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Key indicators

Single-crystal X-ray study
T = 193 K
Mean $\sigma(\text{C}-\text{C}) = 0.005 \text{ \AA}$
R factor = 0.048
wR factor = 0.128
Data-to-parameter ratio = 17.1For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

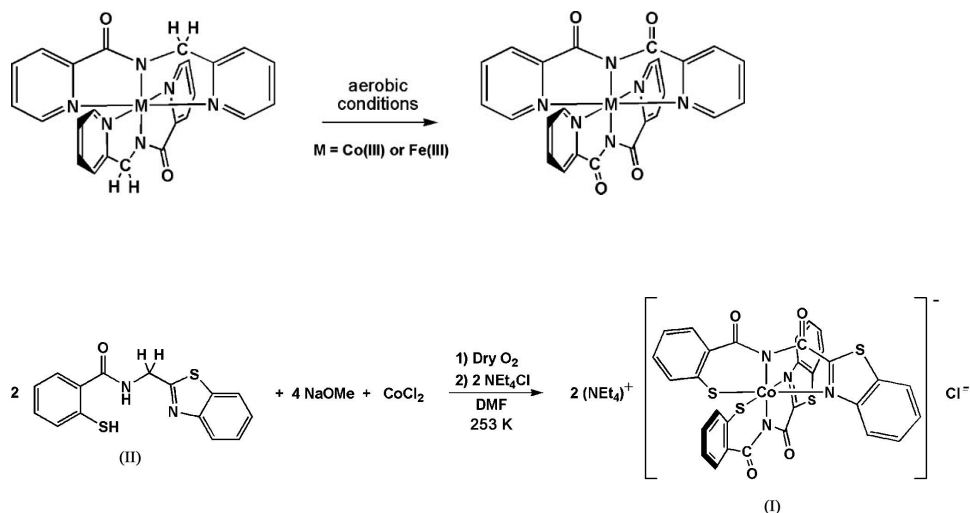
Bis(tetraethylammonium) bis[N-(2-mercaptobenzoyl)-1,3-benzothiazole-2-carboxamidato]-cobaltate(III) chloride

The title coordination compound, $(\text{C}_8\text{H}_{20}\text{N})[\text{Co}(\text{C}_{30}\text{H}_{16}\text{N}_4\text{O}_4\text{S}_4)_2]\text{Cl}$, was formed on aerobic oxidation of a reaction mixture containing the doubly deprotonated *N*-(benzo[*d*]thiazol-2-ylmethyl)-2-mercaptobenzamide ligand and CoCl_2 in a 2:1 ratio. Aerobic conditions were employed to oxidize the complex to the desired cobalt(III) oxidation state, but this also resulted in the oxidation of the coordinated ligand to an *N*-(2-mercaptobenzoyl)-1,3-benzothiazole-2-carboxamide group.

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Comment

In the course of synthetic analogue studies on the nitrile hydratase (NHase) enzyme, we reacted *N*-(benzo[*d*]thiazol-2-ylmethyl)-2-mercaptobenzamide, (II), with CoCl_2 to form an active-site analogue dicarboxamido–dithiolate complex. The reaction was performed using conditions reported by Chottard (Heinrich *et al.*, 2001) for another NHase analogue complex, where the mixture was stirred under aerobic conditions to allow for the oxidation of the complex to cobalt(III), the oxidation state of the native enzyme. Mascharak reported similar aerobic reactions using *N*-(2-picolyl)picolinamide ligands (Rowland *et al.*, 2002) coordinated to iron(III) or cobalt(III), where the ligand itself is also oxidized in the final isolated complex. The oxidation occurs at the α -methylene unit of the bound amide N atom, converting it to a carbonyl group (see first scheme below).



Mascharak proposed that, for ligand frameworks with interrupted conjugation, oxidation would occur to achieve conjugation throughout the entire ligand framework. As ligand (II) had the potential to undergo such an oxidation, it

was anticipated that ligand oxidation would occur, resulting in the formation of $(\text{NEt}_4)[\text{Co}(\text{mbbtca})_2]$ [mbbtca is *N*-(2-mercaptobenzoyl)-1,3-benzothiazole-2-carboxamide] (see second scheme).

