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Incorporation of Thiolate Donation Using 2,2'-Dithiodibenzaldehyde: Complexes of a Pentadentate N₂S₃ Ligand With Relevance to the Active Site of Co Nitrile Hydratase

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Abstract

The use of 2,2'-dithiodibenzaldehyde (DTDB) as a reactant for incorporating thiolate donors into the coordination sphere of a transition metal complex without the need for protecting groups is expanded to include the synthesis of complexes with pentadentate ligands. The ligand N,N'-bis(thiosalicylideneimine)-2,2'-thiobis(ethylamine) (tsaltp) is synthesized at a cobalt center by the reaction of DTDB with a Co complex of thiobis(ethylamine). The resulting Co complexes are thus coordinated by the N₂S₃ pentadentate ligand through two imine N atoms, two thiolate S atoms, and one thioether S atom. A dimeric, bis-thiolate-bridged complex (**1**) is isolated and converted to a monomeric CN adduct (**2**) by treatment with KCN. The N₂S₃ coordination environment provided by the tsaltp ligand is similar to that provided by the protein donors at the active site of the nitrile hydratase enzymes, with **2** being the first octahedral Co complex reported with such a coordination sphere.

Keywords

Cobalt compounds; Thiolates; Nitrile Hydratase

Introduction

A number of metalloenzymes have active-site structures involving sulfur coordination to the transition metal ion, with the sulfur donor generally provided by the side chain of a cysteine residue. Examples include nitrile hydratase [1–10] and the A-cluster of carbon monoxide dehydrogenase/acetyl CoA synthase [11–23]. Understanding the catalytic mechanisms of these enzymes can be greatly aided by the study of small-molecule analogs, or model complexes, which reproduce the active-site structure and/or the function of the enzyme. Synthesis of model complexes for thiolate-containing enzymes is hampered by the difficulty associated with handling thiols, especially their air-sensitivity. We have developed a method for incorporation of thiolate donors to transition metals using 2,2'-dithiodibenzaldehyde (DTDB) as a synthon [24–26]. Reaction of DTDB in methanol with metal complexes containing coordinated primary amines results in a Schiff-base condensation between the aldehyde and the primary amine concomitant with a reductive cleavage of the disulfide bond to provide the thiolate donor. Thus, complexes of ligands containing mixed imine nitrogen/thiolate sulfur donor sets can be

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synthesized using an air-stable thiolate source and without the need for cumbersome protection and deprotection steps. We have previously reported the use of this method for the synthesis of Fe(III), Co(III), Ni(II) and Cu(II) complexes of ligands containing N₃S, N₂S₂, N₂S, and NS₂ donor sets.

The nitrile hydratase enzymes, which catalyze the hydrolysis of nitriles to amides, have an active site consisting of either Co(III) or Fe(III) in an N₂S₃X coordination sphere comprised of two deprotonated amide N donors from the protein backbone, three cysteine thiolates, two of which have been post-translationally modified to sulfenic and sulfinic acid groups, and an exogenous hydroxide ligand [10,27–28]. This unusual active site geometry is likely to be relevant in terms of tuning the electronics of the active-site metal. With the importance of these enzymes both by virtue of their biological functions and as widely used industrial biocatalysts [29–30], there is much interest in understanding these structure-function relationships. As part of a program aimed at modeling the active site of these enzymes, we report herein the application of the DTDB methodology to the synthesis of the first octahedral Co(III) complexes of a pentadentate N₂S₃ ligand.

Experimental

General

Unless otherwise stated, all solvents and reagents were purchased from Sigma-Aldrich or Fisher/ACROS and used as received without further purification. DTDB was synthesized as previously reported [24,31]. IR spectra were recorded on a Nicolet Avatar 360 FTIR. Electrospray mass spectra were obtained on a Finnigan LCQ DECA spectrometer. Elemental analyses were determined by M-H-W Laboratories, Phoenix, Arizona.

