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Crystal structure of pentaaqua(pyridine-3-carboxamide-*N*)cobalt(II) 1,5-naphthalenedisulfonate monohydrate, $[Co(H_2O)_5(C_6H_6N_2O)](C_{10}H_6S_2O_6) \cdot H_2O$

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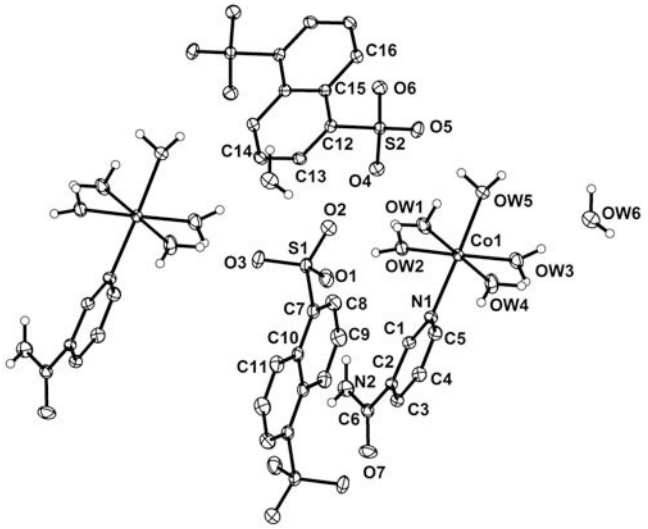

Abstract

$C_{16}H_{24}CoN_2O_{13}S_2$, triclinic, $P\bar{1}$ (no. 2), a = 9.954(1) Å, b = 10.278(1) Å, c = 11.675(1) Å, α = 95.579(2)°, β = 106.855(2)°, γ = 94.513(2)°, V = 1130.5 Å^3, Z = 2, $R_{gt}(F)$ = 0.029, $wR_{ref}(F^2)$ = 0.082, T = 298 K.

Source of material

Nicotinamide (NA, 0.048 g, 0.4 mmol) was added with constant stirring to an aqueous solution (20 ml) of $CoCl_2 \cdot 6H_2O$ (0.048 g, 0.2 mmol). The solution was then treated with disodium naphthalene-1,5-disulfonate (1,5-Na_2NDS, 0.58 g, 0.2 mmol). Yellow crystals of the title complex were collected after a few days (46 % yield based on Co).

Experimental details

The C-bound H atoms were geometrically placed (d(C—H) = 0.93 Å) and refined as riding with U_{iso}(H) = 1.2 U_{eq}(C). The O-bound H atoms were located in difference Fourier maps and refined as riding in their as-found relative positions with U_{iso}(H) = 1.2 U_{eq}(O).

Discussion

Recently, assembling metal complexes through hydrogen bonds to create inorganic-organic hybrid materials has attracted considerable attention [1-8]. However, rationally control of molecular self-assembly into ordered solid state networks with a desired arrangement and dimensionality is a challenge to chemists. In this paper, we chose the appropriate transition metal such as Co^{2+} with well-defined geometries and organic ligands with the inherent coordination and hydrogen bonding donor/acceptor functionalities, nicotinamides as the strategy to construct extended frameworks to evaluate the effect of intermolecular hydrogen bonds upon the assembly process of complex cations.

In the title crystal structure, the Co centre is hexa-coordinated with five aqua ligands and one nicotinamide ligand through the pyridine nitrogen atom, of which one aqua ligand and the nicotinamide ligand are bound to apical positions [d(Co—O) = 2.113(2) Å, d(Co—N) = 2.133(2) Å], other aqua ligands at equatorial positions [d(Co—O) = 2.071(2) - 2.113(2) Å], which is similar to those observed in [9]. The 1,5-NDS anion does not participate in the coordination of the Co(II), and has an inversion centre at the midpoint of the central C—C bond. The hexa-coordinated Co(II) complexes are connected by hydrogen bonds between amides and the coordinated water molecules [d(O1–H···O7) = 2.686(2) Å, d(O3–H···O7) = 2.849(2) Å] to form infinite chains along [100]. The hydrogen bond motif results in the formations of two unique rings in each chain, $C_2^2(16)$ and $C_4^4(12)$, respectively. In the larger ring, the distance between pyridine rings is 3.35 Å, indicating significant aromatic interactions. Adjacent chains are interlinked by 1,5-NDS ligands via hydrogen bonds between the sulfonate oxygen atoms and the remaining N–H protons on the nicotinamide ligands and the coordinated water molecules, respectively, to generate 2D hydrogen bonded sheets. One kind of the 1,5-NDS ligands behave as pillar to sustain the layers through hydrogen bonds formed between the sulfonate oxygen atoms and the coordinated water molecules and between the sulfonate oxygen atoms and the N–H protons on the nicotinamide ligands to form 3D channel structures. Another kind of 1,5-NDS ligands and the lattice water molecules are located in the channels and make contact with host channels through hydrogen bonding interactions between the sulfonate oxygen atoms and the coordinated water molecules, between the sulfonate oxygen atoms and the lattice water molecules, and between the lattice water molecules and the coordinated water molecules.

