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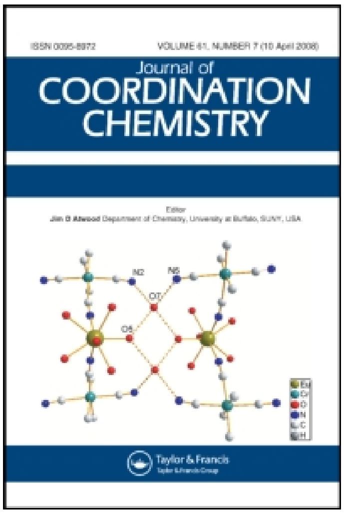

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Synthesis and crystal structure of a 3-d polymeric cobalt(II) and sodium complex with pyrazine-2-carboxylate as a bridging ligand

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SYNTHESIS AND CRYSTAL STRUCTURE OF A 3-D POLYMERIC COBALT(II) AND SODIUM COMPLEX WITH PYRAZINE-2-CARBOXYLATE AS A BRIDGING LIGAND

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A complex with a three-dimensional structure $\{[Na_3Co(pyz)_3(H_2O)_4(ClO_4)_2]\}_n$ (pyz = pyrazine-2-carboxylate anion) has been synthesized and its crystal structure determined by X-ray crystallography. The complex crystallizes in a triclinic system with a space group $P\bar{1}$ and $a = 8.598(11)$, $b = 11.382(15)$, $c = 14.496(19)$ Å, $\alpha = 87.79(2)$, $\beta = 88.21(2)$, $\gamma = 82.08(2)°$. The Co(II) ion is located in a distorted octahedral environment with three oxygen atoms and three nitrogen atoms, from the three pyr ligands. Na(1) ion is coordinated by four oxygen atoms and two nitrogen atoms, in which O(1), O(2), O(2A), N(4A) and N(6A) come from ligand pyr while O(15) comes from H_2O. Na(2) and Na(3) ions are each coordinated by six oxygen atoms. Through coordination of the bridging ligand pyr with Co(II) and Na(I) a three-dimensional net structure is formed.

Keywords: X-ray crystal structure; Cobalt; Pyrazine ligands; Crystal engineering

INTRODUCTION

For a long time research has focused on crystal engineering of coordination polymers because such new compounds may afford new materials with useful properties such as catalytic activity, microporosity, electrical conductivity, non-linear optical activity, co-operative magnetic behavior, etc. The key to synthesis of ideal coordination polymers is design and selection of bridging ligands. Many complexes with pyrazine and its derivatives, such as pyrazine-2-carboxylate [1–13], pyrazine-2,3-dicarboxylate and other ligands, have been synthesized and some physical properties of these complexes investigated. Complexes with pyrazine-2-carboxylate (pyz) as bridging ligand are rare [3,5]; here we report the synthesis and crystal structure of the title complex.

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EXPERIMENTAL

Preparation

The three-dimensional complex $\{[Na_3Co(pyz)_3(H_2O)_4(ClO_4)_2]\}_\infty$ was prepared as follows. Pyrazine-2-carboxylic acid (0.1468 g, 1.18 mmol) and $Co(ClO_4)_2 \cdot 6H_2O$ (0.4320 g, 1.18 mmol) were dissolved in H_2O (25 cm^3), then NaSCN (0.1960 g, 2.42 mmol) was added and the solution was stirred for a few minutes at room temperature. Orange single crystal was obtained after the solution was allowed to stand at room temperature for three weeks (Yield: 0.6526 g, 72%). Anal. Calcd. for $C_{15}H_{17}Cl_2CoN_6Na_3O_{18}$(%): C, 23.45; H, 2.23; N, 10.94; Co, 7.67. Found: C, 24.67; H, 2.62; N, 10.65; Co, 7.20. Infrared spectra were recorded with a Shimadzu 408 IR spectrophotometer using KBr discs.

Crystal Structure Determination

A single crystal with dimensions 0.40 × 0.25 × 0.18 mm was selected and the determination of the single crystal was carried out with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) on a Bruker Smart-1000 diffractometer using the ω scan mode. A total of 6393 reflections were collected in the range of $1.8 \le \theta \le 26.4°$ at 298(2) K, of which 5082 reflections were independent (R(int) = 0.0277) and 3156 reflections with $I > 2\sigma(I)$ were considered to be observed and used in the succeeding refinement. Corrections for Lorentz and polarization factors were applied and all non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were located from a difference Fourier map and refined isotropically using the riding model with displacement parameters. The final refinement including hydrogen atoms converged to $R = 0.0559$ and $wR = 0.1275$, $w = 1/[\sigma^2(F_O)^2 + (0.0723\,P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$, $S = 0.907$, $(\Delta\rho)_{max} = 0.096$ e/Å^3, $(\Delta\rho)_{min} = -1.061$ e/Å^3, $(\Delta/\sigma)_{max} = 0.000$. The programs of structure solution and refinement are SHELXS97 [14] and SHELXL97 [15], respectively.