Bis(2,2'-thiobis(ethylamine))cobalt(II) chloride, [Co(tba)₂]Cl₂

To a solution of 1.0027 g (4.2 mmol) of CoCl₂·H₂O in 20 mL of H₂O is slowly added 1.0 mL (8.7 mmol) of 2,2'-thiobisethylamine to give a brown-red solution. After two hours of stirring, the solvent is removed under reduced pressure and the brown-red solid dissolved in 20 mL methanol, filtered and dried over MgSO₄. After removal of the MgSO₄ by filtration, the solvent is removed by rotary evaporation to give 1.07 g (2.9 mmol, 69%) of a red-brown solid. IR (KBr, cm⁻¹, s, strong; m, medium; w, weak; b, broad) 3408 (b), 1645 (s), 1606 (s), 1505 (m), 1461 (m), 1419 (m), 1376 (w), 1318 (w), 1105 (s), 982 (w), 927 (w), and 619 (b).

Bis[N,N'-bis(thiosalicylideneimine)-2,2'-thiobis(ethylamine)cobalt(III)] chloride, [Co(tsaltp)]₂Cl₂ (1)

A 100 mL round bottom is charged with 0.432 g (1.57 mmol) of DTDB, 0.290 g (0.78 mmol) [Co(tba)₂]Cl₂ and 60 mL of dry MeOH. The solution is refluxed overnight, with stirring, under a nitrogen atmosphere. The cooled solution is filtered, combined with 60 mL of diethyl ether, and chilled overnight to give 0.229 g (0.25 mmole, 65% yield based on Co) of brown/black crystals. IR (KBr pellet, cm⁻¹): 3463 (b), 3401 (b), 3260 (b), 3042 (b), 2904 (b), 2820 (m), 2788 (m), 1612 (s, C=N), 1581 (m), 1559 (m), 1539 (m), 1472 (m), 1457 (m), 1430 (m), 1304 (m), 1252 (m), 1219 (m), 1156 (m), 1120 (m), 1074 (m), 1035 (m), 996 (m), 982 (m), 933 (w), 853 (w), 775 (s), 759 (s), 691 (m), 639 (w), 586 (w), 525 (w) and 457 (m). Elem. Anal. Found (Calcd. for [Co(tsaltp)]₂·8H₂O): C, 40.65 (41.19); H, 4.99 (4.34); N, 5.34 (5.25). Brown rectangular-shaped crystals were grown by slow evaporation of a methanol/toluene solution.

Cyano[N,N'-bis(thiosalicylideneimine)-2,2'-thiobis(ethylamine)]cobalt(III), [Co(tsaltp)CN] (2)

To a slurry of 11.0 mg (0.98 mmol) of KCN in 20 mL of dry MeOH in a 100 mL Schlenk flask is added, via cannula, a solution of **1** (63.4 mg, 0.070 mmol) dissolved in 15 mL of dry MeOH. After stirring overnight under a nitrogen atmosphere, the resulting brown precipitate was

separated by filtration in air and washed with MeOH, H₂O and acetone to give 43.3 mg (0.098 mmol, 70% yield) of **2** as an olive-green solid. IR (KBr pellet, cm⁻¹): 3047 (w), 2961 (w), 2934 (w), 2114 (m, C≡N), 1620 (s, C=N), 1583 (m), 1541(m), 1458 (m), 1429 (m), 1406 (m), 1306 (w), 1250 (m), 1216 (s), 1158 (s), 1123 (s), 1079 (s), 1028 (s), 990 (m), 873 (w), 801 (w), 755 (m), 719 (w), 690 (w) and 463 (b). Elem. Anal. Found (Calcd. for [Co(tsaltp)CN]•H₂O): C, 48.94 (49.46); H, 4.29 (4.37); N, 9.11 (9.11). ESI-M.S. 443.2 (Co(tsaltp)CN⁺), 417.3 (Co(tsaltp)⁺). Brown rectangular crystals were grown by slow evaporation of an acetonitrile/toluene solution.

