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Co(III) Complexes with Coordinated Carboxamido Nitrogens and Thiolato Sulfurs as Models for Co-Containing Nitrile Hydratase and Their Conversion to the Corresponding Sulfinato Species

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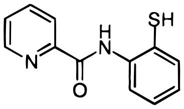
Recent spectroscopic data suggest that the Co(III) site in Co-containing nitrile hydratase is ligated to carboxamido nitrogens and thiolato sulfurs and most possibly one or more of the bound thiolates exist as sulfenato and/or sulfinato groups. The absence of any Co(III) complex with such coordination makes it quite difficult to predict the reactivity of this kind of Co(III) site. In this paper, the Co(III) complexes of two designed ligands $PyPepSH_2$ (**1**) and $PyPepRSH_2$ (**2**) have been reported. The two complexes, namely, $(Et_4N)[Co(PyPepS)_2]$ (**3**) and $Na[Co(PyPepRS)_2]$ (**4**) are the first examples of Co(III) complexes with carboxamido nitrogens and thiolato sulfurs as donors. The average $Co(III)-N_{amido}$ and $Co(III)-S$ distances in these complexes lie in the range 1.90−1.92 and 2.22−2.24 Å, respectively. Reaction of H_2O_2 with both complexes readily affords $Na[Co(PyPepSO_2)_2]$ (**5**) and $Na[Co(PyPepRSO_2)_2]$ (**6**), species in which the thiolato sulfurs are converted to sulfinato (SO_2) groups. Such conversion also occurs when solutions of **3** and **4** are exposed to dioxygen in the presence of activated charcoal. These reactions are clean and the $S \rightarrow SO_2$ transformation does not introduce significant changes in the metric parameters of these complexes. The reactivity of **3** and **4** indicates that the bound Cys-sulfurs around the biological Co(III) site could be oxidized to sulfinato groups.

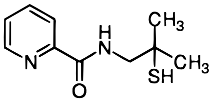
Introduction

The enzyme nitrile hydratase (NHase) catalyzes conversion of nitriles to amides in several microorganisms and has found use in industrial production of selected amides.[1−5] The active site of the heterodimeric enzyme comprises either a low-spin non-heme Fe(III) or a noncorrin Co(III) center nested in a CXXCSC sequence of the α subunit. Recent crystallographic studies on two *Rhodococcus* NHases have revealed that the single low-spin Fe(III) site in the α*β* heterodimer is coordinated to two deprotonated carboxamido nitrogens and three Cys-S centers[6] with at least two of them modified to Cys-sulfenic and -sulfinic groups.[7] Although no crystal structure of a Co-containing NHase has been reported, spectroscopic evidence[8,9] as well as sequence homologies[1] indicate that the coordination structures of the two M(III) sites in NHases are very similar.

The occurrence of the kinetically inert low-spin d^6 Co(III) center in NHase raises an interesting question regarding the role of the unusual donor set in the observed reactivity of the metal site. A close scrutiny of the literature reveals that no Co(III) complex with both carboxamido nitrogen(s) and thiolato sulfur(s) has been reported so far. As a consequence, no corresponding complex with cobalt-bound sulfinato group(s) is available. In our analogue approach to explore the structure and reactivity of the M(III) site in NHases,[10−13] we have now synthesized and characterized Co(III) complexes that contain carboxamido nitrogens and thiolato sulfurs in the first coordination sphere. In this paper, we report the Co(III) complexes of two designed ligands, $PyPepSH_2$ (**1**, *N*-2-mercaptophenyl-2′-pyridinecarboxamide) and $PyPepRSH_2$ (**2**, *N*-2-mercapto-2-methylpropyl-2′-pyridinecarboxamide). The dissociable amide and thiolate protons are denoted as Hs in the abbreviated notations of the two ligands. We have incorporated both aliphatic and aromatic thiolate groups in the ligand design to investigate the chemistry of the bound thiolato sulfur in such species. The two Co(III) complexes, namely, $(Et_4N)[Co(PyPepS)_2]$ (**3**) and $Na[Co(PyPepRS)_2]$ (**4**), are the first two examples of Co(III) complexes with carboxamido nitrogens and thiolato sulfurs as donors.



$PyPepSH_2$ (**1**)



$PyPepRSH_2$ (**2**)

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The post-translational modification of the bound cystinate residues in NHases could be an interesting way nature regulates the reactivity of metal centers bound to cystines in proteins. Although thiolates are normally oxidized to disulfides, it is known that metal-bound thiolates can be oxidized to the corresponding sulfenates and sulfinates.[12] Indeed, oxidation of thiolato sulfurs to sulfinates (and sulfenates) was proposed before as a mechanism of deactivation of the Ni-containing hydrogenases.[14] To investigate the mode of oxidation of the thiolato sulfurs in the present complexes, we have studied their oxidation and have isolated the sulfinato products. In this paper, the two sulfinato complexes, Na[Co(PyPepSO$_2$)$_2$] (**5**) and Na[Co(PyPepRSO$_2$)$_2$] (**6**), are also reported.

