Synthesis, X-ray Structure and Properties of a Trinuclear Mixed-Valence Co^{III}-Co^{II}-Co^{III} Complex with Carboxamido N and Sulfinato S Donors

Mathieu Rat,[a] Rodolphe Alves de Sousa,[a] Alain Tomas,[b] Yves Frapart,[a] Jean-Pierre Tuchagues,[c] and Isabelle Artaud*[a]

Keywords: Cobalt / N ligands / S ligands / Enzyme models

Air oxidation of the six-coordinate $(Et_4N)_2[Co(N_2S_2)(CN)(CH_3CN)]$ complex derived from *N*,*N'*-(3-mercapto-3-methylbutyryl)-*o*-phenylenediamine results in the formation of the trinuclear mixed-valence complex $(Et_4N)_4\{Co^{II}[Co^{III}\{N_2(SO_2)_2\}(CN)(OH)]_2\}$ (**3**) where the thiolates have been oxidized to sulfinates. Its X-ray structure reveals a linear arrangement of cobalt ions with bridging hydroxides and sulfinates. All cobalt ions are in a distorted octahedral environment. The mixed-valence nature of this complex has been demonstrated by temperature-dependent magnetic susceptibility measurements and by EPR spectroscopy both in the solid state and in solution. These data are in agreement with a high-spin Co^{II}. The IR spectrum shows the typical vibrations of cyanide and sulfinate at 2130 cm^{-1} (ν_{CN}), 1175 ($\nu_{as/SO2}$) and 1030 cm^{-1} ($\nu_{s/SO2}$). Trapping of Co^{II} by chelex chromatography after treatment with aqueous HCl, or " in situ" in aqueous solution, yields six-coordinate low-spin complexes with two different axial ligands $Na_3[Co\{N_2(SO_2)_2\}(CN)(Cl)]$ (**5a**) and $(Et_4N)_2[Co\{N_2(SO_2)_2\}(CN)(H_2O)]$ (**5b**). The pK_a of the bound water molecule was estimated as 10.1 by pH-metric titration. While **3** and **5a** were inactive toward acetonitrile hydration, **5b** catalyzes acetamide formation at 50 °C and pH 4.7 and 7 with low efficiency.

Introduction

Nitrile hydratases (NHases) are at the centre of the industrial production of acrylamide. These bacterial enzymes, which catalyze the hydration of nitriles to amides, contain either a non-heme iron(III) or a non-corrinoid cobalt(III) centre. The crystal structure of a Co-type NHase produced from a *Pseudonocardia thermophila* species at 1.8 Å resolution has been reported recently.[1] The ligands to the cobalt atom are two peptide amide nitrogens and three sulfurs from cysteines. The two cysteines in the mean-plane *trans* to the amide nitrogens are oxidized to cysteine-sulfinic and cysteine-sulfenic acids. The apical ligands are one cysteine thiolate and a water molecule. As previously suggested,[2] the cobalt environment is very similar to the iron environment revealed by the X-ray structure of *Rhodococcus* Fe-type NHase crystallised in its NO inactivated form.[3] In this case, NO replaces H_2O as the sixth axial ligand. These results clearly show that the post-translational cysteine oxidations are general among NHases irrespective of whether they contain iron or cobalt at their active site

Most of the cobalt NHase mimics reported so far contain thiolates as sulfur donors; a few contain sulfinates and/or sulfenates.[4−7] One six-coordinate Co^{III} complex with two thiolato S-donors includes CN^- which can be replaced by H_2O at the sixth site.[4a] Most of the complexes containing oxidized thiolates as sulfur donors are six-coordinate and do not have a labile ligand that might be exchanged with H_2O or HO^-. Only one complex containing a sulfinate ligand is five-coordinate and has an open coordination site,[5] but the presence of an apical sulfinate prevents binding of any exogenous ligand at this open coordination site. Recently, we have prepared square planar $(Et_4N)[Co^{III}(N_2S_2)]$ complexes[7,8] containing, similarly to NHase, two carboxamido nitrogens *trans* to two thiolates, and we have described the conversion of the *S*-bound thiolates to *S*-bound sulfinates in the presence of *tert*-butyl isocyanide.[7] The resulting six-coordinate complex $(Et_4N)[Co^{III}(N_2(SO_2)_2](CNtBu)_2]$ has two isocyanide ligands tightly ligated to the cobalt centre. All attempts to exchange one isocyanide with another axial ligand have failed. This contrasts with the behaviour of the precursor square planar Co^{III} complex which has only a low affinity for isocyanide. In this report we show that this $[Co^{III}(N_2S_2)]$ complex interacts with cyanide yielding a six-coordinate complex with apically bonded cy-

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[a] Laboratoire de Chimie et Biochimie Toxicologiques et Pharmacologiques, Université René Descartes, UMR 8601 CNRS,
45 rue des Sts Pères 75270 Paris cedex O6 France
Fax: (internat.) +33-1/42868387
E-mail: artaud@biomedicale.univ-paris5.fr
[b] Laboratoire de Cristallographie et de RMN biologiques UMR 8015, Faculté de Pharmacie,
4 Rue de l'observatoire, 75270 Paris cedex 06 France
[c] Laboratoire de Chimie de Coordination, UPR CNRS 8241, 205 route de Narbonne, 31077 Toulouse Cedex 04 France

anide and solvent molecule. Air oxidation of this complex affords a trinuclear Co^{III}-Co^{II}-Co^{III} species which has been crystallographically and spectroscopically characterised. The ligands at the Co^{III} centre are two nitrogens *trans* to two *S*-bound sulfinates in the mean plane and one cyanide and one hydroxide in the axial positions. Finally we describe its reactivity in solution and show that Co^{II} can be removed, yielding a six-coordinate Co^{III} complex.