X-ray Crystallography

The crystal structures reported in this paper were performed on an Enraf-Nonius CAD4 diffractometer equipped with an Oxford Cryosystems Cryostream 700 Low-temperature apparatus. The crystals were affixed to the tip of a glass fiber with Paratone-N oil (Exxon) and then transferred to the cold stream of the diffractometer operating at 100 K. The unit cells were determined from the setting angles of 24 reflections with 20° < 2θ < 24° and confirmed by axial photographs. The data were processed and the structures solved and refined using the WinGX package [32]. The data were corrected for secondary extinction, Lorentz and polarization effects and an empirical absorption correction based on azimuthal scans of three intense reflections. The structures were solved by direct methods [33] and refined by full-matrix least-squares techniques [34] with values for Δf and Δf' from Creagh and McAuley [35]. All non-hydrogen atoms were refined with anisotropic temperature factors; hydrogen atoms were included at idealized positions, but were not refined. Pertinent details are given in Table 1.

Results and Discussion

Syntheses and Structural Descriptions

Our initial report on the reaction of DTDB with metal complexes containing coordinated primary amines involved reactant nickel complexes of bidentate amine/thiolate ligands and linear triamines [24]. In each of these cases, a thiosalicylaldehyde equivalent condensed with only one amine functionality per ligand, creating tridentate NS₂ ligands and tetradentate N₃S ligands, respectively. Subsequently, we were able to show that two equivalents of thiosalicylaldehyde could be added to a single ligand by reaction of DTDB with ethylenediamine (en) complexes of Ni(II) and Cu(II), resulting in the synthesis of the tsalen complexes [25]. Iron and cobalt complexes of en, however, again displayed condensation of thiosalicylaldehyde equivalents at only one of the two amine groups, resulting in tridentate N₂S ligands [26].

With the goal of synthesizing a Co complex with a pentadentate N₂S₃ ligand as a first-generation model for the active site of Co-containing nitrile hydratase, we decided to investigate the reaction of DTDB with a Co complex of an N₂S ligand, 2,2'-thiobis(ethylamine). The starting Co complex was synthesized by treatment of CoCl₂ with 2,2'-thiobis(ethylamine). Reaction of this complex with DTDB in ethanol produces a brown compound in which the aldehyde stretch of DTDB is replaced by an imine stretch, indicating the formation of the tsaltp ligand. The compound was determined by X-ray crystallography to be Co(III) dimer **1**, an ORTEP drawing [36] of which is shown in Figure 1 and selected bond angles and distances for which are given in Table 2. Each Co atom of the dimer is coordinated by the five donor atoms of tsaltp, which results from the condensation of an equivalent of thiosalicylaldehyde with each of the two amines of 2,2'-thiobis(ethylamine). The coordination environment therefore contains two imine N atoms and three meridionally disposed S atoms. The two thiolate S atoms (S(1) and S(3)) are *cis* to each other and the thioether S(2) is *trans* to one of the thiolates. The octahedral coordination sphere is completed at the site *trans* to one of the imine N atoms by a thiolate from the tsaltp ligand on the other Co atom, which bridges between

the two metal centers. The two halves of the dimer are related by crystallographically imposed inversion symmetry; the two Co atoms and the bridging S atoms are, therefore, coplanar. The two thiophenolate donors bridge asymmetrically, with a Co-S bond distance of 2.218(3) Å to the S atom from the ligand centered on the same Co atom and a Co-S bond distance of 2.278(3) Å to the S atom from the other ligand. The bonds between Co and the terminal thiophenolate, Co-S(1), and one of the bridging thiophenolates, Co-S(3), are within the normal range for Co(III)-thiolate bonds, while the bonds to the other bridging thiophenolate, Co-S(1a), and to the thioether, Co-S(2), are among the longest reported.[37] The dimer crystallizes along with two H₂O molecules and two methanol molecules; one methanol is disordered over three sites.