Experimental Section

Materials. Picolinic acid, 2-aminothiophenol, and 1-amino-2-methyl-2-propanethiol hydrochloride were purchased from Aldrich Chemical Co. Hydrogen peroxide (30%) was purchased from Fisher Scientific Co. [Co(NH$_3$)$_5$Cl]Cl$_2$ was synthesized by following the published procedure.[15] All manipulations were carried out in Schlenk lines and the solvents were dried and distilled before use. The reported complexes afforded satisfactory elemental analyses (Quantitative Technologies Inc.).

Preparation of Compounds. (A) PyPepSH$_2$ (1). The synthesis of this ligand comprises the following steps.

(a) Step 1. Bis-aminothiophenol disulfide: A batch of 5.85 g (0.046 mol) of 2-aminothiolphenol was dissolved in 50 mL of ethanol. To this solution, 50 mL of water was added and air was bubbled through the solution for 24 h. The insoluble disulfide was then filtered and dried under vacuum. Yield: 5.14 g (90%).

(b) Step 2. Acyl chloride of picolinic acid: In neat thionyl chloride, 4.38 g (0.036 mol) of picolinic acid was added and the resultant solution was heated under reflux until the solution became homogeneous. The excess thionyl chloride was removed by vacuum distillation and the resultant pink solid was triturated with chloroform and dried under vacuum.

(c) Step 3. (PyPepS)$_2$, the disulfide of **1**: The acid chloride obtained in step 2 was dissolved in 25 mL of chloroform and slowly added to a solution of 4.21 g (0.016 mol) of the disulfide (step 1) and 10.8 g (0.107 mol) of Et$_3$N in 60 mL of chloroform. The mixture was heated to reflux for 15 min and stirred for 24 h at room temperature. Next, the brown solution was washed with aqueous NaHCO$_3$ and NaCl. The chloroform solution was then dried over MgSO$_4$ and filtered. The solvent was removed by rotary evaporation and the residue was recrystallized from methanol. Yield: 6.50 g (85%).

(d) Step 4. PyPepSH$_2$ (**1**): A solution of 1.64 g (3.60 mmol) of (PyPepS)$_2$ in 20 mL of degassed THF was cooled to 4 °C. To this solution, 0.9 g (0.023 mol) of solid NaBH$_4$ was added in small portions. The dark orange solution thus obtained was stirred for 2 h. It was then concentrated on a rotary evaporator to 10% of its original volume and 5 N acetic acid was slowly added until the pH was 6. The solution was again cooled to 4 °C and stirred. The light cream solid which precipitated within 15 min was collected by filtration and washed with cold aqueous ethanol. The product was dried under high vacuum for 24 h. Yield: 0.67 g (40%). ^{1}H NMR (CDCl$_3$, 250 MHz, δ from TMS): 3.28 (SH, s), 7.06 (1H, s), 7.36 (1H, t), 7.52 (2H, m), 7.91 (1H, t), 8.29 (1H, d), 8.52 (1H, d), 8.68 (1H, d), 10.8 (NH, s). Selected IR bands (KBr pellet, cm^{-1}): 1688 ($\nu_{C=O}$), 2513 (ν_{S-H}), 3285 (ν_{N-H}).

(B) PyPepRSH$_2$ (2). The synthesis of this ligand comprises the following steps.

(a) Step 1. *S*-trityl-1-amino-2-methyl-2-propanethiol: A batch of 10.5 g (0.07 mol) of 1-amino-2-methyl-2-propanethiol hydrochloride was dissolved in 100 mL of trifluoroacetic acid (TFA) and 19.6 g (0.07 mol) of triphenylmethanol was added to it. The mixture was stirred for 1 h. The TFA was then removed by rotary evaporation and the residue was triturated first with chloroform and then with diethyl ether. Finally, the product was dried under high vacuum for 24 h. Yield: 19.4 g (76%).

(b) Step 2. PyPepRStry, *S*-tritylated **2**: A batch of 7.84 g (0.025 mol) of triphenyl phosphite was mixed with a solution of 3.11 g (0.025 mol) of the *S*-tritylated thiol and 3.11 g (0.025 mol) of picolinic acid in 100 mL of pyridine and the mixture was heated to reflux for 8 h. The deep red-brown solution was then evaporated to dryness and the residue was dissolved in chloroform. This solution was then washed with aqueous NaHCO$_3$ followed by aqueous NaCl. Next, the chloroform was removed and the oily residue was redissolved in 10 mL of acetone. Subsequent addition of 0.5 mL of H$_2$O with vigorous stirring afforded a white solid which was recrystallized from aqueous acetone. Yield: 4.72 g (42%). Selected IR bands (KBr pellet, cm^{-1}): 1660 ($\nu_{C=O}$).

(c) Step 3. PyPepRSH$_2$.HCl (**2.HCl**). A batch of 1.54 g (0.013 mol) of Et$_3$SiH was added to a solution of 2.0 g (4.44 mmol) of PyPepRStry in 10 mL of TFA. The addition resulted in a white precipitate and an immediate color change of the solution from red-brown to yellow. The mixture was stirred for 20 min and filtered. TFA was removed from the filtrate under vacuum and the oily residue was redissolved in 15 mL of methanol. Dry HCl gas was then bubbled through this solution to form the hydrochloride salt of **2** which precipitated out as a white solid upon addition of diethyl ether. Yield: 1.0 g (72%). ^{1}H NMR (CDCl$_3$, 250 MHz, δ from TMS): 1.47 (6H, s), 3.67 (2H, d), 7.98(1H, t), 8.45 (1H, t), 8.67 (1H, d), 8.81 (1H, d), 9.54 (NH, s).

