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A linear S-bridged trinuclear cobalt(III) complex with 2-aminobenzenethiol: Synthesis, crystal structure, and spectroscopic characterization

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Abstract

Treatment of cobalt(II) perchlorate hexahydrate with 2 molar equiv. of 2-aminobenzenethiol (Habt) in acetonitrile afforded a tricationic tricobalt complex, $[\text{Co}\{\text{Co}(\text{abt})_3\}_2](\text{ClO}_4)_3 \cdot 2\text{CH}_3\text{CN}$, by aerial oxidation. The molecular structure of the meso ($\Delta\Delta$) form of the complex was determined by X-ray crystallography. In the complex cation, the central Co is coordinated by six thiolate groups from two terminal *fac*(S)- $[\text{Co}(\text{abt})_3]$ units in an octahedral geometry, forming a linear S-bridged tricobalt structure.

Keywords

Trinuclear S-bridged linear Co(III) complex; 2-Aminobenzenethiol; Crystal structure of the meso isomer; Spectral properties

1. Introduction

The chemistry of metal-thiolate compounds has attracted attention because of their utility as structural and functional models for metal-cysteine centers in metalloenzymes [1, 2]. Over the last few years, we have been engaged in synthesis of metal complexes containing mixed N/S-donors [3-5]. Recently, we reported Co(III) complexes with N_2S , N_3S_2 and N_2S_3 donors in an effort to synthesize models for bacterial nitrile hydratase enzymes (NHase), which catalyze the partial hydration of nitriles to amides and which have noncorrinoid cobalt centers with mixed nitrogen/sulfur coordination environments [6, 7].

Chelating N/S donors have been used as ligands to transition metals for the better part of a century [8] and homoleptic metal complexes of both *o*-aminobenzenethiolate (abt) [9] and 2-aminoethanethiolate (aet) [10], including those of the form ML_3 for both $\text{L} = \text{abt}$ and aet , have been known since the 1950's. In addition, the ability of such ML_3 complexes to act as metalloligands to a central metal and form linear trinuclear species of the form $[\text{M}'(\text{ML}_3)_2]^{n+}$ has been known since the 1960's [11, 12]. There are a number of structurally characterized examples of such species with $\text{L} = \text{aet}$ (and closely related $\text{L} = \text{cysteinate}$) [13-29], however there are no structurally characterized examples of such complexes with L

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= abt. We report herein the synthesis and crystal structure of $[\text{Co}\{\text{Co}(\text{abt})_3\}_2](\text{ClO}_4)_3$ – the first structurally characterized species of this class of complex incorporating *o*-aminobenzenethiolate ligands.

2. Experimental

2.1. Materials and physical measurements

All chemicals and solvents were reagent grade and used as received from Aldrich, Acros, and Fisher Scientific without purification. Elemental analyses for C, H, and N were conducted using the Pregl-Dumas technique on a Thermo Fischer Flash EA1112. FT-IR spectra were recorded from 400–4000 cm^{-1} on a Nicolet 750 Magna-IR spectrometer using KBr pellets. UV–Vis data were collected on a Hitachi U-2010 spectrophotometer. Conductivity measurements were made with a Systronics direct reading conductivity meter (model 304).

Caution! Perchlorate salts are potentially explosive and should be handled only in small quantities and with great care.

2.2. Synthesis of $[\text{Co}\{\text{Co}(\text{abt})_3\}_2](\text{ClO}_4)_3 \cdot 2\text{CH}_3\text{CN}$ (1)

To a solution of 2-aminobenzenethiol (250 mg, 2.0 mmol) in acetonitrile (10 mL) was added a solution of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (366 mg, 1.0 mmol) in acetonitrile (10 mL). The resulting brown solution was heated to reflux for 1 h during which a brown microcrystalline solid separated, which was then collected by filtration. The product was washed with acetonitrile and diethyl ether, and dried in air. Brown prismatic crystals suitable for X-ray crystallographic studies were obtained by slow evaporation from a solution in acetonitrile-methanol. Yield 360 mg (0.28 mmol, 83%). Elemental Anal. Calcd for $\text{C}_{36}\text{H}_{36}\text{Cl}_3\text{Co}_3\text{N}_6\text{O}_{12}\text{S}_6 \cdot 1.9\text{CH}_3\text{CN} \cdot 0.4\text{CH}_3\text{OH} \cdot 0.3\text{H}_2\text{O}$: C, 36.69; H, 3.36; N, 8.41. Found: C, 36.69; H, 3.39; N, 8.42%. IR (KBr, cm^{-1}): 3214 m (ν_{NH}); 3136, 3107 w (ν_{CH}); 1600, 1558, 1449 m ($\nu_{\text{C}=\text{C}}$); 1088, 625 S ($\nu_{\text{Cl-O}}$). UV–Vis (MeOH): λ_{max} (ϵ_{M} , $\text{M}^{-1}\text{cm}^{-1}$) 324 (6063); 434 sh; 470 (5490); 595 sh.

