Crystal structure of [3-(*N*-methyl-2-pyridyl-*N*-hydroxymethyl-2-pyridyl)-aminopropionic acid-κ^4N,N',N'',O](flavonolato-κ^2O,O')cobalt(III) chloride — water (1:2), $[Co(C_{15}H_{17}N_3O_3)(C_{15}H_9O_3)]Cl \cdot 2H_2O$

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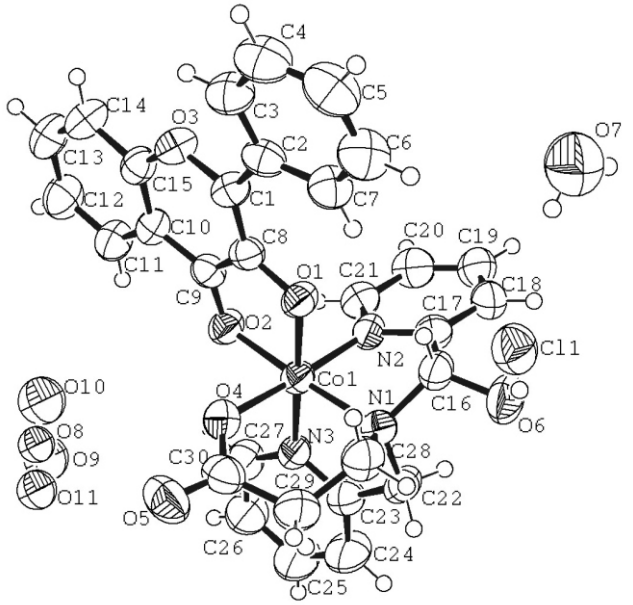

Abstract

$C_{30}H_{30}ClCoN_3O_8$, triclinic, $P\overline{1}$ (no. 2), a = 8.1874(3) Å, b = 12.2733(3) Å, c = 16.6712(6) Å, α = 98.341(1)°, β = 100.289(1)°, γ = 104.827(3)°, V = 1561.1 Å^3, Z = 2, $R_{gt}(F)$ = 0.089, $wR_{ref}(F^2)$ = 0.263, T = 293 K.

Source of material

Lithium salt of *N*,*N*-bis(2-methylpyridyl)propionic acid (bpmpaH, 0.68 g, 2.5 mmol) was dissolved in 10 mL ethanol under Ar atmosphere. $CoCl_2 \cdot 6H_2O$ (1.14 g, 2.25 mmol) in 12 mL ethanol was added to the solution and the mixture was stirred for 8 hours under argon. Flavonol (flaH, 2.5 mmol in 3 mL ethanol) was slowly added prior to the addition of an equivalent amount of triethylamine. After 4 hours of stirring the mixture was filtered under argon and the solid product was washed three times with diethylether. The title complex is formed in 5 % yield upon crystallization from *N*,*N*-dimethylformamide. Residual lithium and triethylammonium chloride salts that are formed during the synthesis provide the source for the chloride counterion. Presumably, the cobalt-assisted oxidation of the original ligand, bpmpa, at a benzylic position gives 3-(*N*-methyl-2-pyridyl-*N*-hydroxymethyl-2-pyridyl)-aminopropionate (bpmpa-O). Cobalt(II) is also oxidized to cobalt(III) during the synthesis.

Experimental details

All H atoms were placed at idealized positions and then constrained during the refinement except those of the solvate water molecules which were not found experimentally. The occupancy for O8 to O11 was obtained by considering the Fourier residual density remaining after the refinement with the well defined part of the structure. Four residual peaks of approximative equal density were found and assigned as a disordered water molecule localized on 4 sites, the occupancy was refined to 0.25.

