Crystal structure of di(2-aminopyridine)-tetrakis[*N*-(2-aminopropyl)-salicylaldiminato)]tricobalt(III) diperchlorate, $Co_3(C_{58}H_{48}N_{12}O_4)(ClO_4)_2$

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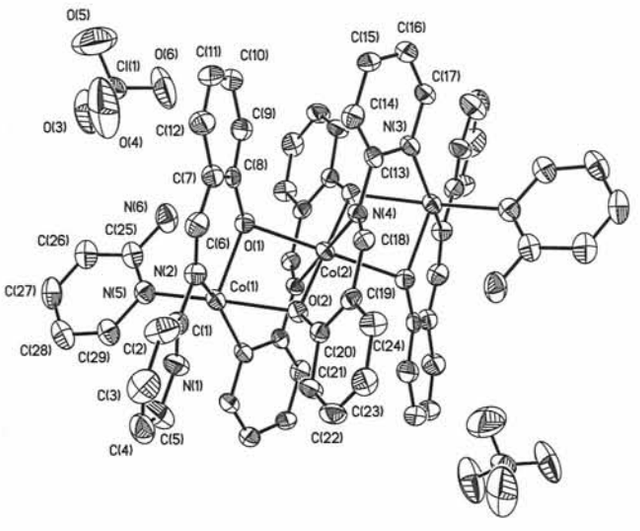
Received August 2, 2003, accepted and available on-line October 31, 2003; CCDC-No. 1267/1132



Abstract

$C_{58}H_{48}Cl_2Co_3N_{12}O_{12}$, triclinic, $P\bar{1}$ (No. 2), $a = 11.640(3)$ Å, $b = 11.693(3)$ Å, $c = 12.218(3)$ Å, $\alpha = 78.968(5)°$, $\beta = 89.827(5)°$, $\gamma = 60.605(4)°$, $V = 1414.0$ Å^3, $Z = 1$, $R_{gt}(F) = 0.062$, $wR_{ref}(F^2) = 0.136$, $T = 293$ K.

Source of material

The title complex was prepared by standing a clear 1:1 (v/v) aqueous alcohol solution (15 ml) containing salicylaldehyde (2 mmol, 212 mg), aminopyridine (2 mmol, 198 mg) and $Co(ClO_4)_2 \cdot 6H_2O$ (1 mmol, 366 mg) overnight, with drying using $CaCl_2$ after filtering and washing the crystals with aqueous alcohol solution twice (yield 92%). Elemental analysis: found – C, 51.22%; H, 3.60%; N, 12.19%, Cl, 5.22%; $C_{58}H_{48}Cl_2Co_3N_{12}O_{12}$ requires C, 51.50%; H, 3.58%; N, 12.42%; Cl, 5.24%).

Experimental details

All the H atoms were added on calculated positions and constrained to ride on their parent atoms with N—H and C—H distances of 0.90 Å and 0.96 Å, respectively, and with $U_{iso}(H) = 1.2U_{eq}(C)$ or $1.2U_{eq}(N)$.