2.3. X-ray Crystallography

Single crystal X-ray diffraction data were collected using a Bruker Kappa ApexII diffractometer (Mo $\text{K}\alpha$, $\lambda = 0.71073 \text{ \AA}$) equipped with an Oxford Cryostream 700 low-temperature apparatus. A suitable single crystal of **1** was identified under a polarizing microscope and affixed with oil in a Hampton Research Cryoloop and transferred to the cold nitrogen stream of the diffractometer. The unit cell was determined from the setting angles of 36 frames of data. Several scans in ϕ and ω directions were made to increase the number of redundant reflections and were averaged during refinement cycles. Data reduction was performed using the Bruker SAINT software package [30]. The structures were solved by direct methods and refined using full-matrix least squares on F^2 (SHELXL-97) [31] within the OLEX2 structure solution package [32]. The intensity data were corrected for Lorentz and polarization effects, and all non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogens were placed at calculated positions, but were not refined. X-ray data collection and structure solution parameters for the complex are listed in table 1.

3. Results and discussion

3.1. Synthesis and structure of **1**

Previously reported syntheses of $[\text{M}'(\text{ML}_3)_2]^{3+}$ complexes have involved the synthesis and isolation of ML_3 followed by treatment of ML_3 with a half-equivalent of a $\text{M}'(\text{III})$ salt or simply treatment of ML_3 with acid (resulting in a complex in which $\text{M} = \text{M}'$). In our hands,

1 is synthesized directly by reaction of $\text{Co}(\text{ClO}_4)_2$ with 2 equivalents of Hbt (scheme 1), with aerobic oxidation responsible for the trivalent state of Co in the final product. The crystal structure of **1** shows $[\text{Co}\{\text{Co}(\text{abt})_3\}_2]^{3+}$ along with three perchlorates and disordered water, methanol, and acetonitrile. The stoichiometry is in agreement with elemental analysis as well as the observed molar conductivity of $345 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, which is consistent with a 1:3 electrolyte [14, 21, 23]. The central Co is situated on a position with $\bar{3}$ symmetry in the rhombohedral space group $R\bar{3}c$, with the three-fold axis coincident with the Co-Co-Co vector. The perchlorate is situated on a two-fold axis and has been modeled with two sets of oxygens, present in an 86/14 ratio. Two solvent positions have been modeled, one with a water disordered over a crystallographic 3-fold axis, with total occupancy of 0.6 per Co trimer, and the other coincident with a 3-fold axis with occupancies of 0.6 methanol and 0.9 acetonitrile molecules per Co trimer. Both the crystal structure and the elemental analyses are best modeled with all three lattice solvents, although the relative abundance of the three solvents differs somewhat between the crystal and the bulk sample. For convenience, **1** is described as a bis(acetonitrile) solvate herein. A perspective drawing of the complex cation is shown in figure 1, and selected bond distances and angles are listed in table 2.