However, the ^1H NMR spectroscopic data obtained for the complex did not conclusively confirm the identity of the product owing to the lack of characteristic ^1H NMR signals. To confirm the identity of the title compound, (I), an X-ray crystallographic analysis was required. Single crystals of the cocrystal $(\text{NEt}_4)[\text{Co}(\text{mbbtca})_2] \cdot (\text{NEt}_4)\text{Cl}$ (see scheme) were obtained by vapor diffusion of Et_2O into a concentrated MeCN solution of the product.

The structure of the $[\text{Co}(\text{mbbtca})_2]^-$ anion of (I) is shown in Fig. 1. The two ligands adopt a meridional coordination geometry, the overall complex having the expected octahedral structure about the cobalt(III) atom. The ligands are bonded to the cobalt through the thiolate (S—Co) and carboxamide N [C(O)N—Co] atoms, as well as through the N atom of the thiazole ring. The Co—S bond lengths are in the range of those reported (2.14–2.28 Å) for cobalt(III)–NHase (Miyana-ga *et al.*, 2001) and other Co-analogue complexes (Tyler *et al.*, 2000). The Co—N1(carboxamide) distance also lies in the range found in Co–NHase (1.96–2.09 Å) and other similar Co-analogue complexes. The thiazole N2/N4—Co bond distances are slightly longer than those found in similar pyridine-based [pyridine N—Co 1.960 (3)–1.995 (3) Å] analogues (Tyler *et al.*, 2000). It is noted that the carboxamide N atoms are *trans* to each other in geometry and that only one isomer of the product is observed (^1H NMR confirms single isomer formation). The preference for the observed isomer, in which the thiolate groups are *cis* to one another, is likely due to the highly donating nature of the thiolate groups, resulting in a strong *trans* influence that prefers *trans* coordination of the imine units *versus* the thiolates. Analogous product formation has been reported for other similar complexes (Rowland *et al.*, 2002).

Experimental

To a 100 ml side-arm flask containing sodium methoxide (0.0713 g, 1.32 mmol) dissolved in MeOH (5 ml) was added a solution of *N*-(benzo[*d*]thiazol-2-ylmethyl)-2-mercaptobenzamide (II) (0.1000 g, 0.333 mmol) in dry DMF (5 ml) under a dry N_2 atmosphere. The solution was stirred for 20 min at room temperature and then cooled to 253 K. To this solution was added a solution of CoCl_2 (0.041 g, 0.32 mmol) in DMF (10 ml) over a 5 min period. The solution was stirred for 10 min and then the septum of the side-arm was replaced with a drying tube to allow dry oxygen into the system and the nitrogen gas was turned off. The reaction was stirred at 253 K for an additional 16 h. The solution was filtered into a 250 ml side-arm flask containing NEt_4Cl (0.1040 g, 0.6275 mmol) under a nitrogen atmosphere. The mixture was stirred for an additional 2 min followed by the removal of the solvent under high vacuum. The residue was re-dissolved in MeCN (approximately 30 ml), filtered through celite, and concentrated to yield a brown–orange solid, (I) (0.0720 g, 0.0704 mmol; 42.3% yield). Compound (I) was crystallized *via* vapor diffusion of Et_2O into a concentrated MeCN solution.

Crystal data

$(\text{C}_8\text{H}_{20}\text{N})[\text{Co}(\text{C}_{30}\text{H}_{16}\text{N}_4\text{O}_4\text{S}_4)_2]\text{Cl}$
 $M_r = 979.59$
 Monoclinic, $P2_1/c$
 $a = 19.807$ (3) Å
 $b = 17.423$ (2) Å
 $c = 13.4721$ (18) Å
 $\beta = 92.435$ (2)°
 $V = 4644.9$ (11) Å³
 $Z = 4$

$D_x = 1.401$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 4197 reflections
 $\theta = 2.1$ – 25.9 °
 $\mu = 0.66$ mm⁻¹
 $T = 193$ (2) K
 Needle, purple
 $0.72 \times 0.15 \times 0.05$ mm

Data collection

Bruker PLATFORM
 diffractometer/SMART 1000
 CCD area detector
 ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2003)
 $T_{\text{min}} = 0.649$, $T_{\text{max}} = 0.968$
 35571 measured reflections