(C) (Et$_4$N)[Co(PyPepS)$_2$] (3). A batch of 80 mg (3.3 mmol) of NaH was added to a solution of 370 mg (1.6 mmol) of **1** in 15 mL of degassed dimethyl formamide (DMF) and the mixture was stirred until all the NaH had reacted. To the light yellow solution was then added 186 mg (0.75 mmol) of [Co(NH$_3$)$_5$Cl]Cl$_2$ and the solutuion was heated to 65 °C for 1 h. The deep red solution thus obtained was stirred for 4 h at room temperature. Next, a batch of 200 mg (1.2 mmol) of Et$_4$NCl was added and the DMF was removed under high vacuum. The dark brown residue was redissolved in 175 mL of acetonitrile and filtered. The filtrate was then concentrated to 30 mL and kept at −20 °C for 25 h. The microcrystalline product was collected by filtration and dried under vacuum. Yield: 232 mg (45%). Selected IR bands (KBr pellet, cm^{-1}): 1585 ($\nu_{C=O}$). Electronic absorption spectrum in ethanol, λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 242 (35 807), 282 (24 552), 344 (5 688), 468 (1 695). ^{1}H NMR (CD$_3$OD, 250 MHz, δ from TMS) of (Et$_4$N)[Co(PyPepS)$_2$]: 1.23 (t, 3H, Et$_4$N), 3.23 (q, 2H, Et$_4$N), 6.73 (t, 1H), 6.86 (t, 1H), 6.98 (d, 1H), 7.31 (t, 1H), 7.90 (m, 2H), 8.08 (d, 1H), 9.06 (d, 1H).

(D) Na[Co(PyPepRS)$_2$] (4). A batch of 63 mg of NaH (2.60 mmol) was added to a solution of 213 mg (0.87 mmol) of **2.HCl** in 10 mL of degassed DMF. After 15 min, 109 mg (0.44 mmol) of [Co(NH$_3$)$_5$Cl]Cl$_2$ was added and the solution heated at 50 °C for 1 h. The red solution was stirred at room temperature for 4 h and then DMF was removed under vacuum. The brown residue was redissolved in 30 mL of acetonitrile and filtered. The volume of the filtrate was then reduced to 15 mL and it was stored at −20 °C for 10 h. The red microcrystalline compound was collected by filtration and dried in vacuo. Yield: 195 mg (81%). Selected IR bands (KBr pellet, cm^{-1}): 1560 ($\nu_{C=O}$). Electronic absorption spectrum in ethanol, λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 505 (727), 409 (3 291), 360 (4 994), 290 (12 619), 257 (14 485). ^{1}H NMR (d_6-DMSO, 250 MHz, δ from TMS) of (Me$_4$N)[Co(PyPepRS)$_2$]: 1.11 (s, 3H), 1.50 (s, 3H), 2.08 (s, 2H), 3.10 (s, 12H, Me$_4$N), 7.31 (t, 1H), 7.70 (d, 1H), 7.81 (t, 1H) 7.87 (d, 1H).

(E) Na[Co(PyPepSO$_2$)$_2$] (5). A batch of 240 mg (0.45 mmol) of the sodium salt of **3** was dissolved in 25 mL of MeOH and cooled to 0 °C. To this solution, 980 μL of 30% H$_2$O$_2$ was added slowly. The solution was stirred for an additional 30 min at room temperature. The product was isolated by slow diffusion of diethyl ether into this solution. Yield: 177 mg (66%). Selected IR bands (KBr pellet, cm^{-1}): 1595 ($\nu_{C=O}$), 1193 (ν_{S-O}) asym, 1070 (ν_{S-O}) sym. Electronic absorption spectrum in methanol, λ_{max}, nm (ϵ, M^{-1} cm^{-1}): 363 (10 584), 272 (36 780), 242 (46 353). ^{1}H NMR (CD$_3$OD, 250 MHz, δ from TMS): 7.14 (t, 1H), 7.48 (m, 3H), 8.07 (m, 3H), 9.34 (d, 1H).

(F) Na [Co(PyPepRSO$_2$)$_2$] (6). This complex was synthesized by following the procedure used for **5**. Yield: 62%. Selected IR bands (KBr pellet, cm^{-1}): 1591 ($\nu_{C=O}$), 1205 (ν_{S-O}) asym, 1046 (ν_{S-O}) sym.

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Table 1. Summary of Crystal Data and Intensity Collection and Structure Refinement Parameters for $(Me_4N)[Co(PyPepS)_2]\cdot 0.5\ H_2O$, $(Me_4N)[Co(PyPepRS)_2]\cdot CH_3CN$, $Na[Co(PyPepSO_2)_2]\cdot 2CH_3OH\cdot H_2O$ (**$5\cdot 2CH_3OH\cdot H_2O$**), and $Na[Co(PyPepRSO_2)_2]\cdot CH_3OH\cdot H_2O$ (**$6\cdot CH_3OH\cdot H_2O$**)