The complex cation consists of three cobalts and six abt ligands. Each of the two terminal cobalts is chelated by three abt ligands to form a *fac*-(S)- $[\text{Co}(\text{abt})_3]$ unit with a CoN_3S_3 chromophore. The three sulfurs of each $[\text{Co}(\text{abt})_3]$ then serve as donors to the central Co(III). The symmetry imposed on the cation results in there being only one unique Co–N distance (2.004(2) Å) and two unique Co–S distances. The Co–S bond distances are in the range of analogous bond distances in $[\text{Co}\{\text{CoL}_3\}_2]^{3+}$ with L = aet [25–27] or cysteinate [27–29]. The Co–S bond distances within the two terminal *fac*-(S)- $[\text{Co}(\text{abt})_3]$ units ($\text{Co}_t\text{--S} = 2.2290(7)$ Å) are slightly shorter than those around the central Co ($\text{Co}_c\text{--S} = 2.2712(6)$ Å). This mirrors the situation in the published structures of analogous trinuclear species involving aet and cysteinate ligands. The Co–N bond distance, while not particularly long, is longer than those for the six $[\text{Co}\{\text{CoL}_3\}_2]^{3+}$ structures, in which the Co–N bond distances range from 1.984 to 2.004 Å. Other metrical parameters are also similar to those reported for $[\text{Co}\{\text{Co}(\text{aet})_3\}_2]^{3+}$, as indicated in table 2. Deviation from ideal octahedral geometry within the terminal *fac*-(S)- $[\text{Co}(\text{abt})_3]$ unit can be seen in the obtuse N–Co–N angles ($97.25(9)^\circ$) and acute S–Co–S angles ($84.83(3)^\circ$). Again, this is comparable to the deviations previously reported for analogous systems. Most importantly, several similar trinuclear metal complexes with aliphatic aminothioliolate ligands such as 2-aminoethanethiolate and L-cysteinate are known, but **1** is the first reported member of this class with the aromatic 2-aminobenzenethiolate.

As the molecule sits on an inversion center, the structure is necessarily the racemic *meso* isomer, with one terminal Co displaying Δ configuration and the other Λ . The overall stereochemistry is best described as $\Delta(\delta\delta\delta)\Lambda(\lambda\lambda\lambda)$, implying that the C–C bonds bridging S and N are parallel to the three-fold axis (*i.e.*, the Co–Co–Co vector). However, there is a significant deviation from the ideal geometry, which would require a 180° torsion angle involving the C–C bond and two Co ions (C6–C1–Co1–Co2e). In the published structures involving aet and cysteinate, this angle is close to the ideal linear value, ranging from 170 – 180° . However, in **1**, this torsion angle is reduced to 146° , indicating the effect of the more rigid sp^2 -hybridized carbons in abt. The molecular packing is stabilized by a complex network of hydrogen bonds, similar to that seen in $[\text{Co}\{\text{Co}(\text{aet})_3\}_2](\text{SO}_4)\text{Cl}$ [25], in which each amine hydrogen is involved in a moderately strong hydrogen bond to perchlorate (table 3). This hydrogen bonding motif results in the cations and anions forming alternate layers parallel to the *ab* plane as shown in figure 2.

3.2. Electronic spectroscopy

The UV-visible spectrum (figure 3) of **1** is similar to those observed for similar S-bridged complexes. The lowest energy visible absorption at 595 nm can be assigned to $^1A_{1g} \rightarrow ^1T_{1g}$ d-d transition. However, assignment of bands in these complexes is complicated by overlap of transitions from two chromophores - the terminal $\text{Co(III)N}_3\text{S}_3$ and the central Co(III)S_6 [12]. The higher energy absorption bands observed for the complex at ca. 470, 434, and 324 nm are much more intense than the d-d band; these bands are attributable to $\text{S} \rightarrow \text{Co(III)}$ charge transfer transitions among the bridging sulfur, and central terminal cobalt ions.

4. Concluding remarks

We have synthesized and characterized an S-bridged tricobalt species bearing the aromatic aminobenzenethiolate by direct treatment of $\text{Co}(\text{ClO}_4)_2$ with 2-aminobenzenethiol in air. The crystal structure of the meso form of the complex has been determined by X-ray crystallography, showing three thiolato-S of each terminal *fac*-(S)-[Co(abt)₃] coordinating to the central Co to form a linear S-bridged tricobalt structure, $[\text{Co}\{\text{Co}(\text{abt})_3\}_2]^{3+}$. Structurally, **1** is quite similar to other trinuclear metal complexes with aliphatic aminothioliates such as 2-aminoethanethiolate and L-cysteinate [25, 27, 29], except for the disposition of the ligand backbond with respect to the Co-Co-Co vector. Complex **1** represents the first reported member of this class with the aromatic 2-aminobenzenethiolate.

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Scheme 1.
Synthetic route to **1**.

Figure 1.