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Table 1. Data collection and handling.

Crystal:	yellow block, size 0.31 × 0.37 × 0.40 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	10.15 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5501, 3933
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3513
$N(param)_{refined}$:	319
Programs:	SHELXS-97, SHELXL-97, SHELXTL [10]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	2*i*	0.1270	0.2252	0.1777	0.09(1)
H(1B)	2*i*	0.0277	0.3170	0.1607	0.049(8)
H(2A)	2*i*	0.3866	0.3052	0.3590	0.057(8)
H(2B)	2*i*	0.3692	0.3930	0.4456	0.054(9)
H(3A)	2*i*	0.1003	0.6532	0.1206	0.080
H(3B)	2*i*	0.1385	0.5908	0.0314	0.080
H(4A)	2*i*	0.4837	0.6566	0.3291	0.057
H(4B)	2*i*	0.3811	0.7366	0.2924	0.080
H(5A)	2*i*	0.1217	0.4950	0.3980	0.054
H(5B)	2*i*	0.0414	0.5678	0.3142	0.090
H(6A)	2*i*	0.0771	0.8794	0.1842	0.110
H(6B)	2*i*	–0.0406	0.7907	0.2095	0.100
H(2C)	2*i*	0.8810	0.3241	0.3348	0.047
H(2D)	2*i*	0.7298	0.3180	0.3310	0.047
H(1)	2*i*	0.5554	0.4264	0.2639	0.029
H(3)	2*i*	0.6084	0.2876	–0.0500	0.034
H(4)	2*i*	0.3696	0.2967	–0.1408	0.036
H(5)	2*i*	0.2309	0.3666	–0.0256	0.035
H(8)	2*i*	0.1534	0.0180	–0.0068	0.049
H(9)	2*i*	0.1699	–0.0088	–0.2022	0.051
H(11)	2*i*	0.6177	0.0240	0.2366	0.043
H(13)	2*i*	0.3466	0.1270	0.5528	0.034
H(14)	2*i*	0.3219	–0.0998	0.4988	0.035
H(16)	2*i*	–0.1073	0.2204	0.5436	0.031

