Crystal structure of 1,3,5-trideoxy-1,3,5-tris((2-pyridylmethyl)amino)-*cis*-inositolcobalt(III) bromide tetrahydrate, $[Co(pmaci)]Br_3 \cdot 4H_2O$

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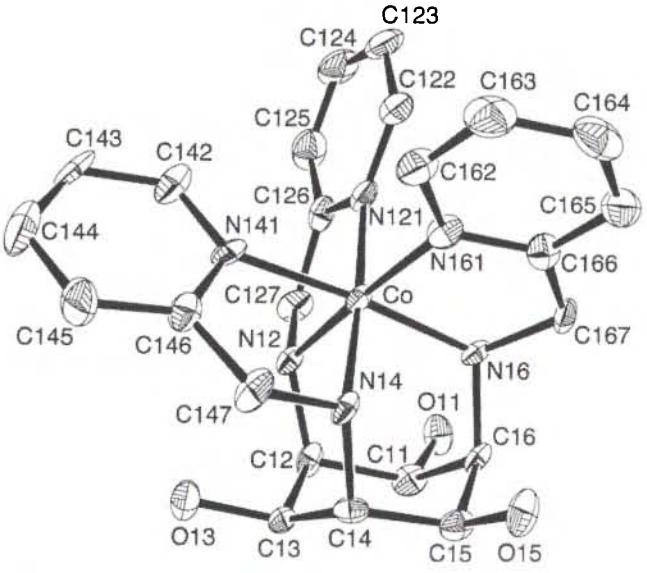

Abstract

$C_{24}H_{38}Br_3CoN_6O_7$, triclinic, $P\bar{1}$ (No. 2), $a = 8.968(2)$ Å, $b = 10.071(2)$ Å, $c = 17.722(4)$ Å, $\alpha = 105.11(3)°$, $\beta = 97.49(3)°$, $\gamma = 98.93(3)°$, $V = 1501.8$ Å^3, $Z = 2$, $R_{gt}(F) = 0.058$, $wR(F^2) = 0.158$, $T = 293$ K.

Source of material

1,3,5-Trideoxy-1,3,5-tris((2-pyridylmethyl)amino)-*cis*-inositol (pmaci) was prepared by the reaction of 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol (taci) [1] with three equivalents of pyridine-2-carbaldehyde in MeOH, followed by the reduction of the resulting Schiff base with $NaBH_4$. $[Co(pmaci)]Br_3 \cdot 4\ H_2O$ was prepared by passing a stream of air through an aqueous solution of pmaci and $CoCl_2 \cdot 6\ H_2O$ at pH = 6 and 353 K for 12 h. The complex was eluted as a yellow fraction from a cation exchange resin with diluted aqueous HBr. Crystals were obtained from EtOH/H_2O/ Et_2O. C,H,N-analysis was in agreement with the composition of the title compound. The ^{1}H-NMR-spectrum (D_2O) confirmed the chiral point group C_3 for the symmetry of the cationic complex in solution, showing a doublet of doublet for the two types of diastereotopic methylene protons.

Three H positions of two water molecules could not be located (two positions of O3 and one of O4).

Discussion

The reaction of aromatic aldehydes with primary amines forming Schiff bases is an efficient route to multidentate chelate ligands [2]. Derivatisation of the versatile ligand taci with O-pendant groups via Schiff bases as intermediates has recently been published [3]. We report here the synthesis of the taci derivative with 2-pyridylmethyl substituents as N-pendant groups (pmaci) and the crystal structure of the corresponding Co(III) complex.