Results and Discussion

The synthesis and spectroscopic characterisation of the square planar $(Et_4N)[Co^{III}(N_2S_2)]$ complex **1** (Scheme 1) has been described previously.[7] Its interaction with CN^- was monitored by UV/Vis spectroscopy under argon. While the electronic spectrum of complex **1** in acetonitrile exhibits an absorption at 695 nm, addition of a CH_3CN solution of Et_4NCN results in the progressive disappearance of this band and appearance of a new one at 820 nm. The conversion is complete after addition of one equivalent of CN^- per Co^{III} centre. Complex **2a** prepared in deaerated DMF and isolated by precipitation with diethyl ether corresponds to the formula $(Et_4N)_2[Co^{III}(N_2S_2)(CN)(DMF)]$. Its ^1H NMR spectrum in $[D_7]DMF$ exhibits only signals between $\delta = 0$ and 10 ppm, indicating that **2** is a six-coordinate low spin Co^{III} complex. The non-equivalence of the CH_3 groups and of the CH_2 protons on either side of the N_2S_2 plane is in agreement with the binding of only one axial cyanide. The sixth position is occupied by a DMF molecule whose methyl resonances are clearly different from those of the free solvent. In the IR spectrum (KBr pellet), the ν_{CN} and ν_{CO} stretching bands corresponding to the axial CN^- and DMF are located at 2080 cm^{-1} and 1670 cm^{-1} respectively. In contrast to a related $[Co^{III}(N_2S_2)]$ complex with two aliphatic carboxamido N donors,[9] addition of cyanide in excess does not result in the formation of a dicyanide species. Consequently, whereas complex **1** can bind two isocyanide molecules, complex **2** binds only one cyanide ion and a solvent molecule such as DMF yielding, in both cases, a six-coordinate low spin Co^{III} complex.

Slow air oxidation of an acetonitrile solution of complex **1** with one equivalent of Et_4NCN (yielding **2b** with CH_3CN at the sixth site, Scheme 1) results in the precipitation of an orange powder, which was collected by filtration. Vapour diffusion of diethyl ether into a highly diluted CH_3CN solution of this species afforded crystals of complex **3** suitable for X-ray analysis. The crystal structure of complex **3** shown in Figure 1 reveals the formation of a linear tetra-

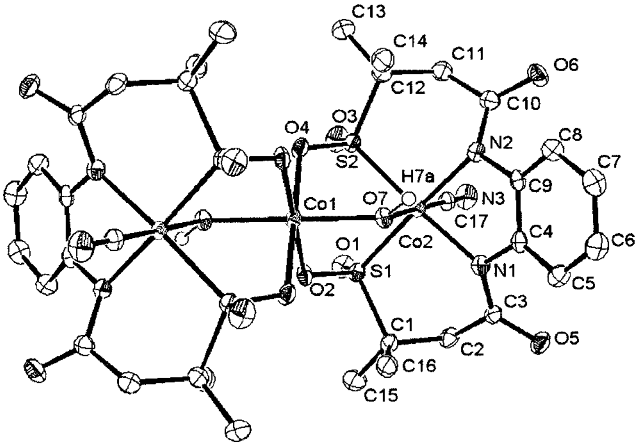
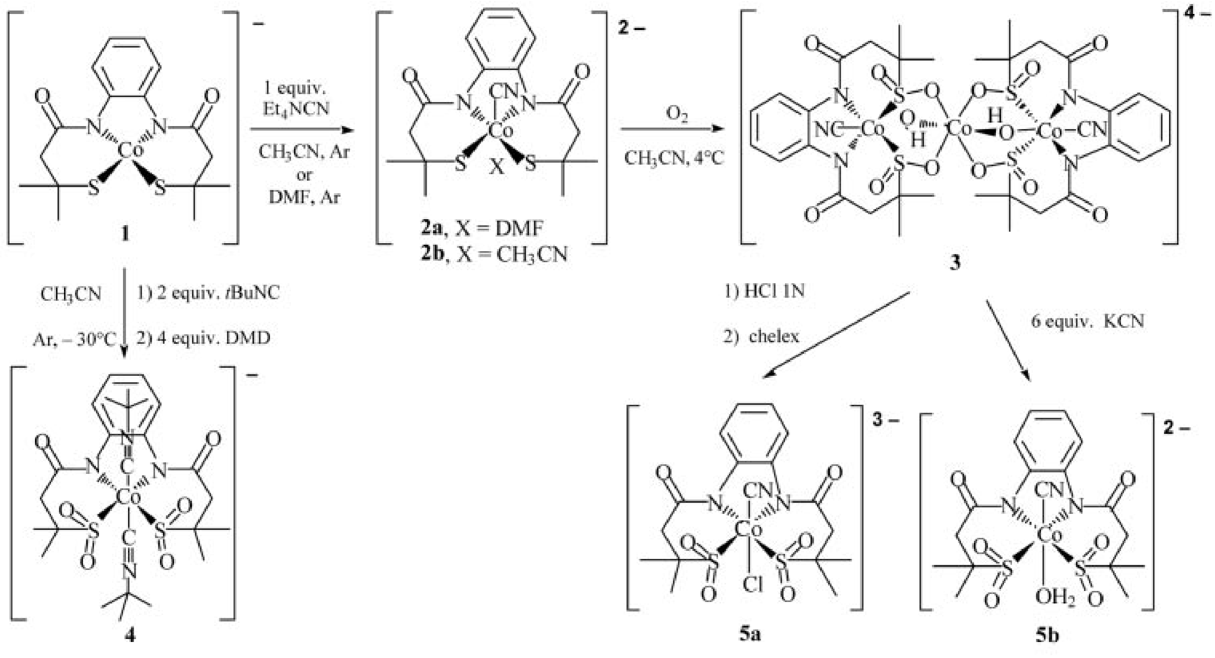