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)	2*i*	0.25402(3)	0.48033(3)	0.23573(2)	0.0221(2)	0.0244(2)	0.0291(2)	0.0055(1)	0.0089(1)	0.0048(1)
S(1)	2*i*	0.34085(7)	0.03324(5)	0.22518(5)	0.0568(4)	0.0265(3)	0.0408(3)	0.0164(3)	0.0271(3)	0.0116(2)
S(2)	2*i*	0.16831(5)	0.31359(5)	0.58452(4)	0.0218(3)	0.0218(3)	0.0246(3)	0.0013(2)	0.0049(2)	0.0029(2)
O(1)	2*i*	0.4353(2)	0.1480(2)	0.2944(2)	0.068(1)	0.0336(9)	0.041(1)	0.0161(8)	0.0233(9)	0.0009(7)
O(2)	2*i*	0.1927(2)	0.0498(2)	0.2092(2)	0.060(1)	0.045(1)	0.062(1)	0.0202(9)	0.0365(9)	0.0162(8)
O(3)	2*i*	0.3812(2)	–0.0882(2)	0.2728(2)	0.080(1)	0.0345(9)	0.061(1)	0.0236(9)	0.040(1)	0.0252(8)
O(4)	2*i*	0.3159(2)	0.3572(1)	0.5981(1)	0.0246(7)	0.0295(8)	0.0383(9)	–0.0021(6)	0.0067(6)	0.0002(6)
O(5)	2*i*	0.0728(2)	0.3692(1)	0.4864(1)	0.0301(8)	0.0298(8)	0.0350(8)	0.0025(6)	0.0020(6)	0.0126(6)
O(6)	2*i*	0.1331(2)	0.3355(1)	0.6970(1)	0.0362(8)	0.0312(8)	0.0288(8)	0.0033(6)	0.0120(6)	–0.0006(6)
O(7)	2*i*	0.8473(2)	0.3630(2)	0.1266(2)	0.0256(8)	0.068(1)	0.050(1)	0.0139(8)	0.0173(7)	0.0207(9)
OW(1)	2*i*	0.1163(2)	0.3095(2)	0.1730(2)	0.0233(8)	0.0290(9)	0.072(1)	0.0042(6)	0.0139(8)	0.0033(8)
OW(2)	2*i*	0.3774(2)	0.3882(2)	0.3778(1)	0.0435(9)	0.0334(9)	0.0292(8)	0.0152(7)	0.0148(7)	0.0080(6)
OW(3)	2*i*	0.1342(2)	0.5818(2)	0.1031(1)	0.046(1)	0.045(1)	0.0338(9)	0.0211(8)	0.0125(7)	0.0129(7)
OW(4)	2*i*	0.3941(2)	0.6513(2)	0.3028(2)	0.0289(9)	0.0259(8)	0.071(1)	0.0017(6)	0.0017(8)	0.0078(8)
OW(5)	2*i*	0.1309(2)	0.5481(2)	0.3445(1)	0.0383(9)	0.0344(8)	0.0409(9)	0.0134(7)	0.0221(7)	0.0113(7)
OW(6)	2*i*	0.0222(2)	0.7969(2)	0.1654(2)	0.056(1)	0.051(1)	0.057(1)	0.0145(9)	0.029(1)	0.0078(9)
N(1)	2*i*	0.3796(2)	0.4052(2)	0.1298(2)	0.0223(8)	0.0261(9)	0.0272(9)	0.0027(7)	0.0075(7)	0.0041(7)
N(2)	2*i*	0.7940(2)	0.3278(2)	0.2957(2)	0.028(1)	0.051(1)	0.035(1)	0.0078(9)	0.0020(8)	0.0107(9)
C(1)	2*i*	0.5176(2)	0.3990(2)	0.1817(2)	0.024(1)	0.025(1)	0.023(1)	0.0009(8)	0.0058(8)	0.0033(8)
C(2)	2*i*	0.6065(2)	0.3540(2)	0.1190(2)	0.023(1)	0.022(1)	0.027(1)	0.0014(8)	0.0079(8)	0.0057(8)
C(3)	2*i*	0.5510(2)	0.3161(2)	–0.0047(2)	0.033(1)	0.026(1)	0.030(1)	0.0049(8)	0.0146(9)	0.0049(8)
C(4)	2*i*	0.4094(2)	0.3218(2)	–0.0583(2)	0.033(1)	0.031(1)	0.023(1)	0.0033(9)	0.0043(8)	0.0024(8)
C(5)	2*i*	0.3270(2)	0.3651(2)	0.0113(2)	0.023(1)	0.030(1)	0.031(1)	0.0019(8)	0.0022(8)	0.0054(9)
C(6)	2*i*	0.7589(2)	0.3484(2)	0.1813(2)	0.025(1)	0.025(1)	0.037(1)	0.0044(8)	0.0090(9)	0.0053(9)
C(7)	2*i*	0.3604(2)	0.0181(2)	0.0773(2)	0.044(1)	0.023(1)	0.032(1)	0.0080(9)	0.017(1)	0.0051(8)
C(8)	2*i*	0.2409(3)	0.0116(2)	–0.0194(2)	0.040(1)	0.039(1)	0.047(1)	0.009(1)	0.016(1)	0.005(1)
C(9)	2*i*	0.2512(3)	–0.0044(2)	–0.1371(2)	0.041(1)	0.044(1)	0.037(1)	0.008(1)	0.002(1)	0.002(1)
C(10)	2*i*	0.4959(2)	0.0082(2)	0.0607(2)	0.042(1)	0.018(1)	0.029(1)	0.0057(9)	0.0122(9)	0.0027(8)
C(11)	2*i*	0.6219(3)	0.0138(2)	0.1577(2)	0.049(1)	0.030(1)	0.027(1)	0.009(1)	0.010(1)	0.0014(9)
C(12)	2*i*	0.1441(2)	0.1404(2)	0.5419(2)	0.027(1)	0.023(1)	0.020(1)	0.0020(8)	0.0054(8)	0.0033(7)
C(13)	2*i*	0.2586(2)	0.0786(2)	0.5356(2)	0.021(1)	0.031(1)	0.032(1)	0.0008(8)	0.0086(8)	0.0039(9)
C(14)	2*i*	0.2436(2)	–0.0580(2)	0.5031(2)	0.025(1)	0.031(1)	0.033(1)	0.0084(8)	0.0107(9)	0.0034(9)
C(15)	2*i*	0.0066(2)	0.0696(2)	0.5165(2)	0.024(1)	0.026(1)	0.020(1)	0.0037(8)	0.0061(8)	0.0042(7)
C(16)	2*i*	–0.1153(2)	0.1299(2)	0.5222(2)	0.029(1)	0.023(1)	0.027(1)	0.0056(8)	0.0085(8)	0.0026(8)