	$(Me_4N)[Co(PyPepS)_2]\cdot 0.5\ H_2O$	$(Me_4N)[Co(PyPepRS)2]\cdot CH_3CN$	**$5\cdot 2CH_3OH\cdot H_2O$**	**$6\cdot CH_3OH\cdot H_2O$**
empirical formula	$C_{28}H_{29}CoN_5O_{2.50}S_2$	$C_{26}H_{39}CoN_6O_2S_2$	$C_{26}H_{26}CoN_4O_9S_2$	$C_{21}H_{30}CoN_4NaO_8S_2$
mol wt	598.61	590.68	684.55	612.53
cryst color, habit	black parallelpiped	black parallelpiped	orange parallelpiped	red block
T, K	140(2)	140(2)	140(2)	298(2)
cryst syst	monoclinic	orthorhombic	monoclinic	monoclinic
space group	I_2/a	$Pna2_1$	$P2_1/c$	$P2_1/c$
a, Å	17.442(4)	21.510(4)	15.050(3)	9.7489(11)
b, Å	11.375(2)	13.485(2)	11.333(2)	13.1151(13)
c, Å	28.162(6)	10.0512(16)	16.478(3)	20.998(3)
α, deg	90	90	90	90
β, deg	93.54(3)	90	97.06(2)	100.481(11)
γ, deg	90	90	90	90
V, Å^3	5576.8(19)	2915.5(9)	2789.2(9)	2640.0(5)
Z	8	4	4	4
d_{calcd}, g cm^{-3}	1.426	1.346	1.630	1.541
abs coeff, μ, mm^{-1}	0.802	0.766	0.843	0.877
GOF^a on F^2	0.985	1.012	1.017	0.890
R_1,^{b} %	5.88	3.43	4.05	4.51
R_{w2},^{c} %	11.39	7.19	8.44	9.34

[a] $GOF = [\sum[w(F_o^2 - F_c^2)^2]/(M - N)]^{1/2}$ (M = number of reflections; N = number of parameters refined). [b] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. [c] $R_{w2} = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Electronic absorption spectrum in methanol, λ_{max}, nm (ϵ, $M^{-1}\ cm^{-1}$): 472 (805), 326 (20 189), 268 (16 968), 250 (16 570). ^1H NMR (CD_3-OD, 250 MHz, δ from TMS): 1.14 (s, 3H) 1.31 (s, 3H), 3.18 (s, 2H), 7.27 (m, 1H), 8.00 (t, 3H).

X-ray Data Collection and Structure Solution and Refinement. Black parallelpipeds of $(Me_4N)[Co(PyPepS)_2]$ and $(Me_4N)[Co(PyPepRS)_2]$, suitable for X-ray analysis, were obtained by slow diffusion of diethyl ether into solutions of **3** and **4** with Me_4NCl in acetonitrile. Orange parallelpipeds of **5** and red blocks of **6** were obtained by slow diffusion of diethyl ether into solutions of the complexes in aqueous methanol. Diffraction data for complexes **3**−**5** were collected with a Siemens R3m/V diffractometer at 140 K while those for complex **6** were collected with a Bruker Platform diffractometer at room temperature. All structures were solved by direct methods (SHELXS-97). Intensities of two standard reflections showed only random fluctuations of less than 1% during the course of data collection. The data were corrected for absorption effects.[16] Machine parameters, crystal data, and data collection parameters are summarized in Table 1. Selected bond distances and angles are listed in Table 2. The four sets of crystallographic data have been submitted as Supporting Information.

Other Physical Measurements. Infrared spectra were obtained with a Perkin-Elmer 1600 FTIR spectrophotometer. Absorption spectra were measured on a Perkin-Elmer Lambda 9 spectrophotometer. ^1H NMR spectra were recorded on a Bruker 250 MHz NMR with a Tecmag data station.

Results and Discussion

Thiolato complexes of Co(III) have mostly been synthesized via air oxidation of reaction mixtures containing different Co(II) starting materials and thiolates.[17−20] However, this method did not work in the case of **3**. A combination of $Co(ClO_4)_2\cdot 6H_2O$ with proton sponge in methanol resulted in a purple solution which turned brown after exposure to air. Such solution did not afford any crystalline solid upon further workup. Various other bases including NaOH were also tried but with no success. Change of solvent to DMF and use of NaH as the base also failed. We therefore decided to start with Co(III) starting materials which in selected cases have afforded desired products.[21−23] In our first attempt, we reacted $[Co(NH_3)_5Cl]Cl_2$ with **1** in water in the presence of NaOH and because Co(III) complexes are kinetically inert, the reaction mixture was heated to 60 °C to accelerate complexation. This procedure resulted in precipitation of intractable brown solid. However, when the same starting material was allowed to react with **1** in DMF and NaH was used as the base, the reaction proceeded smoothly at 60 °C and a homogeneous reddish brown solution was obtained within 1 h. Complex **3** was isolated from this solution upon the addition of Et_4NCl and cooling. The same method was used for the synthesis of **4** except for the addition of Et_4NCl; this complex was isolated as the Na salt.

