9)
H(03)	2*i*	0.8131	0.3822	1.1072	0.7(3)
H(05)	2*i*	0.7653	0.3213	0.7503	0.11(2)
H(04)	2*i*	0.8499	0.4658	0.9542	0.27(8)
H(06)	2*i*	0.6613	0.0685	0.6920	0.18(4)
H(1A)	2*i*	0.0708	–0.0739	0.6719	0.06(1)
H(1B)	2*i*	–0.0339	0.0193	0.7162	0.03(1)
H(2A)	2*i*	0.2560	0.0762	0.8529	0.08(2)
H(2B)	2*i*	0.0899	0.0096	0.8910	0.05(1)
H(3A)	2*i*	0.2149	0.2954	0.8899	0.09(2)
H(3B)	2*i*	0.0505	0.2287	0.9300	0.06(1)
H(12)	2*i*	0.1506	0.3678	0.5518	0.04(1)
H(13)	2*i*	–0.0007	0.2018	0.6301	0.07(2)
H(15)	2*i*	0.3614	0.0784	0.6459	0.09(2)
H(16)	2*i*	0.5034	0.2469	0.5670	0.09(2)
H(22)	2*i*	0.4282	0.5951	0.7695	0.05(1)
H(23)	2*i*	0.5440	0.6869	0.9723	0.09(2)
H(25)	2*i*	0.9588	0.7235	0.8508	0.07(1)
H(26)	2*i*	0.8308	0.6249	0.6498	0.07(2)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	1*h*	1/2	1/2	1/2	0.0414(5)	0.0529(5)	0.0407(5)	0.0213(4)	0.0055(3)	0.0207(4)
C(01)	2*i*	0.6684(9)	0.078(1)	0.881(2)	0.065(5)	0.093(6)	0.25(1)	0.015(4)	0.005(7)	0.066(8)
C(02)	2*i*	0.715(1)	0.178(2)	0.999(1)	0.079(5)	0.16(1)	0.143(8)	0.055(6)	0.027(5)	0.091(8)
C(03)	2*i*	0.781(1)	0.318(1)	1.025(1)	0.103(6)	0.157(9)	0.137(8)	0.084(6)	0.039(5)	0.067(7)
C(05)	2*i*	0.754(1)	0.280(1)	0.811(1)	0.099(6)	0.175(9)	0.118(7)	0.060(6)	0.014(5)	0.092(7)
C(04)	2*i*	0.801(1)	0.366(1)	0.934(1)	0.102(6)	0.136(8)	0.150(9)	0.069(6)	0.025(6)	0.068(7)
C(06)	2*i*	0.690(1)	0.131(2)	0.776(1)	0.075(5)	0.18(1)	0.125(8)	0.042(6)	–0.021(5)	–0.003(8)
C(1)	2*i*	0.0739(6)	0.0234(4)	0.7169(4)	0.062(3)	0.044(2)	0.049(2)	0.014(2)	0.009(2)	0.019(2)
C(2)	2*i*	0.1499(6)	0.0763(5)	0.8524(4)	0.062(3)	0.058(3)	0.048(3)	0.021(2)	0.007(2)	0.028(2)
C(3)	2*i*	0.1569(6)	0.2295(5)	0.9297(4)	0.066(3)	0.070(3)	0.045(2)	0.036(2)	0.000(2)	0.019(2)
N(11)	2*i*	0.3421(4)	0.3261(4)	0.5520(3)	0.046(2)	0.058(2)	0.047(2)	0.023(2)	0.007(2)	0.024(2)
C(12)	2*i*	0.1944(5)	0.3093(5)	0.5715(4)	0.047(3)	0.068(3)	0.060(3)	0.024(2)	0.006(2)	0.035(2)
C(13)	2*i*	0.1026(5)	0.2097(5)	0.6195(4)	0.043(3)	0.072(3)	0.056(3)	0.020(2)	0.005(2)	0.033(2)
C(14)	2*i*	0.1628(5)	0.1215(4)	0.6518(4)	0.051(2)	0.045(2)	0.040(2)	0.015(2)	0.003(2)	0.014(2)
C(15)	2*i*	0.3158(6)	0.1371(5)	0.6286(5)	0.069(3)	0.070(3)	0.082(4)	0.042(3)	0.029(3)	0.046(3)
C(16)	2*i*	0.4006(6)	0.2385(6)	0.5805(5)	0.056(3)	0.075(3)	0.090(4)	0.034(3)	0.029(3)	0.048(3)
N(21)	2*i*	0.6182(4)	0.6002(4)	0.6888(3)	0.047(2)	0.060(2)	0.045(2)	0.023(2)	0.011(2)	0.025(2)
C(22)	2*i*	0.5364(6)	0.6200(6)	0.7857(4)	0.045(3)	0.092(4)	0.050(3)	0.026(2)	0.006(2)	0.021(3)
C(23)	2*i*	0.6057(6)	0.6755(6)	0.9081(4)	0.060(3)	0.099(4)	0.043(3)	0.037(3)	0.010(2)	0.021(3)
C(24)	2*i*	0.7662(5)	0.7145(5)	0.9369(4)	0.057(3)	0.058(3)	0.045(2)	0.027(2)	0.001(2)	0.020(2)
C(25)	2*i*	0.8500(5)	0.6965(5)	0.8370(4)	0.045(3)	0.073(3)	0.048(3)	0.018(2)	–0.002(2)	0.024(2)
C(26)	2*i*	0.7719(5)	0.6381(5)	0.7157(4)	0.045(3)	0.074(3)	0.048(3)	0.021(2)	0.010(2)	0.028(2)
Cl	2*i*	0.2495(1)	0.7036(1)	0.5948(1)	0.0564(7)	0.0629(7)	0.0622(7)	0.0330(6)	0.0109(5)	0.0192(6)
O(1)	2*i*	0.3269(4)	0.6044(4)	0.5496(4)	0.071(2)	0.083(2)	0.106(3)	0.053(2)	0.035(2)	0.045(2)
O(2)	2*i*	0.2014(9)	0.7368(8)	0.4993(6)	0.209(6)	0.219(7)	0.121(4)	0.151(6)	0.014(4)	0.092(5)
O(3)	2*i*	0.1300(7)	0.6515(7)	0.6573(7)	0.132(5)	0.189(6)	0.196(6)	0.090(5)	0.111(5)	0.101(5)
O(4)	2*i*	0.3603(8)	0.8336(6)	0.6785(6)	0.184(6)	0.073(3)	0.157(5)	0.033(4)	–0.051(4)	–0.020(3)