Mascharak's group has reported a similar dimeric Co(III) complex, [NEt₄]₂[Co(PyPS)]₂ {PyPSH₄ = N,N'-bis(2-mercaptophenylpyridine-2,6-dicarboxamide)} which they were able to cleave by reaction with NEt₄CN to form a six-coordinate species with coordinated cyanide [38–39]. By analogy, **1** was reacted with excess KCN in methanol. The IR spectrum shows incorporation of the CN ligand and the X-ray crystal structure confirms the cleavage of the dimer and formation of the mononuclear CN adduct, **2**. An ORTEP diagram of **2** is shown in Figure 2 and selected bond distances and angles are given in Table 3. The molecule crystallizes on a general position in the triclinic space group P 1 along with a water molecule of crystallization. The geometry of the tsaltp ligand is the same as in **1** with meridional coordination of the three S atoms and the two thiolate S atoms *cis* to each other. The CN ligand takes the place of the bridge in **1**, occupying the site *trans* to one of the imine N atoms. All three Co-S bond distances are ca. 0.02 longer in the CN complex than in the dimer.

Comparison to similar models and to active site geometry

The dimeric complex **1** is readily compared to Mascharak's complex of the pentadentate N₃S₂ ligand, PyPS. This ligand has terminal thiolate donors and a tridentate backbone consisting of a pyridine N donor flanked by two amide N donors. The PyPS dimer sits on a two-fold axis, as opposed to the inversion symmetry of **1**. The bridging thiolates in [Co(PyPS)]₂ are also asymmetric, with Co-S bond distances of 2.22 and 2.29–2.32. The NSN backbone of the tsaltp ligand binds to the Co in a facial conformation, while the NNN backbone of PyPS binds in a meridional conformation. This results in the sixth ligand, the thiolate from the symmetry-related ligand, being *trans* to a thiolate in the PyPS dimer and *trans* to a backbone imine N atom in **1**.

The active site of Co nitrile hydratase is unique with its utilization of amide N coordination in conjunction with oxidized and unoxidized thiolate S donors. Model complexes can aid in understanding the importance of these structural features. Compound **2** joins a small group of Co(III) complexes of pentadentate mixed-donor N/S ligands prepared as models for the NHase active site [40–42]. Table 4 shows a comparison of these complexes along with the bond lengths to the Co atom in the structure of Co NHase. Mascharak's compounds, as described above, utilize the PyPS ligand with an N₃S₂ donor set (one pyridyl and two amide N atoms and two aliphatic thiolate S atoms) [38–39]. They have also been able to isolate monomeric and dimeric compounds in which the thiolates have been oxidized, although a crystal structure of the monomeric version has not been published. Kovacs' compounds utilize a ligand with an N₃S₂ donor set consisting of one amino and two imino N atoms and two aliphatic thiolate S atoms [43–45]. Structures of both 5- and 6-coordinate (with azide or thiocyanate coligands) have been reported. The 5-coordinate compound can be converted to one with oxidized S atoms. Ozawa's five-coordinate complex is the only previously reported complex with an N₂S₃ donor set – two amide N atoms, one thioether and two aliphatic sulfinate S atoms coordinate the Co [46]. Coordination of water to this complex has been demonstrated *via* electronic spectroscopy and ESI-MS.

As with **1**, the tsaltp ligand wraps around the Co atom in **2** such that the NSN backbone is in a *facial* conformation. The other species in the table all have backbones (NSN or NNN) which coordinate the Co in a *meridional* manner. Thus, the sixth coordination site in **2** is *trans* to an imine N atom, while the sixth coordination site in the other species, and in Co NHase, is *trans* to a thiolate. With regards to bond lengths, the structures of the six-coordinate complexes are all quite similar. The Co-N bonds in **2** are essentially identical in length to those in Co (S₂Me₂N₃)SCN, which also features imine N atoms. These Co-N bonds are closer in length to those in Co NHase than are the shorter Co-amide bonds in Co(PyPS)CN, although the difference is not very significant. The bonds between Co and the thiolate S atoms are also very similar to those in the other complexes, with the exception of the anomalously long bond *trans* to the CN[−] group in Co(PyPS)CN. As with all of the 6-coordinate species, the bonds in Co(tsaltp)CN are longer than those in the 5-coordinate complexes. The exception is the bond between Co and the thioether which is anomalously long in Co(H₂L1-O₄)[−], a situation that is explained by the thioether being *trans* to the sulfinate ligand. The Co-thioether bond in Co (tsaltp)CN, although shorter, is still relatively long, as such bonds are generally between 2.20 and 2.25 Å.*