The sulfinato complexes **5** and **6** have been synthesized via oxidation of **3** and **4** with either dioxygen or hydrogen peroxide. Oxidation of thilolates coordinated to Co(III) by hydrogen peroxide is a well-known reaction and it has been studied in detail.[24−27] The syntheses of **5** and **6** with peroxide were carried out at 0 °C to prevent any other side reactions. It has been previously shown that oxidation of Co(III)-bound thiolato sulfur also proceeds upon exposure to air and the process of oxidation can be accelerated by the addition of activated charcoal to the solution of the thiolato complex.[28] In the present work, we noted that exposure of methanolic solutions of **3** and **4** to dioxygen did not cause any oxidation, even after 48 h. The addition of activated charcoal to such solutions enhanced the speed of

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Table 2. Selected Bond Distances (Å) and Angles (deg)

$(Me_4N)[Co(PyPepS)_2]\cdot 0.5H_2O$

Bond Distances

Co−N1	1.960(3)	S2−C24	1.767(5)	Co−S1	2.2207(12)	O2−C18	1.250(5)
Co−N2	1.914(3)	N2−C6	1.345(5)	Co−S2	2.2233(13)	C2−C3	1.387(7)
Co−N3	1.973(3)	N4−C18	1.337(5)	S1−C12	1.749(4)	C9−C10	1.385(6)
Co−N4	1.921(3)	O1−C6	1.241(5)				

Bond Angles

N2−Co−N4	178.43(14)	N2−Co−S2	92.92(11)	N1−Co−N3	89.71(14)	C12−S1−Co	97.06(13)
N2−Co−N1	83.60(14)	N4−Co−S2	88.64(11)	N2−Co−S1	88.38(10)	C1−C2−C3	119.1(5)
N4−Co−N1	96.21(14)	N1−Co−S2	90.32(11)	N4−Co−S1	91.77(10)	O1−C6−N2	128.9(4)
N2−Co−N3	95.20(14)	N3−Co−S2	171.83(10)	N1−Co−S1	171.87(11)	C7−C12−S1	119.8(3)
N4−Co−N3	83.24(14)	S1−Co−S2	91.42(5)	N3−Co−S1	89.69(10)	C24−C19−C20	118.7(4)

$(Me_4N)[Co(PyPepRS)_2]\cdot CH_3CN$

Bond Distances

Co−N(1)	1.907(3)	O(1)−C(5)	1.248(5)	Co−S(1)	2.2413(11)	N(3)−C(14)	1.462(4)
Co−N(3)	1.912(3)	O(2)−C(15)	1.254(4)	Co−S(2)	2.2607(9)	C(1)−C(2)	1.532(5)
Co−N(4)	1.984(3)	N(1)−C(5)	1.318(5)	S(1)−C(1)	1.846(4)	C(11)−C(12)	1.520(5)
Co−N(2)	1.995(3)	N(3)−C(15)	1.320(4)	S(2)−C(11)	1.844(3)	C(11)−C(14)	1.520(5)

Bond Angles

N(1)−Co−N(3)	176.55(13)	N(4)−Co−S(2)	167.31(9)	N(1)−Co−S(1)	85.95(10)	C(2)−C(1)−S(1)	108.1(2)
N(1)−Co−N(4)	96.23(12)	N(2)−Co−S(2)	90.17(9)	N(3)−Co−S(1)	97.02(9)	N(1)−C(4)−C(1)	111.6(3)
N(3)−Co−N(4)	82.16(11)	S(1)−Co−S(2)	96.41(3)	N(4)−Co−S(1)	88.03(8)	O(1)−C(5)−N(1)	129.0(4)
N(1)−Co−N(2)	81.91(12)	C(1)−S(1)−Co	99.43(12)	N(2)−Co−S(1)	166.74(9)	C(14)−C(11)−C(13)	109.4(3)
N(3)−Co−N(2)	94.96(13)	C(11)−S(2)−Co	99.24(11)	N(1)−Co−S(2)	95.94(9)	N(3)−C(14)−C(11)	111.3(3)
N(4)−Co−N(2)	87.99(11)	C(3)−C(1)−C(2)	109.2(3)	N(3)−Co−S(2)	85.49(9)	O(2)−C(15)−C(16)	120.8(3)

$Na[Co(PyPepSO_2)_2]\cdot 2CH_3OH\cdot H_2O$ (**$5\cdot 2CH_3OH\cdot H_2O$**)

Bond Distances

Co−N(3)	1.917(3)	S(2)−O(5)	1.477(2)	Co−S(2)	2.1666(10)	O(4)−Na	2.308(3)
Co−N(1)	1.924(3)	S(2)−C(13)	1.786(3)	S(1)−O(1)	1.468(2)	O(6)−C(19)	1.231(4)
Co−N(2)	1.958(3)	O(2)−Na	2.431(3)	S(1)−O(2)	1.468(2)	N(1)−C(7)	1.338(4)
Co−N(4)	1.971(3)	O(3)−C(7)	1.240(4)	S(1)−C(1)	1.776(3)	N(3)−C(19)	1.342(4)
Co−S(1)	2.1646(10)	O(3)−Na	2.284(3)	S(2)−O(4)	1.466(2)	C(19)−C(20)	1.510(4)