The title compound crystallizes in the triclinic space group $P\bar{1}$ as a racemate with either an *RRR* or an *SSS* configuration for the aliphatic amine *N*-donors of the complex molecules. The three secondary amines and the three pyridine nitrogen atoms of pmaci form a cavity in which the Co(III) ion obtains an octahedral coordination. The Co—N bond lengths range from 1.949(6) Å to 1.981(6) Å (average 1.96 Å) and the bond lentghs to the two types of *N*-donors do not differ within significance. The *cis* N–Co–N angles fall in the range of 84.7° – 97.9°, indicating some deviation from ideal octahedral coordination. The structure is completed by a hydrogen bonding network, in which the two different enantiomers are connected by a OH—O hydrogen bond of the non-coordinated hydroxy group (O—O distance: 2.71 Å).

Table 1. Data collection and handling.

Crystal:	orange, plate, size 0.1 × 0.6 × 0.7 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	46.15 cm^{-1}
Diffractometer. scan mode:	Stoe AED 2, ω/θ
$2\theta_{max}$:	45°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	3942, 3942
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 3378
$N(param)_{refined}$:	390
Programs:	SHELXS-97 [4], SHELXL-97 [5]

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

Atom	Site	x	y	z	U_{iso}
H(16N)	2*i*	–0.0405	0.3320	0.8709	0.018
H(14N)	2*i*	0.1172	0.0107	0.8584	0.020
H(12N)	2*i*	0.2758	0.2987	0.7627	0.022
H(11O)	2*i*	0.0531	0.5172	0.9417	0.041
H(15O)	2*i*	0.0637	0.1118	1.0189	0.041
H(13O)	2*i*	0.4552	0.2579	0.7943	0.040
H(123)	2*i*	–0.3872	0.2087	0.5974	0.039

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Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(162)	2*i*	–0.0980	–0.1353	0.6771	0.033
H(16C)	2*i*	0.0629	0.3485	0.9989	0.020
H(14C)	2*i*	0.3627	0.0960	0.9287	0.020
H(163)	2*i*	–0.2966	–0.3041	0.6781	0.043
H(143)	2*i*	0.1894	0.0680	0.5109	0.042
H(15C)	2*i*	0.2790	0.2570	1.0247	0.026
H(12C)	2*i*	0.3867	0.4669	0.8751	0.024
H(142)	2*i*	0.0459	0.1485	0.6047	0.034
H(13C)	2*i*	0.4774	0.3214	0.9410	0.024
H(125)	2*i*	–0.0222	0.5210	0.6558	0.042
H(165)	2*i*	–0.3718	–0.0536	0.8777	0.035
H(11C)	2*i*	0.3013	0.4710	0.9942	0.027
H(122)	2*i*	–0.2650	0.1024	0.6809	0.028
H(144)	2*i*	0.3753	–0.0581	0.5394	0.054

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(47A)	2*i*	0.3542	–0.0370	0.8020	0.033
H(47B)	2*i*	0.1904	–0.1336	0.7724	0.033
H(124)	2*i*	–0.2591	0.4141	0.5804	0.048
H(67A)	2*i*	–0.1320	0.1586	0.9471	0.026
H(67B)	2*i*	–0.2344	0.2214	0.8920	0.026
H(45)	2*i*	–0.5982	–0.1093	0.6599	0.046
H(164)	2*i*	–0.4347	–0.2682	0.7807	0.042
H(27A)	2*i*	0.1323	0.5108	0.8105	0.033
H(27B)	2*i*	0.2161	0.4771	0.7373	0.033
H(100)	2*i*	–0.10(1)	0.21(1)	1.124(7)	0.06(4)
H(101)	2*i*	0.413(8)	0.395(8)	0.661(5)	0.01(2)
H(2A)	2*i*	0.51(2)	0.44(2)	0.72(1)	0.12(6)
H(4A)	2*i*	–0.03(1)	0.29(1)	0.459(8)	0.05(4)
H(1A)	2*i*	0.04(1)	0.28(1)	1.137(5)	0.02(3)