Discussion

The asymmetric unit of the title crystal structure consists of one [3-(*N*-methyl-2-pyridyl-*N*-hydroxymethyl-2-pyridyl)-aminopropionic acid-κ^4N,N',N'',O](flavonolato-κ^2O,O')-cobalt(III) cation, one chloride anion and two water molecules as solvate. Prior to the title compound, only one flavonolato-cobalt(III) complex has been reported with an N_2,O_2 donor co-ligand as model for the cobalt-containing flavonol 2,4-dioxygenase [1]. The title crystal structure is the first structurally relevant model for the metal-binding site of the enzyme [2] with its N_3,O donor co-ligand. The title compound contains a cationic six-coordinated cobalt(III) center surrounded by 3 N atoms of the ligand in a facial fashion, one O atom from the carboxylate function of the ligand and two O atoms of the flavonolate ligand occupying the remaining sites.

Table 1. Data collection and handling.

Crystal:	red prism, size 0.05 × 0.10 × 0.25 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	6.88 cm^{-1}
Diffractometer, scan mode:	KappaCCD, φ/ω
$2\theta_{max}$:	54.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	17399, 6612
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 4372
$N(param)_{refined}$:	396
Programs:	SIR92 [3], SHELXL-97 [4], ORTEP-3 [5], WinGX [6]

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

Atom	Site	x	y	z	U_{iso}
H(3)	2*i*	0.8159	–0.0942	0.4319	0.077
H(4)	2*i*	0.8859	–0.2646	0.4119	0.094
H(5)	2*i*	0.9041	–0.3670	0.5165	0.100
H(6)	2*i*	0.8594	–0.2975	0.6428	0.092
H(7)	2*i*	0.7870	–0.1289	0.6654	0.073
H(11)	2*i*	0.6175	0.3757	0.5950	0.073
H(12)	2*i*	0.5786	0.4273	0.4675	0.084
H(13)	2*i*	0.6011	0.3061	0.3514	0.086
H(14)	2*i*	0.6636	0.1357	0.3638	0.076
H(16)	2*i*	0.7065	–0.0672	0.8099	0.065
H(18)	2*i*	0.3240	–0.1499	0.8368	0.074
H(19)	2*i*	0.0784	–0.1125	0.7709	0.079
H(20)	2*i*	0.1025	0.0511	0.7155	0.079
H(21)	2*i*	0.3759	0.1757	0.7260	0.066
H(22A)	2*i*	0.6375	0.1064	0.9686	0.071
H(22B)	2*i*	0.8364	0.1588	1.0090	0.071

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(24)	2*i*		0.7353	0.3336	1.0686	0.108
H(25)	2*i*		0.7095	0.5111	1.0438	0.118
H(26)	2*i*		0.7023	0.5487	0.9137	0.100
H(27)	2*i*		0.7112	0.4096	0.8073	0.078
H(28A)	2*i*		0.9895	0.0476	0.9479	0.076
H(28B)	2*i*		0.9885	0.0380	0.8530	0.076
H(29A)	2*i*		1.0812	0.2497	0.9649	0.087
H(29B)	2*i*		1.2183	0.1908	0.9403	0.087
H(6A)	2*i*		0.7026	–0.1386	0.9104	0.110
H(1O7)	2*i*		0.6708	–0.3937	0.7409	0.184
H(2O7)	2*i*		0.5113	–0.4729	0.7276	0.184
O(8)	2*i*	0.25	1.268(2)	0.453(1)	0.7256(9)	0.045(3)
O(9)	2*i*	0.25	1.093(3)	0.553(2)	0.748(1)	0.075(5)
O(10)	2*i*	0.25	1.075(3)	0.480(2)	0.684(1)	0.083(6)
O(11)	2*i*	0.25	1.284(2)	0.513(1)	0.773(1)	0.055(4)