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RESULTS AND DISCUSSION

Crystal Structure

Crystal Data

$C_{15}H_{17}Cl_2CoN_6Na_3O_{18}$, $M = 768.15$, triclinic, space group $P\bar{1}$, $a = 8.598(11)$, $b = 11.382(15)$, $c = 14.496(19)$ Å, $\alpha = 87.79(2)$, $\beta = 88.21(2)$, $\gamma = 82.08(2)°$, $V = 1404(3)$ Å^3, $Z = 2$, $D_c = 1.817$ g cm^{-3}, $F(000) = 774$, μ (Mo Kα) = 0.940 mm^{-1}. Selected bond distances and angles are listed in Table I.

Figure 1 shows the coordination diagram of the complex with the atom numbering scheme, in which the bonds involving the Na(I) ions are indicated by dotted lines. Co(1) is coordinated by O(1), O(3), O(5), N(1), N(3) and N(5), the six coordinating atoms coming from three pyr ligands with each pyr ligand contributing one oxygen atom and one nitrogen atom to the octahedron. The bond lengths and the associated angles relating to Co(1) indicate that the atom is located in a distorted octahedral environment. The coordination bond lengths for Co(1) range from 2.063(4) to 2.147(5) Å,

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TABLE I Selected bond lengths (Å) and bond angles (°)

Co(1)–O(5)	2.063(4)	Co(1)–O(1)	2.063(4)	Co(1)–O(3)	2.086(4)
Co(1)–N(5)	2.136(4)	Co(1)–N(3)	2.138(4)	Co(1)–N(1)	2.147(5)
Na(1)–O(2A)	2.297(5)	Na(1)–O(15)	2.319(6)	Na(1)–O(1)	2.445(5)
Na(1)–O(2)	2.551(5)	Na(1)–N(4A)	2.566(6)	Na(1)–N(6A)	2.621(6)
Na(2)–O(4)	2.273(5)	Na(2)–O(16)	2.349(6)	Na(2)–O(17)	2.409(5)
Na(2)–O(18)	2.417(5)	Na(2)–O(6A)	2.627(5)	Na(2)–O(6B)	2.977(5)
Na(3)–O(18)	2.315(5)	Na(3)–O(6A)	2.333(5)	Na(3)–O(17A)	2.376(5)
Na(3)–O(7)	2.412(6)	Na(3)–O(14)	2.460(6)	Na(3)–O(11)	2.535(7)
O(5)–Co(1)–O(1)	106.48(14)	O(5)–Co(1)–O(3)	86.30(13)		
O(1)–Co(1)–O(3)	165.87(14)	O(5)–Co(1)–N(5)	77.84(13)		
O(1)–Co(1)–N(5)	90.58(13)	O(3)–Co(1)–N(5)	98.14(13)		
O(5)–Co(1)–N(3)	160.22(13)	O(1)–Co(1)–N(3)	91.41(13)		
O(3)–Co(1)–N(3)	76.99(13)	N(5)–Co(1)–N(3)	93.95(13)		
O(5)–Co(1)–N(1)	95.82(15)	O(1)–Co(1)–N(1)	78.91(15)		
O(3)–Co(1)–N(1)	94.10(15)	N(5)–Co(1)–N(1)	165.77(15)		
N(3)–Co(1)–N(1)	95.86(15)				
O(2A)–Na(1)–O(15)	95.10(16)	O(2A)–Na(1)–O(1)	134.48(14)		
O(15)–Na(1)–O(1)	94.37(15)	O(2A)–Na(1)–O(2)	82.15(12)		
O(15)–Na(1)–O(2)	93.75(15)	O(1)–Na(1)–O(2)	52.85(11)		
O(2A)–Na(1)–N(4A)	90.03(14)	O(15)–Na(1)–N(4A)	174.84(17)		
O(1)–Na(1)–N(4A)	81.66(14)	O(2)–Na(1)–N(4A)	86.50(14)		
O(2A)–Na(1)–N(6A)	104.22(14)	O(15)–Na(1)–N(6A)	90.73(16)		
O(1)–Na(1)–N(6A)	120.07(14)	O(2)–Na(1)–N(6A)	171.88(14)		
N(4A)–Na(1)–N(6A)	88.43(15)				
O(4)–Na(2)–O(16)	101.09(15)	O(4)–Na(2)–O(17)	93.12(13)		
O(16)–Na(2)–O(17)	99.53(14)	O(4)–Na(2)–O(18)	98.42(13)		
O(16)–Na(2)–O(18)	85.41(13)	O(17)–Na(2)–O(18)	166.36(14)		
O(4)–Na(2)–O(6A)	90.45(13)	O(16)–Na(2)–O(6A)	165.41(14)		
O(17)–Na(2)–O(6A)	88.60(12)	O(18)–Na(2)–O(6A)	84.09(12)		
O(4)–Na(2)–O(6B)	166.44(14)	O(16)–Na(2)–O(6B)	81.45(16)		
O(17)–Na(2)–O(6B)	73.32(13)	O(18)–Na(2)–O(6B)	95.06(13)		
O(6A)–Na(2)–O(6B)	89.41(15)				
O(18)–Na(3)–O(6A)	93.37(13)	O(18)–Na(3)–O(17A)	94.08(13)		
O(6A)–Na(3)–O(17A)	87.21(13)	O(18)–Na(3)–O(7)	90.16(15)		
O(6A)–Na(3)–O(7)	91.73(15)	O(17A)–Na(3)–O(7)	175.68(16)		
O(18)–Na(3)–O(14)	156.41(17)	O(6A)–Na(3)–O(14)	109.92(16)		
O(17A)–Na(3)–O(14)	90.93(15)	O(7)–Na(3)–O(14)	85.50(17)		
O(18)–Na(3)–O(11)	103.23(16)	O(6A)–Na(3)–O(11)	163.21(17)		
O(17A)–Na(3)–O(11)	89.09(16)	O(7)–Na(3)–O(11)	90.74(18)		
O(14)–Na(3)–O(11)	53.75(17)				