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}
Br(1)	2*i*	0.25816(9)	0.51555(9)	0.16044(5)	0.0343(5)	0.0274(5)	0.0216(5)	0.0006(4)	0.0062(4)	0.0029(4)
Br(2)	2*i*	0.37435(9)	0.79858(9)	0.93055(6)	0.0301(5)	0.0317(5)	0.0410(6)	–0.0003(4)	0.0050(4)	0.0203(4)
Br(3)	2*i*	0.2948(1)	0.5453(1)	0.58386(8)	0.0694(8)	0.0818(9)	0.0551(8)	0.0106(6)	0.0120(6)	0.0416(7)
Co	2*i*	0.0532(1)	0.1607(1)	0.78228(6)	0.0210(6)	0.0176(6)	0.0100(6)	0.0021(4)	0.0037(4)	0.0032(5)
N(16)	2*i*	–0.0100(7)	0.2549(6)	0.8805(3)	0.022(3)	0.014(3)	0.009(3)	0.001(2)	0.001(3)	0.004(3)
N(14)	2*i*	0.1838(7)	0.0647(6)	0.8386(4)	0.024(3)	0.012(3)	0.010(3)	–0.002(3)	0.006(3)	0.000(3)
N(12)	2*i*	0.2113(7)	0.3282(6)	0.7963(4)	0.023(3)	0.021(4)	0.012(3)	0.004(3)	0.005(3)	0.007(3)
N(161)	2*i*	–0.1145(7)	0.0065(6)	0.7744(4)	0.027(4)	0.014(4)	0.018(4)	0.004(3)	0.003(3)	–0.001(3)
N(141)	2*i*	0.1357(7)	0.0706(6)	0.6876(4)	0.027(4)	0.016(3)	0.009(4)	0.000(3)	–0.001(3)	–0.003(3)
N(121)	2*i*	–0.0748(7)	0.2476(7)	0.7195(4)	0.028(4)	0.030(4)	0.013(4)	0.004(3)	0.007(3)	0.008(3)
O(11)	2*i*	0.1431(6)	0.5428(6)	0.9390(3)	0.029(3)	0.022(3)	0.036(4)	0.009(2)	0.015(3)	0.011(3)
O(15)	2*i*	0.1149(6)	0.0879(5)	0.9845(3)	0.039(3)	0.020(3)	0.028(3)	0.001(2)	0.017(3)	0.012(3)
O(13)	2*i*	0.4732(6)	0.2205(6)	0.8296(3)	0.031(3)	0.031(3)	0.025(3)	0.012(2)	0.014(3)	0.011(3)
C(123)	2*i*	–0.289(1)	0.250(1)	0.6254(5)	0.037(5)	0.045(6)	0.014(5)	0.014(4)	–0.001(4)	0.004(4)
C(162)	2*i*	–0.1540(9)	–0.1182(9)	0.7181(5)	0.032(5)	0.027(5)	0.020(5)	0.003(4)	0.002(4)	0.005(4)
C(16)	2*i*	0.1127(8)	0.3126(8)	0.9538(4)	0.025(4)	0.017(4)	0.010(4)	0.003(3)	0.005(3)	0.006(3)
C(14)	2*i*	0.2970(8)	0.1546(8)	0.9103(5)	0.019(4)	0.014(4)	0.017(4)	0.006(3)	–0.002(3)	0.005(3)
C(163)	2*i*	–0.272(1)	–0.2200(9)	0.7186(6)	0.037(5)	0.026(5)	0.033(6)	–0.005(4)	–0.002(4)	0.000(4)
C(143)	2*i*	0.205(1)	0.049(1)	0.5597(5)	0.053(6)	0.041(6)	0.006(4)	0.007(4)	0.006(4)	0.001(4)
C(126)	2*i*	–0.0039(9)	0.3723(8)	0.7129(5)	0.031(4)	0.021(4)	0.021(4)	0.017(3)	0.014(4)	0.009(4)