Bond Angles

N(3)−Co−N(1)	177.68(11)	N(4)−Co−S(2)	169.49(8)	N(1)−Co−S(1)	88.39(8)	C(13)−S(2)−Co	99.08(11)
N(3)−Co−N(2)	98.27(11)	S(1)−Co−S(2)	94.51(4)	N(2)−Co−S(1)	171.09(8)	C(6)−C(1)−S(1)	117.3(2)
N(1)−Co−N(2)	83.33(11)	O(1)−S(1)−O(2)	112.44(13)	N(4)−Co−S(1)	90.66(8)	C(3)−C(2)−C(1)	119.7(3)
N(3)−Co−N(4)	83.42(11)	O(1)−S(1)−C(1)	107.79(15)	N(3)−Co−S(2)	87.44(8)	O(3)−C(7)−C(8)	120.0(3)
N(1)−Co−N(4)	95.03(11)	O(2)−S(1)−C(1)	106.85(15)	N(1)−Co−S(2)	94.26(8)	N(2)−C(8)−C(7)	115.6(3)
N(2)−Co−N(4)	86.79(11)	O(1)−S(1)−Co	111.98(10)	N(2)−Co−S(2)	89.42(8)	O(6)−C(19)−C(20)	119.7(3)
N(3)−Co−S(1)	89.91(8)	O(2)−S(1)−Co	117.46(10)				

$Na[Co(PyPepRSO_2)_2]\cdot CH_3OH\cdot H_2O$ (**$6\cdot CH_3OH\cdot H_2O$**)

Bond Distances

Co−N(2)	1.908(4)	S(1)−O(3)	1.454(4)	Na−O(4)	2.211(4)	O(4)−C(16)	1.252(6)
Co−N(4)	1.912(4)	S(1)−C(8)	1.868(6)	Na−O(3)	2.277(4)	N(1)−C(1)	1.322(7)
Co−N(3)	1.987(4)	S(2)−O(5)	1.474(4)	Na−O(7)	2.377(5)	N(2)−C(6)	1.333(6)
Co−N(1)	2.003(4)	S(2)−O(6)	1.476(4)	Na−O(6)	2.478(4)	N(4)−C(16)	1.312(7)
Co−S(1)	2.1962(15)	S(2)−C(18)	1.870(5)	S(1)−O(2)	1.452(4)	C(9A)−C(8)	1.482(10)
Co−S(2)	2.2288(16)	O(1)−C(6)	1.254(6)				

Bond Angles

N(2)−Co−N(4)	177.51(19)	O(4)−Na−O(7)	100.2(18)	N(4)−Co−S(1)	92.83(13)	O(6)−S(2)−Co	119.04(16)
N(2)−Co−N(3)	100.09(18)	O(3)−Na−O(7)	98.24(16)	N(3)−Co−S(1)	89.06(12)	C(17)−N(4)−Co	119.5(3)
N(4)−Co−N(3)	82.23(18)	O(2)−S(1)−O(3)	112.7(2)	N(1)−Co−S(1)	164.95(14)	N(1)−C(1)−C(2)	122.7(6)
N(2)−Co−N(1)	81.80(17)	O(2)−S(1)−C(8)	106.7(3)	N(2)−Co−S(2)	92.26(14)	N(1)−C(5)−C(6)	114.6(4)
N(4)−Co−N(1)	99.39(18)	O(2)−S(1)−Co	110.78(17)	N(4)−Co−S(2)	85.55(13)	O(1)−C(6)−N(2)	126.4(5)
N(3)−Co−N(1)	83.96(16)	O(5)−S(2)−O(6)	112.1(2)	N(3)−Co−S(2)	165.75(13)	N(2)−C(6)−C(5)	112.8(5)
N(2)−Co−S(1)	86.34(13)	O(6)−S(2)−C(18)	105.6(2)	N(1)−Co−S(2)	90.86(13)	O(4)−C(16)−N(4)	128.0(5)

oxidation and complete oxidation was achieved within 36 h. The role of charcoal in the formation of the sulfinato complexes is not clear at this time. Since activated charcoal promotes the formation of Co(II) species,[29] we hypothesize that molecular oxygen is converted to peroxide by small amounts of the Co(II) forms of **3** and **4** in the reaction mixtures and the sulfinato complexes are finally obtained as a result of the oxidation of **3** and **4** by peroxide generated in situ. Although both methods afford **5** and **6** in similar yields, oxidation with hydrogen peroxide is the preferred method because such reactions are clean and proceed rapidly at low temperatures.

Structure of $(Me_4N)[Co(PyPepS)_2]\cdot 0.5H_2O$. The structure of $[Co(PyPepS)_2]^-$ is shown in Figure 1. The coordination geometry around cobalt is distorted octahedral and the two deprotonated $PyPepS^{2-}$ ligands are ligated to the Co(III) center in *mer* fashion. The two deprotonated carboxamido nitrogens are trans to each other while the two thiolato sulfurs occupy positions that are cis to each other. The lattice water molecules

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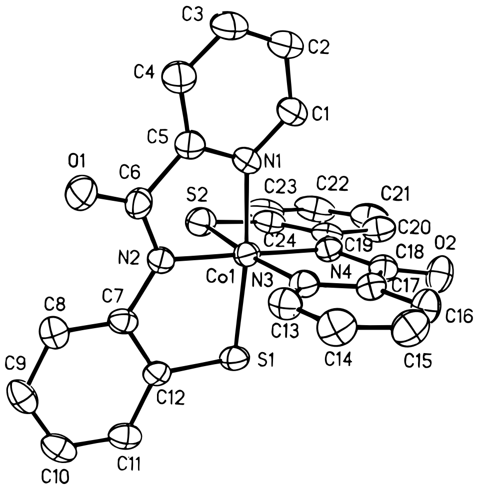

Figure 1. Thermal ellipsoid (probability level 50%) plot of [Co(PyPepS)$_2$]$^-$ (anion of **3**) with an atom-labeling scheme. H atoms are omitted for the sake of clarity.