in which the Co–N bond lengths (2.136(4), 2.138(4) and 2.147(5) Å) are longer than Co–O bond lengths (2.063(4), 2.086(4) Å). These bond lengths fall within the normal range. Na(1) is coordinated by O(1), O(2), O(2A), O(15), N(4A) and N(6A), in which O(15) comes from an H_2O molecule and the other coordinating atoms are from four pyr ligands. Na(2) is coordinated by six oxygen atoms with O(4), O(6A) and O(6B) from three pyr ligands and O(16), O(17) and O(18) from three H_2O molecules. Na(3) is also coordinated by six oxygen atoms, with O(6A) from a pyr ligand, O(17A) and O(18) from H_2O molecules and O(7), O(11) and O(14) from two perchlorate ions. Except for Na(2)–O(6B) which is a little longer, the Na–O bond lengths range from 2.273(5) to 2.627(5) Å, and the Na–N bond lengths are 2.566(6) and 2.621(6) Å. All these bond lengths are similar to those previously observed [16–23] and are consistent with the existence of a significant bonding interaction between sodium and oxygen atoms and between sodium and nitrogen atoms [24]. The bond lengths and bond angles for the three Na(I) ions indicate that their coordination environments are distorted

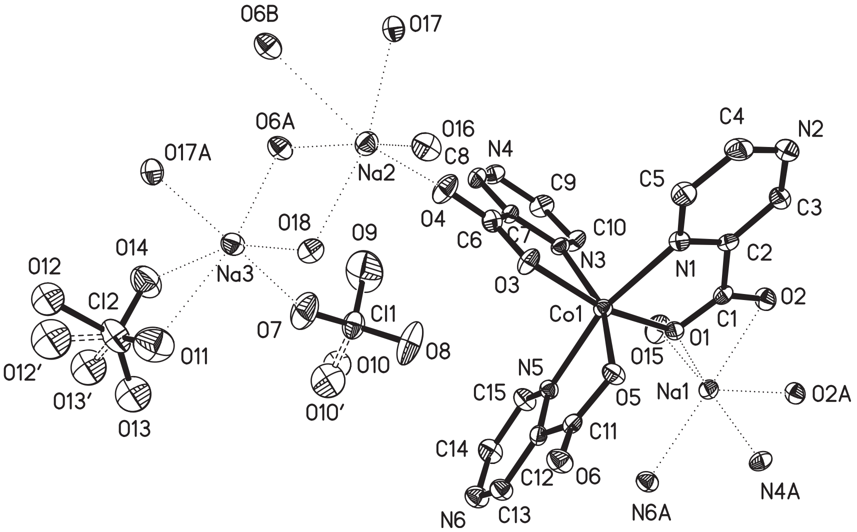

FIGURE 1 Perspective view of the title complex with atom numbering scheme.