Electrochemistry

The electrochemical properties of the dimeric species **1** were investigated in acetonitrile. Scanning in the anodic direction, initially there is no electrochemical response to 1.5 V (vs. Ag/AgCl). On the reverse scan, an irreversible cathodic peak is apparent at ca. −770 mV. Continuing with a second scan results in the appearance of an irreversible anodic peak at ca. 530 mV. Subsequent scans show both the anodic and cathodic peaks. A possible explanation of this behavior is reduction of the Co(III)₂ dimer resulting in cleavage and appearance of a Co(II) monomer which undergoes oxidation in the second scan.

Reactivity with nitriles

Mascharak has also demonstrated the ability to catalyze, using Co(PyPS)CN, the hydrolysis of acetonitrile to acetamide, mimicking the enzymatic activity of the nitrile hydratase enzymes. In aqueous solution at pH 7, the CN[−] ligand is replaced by H₂O, which can be deprotonated with a pK_a of 8.3. The resulting OH[−] species, heated with acetonitrile at a pH of 9.5, results in the appearance of acetamide with a rate of 18 turnovers in four hours. It is, of course, highly desirable to gain an understanding of the factors necessary for the enzyme to be able to catalyze this difficult reaction, particularly in view of the unusual ligands utilized at the active site. We carried out similar reactions with **2** in solutions with pH ranging from 10.5 to 12.7. Control reactions were carried out under the same conditions with no Co complexes present. In reactions carried out above a pH of 12, the appearance of acetamide was confirmed by the presence of a peak in the ¹H NMR (CDCl₃) at 1.99 ppm for the methyl resonance (acetonitrile displayed a methyl peak at 2.06). However, the same result in approximately the same efficiency was observed in the control experiments. At lower pH values, no acetamide was observed in either the control or metal-containing reactions. Thus, it appears that **1**, unlike Co (PyPS)CN, is not a catalyst for nitrile hydrolysis. This suggests that factors such as amide coordination or a *trans* thiolate [45] may be necessary for this type of reactivity, although there are enough other differences among **1**, Co(PyPS)CN, and the nitrile hydratase active site that further model studies are needed to isolate the required structural features.

Conclusions

The methodology involving the use of DTDB for the synthesis of metal complexes with mixed N/S ligation has been extended to include the preparation of pentadentate ligands. The two

*Range established by a search of the Cambridge Structural Database (see reference 37).

complexes reported herein are the first to feature a six-coordinate Co atom coordinated by a pentadentate N_2S_3 ligand. This donor set mimics that provided to the Co atom by the protein at the active site of nitrile hydratase. The complexes reported herein do not, however, duplicate the coordination geometry, the amide N donors, or the oxidized thiolate donors present at the enzyme's active site. These features are represented in some complexes previously reported in the literature, although none of these compounds have an octahedral Co atom in a N_2S_3X coordination environment. Ultimately, a complete understanding of how the peculiar features of the nitrile hydratase active site affect the enzymatic mechanism will require model complexes that allow isolation and investigation of each feature. Compound **2** represents a new entry in that series and work is underway to synthesize analogous complexes with amide N donors replacing the imines and with oxidized thiolates.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
ORTEP drawing of the cation in **1** showing the 50% thermal ellipsoids. H atoms have been omitted for clarity.

Figure 2.
ORTEP drawing of **2** showing the 50% thermal ellipsoids. H atoms have been omitted for clarity.