Figure 1. ORTEP picture of the anionic complex **3** $\{Co[Co\{N_2(SO_2)_2\}(CN)(OH)]_2\}^{4-}$ with atom labelling (40% probability level of displacement ellipsoids); the H atoms, the water molecule and Et_4N^+ are omitted for clarity



Scheme 1. Synthesis of the complexes

Table 1. Crystallographic data from the X-ray diffraction of **3**

Empirical formula	$C_{34}H_{42}Co_3N_6O_{14}S_4\cdot 4C_8H_{20}N\cdot 6H_2O$
Molecular mass	1692.90
Crystal System	Monoclinic
Space	*C*2/*c*
a[Å]	28.598(2)
b [Å]	12.9144(7)
c [Å]	22.916(2)
α [°]	90
β [°]	100.81 (1)
V [Å^3]	8313.2(11)
Z	4
F(000)	
3620	
$D_{calcd.}$ [g.cm^{-3}]	1.353
λ (Mo-K_α) [mm^{-1}]	0.8
Temperature (K)	100
Index ranges	$-34 < h < 34$ $-14 < k < 14$ $-27 < l < 27$
Observed data [$I > 2.0\ \sigma(I)$]	5531
No. of reflns. Collected	29402
No. of unique reflns	7020
θ limits [°]	2.4, 25.0
R_{int}	0.078
Data/restraints/parameters	7020/7/499
*R*1, *wR*2 [$I > 2\sigma(I)$]	0.0589, 0.1509
*R*1, *wR*2 (all data)	0.0738, 0.1616
$\Delta\delta_{min.}/\Delta\delta_{max.}$ [e·Å^{-3}]	−0.59/1.32
GOF	1.08

Table 2. Selected bond lengths [Å] and angles [°] for **3** ($C_{34}H_{42}Co_3N_6O_{14}S_4\cdot 4C_8H_{20}N\cdot 6H_2O$)

Co1−O2	2.130(3)	Co1−O7	2.015(3)
Co1−O4	2.118(3)		
Co2−S1	2.1968(12)	Co2−S2	2.2102(10)
Co2−O7	1.940(3)	Co2−S2	2.2102(10)
Co2−N1	2.002(3)	Co2−C17	1.876(4)
Co2−N2	1.980(4)		
S1−O1	1.461(3)	C1−C16	1.532(6)
S1−O2	1.490(3)	C1−C2	1.526(6)
S1−C1	1.838(4)	C1−C15	1.529(6)
S2−O3	1.448(4)	C2−C3	1.502(6)
S2−C12	1.834(5)	C4−C5	1.404(6)
S2−O4a	1.495(3)	C4−C9	1.397(5)
O5−C3	1.264(5)	C5−C6	1.388(7)
O6−C10	1.251(6)	C6−C7	1.381(7)
C7−C8	1.389(7)	C8−C9	1.387(6)
C10−C11	1.516(6)	C11−C12	1.537(7)
C12−C14	1.534(6)	C12−C13	1.531(6)
N1−C44	1.404(5)	N1−C3	1.339(5)
N2−C99	1.425(5)	N2−C10	1.339(5)
N3−C17	1.155(6)		
O2−Co1−O4	91.57(10)	O2−Co1−O7	84.24(10)
O4−Co1−O7	94.38(10)		
N1−Co2−C17	90.53(15)	N2−Co2−C17	90.02(15)
S1−Co2−S2	88.62(4)	S1−Co2−O7	87.27(8)
S1−Co2−N1	95.18(11)	N1−Co2−N2	82.11(14)
S1−Co2−C17	91.49(12)	S2−Co2−O7	87.78(8)
S2−Co2−N2	94.03(10)	S2−Co2−C17	91.94(12)
O7−Co2−N1	89.84(12)	O7−Co2−N2	91.23(12)