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}
C(1)	2*i*	0.7491(7)	0.0163(5)	0.5641(3)	0.046(3)	0.057(3)	0.041(3)	0.018(3)	0.008(2)	0.008(3)
C(2)	2*i*	0.7929(7)	–0.0909(5)	0.5520(4)	0.043(3)	0.052(3)	0.057(4)	0.013(3)	0.005(3)	0.000(3)
C(3)	2*i*	0.8237(9)	–0.1345(6)	0.4748(4)	0.065(4)	0.069(4)	0.062(4)	0.026(3)	0.019(3)	0.002(3)
C(4)	2*i*	0.865(1)	–0.2366(7)	0.4630(5)	0.080(5)	0.073(5)	0.083(5)	0.034(4)	0.024(4)	–0.008(4)
C(5)	2*i*	0.877(1)	–0.2977(7)	0.5254(6)	0.080(5)	0.060(4)	0.109(7)	0.031(4)	0.017(5)	0.004(4)
C(6)	2*i*	0.850(1)	–0.2567(6)	0.6002(5)	0.082(5)	0.068(5)	0.086(5)	0.036(4)	0.017(4)	0.013(4)
C(7)	2*i*	0.8068(8)	–0.1551(5)	0.6139(4)	0.064(4)	0.056(4)	0.064(4)	0.024(3)	0.016(3)	0.009(3)
C(8)	2*i*	0.7369(7)	0.0818(5)	0.6366(3)	0.037(3)	0.050(3)	0.042(3)	0.009(2)	0.009(2)	0.005(2)
C(9)	2*i*	0.6929(7)	0.1862(5)	0.6341(3)	0.040(3)	0.045(3)	0.047(3)	0.009(2)	0.006(2)	0.007(2)
C(10)	2*i*	0.6654(7)	0.2248(5)	0.5575(3)	0.048(3)	0.055(3)	0.045(3)	0.017(3)	0.014(2)	0.014(3)
C(11)	2*i*	0.6271(9)	0.3276(6)	0.5487(4)	0.070(4)	0.062(4)	0.059(4)	0.024(3)	0.020(3)	0.018(3)
C(12)	2*i*	0.604(1)	0.3586(6)	0.4728(5)	0.084(5)	0.068(4)	0.070(5)	0.033(4)	0.019(4)	0.028(4)
C(13)	2*i*	0.618(1)	0.2856(7)	0.4031(4)	0.085(5)	0.086(5)	0.057(4)	0.032(4)	0.019(4)	0.035(4)
C(14)	2*i*	0.6549(9)	0.1841(6)	0.4102(4)	0.072(4)	0.082(5)	0.044(3)	0.034(4)	0.016(3)	0.017(3)
C(15)	2*i*	0.6792(7)	0.1555(5)	0.4874(4)	0.044(3)	0.063(4)	0.047(3)	0.016(3)	0.013(2)	0.016(3)
C(16)	2*i*	0.6666(8)	–0.0261(5)	0.8538(4)	0.067(4)	0.050(3)	0.049(3)	0.018(3)	0.016(3)	0.017(3)
C(17)	2*i*	0.4940(8)	–0.0104(5)	0.8171(4)	0.064(4)	0.050(3)	0.046(3)	0.015(3)	0.019(3)	0.003(3)
C(18)	2*i*	0.3328(9)	–0.0850(6)	0.8133(4)	0.069(4)	0.055(4)	0.057(4)	0.005(3)	0.022(3)	0.009(3)
C(19)	2*i*	0.1871(9)	–0.0622(6)	0.7747(4)	0.055(4)	0.078(5)	0.061(4)	0.010(3)	0.020(3)	0.015(4)
C(20)	2*i*	0.2013(8)	0.0349(6)	0.7416(4)	0.051(4)	0.081(5)	0.067(4)	0.021(3)	0.018(3)	0.008(4)
C(21)	2*i*	0.3656(8)	0.1090(6)	0.7475(4)	0.056(4)	0.061(4)	0.053(3)	0.023(3)	0.015(3)	0.010(3)