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References

1. Aakeröy, C. B.; Beatty, A. M.; Leinen, D. S.: A Versatile Route to Porous Solids: Organic-Inorganic Hybrid Materials Assembled through Hydrogen Bonds. Angew. Chem., Int. Ed. **38** (1998) 1815-1819.
2. Zelenák, V.; Sabo, M.; Massa, W.; Llewellyn, P.: Preparation, characterisation and crystal structure of two zinc(II) benzoate complexes with pyridine-based ligands nicotinamide and methyl-3-pyridylcarbamate. Inorg. Chim. Acta **357** (2004) 2049-2059.
3. Bera, J. K.; Vo, T. T.; Walton, R. A.; Dunbar, K. R.: Hydrogen-bonding as a tool for building one-dimensional structures based on dimetal building blocks. Polyhedron **22** (2003) 3009-3014.
4. Aakeröy, C. B.; Beatty, A. M.: Supramolecular assembly of low-dimensional silver(I) architectures via amide-amide hydrogen bonds. Chem. Commun. (1998) 1067-1068.
5. Aakeröy, C. B.; Beatty, A. M.; Helfrich, B. A.: Two-fold interpenetration of 3-D nets assembled via three-coordinate silver(I) ions and amide-amide hydrogen bonds. J.Chem. Soc., Dalton Trans. (1998) 1943-1945.
6. Rivas, J. C. M.; Brammer, L.: Supramolecular assembly of anion-channel and anion-layer structures of $[PtL_4]X_2$ (L = nicotinamide; X = Cl or PF_6]: surprisingly robust arene ring 'herringbone' motifs and adaptable amide-amide hydrogen bonding. New J. Chem. (1998) 1315-1318.
7. Aakeröy, C. B.; Beatty, A. M.; Leinen, D. S.; Lorimer, K. R.: Deliberate combination of coordination polymers and hydrogen bonds in a supramolecular design strategy for inorganic/organic hybrid networks. Chem. Commun. (2000) 935-936.
8. Brammer, L.; Rivas, J. C. M.; Atencio, R.; Fang, S, Y.; Pigge, F. C.: Combining hydrogen bonds with coordination chemistry or organometallic π-arene chemistry: strategies for inorganic crystal engineering. J. Chem. Soc., Dalton Trans. (2000) 3855-3867.
9. Lu, Y. L.; Wu, J.-Y.; Chan, M. C.; Huang, S. M.; Lin, C. S.; Chiu, T. W.; Liu, Y. H.; Wen, Y. S.; Ueng, C. H.; Chin, T. M.; Hung, C. H.; Lu, K. L.: Influence of Water Content on the Self-Assembly of Metal-Organic Frameworks Based on Pyridine-3,5-dicarboxylate. Inorg. Chem. **45** (2006) 2430-2437.
10. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112-122.