Molecular structure of $[\text{Co}\{\text{Co}(\text{abt})_3\}_2](\text{ClO}_4)_3 \cdot 2\text{CH}_3\text{CN}$; ellipsoids are drawn at 30% probability. Perchlorates, acetonitrile and hydrogens are omitted for clarity. Symmetry code: a = $y-1, -x+y, -z$; b = $-y+1, x-y+2, z$; c = $x-y+1, x+1, -z$; d = $-x+y-1, -x+1, z$; e = $-x, -y+2, -z$.

Figure 2. Molecular packing of $[\text{Co}\{\text{Co}(\text{abt})_3\}_2](\text{ClO}_4)_3 \cdot 2\text{CH}_3\text{CN}$ viewed along the b axis. Hydrogens are omitted for clarity.

Figure 3.
Electronic absorption spectrum of $[\text{Co}\{\text{Co}(\text{abt})_3\}_2](\text{ClO}_4)_3 \cdot 2\text{CH}_3\text{CN}$ in methanol.

Table 1Crystal data and structure refinement for [Co{Co(abt)₃}₂](ClO₄)₃·2CH₃CN (**1**).

Empirical formula	C _{36.80} H _{38.90} Cl ₃ O ₁₂ Co ₃ N _{6.30} S ₆	
Formula weight	1249.74	
Temperature (K)	150(2)	
Wavelength (Å)	0.71073	
Crystal system	Rhombohedral	
Space group	R-3c	
Unit cell dimensions (Å, °)	a = 11.5120(4)	α = 90
	b = 11.5120(4)	β = 90
	c = 67.054(2)	γ = 120
Volume (Å ³)	7695.8(6)	
Z	6	
Density (calculated) (Mg/m ³)	1.618	
Absorption coefficient (mm ⁻¹)	1.422	
F(000)	3805	
θ range for data collection (°)	1.82 to 26.00	
Index ranges	-14 h 14, -14 k 14, -85 l 85	
Reflections collected	54369	
Independent reflections	1903 [R(int) = 0.0296]	
Completeness to θ = 26.00° (%)	100.0	
Data / restraints / parameters	1638 / 5 / 130	
Goodness-of-fit on F ²	1.075	
Final R indices [I > 2σ(I)]	R ₁ = 0.0342, wR ₂ = 0.0892	
R indices (all data)	R ₁ = 0.0408, wR ₂ = 0.1945	
Largest diff. peak and hole (e Å ⁻³)	0.459 and -0.545	

Table 2

Selected bond distances (Å) and angles (°) for **1** and averages of analogous measurements for [Co{Co(aet)₃}₂](SO₄)Cl [25].

Bond/angle	1	[Co{Co(aet) ₃ } ₂] ³⁺	Bond/angle type
Co(2)-S(1)	2.2712(6)	2.262	Co _c -S
Co(1)-S(1)	2.2290(7)	2.238	Co _t -S
Co(1)-N(1)	2.004(2)	1.986	Co _t -N
Co1...Co2	2.8622(7)	2.857	
S(1)-Co(2)-S(1) ^a	97.11(2)	97.43	across trimer
S(1)-Co(2)-S(1) ^b	82.89(2)	82.57	across trimer
N(1)-Co(1)-S(1) ^b	170.90(7)	173.16	interligand trans
N(1)-Co(1)-S(1)	87.26(6)	88.22	abt bite angle
S(1)-Co(1)-S(1) ^b	84.83(3)	84.5	same side of trimer
S(1)-Co(2)-S(1) ^c	180.0	180.0	across trimer
S(1)-Co(1)-N(1) ^b	89.98(7)	92.76	interligand cis
N(1)-Co(1)-N(1) ^b	97.25(9)	94.6	interligand

Symmetry transformations used to generate equivalent atoms:

^a y-1, -x+y, -z

^b -y+1, x-y+2, z

^c -x, -y+2, -z.

Table 3Hydrogen bonds (Å, °) between complex cation and perchlorate for [Co{Co(abt)₃}₂](ClO₄)₃·2CH₃CN.

D-H...A	D...A	∠D-H...A
N1-H1B...O1B ^d	2.94(2)	124(2)
N1-H1A...O2B ^e	3.06(2)	151(3)
N1-H1B...O1	3.008(4)	179(3)

Symmetry transformation used to generate equivalent atoms:

^d
 $y+1/3, x-1/3, -z+1/6$ ^e
 $x-y-2/3, -y-1/3, -z+1/6$