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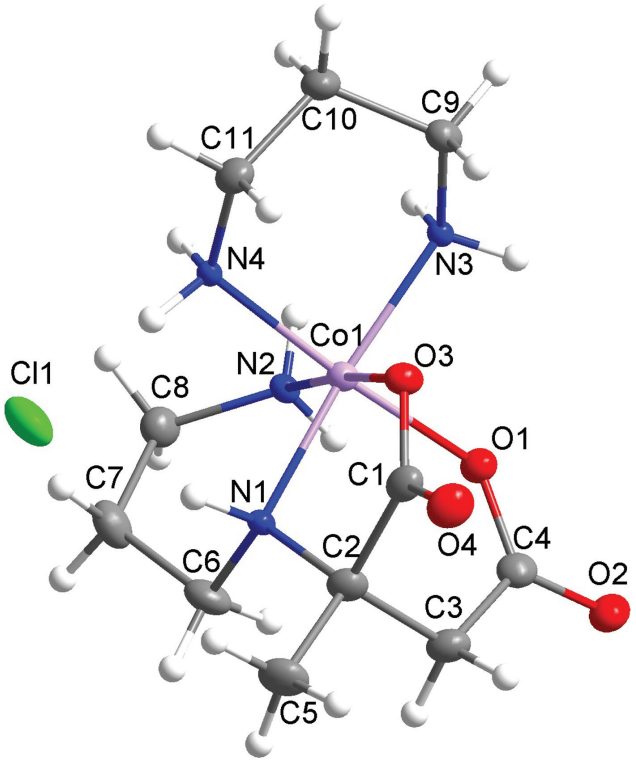
Crystal structure of (1,3-propanediamine-κ²*N*,*N*′)(*N*-(3-aminopropyl)-α-methyl aspartato-κ⁴*N*,*N*′,*O*,*O*′)cobalt(III) chloride, $C_{11}H_{24}ClCoN_4O_4$



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Abstract

$C_{11}H_{24}ClCoN_4O_4$, monoclinic, $P2_1/c$ (no. 14), $a = 11.4214(1)$ Å, $b = 9.8842(1)$ Å, $c = 13.6893(1)$ Å, $\beta = 106.436(1)°$, $V = 1482.25(2)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0238$, $wR_{ref}(F^2) = 0.0616$, $T = 296(2)$ K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Red polyhedron
Size:	0.26 × 0.23 × 0.19 mm
Wavelength:	Mo *Kα* radiation (0.71073 Å)
μ:	1.36 mm^{-1}
Diffractometer, scan mode:	Bruker P4, ω
θ_{max}, completeness:	28.3°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	19734, 3684, 0.017
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3498
$N(param)_{refined}$:	191
Programs:	Bruker [1], SHELX [2, 3], Diamond [4]

Source of material

The mixture of $CoCl_2{\cdot}6\ H_2O$ (0.071 g, 0.3 mmol), 1,3-diaminopropane (0.075 mL, 0.9 mmol), citraconic acid (0.039 g, 0.3 mmol) in ethanol (1.0 mL) was sealed under vacuum in a Pyrex tube and heated to 70 °C for 68 h, then cooled to room temperature at 20 °C/h. The pH before and after the reaction were 7 and 6, respectively. The red polyhedral crystals were recovered by vacuum filtration and washed with distilled water. The product is stable in air.

Experimental details

All hydrogen atoms were placed in calculated positions and refined as riding model.

Comment

We previously published a series of tailor-made α-amino acid metal complexes, which are formed under mild hydrothermal conditions *in situ* by Michael addition of amine to *α*,*β*-unsaturated dicarboxylic acid [5–8]. Several metal complexes with various *N*-substituted aspartates and diacetate were formed by the direct amination of *α*,*β*-unsaturated dicarboxylic acids such as fumaric acid, maleic acid, and muconic acid. In this study we report a racemic