2. {[Zn(ClO4)2(C13H14N2)2] · 2C6H6}n

Table 4. Data collection and handling.

Crystal:	colorless fragment, size 0.06 × 0.06 × 0.18 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	8.32 cm^{-1}
Diffractometer, scan mode:	Siemens SMART CCD, ω
$2\theta_{max}$:	46.52°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4309, 2734
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2551
$N(param)_{refined}$:	262
Programs:	SIR97 [3], SHELXTL [4], SADABS [5]

Table 5. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{iso}
H(01)	2*i*	0.3830	0.4735	0.1500	0.22(6)
H(02)	2*i*	0.3014	0.6322	–0.0583	0.24(7)
H(03)	2*i*	0.1891	0.8732	–0.1080	0.18(5)
H(04)	2*i*	0.1585	0.9668	0.0410	0.21(6)
H(05)	2*i*	0.2377	0.8230	0.2452	0.15(4)
H(06)	2*i*	0.3421	0.5762	0.3083	0.16(4)
H(1A)	2*i*	–0.0383	0.4788	0.7149	0.04(1)
H(1B)	2*i*	0.0643	0.5737	0.6686	0.06(2)
H(2A)	2*i*	0.2508	0.4245	0.8513	0.05(2)
H(2B)	2*i*	0.0848	0.4910	0.8894	0.06(2)
H(3A)	2*i*	0.0475	0.2719	0.9319	0.06(2)
H(3B)	2*i*	0.2110	0.2052	0.8904	0.07(2)
H(12)	2*i*	0.1495	0.1267	0.5568	0.06(2)
H(13)	2*i*	–0.0007	0.2916	0.6366	0.04(1)
H(15)	2*i*	0.3519	0.4256	0.6393	0.08(2)
H(16)	2*i*	0.4947	0.2574	0.5612	0.07(2)
H(22)	2*i*	0.5701	0.0985	0.2285	0.06(2)
H(23)	2*i*	0.4516	0.1909	0.0261	0.06(2)
H(25)	2*i*	0.0414	0.2219	0.1508	0.06(2)
H(26)	2*i*	0.1686	0.1248	0.3517	0.07(2)