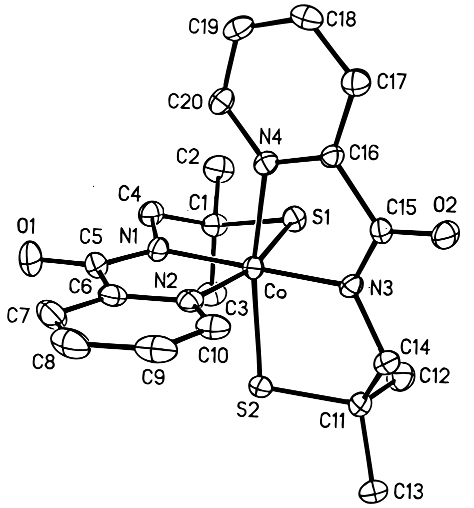

Figure 2. Thermal ellipsoid (probability level 50%) plot of [Co(PyPepRS)$_2$]$^-$ (anion of **4**) with an atom-labeling scheme. H atoms are omitted for the sake of clarity.

are hydrogen-bonded to the oxygens of the carbonyl groups of the ligands. The average Co−S bond length (2.2220(12) Å) compares well with reported Co−S bond lengths in Co(III) complexes of aromatic thiolates.[23,30] The average Co−N$_{amido}$ and Co−N$_{py}$ bond distances (1.9175(3) and 1.9665(3) Å, respectively) are also within the ranges for such distances observed in reported complexes.[31−33]

Structure of (Me$_4$N)[Co(PyPepRS)$_2$]·CH$_3$CN. The spatial arrangement of donor atoms around the Co(III) center in [Co(PyPepRS)$_2$]$^-$ (Figure 2) is similar to that noted in [Co(PyPepS)$_2$]$^-$. The overall geometry is however more distorted. For example, the N(4)−Co−S(2) angle in [Co(PyPepRS)$_2$]$^-$ is 167.31(9)°, while the N(1)−Co-S(1) angle in [Co(PyPepS)$_2$]$^-$ is 171.87 (11)°. The average Co−S bond length (2.2510(10) Å) in [Co(PyPepRS)$_2$]$^-$ is similar to that reported for other Co(III) complexes of aliphatic thiolates.[20,34]

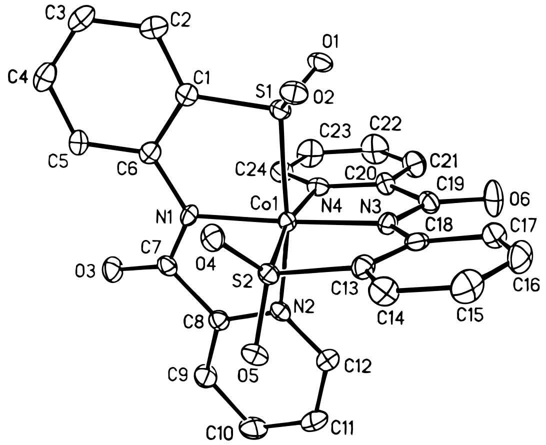

Figure 3. Thermal ellipsoid (probability level 50%) plot of [Co(PyPepSO$_2$)$_2$]$^-$ (anion of **5**) with an atom-labeling scheme. H atoms are omitted for the sake of clarity.

Structure of Na[Co(PyPepSO$_2$)$_2$]·2CH$_3$OH·H$_2$O (5·2CH$_3$OH·H$_2$O). The structure of this complex has been briefly reported in an earlier account.[12] A different view of the anion is shown in Figure 3. It is important to note that both the disposition of donor atoms and the overall geometry of [Co(PyPepSO$_2$)$_2$]$^-$ and [Co(PyPepS)$_2$]$^-$ are very similar. The only noticeable difference is the shortening of the Co−S(thiolato) bond from 2.2220(12) Å (average value) to the Co−S(sulfinato) distance of 2.1656(10) Å (average value). Such shortening has previously been reported and attributed to the increasd ligand field of the sulfinato (SO$_2$) group.[35,36] The increase in ligand field strength is also reflected in the small increase in the Co−N$_{py}$ distance trans to the sulfinato moiety in [Co(PyPepSO$_2$)$_2$]$^-$ compared to that in [Co(PyPepS)$_2$]$^-$ (Table 2). The average S−O distance (1.470 (2) Å) noted for **5** is very close to that observed in other Co(III) complexes with bound sulfinates.[35,36] The sodium ion is associated with the oxygen atoms of the carbonyl and the sulfinate moieties, and also with the lattice solvents (methanol and water).

Structure of Na[Co(PyPepRSO$_2$)$_2$]·CH$_3$OH·H$_2$O (6·CH$_3$OH·H$_2$O). The structure of [Co(PyPepRSO$_2$)$_2$]$^-$ (Figure 4) also indicates that oxidation of thiolates to sulfinates does not introduce major changes in the metric parameters of [Co(PyPepRSO$_2$)$_2$]$^-$ compared to [Co(PyPepRS)$_2$]$^-$. Again, there is a slight shortening of the average Co−S bond length to 2.2125(15) Å. This length is in good agreement with those previously reported for Co(III) complexes with ligated sulfinates.[28,36] The sodium ions are also associated with the oxygen atoms of the sulfinate groups and lattice water molecules.