Discussion

Analysis of the structure reveals that the title complex is a trimeric nuclear cobalt(II) cation structure. It consists of a discrete trimeric nuclear cobalt(II) dication, and two perchlorate anions. Each of the cation in the complex composes of three cobalt(II) atoms, four Schiff base ligands (L), and two 2-aminopyridine molecules. All the four Schiff bases are tridentate ligands with one phenate oxygen, one aromatic imine nitrogen, and one aliphatic imine nitrogen as donor atoms, coordinating to two or three cobalt(II) atoms. All the phenate oxygen atoms are μ_2-bridged donors. Co(2) atom is located in the symmetry center of the cation, with Co(1) and Co(1A) are equivalent. Co(II) atom has slightly distorted octahedral coordination, and is six-coordinated by two aliphatic imine nitrogen atoms and four phenate oxygen atoms from all the four Schiff bases. The three angles of the diagonals in the Co(2) octahedrons for the two complexes are exactly 180°. The other angles around Co(2) are between 82.5° – 97.53°. The metals are bridged by a pair of μ_2-phenate groups from two Schiff bases, constituting a trimeric structure with the adjacent metal-metal separations of 3.040Å, which is in normal range for μ_2-phenate-bridged cobalt(II) complexes. This is mainly due to the smaller Co–O–Co angles (average 93.3°) in the four-membered cycle Co_2O_2. Co(1), Co(1A), O(1), O(1A), O(2) and O(2A) constitute a hexagon in *trans*-conformation, and Co(2) atom locates in the position of the symmetry center of the hexagon. Co(1) atom is five-ligated by an aliphatic imine nitrogen atom (N(2)), an aromatic nitrogen atom (N(3A)), two phenate oxygen atoms (O(1) and O(2)) from three Schiff bases, and an aromatic nitrogen atom N(5) from the 2-aminopyridine. The metal atom has a distorted square pyramidal coordination, with O(2), N(2), N(3A) and N(5) constituting the basal plane. Co(1) atom is located above the basal plane at the distance of 0.119Å, towards the apical O(1) atom. Presumably because of the larger steric effects, some of the Co—O contacts (d(Co1—O2) = 2.129(4) Å and d(Co2—O2) = 2.152(3) Å) are slightly longer than those trivalent cobalt complexes. The other Co—O bond lengths (from 1.985(3) Å to 2.073(3) Å) are in normal range for the bond length between divalent cobalt atoms and phenate oxygen atoms.

Table 1. Data collection and handling.

Crystal:	dark prism, size 0.13 × 0.22 × 0.26 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	10.40 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	52.96°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	8179, 5581
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2232
$N(param)_{refined}$:	394
Programs:	SHELXTL [1], SHEXTL-plus [2]

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

Atom	Site	x	y	z	U_{iso}
H(6A)	2*i*	0.7423	0.5287	0.3164	0.088
H(6B)	2*i*	0.8472	0.5592	0.2761	0.088
H(2)	2*i*	0.2745	0.4913	0.0306	0.093
H(3)	2*i*	0.2907	0.3039	–0.0236	0.114
H(4)	2*i*	0.4706	0.0960	0.0507	0.099
H(5)	2*i*	0.6257	0.0772	0.1765	0.104
H(6)	2*i*	0.3053	0.6387	0.0928	0.066
H(9)	2*i*	0.5473	0.7728	0.3606	0.072
H(10)	2*i*	0.4224	0.9869	0.2585	0.083
H(11)	2*i*	0.2705	1.0318	0.1097	0.081
H(12)	2*i*	0.2475	0.8625	0.0677	0.075
H(14)	2*i*	0.1400	0.8654	0.3146	0.062

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(15)	2*i*	0.0668	1.0817	0.3372	0.063
H(16)	2*i*	0.1089	1.1117	0.5120	0.068
H(17)	2*i*	0.2271	0.9309	0.6525	0.060
H(18)	2*i*	0.1211	0.6680	0.4141	0.049
H(21)	2*i*	0.4699	0.1714	0.3973	0.061
H(22)	2*i*	0.2908	0.1431	0.3823	0.075
H(23)	2*i*	0.0806	0.3168	0.3832	0.076
H(24)	2*i*	0.0480	0.5206	0.4008	0.063
H(26)	2*i*	0.9899	0.4532	0.1485	0.086
H(27)	2*i*	1.0638	0.2887	0.0469	0.091
H(28)	2*i*	0.9612	0.1563	0.0543	0.089
H(29)	2*i*	0.7882	0.2034	0.1561	0.072