anionic trinuclear complex in which the thiolates of the tetradentate ligand have been oxidized to sulfinates. For crystal data of **3** see also Table 1. All three Co centres are in distorted coordination environments. The distortion from ideal octahedral geometry for each cobalt atom is due to restrictions imposed by the ligand, as evidenced by the bite angles [O(2)−Co(1)−O(7): 84.2°, O(4)−Co(1)−O(7): 85.6° and O(2)−Co(1)−O(4): 91.6° for Co(1) and N(1)−Co(2)−N(2): 82.1(1)° for Co(2)]. The terminal Co atoms are related by an inversion centre occupied by the central Co(1) atom. Each outer Co is surrounded by two carboxamido-N and two sulfinato-S donors, *trans* to the nitrogens in the equatorial plane, and by one cyanide and one hydroxide at the axial coordination sites [Co(2)−O(7)−Co(1): 116.2(1)°]. Co(2) lies 0.037(1) Å out of the best least-squares plane defined by S(1), S(2), N(1) and N(2) [maximum deviation of −0.008(1) Å for S(2)]. The Co(1)−Co(2) distance is 3.359 Å. The sulfinates and the hydroxide bridge the terminal and central cobalt ions, the latter being coordinated to the two bridging hydroxides and four oxygens from the four bridging sulfinates. Selected bond angles and distances are listed in Table 2. The Co-N distances are equivalent to those determined for complex **4**[7] (Scheme 1) and related complexes,[4−6] and for the Co-NHase active site.[1] They are in agreement with cobalt coordination to deprotonated amide nitrogens. The sulfur-to-Co bond lengths are about 0.025 Å shorter than in complex **4**.[7] O-coordination of the sulfinates to the central Co atom differentiates the two S−O bonds. The sulfur distances to the bonded oxygen atoms [S(1)−O(2), 1.488(3) Å; S(2)−O(4), 1.493(9) Å] are significantly longer than those to the non-coordinated oxygen atoms [S(1)−O(1) 1.4621 Å; S(2)−O(3) 1.4488 Å). The Co(1)−O(2)−S(1)−Co(2) and Co(1)−O(4)−S(2)−Co(2) bridges are slightly twisted with torsion angles of −0.4(2)° and +2.9(2)°, respectively. The Co(2)−CN and C−N distances fall within the range so far determined for other mono- or dicyanide Co^{III} complexes containing carboxamido nitrogens and pyridine nitrogens[10] or thiolates.[11]

The stoichiometry of four Et$_4$N cations per trinuclear cobalt cluster and the charge balance suggest a Co^{III}-Co^{II}-Co^{III} distribution of oxidation states. This hypothesis is supported by the length of the Co−OH bonds: as expected from the larger ionic radius of Co^{II} compared to Co^{III},[12] the Co(1)−O(7) bond length is noticeably longer than the Co(2)−O(7) one. Furthermore the *N*-amidate- bonded Co(2) centre is expected to be Co^{III} as in complex **4**.[7] Interestingly, the Co^{III}(2)−O(7) distance (1.94 Å) is shorter than the corresponding Co-O distance (2.58 Å) reported for Co-NHase.[1] This result supports the proposal of the Japanese group[1] that a water molecule, rather than a hydroxide ion, is coordinated to the Co centre of NHase.

In the CSD database,[13]we found few trinuclear cobalt complexes with a Co^{III}-Co^{II}-Co^{III} arrangement where the central Co^{II} is octahedrally coordinated to six oxygens.[14] Complex **3** is the first example of such a trinuclear complex containing bridging sulfinato groups.

Further characterisation of the trinuclear complex **3** has been performed both in the solid state and in solution.

Infrared Spectroscopy

Thiolate to sulfinate oxidation results in a shift of the ν_{CN} band from 2080 cm^{-1} in **2** to 2130 cm^{-1} in **3**. As previously discussed,[7] this shows that the cyanide is a weaker π-acceptor and a stronger σ-donor ligand in **3** than in **2**. In addition, comparison of the IR spectra of complexes **3** and **4** shows a decrease of the $\nu_{as}(SO_2)$ and $\nu_s(SO_2)$ from 1210 and 1070 cm^{-1} (**4**) to 1175 and 1030 cm^{-1} (**3**). This shift to lower energy associated with the shorter C−S distances found in the structure of **3** shows that the metal-to-ligand back donation is stronger in the N_2S_2 mean plane of **3** than in **4**.

Magnetic Properties

The temperature dependence of the magnetic susceptibility in the 300−2 K range is shown in Figure 2. The room temperature effective magnetic moment (μ_{eff} = 4.73 BM) lies in the 4.40−5.00 BM range corresponding to one high-spin cobalt(II) (S = 3/2).[15] It decreases slowly to 3.99 BM at 20 K and then drops to 3.63 BM at 4 K. This behaviour may be understood as arising from the combined effects of orbital degeneracy and zero-field splitting (ZFS). These magnetic data are very similar to those previously reported for a sulfito-bridged trinuclear cobalt complex,[14b] and confirm that complex **3** is in the mixed valence state Co^{III}(S = 0)-Co^{II}(S = 3/2)-Co^{III}(S = 0) as suggested by the X-ray structural analysis.