9543 independent reflections
 6275 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.075$
 $\theta_{\text{max}} = 26.5$ °
 $h = -24 \rightarrow 24$
 $k = -21 \rightarrow 21$
 $l = -16 \rightarrow 16$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.128$
 $S = 1.00$
 9543 reflections
 559 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0609P)^2 + 1.9315P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.50$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.28$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Co—S1	2.2255 (10)	O1—C7	1.220 (4)
Co—S3	2.2182 (9)	O2—C8	1.225 (4)
Co—N1	1.957 (2)	O3—C27	1.210 (4)
Co—N2	2.011 (2)	O4—C28	1.229 (3)
Co—N3	1.957 (2)	N1—C7	1.403 (4)
Co—N4	2.042 (2)	N1—C8	1.364 (4)
S1—C1	1.744 (3)	N2—C9	1.304 (4)
S2—C9	1.712 (3)	N2—C11	1.390 (4)
S2—C10	1.735 (3)	N3—C27	1.414 (4)
S3—C21	1.759 (3)	N3—C28	1.349 (4)
S4—C29	1.711 (3)	N4—C29	1.304 (4)
S4—C30	1.729 (3)	N4—C31	1.402 (4)
S1—Co—S3	92.58 (4)	Co—N1—C7	127.3 (2)
S1—Co—N1	95.43 (8)	Co—N1—C8	115.2 (2)
S1—Co—N2	178.69 (8)	C7—N1—C8	117.3 (2)
S1—Co—N3	83.96 (8)	Co—N2—C9	110.2 (2)
S1—Co—N4	93.31 (7)	Co—N2—C11	138.6 (2)
S3—Co—N1	86.94 (7)	C9—N2—C11	111.1 (3)
S3—Co—N2	87.96 (7)	Co—N3—C27	126.3 (2)
S3—Co—N3	96.27 (8)	Co—N3—C28	116.4 (2)
S3—Co—N4	173.74 (7)	C27—N3—C28	116.8 (3)
N1—Co—N2	83.41 (10)	Co—N4—C29	110.0 (2)
N1—Co—N3	176.75 (10)	Co—N4—C31	139.18 (19)
N1—Co—N4	94.60 (10)	C29—N4—C31	110.2 (3)
N2—Co—N3	97.16 (10)	S1—C1—C6	123.0 (3)
N2—Co—N4	86.19 (10)	O1—C7—N1	122.2 (3)
N3—Co—N4	82.25 (10)	O2—C8—N1	130.0 (3)
Co—S1—C1	107.03 (11)	S3—C21—C22	117.9 (3)
C9—S2—C10	88.64 (15)	O3—C27—N3	121.9 (3)
Co—S3—C21	106.38 (11)	O4—C28—N3	130.3 (3)
C29—S4—C30	88.79 (15)		

H atoms were placed in idealized positions (according to the sp^2 or sp^3 geometries of their parent C atoms), and then refined using a riding model with fixed C—H distances (C—H = 0.95–1.00 Å) and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

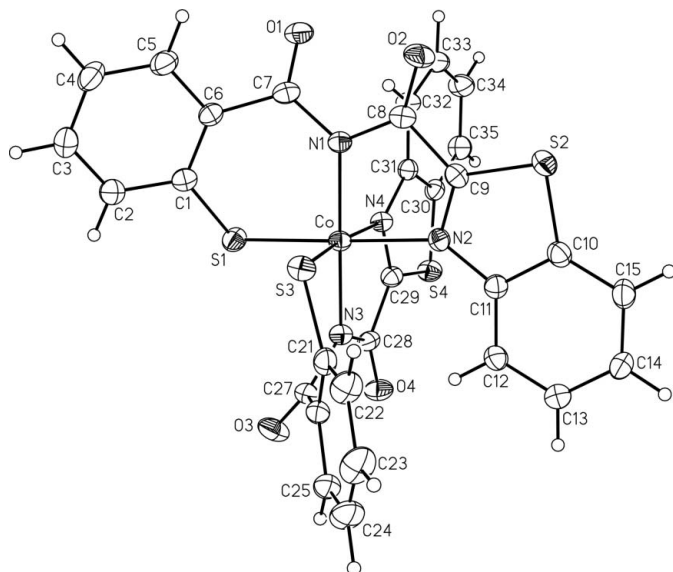


Figure 1

Perspective view of the $[\text{Co}(\text{mbtbca})_2]^-$ anion of compound (I), showing the atom-labeling scheme (NEt_4^+ cations and the chloride anion have been omitted for clarity). Non-H atoms are represented by displacement ellipsoids drawn at the 30% probability level. H atoms are shown as circles of arbitrary size.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINTE* (Bruker, 1997); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 1997a); molecular graphics: *SHELXTL* (Sheldrick, 1997b); software used to prepare material for publication: *SHELXTL*.

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