C(15)	2*i*	0.2067(9)	0.2093(8)	0.9750(5)	0.024(4)	0.021(4)	0.020(4)	–0.001(3)	0.001(3)	0.011(4)
C(12)	2*i*	0.3114(9)	0.3862(8)	0.8764(5)	0.027(4)	0.016(4)	0.018(4)	0.000(3)	0.010(3)	0.009(3)
C(142)	2*i*	0.119(1)	0.0966(9)	0.6161(5)	0.044(5)	0.022(5)	0.017(5)	0.003(4)	0.009(4)	0.002(4)
C(13)	2*i*	0.3982(8)	0.2757(8)	0.8937(5)	0.019(4)	0.030(5)	0.014(4)	0.008(3)	0.004(3)	0.012(4)
C(125)	2*i*	–0.072(1)	0.436(1)	0.6606(5)	0.040(5)	0.042(6)	0.033(6)	0.016(4)	0.012(4)	0.021(5)
C(165)	2*i*	–0.3164(9)	–0.0713(9)	0.8366(5)	0.027(4)	0.031(5)	0.029(5)	0.001(4)	0.004(4)	0.013(4)
C(11)	2*i*	0.2251(9)	0.4349(8)	0.9451(5)	0.028(4)	0.013(4)	0.019(4)	0.000(3)	0.001(3)	–0.001(3)
C(122)	2*i*	–0.2159(9)	0.1875(9)	0.6763(5)	0.029(5)	0.026(5)	0.017(4)	0.008(4)	0.004(4)	0.006(4)
C(146)	2*i*	0.2394(9)	–0.0060(8)	0.7033(5)	0.029(4)	0.022(4)	0.020(5)	0.006(3)	0.008(4)	0.002(4)
C(144)	2*i*	0.314(1)	–0.027(1)	0.5762(6)	0.058(6)	0.054(7)	0.027(6)	0.011(5)	0.025(5)	0.007(5)
C(147)	2*i*	0.248(1)	–0.0397(9)	0.7806(5)	0.043(5)	0.019(4)	0.017(5)	0.012(4)	0.009(4)	–0.004(4)
C(124)	2*i*	–0.213(1)	0.374(1)	0.6166(6)	0.046(6)	0.058(7)	0.023(5)	0.020(5)	0.002(4)	0.022(5)
C(166)	2*i*	–0.1952(9)	0.0311(8)	0.8338(5)	0.024(4)	0.019(4)	0.024(5)	0.006(3)	0.006(3)	0.011(4)
C(167)	2*i*	–0.1508(9)	0.1711(8)	0.8945(5)	0.024(4)	0.028(5)	0.015(4)	0.001(3)	0.010(3)	0.008(4)
C(145)	2*i*	–0.669(1)	–0.056(1)	0.6480(6)	0.034(5)	0.043(6)	0.033(6)	0.013(4)	0.013(4)	–0.006(5)
C(164)	2*i*	–0.355(1)	–0.1988(9)	0.7788(6)	0.025(4)	0.031(5)	0.047(6)	–0.006(4)	–0.001(4)	0.016(5)
O(1)	2*i*	–0.0020(9)	0.2060(7)	1.1242(4)	0.036(4)	0.020(4)	0.035(4)	0.001(3)	0.007(3)	0.008(3)
O(2)	2*i*	0.4311(9)	0.355(1)	0.6931(5)	0.059(5)	0.087(7)	0.033(4)	0.017(5)	0.007(4)	0.034(5)
O(3)	2*i*	0.4339(9)	0.247(1)	0.4741(5)	0.060(5)	0.105(7)	0.058(6)	0.017(5)	0.009(4)	0.035(5)
C(127)	2*i*	0.1456(9)	0.4363(9)	0.7660(5)	0.033(5)	0.036(5)	0.024(5)	0.009(4)	0.003(4)	0.026(4)
O(4)	2*i*	0.028(2)	0.287(1)	0.4451(8)	0.096(9)	0.060(7)	0.13(1)	0.014(6)	0.062(8)	–0.011(6)

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