Properties

Ligation of carboxamido nitrogens to Co(III) in all four complexes is evident in the red shift of ν_{CO}.[30,31] For example, ν_{CO} for **3** and **4** appear at 1560 and 1585 cm^{-1} compared to 1688 and 1660 cm^{-1} in **1** and **2.HCl**, respectively. The coordinated sulfinate group in **5** and **6** exhibits strong stretching frequencies in the region of 1200 and 1100 cm^{-1} which have

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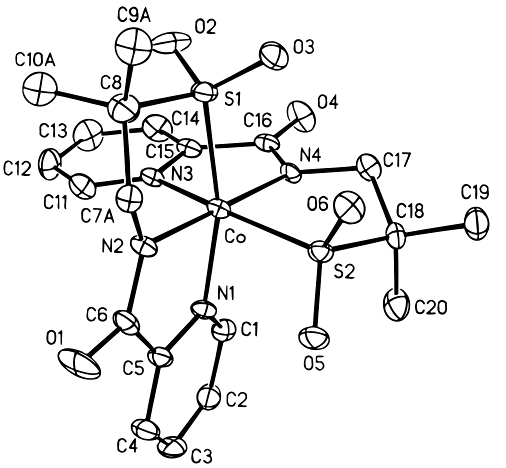

Figure 4. Thermal ellipsoid (probability level 50%) plot of [Co(PyPepRSO$_2$)$_2$]$^-$ (anion of **6**) with an atom-labeling scheme. H atoms are omitted for the sake of clarity.

been assigned to the ν(asym) and ν(sym) bands of the $-SO_2$ moiety.[37] In the solid state, **3** and **4** are quite stable. However, solutions of these thiolato complexes are slowly converted to other oxygenated species (including the sulfinato complexes) when kept in air for long periods of time.[28]

The complexes **3** and **4** dissolve in a variety of protic and aprotic solvents to give deep reddish brown solutions. These solutions exhibit strong absorption bands with maxima at ~500, ~350, and ~280 nm. The ~500-nm band most possibly arises from a thiolate-to-Co(III) charge transfer (LMCT) transition because conversion of **3** to **5** results in the disappearance of this absorption (Figure 5). Similar behavior is observed with **4**. Oxidation of the coordinated thiolato sulfur to sulfinato group also causes a blue shift of the ~280-nm band of **3** and **4**. This band has also been assigned to LMCT transition in other Co(III) complexes of similar kinds.[35,36] The blue shift of this band indicates that the sulfinate group exerts a stronger ligand field in **5** and **6**.

Conversion of Co(III)-bound thiolato sulfurs of **3** to sulfinato groups results in upfield shift (by 0.3 ppm) of the ^{1}H NMR peaks for the protons ortho to the sulfinato groups of **5**. Another change upon oxidation is noted with the methyl groups of **4**. The single peak for the methyl groups of **4** splits into two in the ^{1}H NMR spectrum of **6**. The reason for this inequivalency is most possibly related to the spatial arrangements of the methyl groups in relation to the sulfinato oxygens in **5** (Figure 4).

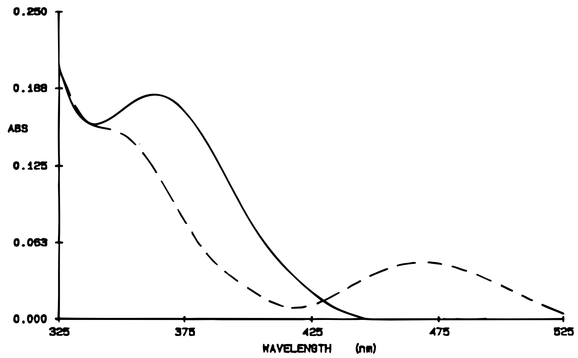

Figure 5. Changes in the electronic absorption spectrum upon conversion of [Co(PyPepS)$_2$]$^-$ (broken line) to [Co(PyPepSO$_2$)$_2$]$^-$ (solid line) in methanol.

Summary and Conclusions

The following are the summary and conclusions of this study.

(a) Two complexes, **3** and **4**, with carboxamido nitrogens and thiolato sulfurs ligated to Co(III) centers have been characterized for the first time.

(b) The thiolato sulfurs of **3** and **4** are readily converted to sulfinates upon reaction with hydrogen peroxide. The resulting complexes, **5** and **6**, comprise both carboxamido nitrogens and sulfinato groups around Co(III) much like the proposed coordination structure of the Co(III) site of the Co−NHases. The S → SO$_2$ conversion occurs, albeit slowly, upon exposure to dioxygen in the presence of activated charcoal.

(c) Although the presence of aliphatic thiolates and sulfinate in **4** and **6** make them better models of the biological Co(III) site in NHase, it is important to note that the properties and reactivities of **3** and **5** are very similar to those of **4** and **6**. This suggests that aromatic thiolato sulfurs can substitute for aliphatic ones in the design of more complicated ligands for modeling the active site of NHases.

Supporting Information Available: X-ray crystallographic files, in CIF format, for the structure determination of **3**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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