C(22)	2*i*	0.7466(9)	0.1520(6)	0.9604(4)	0.080(4)	0.061(4)	0.040(3)	0.022(3)	0.017(3)	0.013(3)
C(23)	2*i*	0.7339(9)	0.2696(5)	0.9508(4)	0.074(4)	0.052(4)	0.047(3)	0.015(3)	0.013(3)	0.007(3)
C(24)	2*i*	0.729(1)	0.3498(7)	1.0155(5)	0.147(8)	0.066(5)	0.055(4)	0.032(5)	0.035(5)	–0.005(4)
C(25)	2*i*	0.715(1)	0.4557(7)	1.0008(5)	0.171(9)	0.057(5)	0.070(5)	0.037(5)	0.042(6)	0.000(4)
C(26)	2*i*	0.710(1)	0.4775(6)	0.9241(5)	0.130(7)	0.047(4)	0.072(5)	0.026(4)	0.025(5)	0.004(3)
C(27)	2*i*	0.7160(9)	0.3944(6)	0.8605(4)	0.084(5)	0.053(4)	0.063(4)	0.024(3)	0.022(3)	0.014(3)
C(28)	2*i*	0.9719(8)	0.0852(6)	0.9011(4)	0.057(4)	0.072(4)	0.065(4)	0.024(3)	0.007(3)	0.024(3)
C(29)	2*i*	1.1055(9)	0.2009(7)	0.9201(5)	0.061(4)	0.084(5)	0.063(4)	0.013(4)	0.001(3)	0.016(4)
C(30)	2*i*	1.1164(9)	0.2629(6)	0.8488(4)	0.059(4)	0.057(4)	0.061(4)	0.009(3)	0.015(3)	–0.002(3)
N(1)	2*i*	0.7885(6)	0.0927(4)	0.8840(3)	0.055(3)	0.046(3)	0.043(3)	0.012(2)	0.009(2)	0.008(2)
N(2)	2*i*	0.5095(6)	0.0852(4)	0.7839(3)	0.055(3)	0.047(3)	0.044(3)	0.016(2)	0.016(2)	0.014(2)
N(3)	2*i*	0.7288(6)	0.2916(4)	0.8747(3)	0.066(3)	0.045(3)	0.040(3)	0.012(2)	0.014(2)	0.010(2)
O(1)	2*i*	0.7628(5)	0.0523(3)	0.7108(2)	0.062(2)	0.049(2)	0.040(2)	0.020(2)	0.014(2)	0.010(2)
O(2)	2*i*	0.6805(5)	0.2420(3)	0.7027(2)	0.066(3)	0.049(2)	0.043(2)	0.020(2)	0.017(2)	0.010(2)
O(3)	2*i*	0.7176(5)	0.0539(4)	0.4908(2)	0.061(3)	0.064(3)	0.042(2)	0.026(2)	0.010(2)	0.009(2)
O(4)	2*i*	0.9759(5)	0.2530(4)	0.7951(3)	0.057(3)	0.061(3)	0.055(2)	0.009(2)	0.016(2)	0.014(2)
O(5)	2*i*	1.2571(6)	0.3230(4)	0.8438(3)	0.058(3)	0.072(3)	0.093(4)	0.001(2)	0.020(3)	0.005(3)
O(6)	2*i*	0.6533(7)	–0.0886(4)	0.9168(3)	0.098(4)	0.062(3)	0.073(3)	0.028(3)	0.029(3)	0.032(3)
O(7)	2*i*	0.6017(9)	–0.4541(6)	0.7084(4)	0.125(6)	0.118(5)	0.124(6)	0.025(4)	0.036(4)	0.028(4)
Co(1)	2*i*	0.7440(1)	0.17110(6)	0.79259(4)	0.0520(5)	0.0449(4)	0.0396(4)	0.0135(3)	0.0123(3)	0.0086(3)
Cl(1)	2*i*	0.8669(3)	–0.2381(2)	0.8578(1)	0.091(1)	0.061(1)	0.080(1)	0.0228(9)	0.022(1)	0.0195(9)

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