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)	2*i*	0.61226(7)	0.37602(7)	0.30020(6)	0.0415(5)	0.0422(5)	0.0388(5)	–0.0151(4)	0.0020(4)	–0.0137(4)
Co(2)	1*h*	1/2	1/2	1/2	0.0351(6)	0.0371(6)	0.0370(6)	–0.0156(5)	0.0021(5)	–0.0133(5)
Cl(1)	2*i*	0.9043(2)	0.8114(2)	0.1893(2)	0.093(2)	0.058(1)	0.058(1)	–0.023(1)	–0.010(1)	–0.016(1)
N(1)	2*i*	0.5473(5)	0.2649(5)	0.1818(4)	0.054(3)	0.052(3)	0.079(4)	–0.030(3)	0.016(3)	–0.029(3)
N(2)	2*i*	0.4542(4)	0.4834(5)	0.1798(4)	0.046(3)	0.047(3)	0.036(3)	–0.022(2)	–0.008(2)	–0.005(2)
N(3)	2*i*	0.2577(4)	0.7905(4)	0.5716(4)	0.045(3)	0.041(3)	0.041(3)	–0.016(2)	0.006(2)	–0.015(2)
N(4)	2*i*	0.2901(4)	0.6379(4)	0.4618(3)	0.040(3)	0.035(2)	0.033(3)	–0.016(2)	0.000(2)	–0.010(2)
N(5)	2*i*	0.7781(5)	0.3543(5)	0.2133(4)	0.054(3)	0.057(3)	0.042(3)	–0.026(3)	0.000(3)	–0.013(3)
N(6)	2*i*	0.8065(5)	0.5146(6)	0.2759(4)	0.064(4)	0.105(4)	0.076(4)	–0.054(4)	0.025(3)	–0.038(4)
O(1)	2*i*	0.5571(3)	0.5591(3)	0.3408(3)	0.037(2)	0.040(2)	0.038(2)	–0.014(2)	–0.001(2)	–0.002(2)
O(2)	2*i*	0.4772(3)	0.3778(3)	0.4211(3)	0.039(2)	0.051(2)	0.046(2)	–0.026(2)	0.007(2)	–0.019(2)
O(3)	2*i*	1.0401(7)	0.7269(7)	0.1831(5)	0.114(5)	0.197(7)	0.091(5)	0.030(5)	0.008(4)	–0.015(5)
O(4)	2*i*	0.837(1)	0.776(1)	0.1373(7)	0.38(1)	0.52(2)	0.204(9)	–0.39(1)	0.156(9)	–0.25(1)
O(5)	2*i*	0.878(1)	0.9322(7)	0.130(1)	0.26(1)	0.089(5)	0.34(1)	–0.043(6)	0.12(1)	0.013(7)
O(6)	2*i*	0.8734(6)	0.8156(7)	0.2959(5)	0.152(6)	0.195(7)	0.084(4)	–0.025(5)	0.030(4)	–0.068(5)
C(1)	2*i*	0.4427(6)	0.3861(6)	0.1361(5)	0.062(4)	0.058(4)	0.042(4)	–0.039(4)	0.006(3)	–0.016(3)
C(2)	2*i*	0.3453(7)	0.4056(7)	0.0598(6)	0.100(5)	0.074(5)	0.068(5)	–0.055(4)	–0.036(4)	0.001(4)
C(3)	2*i*	0.3553(9)	0.295(1)	0.0275(6)	0.137(8)	0.130(8)	0.060(5)	–0.099(7)	–0.015(5)	–0.018(5)
C(4)	2*i*	0.4610(9)	0.1723(9)	0.0716(7)	0.111(7)	0.110(7)	0.076(6)	–0.081(6)	0.037(5)	–0.054(5)
C(5)	2*i*	0.5536(7)	0.1622(8)	0.1474(7)	0.075(5)	0.079(5)	0.111(7)	–0.032(4)	0.022(5)	–0.052(5)
C(6)	2*i*	0.3758(6)	0.6099(6)	0.1465(5)	0.054(4)	0.058(4)	0.043(4)	–0.025(3)	–0.006(3)	0.000(3)
C(7)	2*i*	0.3899(5)	0.7096(6)	0.1869(5)	0.044(3)	0.048(4)	0.046(4)	–0.019(3)	0.002(3)	–0.009(3)
C(8)	2*i*	0.4810(5)	0.6831(6)	0.2769(4)	0.038(3)	0.045(3)	0.034(3)	–0.018(3)	0.013(3)	–0.010(3)
