Crystal structure of tris(2,2′-bipyridine)cobalt(II) diperchlorate, $[Co(C_{10}H_8N_2)_3][ClO_4]_2$

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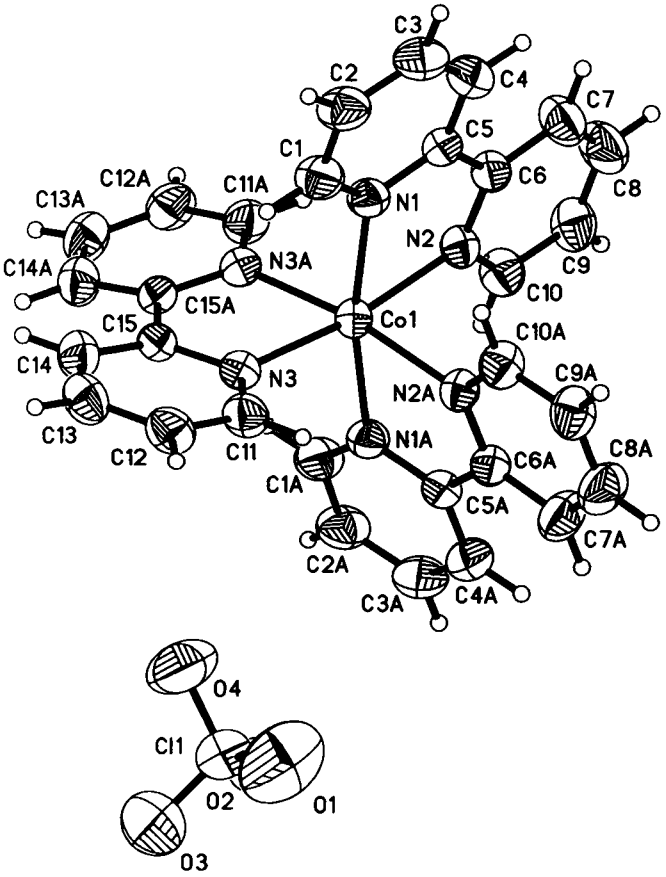

Abstract

$C_{30}H_{24}Cl_2CoN_6O_8$, monoclinic, $C12/c1$ (no. 15), $a = 17.538(4)$ Å, $b = 10.897(2)$ Å, $c = 16.078(3)$ Å, $\beta = 91.01(3)°$, $V = 3072.2$ Å^3, $Z = 4$, $R_{gt}(F) = 0.044$, $wR_{ref}(F^2) = 0.113$, $T = 293$ K.

Source of material

Compound $[Co(bipy)_3](ClO_4)_2$ (bipy = 2,2′-bipyridine) was synthesized by adding a solution of bipy (0.2348 g, 1.5 mmol) and 3,5-pyrazoledicarboxylate (0.0766 g, 0.5 mmol) in 20.0 mL ethanol to a stirred aqueous solution of $Co(ClO_4)_2 \cdot 6H_2O$ (0.183 g, 0.5 mmol) with $NaClO_4$ (0.031 g, 0.25 mmol) in 5.0 mL ethanol with slight acidity. The resulting pink solution was stirred for 15 hours at 318 K, a little solid was filtrated and washed by ethanol. The filtrate was allowed to evaporate slowly in the atmosphere at room temperature for 5 days, and the dark-yellow block-shaped crystals suitable for X-ray single-crystal diffraction were isolated (yield 63.8 %).

Discussion

The crystal structures of tris-chelated first-row transition-metal complexes of $[M(bipy)_3](ClO_4)_2$ (M = Mn, Fe, Ni, Cu, Zn) have been synthesized in the past decades [1-5]. The known complexes containing the $[Co(bipy)_3]^{2+}$ subunit crystallize in a complicated double salt form and have been extensively investigated [6-13], so far as we know, there are no available structural data for simple anhydrous $[Co(bipy)_3]^{2+}(X^-)_2$ (X = anion such as ClO_4^-, NO_3^-) type compounds. Especially to our great interest, when trying to prepare the cobalt(II) complex containing bipy and 3,5-pyrazoledicarboxylate ligands, we did not obtain the expected compound but, instead, yellow prismatic crystals of tris(2,2′-bipyridine)-cobalt(II) diperchlorate.

The new compound, $[Co(bipy)_3](ClO_4)_2$, is composed of a monomeric $[Co(bipy)_3]^{2+}$ cation and two perchlorate anions, being isostructural with the iron(II) [2], nickel(II) [3] and zinc(II) [5] complexes. The asymmetric unit contains one half cation and one anion. A twofold rotation axis passes through the cobalt(II) and bisects one bipy ligand. The Co(II) is coordinated by six N atoms from three bidentate chelating bipy ligands, forming three five-membered chelated rings, with Ni—N bond lengths ranging from 2.119(2) Å to 2.136(2) Å with the average value of 2.129 Å, shorter than those of the isomorphous Zn(II) compound [2.135(2) Å – 2.172(3) Å, mean value of 2.157 Å], larger than those of the isomorphous Ni(II) compound [2.071(4) Å – 2.091(4) Å, mean value of 2.082 Å]. The N–Co–N bond angles of the bipy ligands in the title compound are in a range of 77.1(1)° to 77.7(1)°, smaller than those of the Ni(II) isomorph [78.6(1)° – 79.1(2)°]. The dihedral angles between each pair of pyridine rings in three non-planar bipy ligands are 7.3° to 17.8°. Thus, the coordination polyhedron around the Co(II) center could be best described as a distorted octahedron. The crystal packing of the title structure is formed by two-dimensional layers of cations and anions parallel to the a,b plane.

Table 1. Data collection and handling.