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	x	y	z	U_{iso}*/U_{eq}
Co1	0.20161(2)	0.91803(2)	0.18192(2)	0.01249(6)
N1	0.25900(10)	0.73449(11)	0.21961(8)	0.0163(2)
H1	0.336527	0.726245	0.202699	0.020*
Cl1	0.52749(4)	0.72731(4)	0.17210(3)	0.02944(9)
O1	0.04236(8)	0.87559(10)	0.19455(7)	0.01752(18)
O2	−0.11854(9)	0.75361(11)	0.19707(8)	0.0238(2)
N2	0.23774(10)	0.97809(12)	0.32387(8)	0.0184(2)
H2A	0.238205	1.068124	0.323025	0.022*
H2B	0.174745	0.953390	0.345976	0.022*
O3	0.15885(8)	0.84642(9)	0.04661(7)	0.01651(18)
N3	0.12924(10)	1.09337(11)	0.12792(8)	0.0161(2)
H3A	0.048585	1.085968	0.114592	0.019*
H3B	0.153563	1.154491	0.177252	0.019*
O4	0.10406(10)	0.65386(11)	−0.03844(8)	0.0244(2)
N4	0.35955(10)	0.98054(11)	0.17217(8)	0.0161(2)
H4A	0.387446	1.042040	0.220666	0.019*
H4B	0.410943	0.910837	0.185834	0.019*
C1	0.14272(12)	0.71685(13)	0.04140(10)	0.0172(2)
C2	0.17047(12)	0.64404(13)	0.14604(10)	0.0186(2)
C3	0.05011(13)	0.63140(14)	0.17366(11)	0.0211(3)
H12A	−0.006365	0.580256	0.120147	0.025*
H12B	0.065436	0.578380	0.235633	0.025*
C4	−0.01306(12)	0.76159(14)	0.18952(10)	0.0188(3)
C5	0.22429(15)	0.50312(14)	0.14144(12)	0.0257(3)
H5A	0.304240	0.511650	0.132263	0.039*
H5B	0.172540	0.453589	0.085369	0.039*
H5C	0.229847	0.455767	0.203820	0.039*
C11	0.36397(12)	1.04028(14)	0.07366(10)	0.0191(2)
H11A	0.331312	0.975949	0.019259	0.023*
H11B	0.448174	1.058473	0.075988	0.023*
C10	0.29100(12)	1.17069(14)	0.05131(11)	0.0206(3)
H10A	0.321219	1.232971	0.107569	0.025*
H10B	0.303227	1.212106	−0.009297	0.025*
C9	0.15579(12)	1.14814(13)	0.03540(10)	0.0176(2)
H9A	0.112968	1.233255	0.016952	0.021*
H9B	0.125532	1.085505	−0.020626	0.021*
C6	0.28615(14)	0.69836(14)	0.32907(10)	0.0227(3)
H6A	0.310840	0.604289	0.338956	0.027*
H6B	0.213747	0.710490	0.351826	0.027*
C7	0.38810(13)	0.78889(16)	0.39021(10)	0.0247(3)
H7A	0.452962	0.790005	0.357296	0.030*
H7B	0.421103	0.749601	0.457320	0.030*
C8	0.35038(13)	0.93470(14)	0.40271(10)	0.0218(3)
H8A	0.337361	0.944445	0.469371	0.026*
H8B	0.416798	0.994465	0.400118	0.026*

cobalt complex containing *N*-(3-aminopropyl)-α-methyl aspartate, which is formed *in situ* by Michael addition of 1,3-diaminopropane to citraconic acid.

The title structure contains a discrete mononuclear $Co[C_{11}H_{24}N_4O_4]^+$ cation. One unique cobalt atom is coordinated by two nitrogen atoms and two oxygen atoms in a *N*-(3-aminopropyl)-α-methyl aspartate. The other two oxygen atoms in each carboxylate group of the *N*-(3-aminopropyl)-α-methyl aspartate remain uncoordinated. Two additional nitrogen atoms from 1,3-diaminopropane ligand in a *cis*-configuration complete a slightly distorted octahedral arrangement with distances in the range of 1.9128(9) Å–1.9717(11) Å. A bond valence sum (BVS) calculation gives a value of 2.88 for Co indicating an oxidation state of +3 [9]. The $Co[C_{11}H_{24}N_4O_4]^+$ cation charge is balanced by one chloride anion. Each chloride anion bridges two Co[(*N*-(3-aminopropyl)-α-methyl aspartate)(1,3-diaminopropane)]$^+$ cations through weak hydrogen bonds (NH$\cdots$Cl) with the distance of 3.154(1) Å, 3.256(1) Å, and 3.311(1) Å, which result in the formation of zigzag chains along the *b*-axis. Furthermore, the chains are stabilized by the presence of hydrogen bonds between the nitrogen atoms and the carboxylate oxygen atoms [d(NH$\cdots$O) = 2.9034(15) Å, 3.0217(15) Å, and 3.0354(15) Å] in adjacent cobalt(III) complex moieties, which result in double layers on the *bc*-plane. Thus Co[(*N*-(3-aminopropyl)-α-methyl aspartate)(1,3-diaminopropane)]$^+$ cations forms an extended 3D network.

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