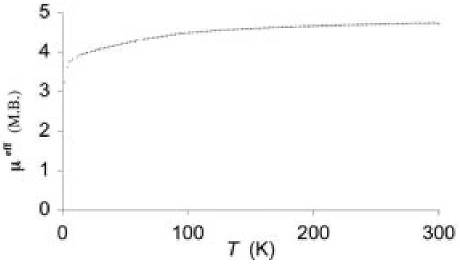


Figure 2. Temperature dependence of the effective magnetic moment for complex **3**

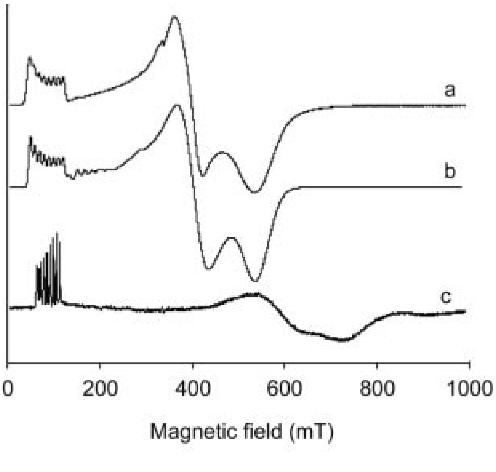


Figure 3. X-band EPR spectra of **3** at 10 K in the polycrystalline state (a) and in methanol solution (c); **3b**) simulation of spectrum **3a** using the Xsophe software package (g_x^{eff}=1.26, g_y^{eff}=1.71, g_z^{eff}=7.91 and A_z = 10 mT, and linewidths Θ_x = 20.2 mT, Θ_Θ = 31.3 mT, Θ_Θ = 15.1 mT); experimental conditions: microwave frequency: 9.45 GHz, modulation frequency 100 kHz, modulation amplitude 1 mT, microwave power 20 mW

EPR Spectroscopy

The EPR spectrum of compound **3** as a polycrystalline powder recorded at 10 K is shown in Figure 3, part a. The simulation (Figure 3, part b) yields the effective *g* values g_x^{eff}=1.26, g_y^{eff}=1.71, g_z^{eff}=7.91 and a hyperfine splitting value A_z of 10 mT, which are characteristic of a single S = 3/2 Co^{II} ion. The eight-line hyperfine structure observed at g_z is due to the coupling between the electronic spin and the nuclear spin of Co^{II} (I = 7/2). The g^{eff} values can be analysed on the basis of the spin hamiltonian for an S = 3/2 centre:

$$\hat{H}_{eff} = \mu_b \vec{S}\,\bar{g}\,\vec{B} + D\,[\hat{S}^2_z - 1/3\,S\,(S+1) + E/D\,(\hat{S}^2_x - \hat{S}^2_y)] + \vec{S}\,\bar{A}\,\vec{I} \quad (1)$$

μ_b is the Bohr magneton, $\vec{B}$ is the external magnetic field, $\bar{g}$ the electronic tensor, $\bar{A}$ the hyperfine coupling tensor, and I the nuclear spin quantum number. *D* and *E*/*D* correspond to the zero-field splitting and rhombicity parameters, respectively. Such *g* values are due to a large axial distortion giving rise to a large zero-field splitting (10 cm^{-1} ≤ D ≤ 30 cm^{-1}) and a large rhombicity ($E/D \geq 0.27$).[16,17] Finally, the EPR spectra of compound **3** in solution (*g* = 7.55, 1.15 and 0.9 in MeOH) (Figure 3, part c) and in the solid state (Figure 3, part a) are very similar. Therefore the same Co^{II} (S = 3/2, I = 7/2) formalism can be used to analyze the spectrum of compound **3** in solution. The signals broaden with temperature, and disappear above 30 K as expected for high-spin Co^{II} complex for which electron spin-lattice relaxation is very fast. It is very likely that the trinuclear structure determined in the solid state is retained in solution.

^{1}H NMR Spectroscopy

Complex **3** is paramagnetic as evidenced by its ^{1}H NMR spectrum in D_2O which extends over 70 ppm. The assignment of only six resonances to the $N_2(SO_2)_2$ ligand is consistent with the presence of an inversion centre in the overall structure and with the absence of a symmetry plane for the terminal Co^{III} centres. Consequently, the two signals at δ = −41 and +11.6 ppm were attributed to the methyl groups on the basis of the integration ratios. The four remaining signals, each accounting for two protons, were not assigned.

The purpose of the investigation reported below was to find proper conditions for removing the Co^{II} cation with the aim of recovering a six-coordinate Co^{III} mononuclear complex. In a first experiment, the trinuclear complex was treated with an excess of aqueous HCl solution and the resulting complex **5a** (Scheme 1) was purified over chelex chromatography, to retain the cobalt(II), and isolated as a powder after lyophilization. The characteristics of complex **5a** are consistent with the formation of a six-coordinate

Co^{III} complex with both cyanide and chloride axial ligands: (i) electrospray mass ionization (ESI^-) exhibits two peaks at 565.85 and 507.93 corresponding to the mass of the $\{(Na)_2[Co^{III}\{N_2(SO_2)_2\}(CN)(Cl)]\}^-$ and $\{(Na)[Co^{III}\{N_2(SO_2)_2\}(CN)]\}^-$ anions, respectively; (ii) elemental analysis corresponds to the formula $C_{19}H_{20}ClN_3O_6S_2Na_3Co\cdot3NaCl\cdot2H_2O$; (iii) IR spectroscopy shows a ν_{CN} vibration located at 2130 cm^{-1}; (iv) ^1H NMR spectroscopy is consistent with a low-spin six-coordinate Co^{III} with two different axial ligands. As expected, the methyl protons on both sides of the mean plane are non-equivalent, as are the protons of the CH_2 groups.