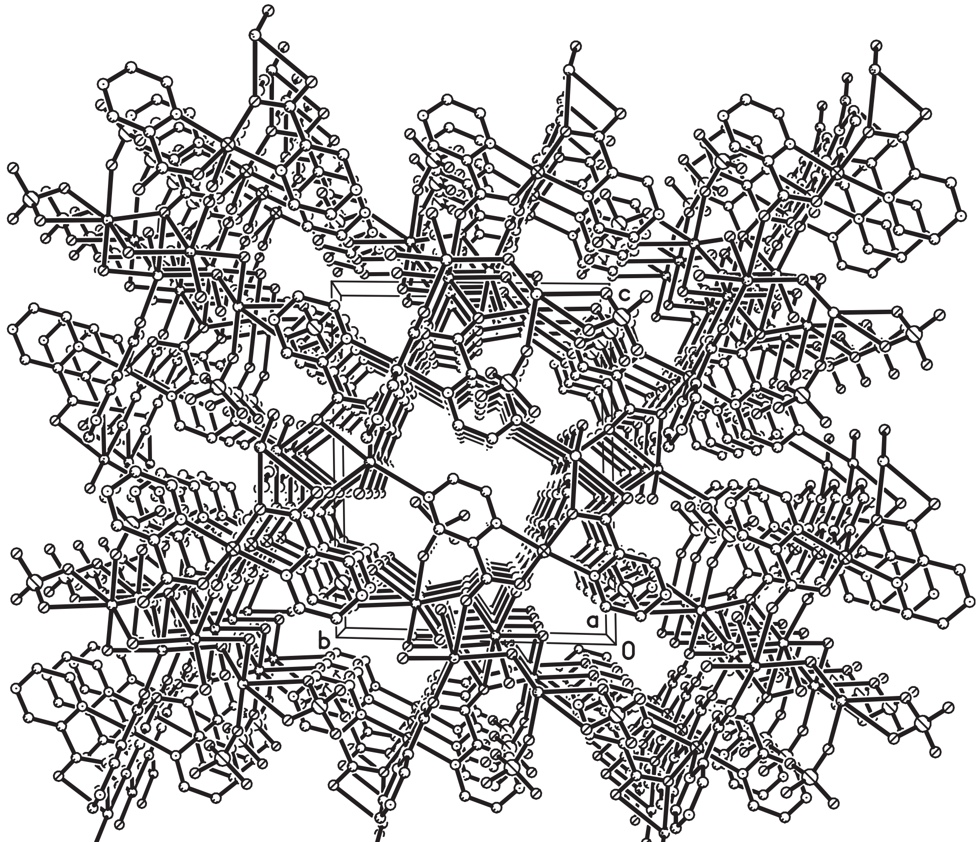

FIGURE 2 Unit cell and the three-dimensional structure.

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octahedra. Figure 1 also indicates that Co(II) ions and Na(I) ions are bridged by pyr bridging ligands, while one water molecule (containing O(18)) and one carboxylate oxygen atom act as bridging ligands between Na(2) and Na(3). It is these bridging ligands that lead to the connections between Co(II) ions and Na(I) ions and the formation of the three-dimensional net structure, which is shown in Figure 2.

Infrared Spectrum

The IR absorption bands of free pyrazine-2-carboxylic acid that occur at 1720 cm^{-1} (br, vs) and 1315 cm^{-1}(vs) for vibration of $\nu(\text{C}=\text{O})$, 1272 cm^{-1}(m), 1152 cm^{-1}(vs), 1052 cm^{-1}(s), 1020 cm^{-1}(s), 890 cm^{-1}(m) and 820 cm^{-1}(m) for pyrazine ring vibration, appeared in the complex at 1640 cm^{-1}(vs) and 1370 cm^{-1}(vs) for vibration of $\nu_{\text{as}}(\text{C}=\text{O})$ and $\nu_{\text{s}}(\text{C}=\text{O})$, respectively, and 865 cm^{-1}(s) for pyrazine ring vibration. The typical strong and broad peaks at 1095 and 1125 cm^{-1} for the vibrations of perchlorate ion cover the peaks from the pyrazine ring in this region.

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Supplementary Material

The X-ray crystallographic file, in CIF format, is available from the Cambridge Crystallographic Data Centre on quoting the deposition number CCDC 197279.

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