Table 6. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Zn	1*h*	1/2	0	1/2	0.0335(5)	0.0419(5)	0.0311(5)	–0.0139(4)	0.0059(3)	–0.0147(4)
C(01)	2*i*	0.337(1)	0.574(1)	0.129(2)	0.063(6)	0.101(9)	0.24(2)	–0.006(5)	–0.003(8)	–0.07(1)
C(02)	2*i*	0.288(1)	0.669(2)	0.006(2)	0.068(6)	0.18(1)	0.19(1)	–0.062(8)	0.051(7)	–0.14(1)
C(03)	2*i*	0.223(1)	0.811(2)	–0.024(1)	0.096(7)	0.19(1)	0.100(8)	–0.098(8)	0.038(6)	–0.058(9)
C(04)	2*i*	0.204(1)	0.866(1)	0.064(1)	0.103(7)	0.115(9)	0.132(9)	–0.065(6)	0.016(7)	–0.047(7)
C(05)	2*i*	0.250(1)	0.781(2)	0.185(1)	0.093(7)	0.15(1)	0.112(8)	–0.066(7)	0.031(6)	–0.078(8)
C(06)	2*i*	0.314(1)	0.635(2)	0.223(1)	0.086(7)	0.14(1)	0.110(9)	–0.040(7)	–0.010(6)	–0.010(8)
C(1)	2*i*	0.0688(6)	0.4758(5)	0.7151(4)	0.050(3)	0.038(3)	0.039(3)	–0.009(2)	0.007(2)	–0.012(2)
C(2)	2*i*	0.1452(7)	0.4238(6)	0.8515(4)	0.061(4)	0.052(3)	0.038(3)	–0.020(3)	0.009(2)	–0.021(3)
C(3)	2*i*	0.1536(7)	0.2714(6)	0.9304(5)	0.058(4)	0.060(4)	0.037(3)	–0.029(3)	–0.001(2)	–0.011(3)
N(11)	2*i*	0.3398(5)	0.1722(4)	0.5518(4)	0.046(3)	0.047(3)	0.036(2)	–0.021(2)	0.008(2)	–0.017(2)
C(12)	2*i*	0.1924(6)	0.1866(6)	0.5745(5)	0.040(3)	0.060(3)	0.050(3)	–0.022(3)	0.008(2)	–0.029(3)
C(13)	2*i*	0.1011(6)	0.2860(6)	0.6228(5)	0.034(3)	0.061(3)	0.054(3)	–0.014(3)	0.007(2)	–0.030(3)
C(14)	2*i*	0.1592(6)	0.3772(5)	0.6509(4)	0.043(3)	0.041(3)	0.027(2)	–0.009(2)	0.001(2)	–0.009(2)
C(15)	2*i*	0.3080(7)	0.3647(6)	0.6247(6)	0.068(4)	0.062(4)	0.081(4)	–0.037(3)	0.031(3)	–0.047(3)
C(16)	2*i*	0.3934(7)	0.2631(6)	0.5769(6)	0.050(3)	0.067(4)	0.079(4)	–0.032(3)	0.028(3)	–0.039(3)
N(21)	2*i*	0.3818(5)	0.1001(4)	0.3121(3)	0.044(2)	0.050(3)	0.034(2)	–0.020(2)	0.009(2)	–0.016(2)
C(22)	2*i*	0.4622(6)	0.1221(6)	0.2134(5)	0.042(3)	0.081(4)	0.040(3)	–0.027(3)	0.009(2)	–0.017(3)
C(23)	2*i*	0.3913(7)	0.1779(7)	0.0914(5)	0.056(4)	0.092(5)	0.035(3)	–0.033(3)	0.014(3)	–0.016(3)
C(24)	2*i*	0.2324(6)	0.2148(6)	0.0642(4)	0.052(3)	0.051(3)	0.034(3)	–0.024(3)	0.002(2)	–0.012(2)
C(25)	2*i*	0.1499(6)	0.1958(6)	0.1644(5)	0.037(3)	0.063(4)	0.041(3)	–0.016(3)	0.001(2)	–0.018(3)
C(26)	2*i*	0.2273(6)	0.1380(6)	0.2853(5)	0.040(3)	0.063(4)	0.040(3)	–0.017(3)	0.012(2)	–0.020(3)
Cl	2*i*	0.7515(2)	0.2073(2)	0.4065(1)	0.0509(8)	0.0558(9)	0.0579(9)	–0.0299(7)	0.0124(7)	–0.0177(7)
O(1)	2*i*	0.6699(5)	0.1125(4)	0.4453(4)	0.066(3)	0.073(3)	0.100(3)	–0.052(2)	0.038(2)	–0.044(2)
O(2)	2*i*	0.795(1)	0.2361(9)	0.5045(6)	0.220(8)	0.252(9)	0.128(5)	–0.173(7)	0.027(5)	–0.112(6)
O(3)	2*i*	0.8734(8)	0.1538(8)	0.3484(8)	0.130(5)	0.185(7)	0.234(8)	–0.098(5)	0.132(6)	–0.120(6)
O(4)	2*i*	0.647(1)	0.3387(7)	0.3200(7)	0.200(8)	0.077(4)	0.157(6)	–0.035(5)	–0.054(6)	0.029(4)

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