Using the same procedure, the corresponding aquo or hydroxo complex **5b** (Scheme1) was prepared upon stirring an aqueous (H_2O or D_2O) solution of **3** with chelex. However, **5b** could not be isolated in the solid state since it was destroyed during the lyophilisation step; it was characterised "in situ" in solution after filtration. Its ^1H NMR spectrum in D_2O is characteristic of a low-spin mononuclear Co^{III} species with two different axial ligands (CN^-/H_2O or CN^-/HO^-). The pK_a of the bound water molecule was determined by pH-metry. Titration of **5b** (2.7 10^{-4} M) with aqueous HCl (10^{-3} M) reveals two acidic functions with pK_a values of 10.1 and 6.5 (Figure 4, part b). The former is attributed to the bound water in $[Co^{III}\{N_2(SO_2)_2\}(CN)(H_2O)]^{2-}$ and the latter to a bound HNC in $[Co^{III}\{N_2(SO_2)_2\}(HNC)(H_2O)]^-$. None of these p$K_a$ values can correspond to an amide coordinated in its protonated tautomer iminol form, since in complex **4**, which has two *tert*-butyl isocyanides at the axial sites, no protonation site was identified upon acidic titration (Figure 4, part a).

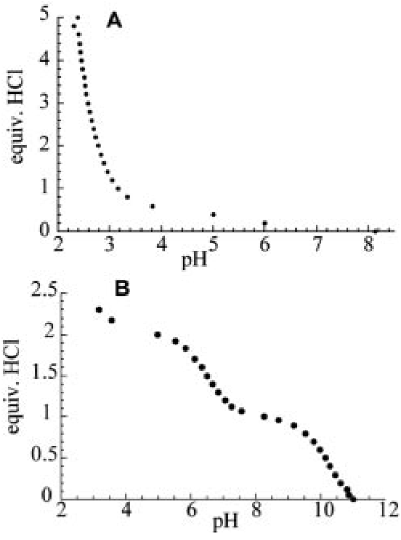
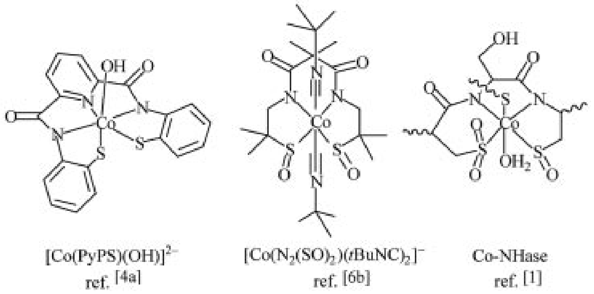


Figure 4. pH-metric titration of complex **4** a) and complex **5b** b) with aqueous HCl

A more efficient way for preparing a more concentrated solution of **5b** "in situ" is to trap the Co^{II} cation with cyanide as $K_3[Co(CN)_6]$. This reaction was monitored by ^1H NMR spectroscopy. Progressive addition of six equivalents of KCN to a D_2O solution of **3** resulted in the formation of a low-spin species identical to **5b**. Finally the reactivity of complexes **3**, **5a**, **5b** (prepared as mentioned previously) was assayed toward acetonitrile hydration in buffered solution at pH 4.7, 7.3 and 10.3. The amide conversion was estimated by ^1H NMR spectroscopy after lyophilisation and dissolution of the residue in [D$_6$]DMSO. While the trinuclear and chloro complexes were inactive, amide formation corresponding to 7 and 14 turnovers of complex **5b** was determined after 24 h at 50 °C at pH 4.7 and 7, respectively. The catalyst was destroyed at higher pH. Under the same conditions, formation of amide was not detected either in the absence of complex **5b** or in the presence of the unique $K_3[Co(CN)_6]$ species. Two other mimics of NHase catalyze acetonitrile hydration with low efficiency (Scheme 2): a dithiolato hydroxo Co^{III} complex, $[Co(PyPS)(OH)]^{2-}$, prepared by Mascharak et al.[4a] and a di-sulfenato Co^{III} complex, $[Co\{N_2(SO)_2\}(tBuNC)_2]^-$, described by Chottard et al.[6b] These two complexes, as well as **5b**, reproduce some of the structural features characteristic of the Co-NHase active site but not all of them. Accordingly, the presence of both a sulfenate and an aquo or hydroxo ligand seems to be required for a high activity.



