Crystal Structure of Azidobis[2,4-dichloro-6-[(2-dimethylaminoethylimino)methyl]phenolate]cobalt(III) Perchlorate

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The crystal of the complex $[\text{Co}(\text{DMP})_2(\text{N}_3)]\cdot\text{ClO}_4$ (DMP = 2,4-dichloro-6-[(2-dimethylaminoethylimino)methyl]phenol) was synthesized and its structure characterized by an X-ray single-crystal determination. The complex consists of a $[\text{Co}(\text{DMP})_2(\text{N}_3)]^+$ cation and a disordered perchlorate anion. The Co^{III} atom in the cationic moiety is six-coordinated in an octahedral coordination.

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There has been considerable interest in metal Schiff-base complexes; for example, they have been studied as reagents for oxygen separation and transport,¹ as models for biological dioxygen carriers² or magnetism or used in catalytic reactions.^{3,4} Nevertheless, in systems as simple as bis-bidentate Schiff-base complexes there are still some stereochemical and conformational questions that remain to be solved.⁵ We have focused our attention on the assembly of transition metal ions with flexible ligands, since they can adopt diverse coordination

modes according to the geometric needs of the metal ions.^{6,7} As a subsequent study of such complexes, the author reports here on a new cobalt(III) complex, (I), derived from a Schiff-base ligand, 2,4-dichloro-6-[(2-dimethylaminoethylimino)methyl]phenol (DMP).

To prepare the complex, 3,5-dichlorosalicylaldehyde (0.1 mmol, 19.2 mg) and *N,N*-dimethylethane-1,2-diamine (0.1 mmol, 8.8 mg) were dissolved in MeOH (10 ml). The mixture was stirred at room temperature for 10 min to give a clear-yellow solution, to which was added an aqueous solution (2 ml) of $\text{Co}(\text{ClO}_4)_3\cdot 6\text{H}_2\text{O}$ (0.1 mmol, 46.5 mg) and NaN_3 (0.1 mmol, 6.5 mg) with stirring. The mixture was stirred for another 10 min at room temperature. After keeping the filtrate in air for 7 d, brown block-shaped crystals were formed. A chemical diagram of the complex is illustrated in Fig. 1. The molecular structure is shown in Fig. 2. A summary of the crystal and experimental data are given in Table 1. Atomic coordinates and temperature factors are listed in Table 2. Selected bond distances and angles are given in Table 3.

Fig. 1 Structural chemical diagram of (I).

Fig. 2 Structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Only the major components of the disordered perchlorate anion are shown.

Table 1 Crystal and experimental data

CCDC: 295155	
Formula: $\text{C}_{22}\text{H}_{27}\text{Cl}_2\text{CoN}_7\text{O}_6$	
Formula weight = 721.69	
Crystal system: triclinic	
Space group: $P\bar{1}$	$Z = 2$
$a = 8.246(1)$	$\alpha = 68.001(1)$
$b = 13.651(1)$	$\beta = 82.999(1)$
$c = 15.136(1)$	$\gamma = 88.537(1)$
$V = 1567.6(2)\text{\AA}^3$	
$D_x = 1.529\text{ g/cm}^3$	$D_m = 1.532\text{ g/cm}^3$
No. of reflections used = 6939	
$2\theta_{\text{max}} = 56.4^\circ$ with Mo K_α	
$R = 0.0700$	
$(\Delta/\sigma)_{\text{max}} = 0.000$	
$(\Delta\rho)_{\text{max}} = 1.683\text{ e\AA}^{-3}$	
$(\Delta\rho)_{\text{min}} = -0.553\text{ e\AA}^{-3}$	
Measurement: Bruker SMART CCD Area Detector	
Program system: SHELX-97	
Structure determination: direct method	
Refinement: full-matrix least-squares on F^2	