Crystal:	dark-yellow, prismatic, size 0.20 × 0.20 × 0.30 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	7.95 cm^{-1}
Diffractometer, scan mode:	Rigaku R-AXIS RAPID, ω/φ
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4365, 2492
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2149
$N(param)_{refined}$:	214
Programs:	SHELXS-97 [14], SHELXL-97 [15]

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

Atom	Site	x	y	z	U_{iso}
H(1A)	8f	0.4099	0.3570	0.4009	0.058
H(2A)	8f	0.3135	0.4133	0.4883	0.063
H(3A)	8f	0.2433	0.5883	0.4581	0.063
H(4A)	8f	0.2682	0.6986	0.3390	0.058
H(7A)	8f	0.2901	0.7798	0.2172	0.067
H(8A)	8f	0.3278	0.8709	0.0944	0.075
H(9A)	8f	0.4375	0.8042	0.0315	0.064
H(10A)	8f	0.5047	0.6452	0.0898	0.054
H(11A)	8f	0.6000	0.4052	0.4095	0.053
H(12A)	8f	0.6200	0.2364	0.4927	0.060
H(13A)	8f	0.5746	0.0469	0.4483	0.063
H(14A)	8f	0.5141	0.0302	0.3192	0.060

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)	4e	½	0.47366(5)	¼	0.0348(3)	0.0291(3)	0.0348(3)	0	0.0005(2)	0
Cl(1)	8f	0.32473(5)	0.00771(8)	0.36353(5)	0.0550(6)	0.0664(6)	0.0389(4)	−0.0076(4)	0.0009(4)	0.0029(3)
N(1)	8f	0.3987(1)	0.4930(2)	0.3207(2)	0.034(1)	0.038(1)	0.041(1)	−0.001(1)	0.003(1)	0.004(1)
N(2)	8f	0.4398(1)	0.6161(2)	0.1859(1)	0.041(2)	0.033(1)	0.036(1)	0.001(1)	0.001(1)	0.0012(9)
N(3)	8f	0.5434(1)	0.3222(2)	0.3186(1)	0.033(1)	0.036(1)	0.039(1)	0.001(1)	−0.002(1)	0.000(1)
C(1)	8f	0.3816(2)	0.4272(3)	0.3889(2)	0.044(2)	0.052(2)	0.048(2)	0.000(2)	0.005(1)	0.015(1)
C(2)	8f	0.3239(2)	0.4599(3)	0.4414(2)	0.042(2)	0.065(2)	0.050(2)	−0.003(2)	0.010(2)	0.010(2)
C(3)	8f	0.2819(2)	0.5633(3)	0.4229(2)	0.039(2)	0.069(2)	0.051(2)	−0.003(2)	0.012(2)	−0.000(2)
C(4)	8f	0.2969(2)	0.6294(3)	0.3524(2)	0.039(2)	0.047(2)	0.058(2)	0.006(2)	0.006(2)	−0.002(2)
C(5)	8f	0.3559(2)	0.5916(3)	0.3012(2)	0.032(2)	0.034(2)	0.042(2)	−0.004(1)	−0.002(1)	−0.001(1)
C(6)	8f	0.3762(2)	0.6570(3)	0.2236(2)	0.038(2)	0.033(2)	0.044(2)	0.000(1)	−0.003(1)	−0.002(1)
C(7)	8f	0.3336(2)	0.7526(3)	0.1906(2)	0.056(2)	0.049(2)	0.062(2)	0.016(2)	0.007(2)	0.012(2)
C(8)	8f	0.3564(2)	0.8073(4)	0.1177(2)	0.062(3)	0.054(2)	0.071(2)	0.016(2)	0.000(2)	0.022(2)
C(9)	8f	0.4209(2)	0.7675(3)	0.0802(2)	0.066(2)	0.045(2)	0.048(2)	0.000(2)	0.002(2)	0.016(1)
C(10)	8f	0.4608(2)	0.6722(3)	0.1157(2)	0.051(2)	0.044(2)	0.040(2)	0.003(2)	0.006(1)	0.006(1)
C(11)	8f	0.5815(2)	0.3293(3)	0.3920(2)	0.042(2)	0.045(2)	0.046(2)	0.003(1)	−0.008(1)	0.001(1)
C(12)	8f	0.5942(2)	0.2287(3)	0.4420(2)	0.049(2)	0.054(2)	0.046(2)	0.009(2)	−0.008(2)	0.003(1)
C(13)	8f	0.5678(2)	0.1160(3)	0.4151(2)	0.059(2)	0.046(2)	0.054(2)	0.011(2)	−0.000(2)	0.012(2)
C(14)	8f	0.5310(2)	0.1060(3)	0.3386(2)	0.055(2)	0.037(2)	0.057(2)	0.002(2)	−0.002(2)	0.006(1)
C(15)	8f	0.5199(2)	0.2114(2)	0.2910(2)	0.030(2)	0.033(2)	0.043(2)	0.003(1)	0.003(1)	0.001(1)
O(1)	8f	0.3313(3)	0.0852(5)	0.4323(2)	0.150(4)	0.161(4)	0.086(2)	−0.046(3)	0.012(2)	−0.061(3)
O(2)	8f	0.3355(2)	0.0711(4)	0.2903(2)	0.093(3)	0.174(4)	0.071(2)	0.004(3)	0.010(2)	0.062(2)
O(3)	8f	0.3827(2)	−0.0859(4)	0.3713(3)	0.093(3)	0.091(3)	0.177(4)	0.011(2)	−0.028(3)	0.023(3)
O(4)	8f	0.2510(2)	−0.0480(3)	0.3625(2)	0.067(2)	0.110(3)	0.120(3)	−0.029(2)	0.011(2)	−0.008(2)

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