Scheme 2. Schematic drawing of the two previously reported mimics of Co-NHase activity and of the Co-NHase active site

Conclusion

This work describes the first example of thiolate to sulfinate oxidation in a six-coordinate Co^{III} complex whose apical sites are occupied by a cyanide and a labile solvent molecule. This oxidation results in the formation of a new trinuclear mixed valence Co^{III}-Co^{II}-Co^{III} complex with bridging sulfinates which has been characterised both in the solid state and in solution. The terminal Co^{III} ions retain the environment of the starting Co^{III} compound but with S-bonded sulfinates and a hydroxide replacing the solvent molecule in the sixth coordination position. The high-spin Co^{II} is held by interactions with the six oxygens of the bridging hydroxides and sulfinates. The central Co^{II} ion is easily trapped by chelating agents, yielding the first example of a six-coordinate low-spin $[Co^{III}\{N_2(SO_2)_2\}(CN)(H_2O)](Et_4N)_2$ complex including an exchangeable coordination site able to bind Cl^-. Preliminary experiments show that the aquo complex catalyzes hydration of acetonitrile, although with a low efficiency.

Experimental Section

Complex 2: Et_4NCN (14.8 mg, 0.095 mmol) in deaerated CH_3CN was added to a deaerated DMF solution of $(Et_4N)[Co(N_2S_2)]$ **1** (50 mg, 0.095 mmol, 1 mL). The resulting brown mixture was stirred at room temp. for 5 min. Cooling to −20 °C and addition of cold Et_2O afforded complex **2** as a brown powder. The solid was dried under vacuum and stored in a glovebox. (35 mg, 45%). $C_{36}H_{67}CoN_6O_3S_2\cdot CH_3CN\cdot 2H_2O$ (832.10): calcd. C 54.85, H 8.96, N 11.78; found C 55.06, H 9.36, N 11.99. UV/Vis (CH_3CN): λ_{max} (ε, $\text{M}^{-1}\text{cm}^{-1}$) = 232 (24000), 259 (21800), 470 (1100), 822 (800) nm. IR (KBr): $\tilde{\nu}$ = 2080 (ν_{CN}), 1620 (ν_{CO} DMF), 1545 (ν_{CO}) cm^{-1}. ^1H NMR (250 MHz, $[D_7]$DMF, 300 K): δ = 1.16 (s, 24 H, Me Et_4N), 1.25 (s, 6 H, Me), 1.43 (s, 6 H, Me), 2.23 (d, J = 12 Hz, 2 H, CH_2,), 2.66 (s, 3 H, Me DMF), 2.82 (s, 3 H, Me DMF), 2.98 (s,16 H, CH_2 Et_4N), 3.42 (d, J = 12 Hz, 2 H, CH_2), 6.36 (dd, 2 H, H_{ar}), 7.90 (s, HCO DMF), 8.52 (dd, 2 H, H_{ar}) ppm. MS (FAB^-): m/z (%) = 395 (100) $[Co(N_2S_2)]^-$.

Complex 3: Et_4NCN (60 mg, 0.4 mmol) was added to a CH_3CN solution of $(Et_4N)[Co(N_2S_2)]$ **1** (200 mg, 0.4 mmol, 4 mL). The resulting brown mixture was stirred under a dioxygen atmosphere at 4 °C for a week. An orange precipitate was collected (95 mg, 41%), washed with Et_2O and dried under vacuum. $C_{66}H_{122}Co_3N_{10}O_{14}S_4\cdot 6H_2O\cdot CH_3CN$ (1733.97): calcd. C 47.10, H 7.96, N 8.89; found C 46.94, H 8.02, N 8.83. UV/Vis (H_2O): λ_{max} (ε, $\text{M}^{-1}\text{cm}^{-1}$) = 252 (33800), 279 (44300), 300 (sh), 460 (1400) nm. IR (KBr): $\tilde{\nu}$ = 2130 (ν_{CN}), 1540 (ν_{CO}), 1175 and 1030 (ν_{SO2}) cm^{-1}. ^1H NMR (250 MHz, D_2O): δ = 27 (2 H), 22 (2 H), 11.7 (6 H), 3.33 (32 H, CH_2 Et_4N), 1.55 (2 H), 1.50 (s, 48 H, Me Et_4N) −8 (2 H), −42.2 (6 H) ppm. MS(ESI^- in MeOH): m/z (%) = 242.5 (100) $[Co\{N_2(SO_2)_2\}(CN)]^{2-}$.

Complex 5a: A batch of **3** (50 mg, 0.029 mmol) was dissolved in 10 mL of 1 N HCl and stirred for 15 min. After lyophilisation, the residue was dissolved in methanol and loaded onto a Chelex 100 resin column. The first pink band eluted with methanol was collected. Addition of Et_2O afforded complex **5a** as a pink powder (20 mg, 42%) upon cooling. $C_{17}H_{20}CoN_3Na_3O_6S_2Cl\cdot 3NaCl\cdot 3H_2O$ (819.22): calcd. C 24.92, H 3.20, N 5.13; found C 25.18, H 3.27, N 5.22. UV/Vis (H_2O): λ_{max} (ε, $\text{M}^{-1}\text{cm}^{-1}$) = 250 (36700), 281 (51700), 302 (42800), 470 (1400) nm. IR (KBr): $\tilde{\nu}$ = 2130 (ν_{CN}), 1535 (ν_{CO}), 1175 and 1060 (ν_{SO2}) cm^{-1}. ^1H NMR (250 MHz, D_2O): δ = 1.30 (s, 6 H, Me), 1.42 (s, 6 H, Me), 2.43 (d, J = 17 Hz, 2 H CH_2), 2.91 (d, J = 17 Hz, 2 H, CH_2), 6.90 (dd, 2 H, H_{ar}), 7.42 (dd, 2 H, H_{ar}) ppm. MS (ESI^- in MeOH): m/z (%) = 507.93 (100) $\{(Na)[Co\{N_2(SO_2)_2\}(CN)]\}^-$, 565.83 (25) $\{(Na)_2[Co\{N_2(SO_2)_2\}(CN)(Cl)]\}^-$.