C(9)	2*i*	0.4883(6)	0.7892(6)	0.3006(5)	0.080(5)	0.053(4)	0.043(4)	–0.030(4)	0.008(3)	–0.010(3)
C(10)	2*i*	0.4133(7)	0.9178(6)	0.2406(6)	0.094(5)	0.052(4)	0.072(5)	–0.041(4)	0.031(5)	–0.022(4)
C(11)	2*i*	0.3223(7)	0.9444(6)	0.1514(6)	0.073(5)	0.037(4)	0.068(5)	–0.015(4)	0.009(4)	0.001(4)
C(12)	2*i*	0.3097(6)	0.8437(6)	0.1259(5)	0.059(4)	0.048(4)	0.055(4)	–0.011(3)	–0.007(3)	0.001(3)
C(13)	2*i*	0.2332(5)	0.7744(5)	0.4702(5)	0.031(3)	0.043(3)	0.045(4)	–0.015(3)	0.009(3)	–0.015(3)
C(14)	2*i*	0.1592(5)	0.8803(6)	0.3826(5)	0.049(4)	0.057(4)	0.044(4)	–0.025(3)	–0.002(3)	–0.005(3)
C(15)	2*i*	0.1140(5)	1.0081(5)	0.3964(5)	0.060(4)	0.034(3)	0.050(4)	–0.016(3)	0.004(3)	–0.001(3)
C(16)	2*i*	0.1399(6)	1.0256(6)	0.4999(6)	0.056(4)	0.043(4)	0.067(5)	–0.020(3)	0.018(4)	–0.015(4)
C(17)	2*i*	0.2103(5)	0.9173(6)	0.5832(5)	0.057(4)	0.043(3)	0.050(4)	–0.021(3)	0.012(3)	–0.019(3)
C(18)	2*i*	0.2099(5)	0.6016(5)	0.4297(4)	0.039(3)	0.040(3)	0.036(3)	–0.015(3)	–0.004(3)	–0.002(3)
C(19)	2*i*	0.2418(5)	0.4704(5)	0.4153(4)	0.048(3)	0.043(3)	0.034(3)	–0.024(3)	–0.002(3)	–0.001(3)
C(20)	2*i*	0.3711(5)	0.3640(5)	0.4139(4)	0.046(3)	0.048(3)	0.035(3)	–0.028(3)	0.004(3)	–0.013(3)
C(21)	2*i*	0.3856(6)	0.2426(5)	0.3999(5)	0.052(4)	0.041(3)	0.066(4)	–0.023(3)	0.012(3)	–0.024(3)
C(22)	2*i*	0.2784(6)	0.2260(6)	0.3898(5)	0.071(5)	0.054(4)	0.085(5)	–0.044(4)	0.019(4)	–0.031(4)
C(23)	2*i*	0.1529(6)	0.3294(7)	0.3905(5)	0.058(4)	0.084(5)	0.075(5)	–0.052(4)	0.015(4)	–0.030(4)
C(24)	2*i*	0.1338(5)	0.4501(6)	0.4019(5)	0.042(3)	0.057(4)	0.062(4)	–0.028(3)	–0.007(3)	–0.010(3)
C(25)	2*i*	0.8433(6)	0.4230(7)	0.2123(5)	0.038(4)	0.071(4)	0.046(4)	–0.018(3)	–0.003(3)	–0.014(4)
C(26)	2*i*	0.9496(6)	0.4013(7)	0.1494(6)	0.058(4)	0.090(5)	0.060(5)	–0.032(4)	0.004(4)	–0.014(4)
C(27)	2*i*	0.9935(6)	0.3038(8)	0.0896(6)	0.056(4)	0.114(6)	0.059(5)	–0.040(5)	0.019(4)	–0.025(5)
C(28)	2*i*	0.9319(7)	0.2254(7)	0.0928(6)	0.061(5)	0.083(5)	0.059(5)	–0.015(4)	0.003(4)	–0.030(4)
C(29)	2*i*	0.8289(6)	0.2551(6)	0.1539(5)	0.055(4)	0.071(5)	0.047(4)	–0.024(4)	–0.004(3)	–0.017(4)

Acknowledgments. The authors thank the Education Office of Hubei Province, P. R. China, for the research grant No. 2002B29002 and the Natural Science Foundation of Hubei Province, P. R. China, for the research grant No. 2003ABB010.

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