Table 1Crystallographic Data for **1** and **2**

	1•H₂O•2CH₃OH	2•H₂O
formula	C ₃₈ H ₄₄ Co ₂ N ₄ O ₃ S ₆ Cl ₂	C ₁₉ H ₂₀ CoN ₃ OS ₃
fw	985.90	461.49
crystal system	monoclinic	triclinic
space group	C2/c	P1
Z	4	2
a (Å)	25.525 (14)	7.096 (6)
b (Å)	12.496 (3)	7.434 (2)
c (Å)	17.786 (6)	18.076 (3)
α (deg)		83.30 (3)
β (deg)	132.38 (3)	86.22 (4)
γ (deg)		86.92 (4)
V (Å ³)	4187 (3)	943.9 (9)
d _{calc} (g cm ⁻³)	1.564	1.624
temp (K)	100	100
λ (Å, Mo K _α)	0.71073	0.71073
μ (mm ⁻¹)	1.262	1.256
R ₁ ^a	0.069	0.0406
wR ₂ ^b	0.1410	0.1122

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b wR_2 = \left[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \right]^{1/2}$$

Table 2Selected bond lengths (Å) and angles (deg) for **1**.

S(1)-Co(1)	2.218(3)	S(3)-Co(1)	2.222(3)
S(1a)-Co(1)	2.278(3)	N(1)-Co(1)	1.971(7)
S(2)-Co(1)	2.277(3)	N(2)-Co(1)	1.961(8)
Co(1)···Co(1a)	3.368	S(1)···S(1a)	2.980
N(1)-Co(1)-S(3)	175.7(2)	S(2)-Co(1)-S(3)	90.69(11)
S(1)-Co(1)-S(2)	178.69(11)	N(1)-Co(1)-N(2)	93.6(3)
N(2)-Co(1)-S(1a)	177.2(2)	S(2)-Co(1)-N(2)	86.7(2)
S(1)-Co(1)-S(1a)	82.97(9)	Co(1)-S(1)-Co(1a)	97.0(1)

Table 3Selected bond distances and angles (deg) for **2**

Bond Distances (Å)			
Co(1)-S(1)	2.2405(15)	Co(1)-C(19)	1.883(5)
Co(1)-S(2)	2.3009(17)	Co(1)-N(1)	1.963(4)
Co(1)-S(3)	2.2375(17)	Co(1)-N(2)	1.966(4)
Bond Angles (deg)			
N(3)-C(19)-Co(1)	177.8(4)	N(1)-Co(1)-C(19)	172.83(17)
N(2)-Co(1)-S(1)	176.56(12)	S(2)-Co(1)-S(3)	175.99(5)

Table 4
Comparison of Co(III) complexes with pentadentate mixed N/S ligands (bonds in Å)

	# ^a	donors	N types ^b	S types	<i>trans</i> L ^c	Co-N	Co-S	Co-S	Co-SR ₂	ref
Co(tsaltp)/CN	6	N ₂ S ₃	imine	ArS ⁻ /RS ₂	imine	1.963	1.966	2.238	2.301	this work
Co(PyPS)/CN	6	N ₃ S ₂	amide	RS ⁻	RS ⁻	1.930	1.937	2.249	2.325	38
Co(S ₂ Me ₂ N ₃)/N ₃	6	N ₃ S ₂	imine	RS ⁻	RS ⁻	1.944	1.946	2.216	2.223	44
Co(S ₂ Me ₂ N ₃)/SCN	6	N ₃ S ₂	imine	RS ⁻	RS ⁻	1.956	1.962	2.218	2.231	45
Co(S ₂ Me ₂ N ₃) ⁺	5	N ₃ S ₂	imine	RS ⁻	RS ⁻	1.923	1.923	2.158	2.162	43
Co(H ₂ L1-O ₄) ⁻	5	N ₂ S ₃	amide	RSO ₂ ⁻ /RS ₂	RS ⁻	1.907	1.931	2.101	2.107	46
Co NHase	6	N ₂ S ₃	amide	RSO ₂ H/ ⁻ RSOH/RS ⁻	RS ⁻	1.96	2.09	2.28 (RS ⁻)	2.322 2.14 (RSO ₂ H)	10

^a coordination number
^b not including central N of N₃S₂ ligands
^c identity of substituent *trans* to 6th site