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Table 2 Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for the complex. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U(\text{eq})$
Co(1)	5118(1)	6488(1)	6795(1)	34(1)
Cl(1)	11320(2)	2835(1)	8812(2)	95(1)
Cl(2)	9134(1)	6611(1)	8727(1)	55(1)
Cl(3)	9179(2)	6495(1)	4291(1)	61(1)
Cl(4)	10172(2)	10694(1)	3168(1)	84(1)
Cl(5)	5497(2)	1228(1)	7633(1)	81(1)
O(1)	6852(3)	6343(2)	7539(2)	41(1)
O(2)	6680(3)	6770(2)	5686(2)	43(1)
O(3)	6037(18)	572(9)	7144(10)	120(5)
O(4)	6816(17)	1573(14)	7954(15)	179(8)
O(5)	4585(17)	2079(10)	7107(9)	132(6)
O(6)	4418(18)	621(8)	8480(7)	121(5)
O(3')	5360(20)	702(12)	7006(10)	126(6)
O(4')	6914(11)	1928(7)	7267(9)	92(4)
O(5')	4179(14)	1874(11)	7683(17)	197(12)
O(6')	5790(20)	491(11)	8541(8)	155(7)
N(1)	5191(4)	5081(2)	6848(2)	40(1)
N(2)	3205(4)	6640(3)	6018(3)	46(1)
N(3)	5086(4)	7962(2)	6691(2)	39(1)
N(4)	4329(6)	8246(4)	9089(3)	62(1)
N(5)	3588(4)	6044(3)	7954(2)	45(1)
N(6)	3960(4)	5288(3)	8628(3)	50(1)
N(7)	4213(7)	4563(4)	9272(4)	86(2)
C(1)	7624(5)	4587(3)	7636(3)	42(1)
C(2)	7742(4)	5521(3)	7838(3)	38(1)
C(3)	8969(5)	5519(3)	8424(3)	41(1)
C(4)	10034(5)	4699(3)	8733(3)	52(1)
C(5)	9909(5)	3841(3)	8471(4)	56(1)
C(6)	8733(5)	3760(3)	7945(3)	50(1)
C(7)	6304(5)	4422(3)	7162(3)	43(1)
C(8)	3891(6)	4802(4)	6385(4)	58(1)
C(9)	2555(8)	5509(5)	6356(5)	79(2)
C(10)	3598(8)	7205(8)	5003(4)	109(3)
C(11)	1794(7)	7180(6)	6314(5)	85(2)
C(12)	7129(5)	8616(3)	5296(3)	45(1)
C(13)	7449(4)	7655(3)	5171(3)	38(1)
C(14)	8684(5)	7676(3)	4426(3)	42(1)
C(15)	9509(5)	8585(4)	3813(3)	52(1)
C(16)	9132(6)	9530(3)	3943(4)	57(1)
C(17)	8004(6)	9557(3)	4665(4)	57(1)
C(18)	6004(5)	8701(3)	6054(3)	44(1)
C(19)	4154(5)	8258(3)	7445(3)	42(1)
C(20)	5182(5)	8018(3)	8270(3)	47(1)
C(21)	5444(10)	8219(6)	9779(5)	90(2)
C(22)	2908(9)	7471(8)	9584(5)	118(3)

Complex (I) is a mononuclear cobalt(III) compound, which consists of a $[\text{Co}(\text{DMP})_2(\text{N}_3)]^+$ cation and a disordered perchlorate anion. In the cationic moiety of (I), the Co(1) atom is in an octahedral coordination and is six-coordinated by one O and two N atoms of one DMP ligand and by another imine N atom of the other DMP ligand, defining the basal plane, and by the phenolate O atom of the other DMP, together with one terminal N atom of the azide anion, occupying the axial positions. One of the DMP ligands acts as a tridentate ligand, while the other one acts as a bis-dentate ligand. The three *trans* angles at Co(1) lie in the range $173.89(13)$ to $178.63(13)^\circ$. The other angles subtended at the Co(1) atom range from $84.31(13)$ to $94.95(13)^\circ$, indicating a slightly distorted octahedral geometry. The bond lengths subtended at Co(1) are comparable to the values observed in other Schiff-base cobalt(III)

Table 3 Selected bond lengths ($\text{\AA}$) and angles ($^\circ$)

Co(1)-O(1)	1.887(3)	Co(1)-N(1)	1.890(3)
Co(1)-O(2)	1.907(3)	Co(1)-N(5)	1.935(3)
Co(1)-N(3)	1.960(3)	Co(1)-N(2)	2.041(3)
O(1)-Co(1)-N(1)	94.95(13)	O(1)-Co(1)-O(2)	89.13(12)
N(1)-Co(1)-O(2)	84.31(13)	O(1)-Co(1)-N(5)	89.62(14)
N(1)-Co(1)-N(5)	89.84(14)	O(2)-Co(1)-N(5)	173.89(13)
O(1)-Co(1)-N(3)	85.46(12)	N(1)-Co(1)-N(3)	177.89(14)
O(2)-Co(1)-N(3)	93.63(12)	N(5)-Co(1)-N(3)	92.22(14)
O(1)-Co(1)-N(2)	178.63(13)	N(1)-Co(1)-N(2)	85.32(14)
O(2)-Co(1)-N(2)	92.22(14)	N(5)-Co(1)-N(2)	89.05(15)
N(3)-Co(1)-N(2)	94.31(14)		

complexes.⁸ The azide group is nearly linear, and shows a bent coordination mode with the Co(1) atom $[\text{N}5-\text{N}6-\text{N}7 = 175.9(5)^\circ$, and $\text{Co}1-\text{N}5-\text{N}6 = 116.7(3)^\circ$].

Atom H4A linked to N4 was located in a difference Fourier map and refined isotropically with the N-H distance restrained to $0.90(1)\text{\AA}$. The other H atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms with C-H distances in the range $0.93 - 0.97\text{\AA}$, and with $U_{\text{iso}}(\text{H}) = 1.2$ or $1.5U_{\text{eq}}(\text{C})$. The O atoms of the perchlorate anion are disordered over two distinct sites with occupancies of $0.509(2)$ and $0.491(2)$. The Cl-O and O-O distances in both disordered components were restrained to be equal. The structure contains solvent-accessible voids of $122\text{\AA}^3$, which might accommodate a disordered MeOH molecule. An unassigned maximum residual density was observed at $1.99\text{\AA}$ from atom H4A.

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