Crystal Structure Determination of 3: A brown crystal with dimensions 0.6 × 0.6 × 0.3 mm^3 was stuck on a glass fibre and mounted on a Stoe IPDS Imaging Plate Diffraction System (IPDS) equipped with an Oxford Cryosystems Cooler Device.[18] The final unit cell parameters were obtained by the least-squares refinement of 5000 reflections. Only statistical fluctuations were observed in the intensity monitors over the course of the data collection. Crystal data and data collection parameters are listed in Table 1. Corrections for Lorentz and polarisation effects were applied. The structure was solved by direct methods using SHELXS-97.[19] Refinement, based on F^2, was carried out by full-matrix least-squares with anisotropic thermal parameters for all non-hydrogen atoms using SHELXL-97.[20] All hydrogen atoms were located on a difference Fourier map and refined as riding models with isotropic parameters constrained to be 1.2-times the Ueq of the carrier atom. Least-squares refinements were carried out by minimising the function $\Sigma w(F_o^2 - F_c^2)^2$, where F_o and F_c are the observed and calculated structure factors. The weighting scheme used in the last refinement was $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. Models reached convergence with $R1 = \Sigma(||F_o| - |F_c||)/\Sigma(|F_o|)$ and $wR2 = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w\,(F_o^2)^2\}^{1/2}$, having the values listed in Table 1. ORTEP-II was used to produced molecular graphics.[21] Fractional atomic coordinates, anisotropic thermal parameters for non-hydrogen atoms and atomic coordinates for H atoms have been deposited with the Cambridge Crystallographic Data Centre.

CCDC-182354 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

Complex 5b: A D_2O solution of complex **3** (1.7 mg in 1 mL) was stirred with chelex (10 mg) resulting in the formation of **5b**. The supernatant was analysed by ^1H NMR spectroscopy. ^1H NMR (250 MHz, D_2O): δ = 1.34 (s, 3 H, Me), 1.46 (s, 3 H, Me), 2.48 (d, J = 17 Hz, 2 H, CH_2), 2.95 (d, J = 17 Hz, 2 H, CH_2), 6.95 (m, 2 H_{ar}), 7.78 (m, 2 H_{ar}) ppm.

pH-metric Titration of Complex 5b: 5 mL of an aqueous solution of complex **3** (3.5 mg) was stirred at room temp. with chelex (50 mg) for 3 hours. After filtration the resin was washed with water (2.5 mL) and the filtrate (**5b**: 2.7 10^{-4} M) was titrated with HCl (10^{-3} M).

Catalytic Assays: 50 µL of an aqueous solution of KCN (1.8 M, 90 µmoL) was added to 950 µL of an aqueous solution of **3** (26 mg, 15 µmoL) yielding a 3 10^{-3} M solution of **5b**. 100 µL was withdrawn and added to a mixture of 500 µL of a 0.1 M buffered solution (acetate pH 4.7, Hepes pH 7.3 and carbonate pH 10.3) and CH_3CN (100 µL). The mixture was heated to 50 °C for 48 H. After cooling and lyophilization, the residue was dissolved in $[D_6]$DMSO in the presence of trimethoxybenzene as an internal standard. The filtrate was analysed by ^1H NMR spectroscopy.

Acknowledgments

This work was supported by the European Commission TMR-NOHEMIP research network N° ERBFMRXCT98-0174.

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[1] A. Miyanaga, S. Fushinobu, K. Ito, T. Wakagi, *Biochem. Biophys. Res. Commun.* **2001**, *288*, 1169−1174.

[2] B. A. Brennan, G. Alms, M. J. Nelson, L. T. Durney, R. C. Scarrow, *J. Am. Chem. Soc.* **1996**, *118*, 9194−9195.

[3] S. Nagashima, M. Nakasako, N. Dohmae, M. Tsujimura, K. Takio, M. Odaka, M. Yohda, N. Kamiya, I. Endo, *Nature Struct. Biol.* **1998**, *5*, 347−351.

[4] [4a] J. C. Noveron, M. M. Olmstead, P. K. Mascharak, *J. Am. Chem. Soc.* **1999**, *121*, 3553−3554. [4b] L. A. Tyler, J. C. Noveron, M. M. Olmstead, P. K. Mascharak, *Inorg. Chem.* **2000**, *39*, 357−362. [4c] L. A. Tyler, M. M. Olmstead, P. K. Mascharak, *Inorg. Chem.* **2001**, *40*, 5408−5414.

[5] I. Kung, D. Schweitzer, J. Shearer, W. D. Taylor, H. L. Jackson, S. L. Ovell, J. A. Kovacs, *J. Am. Chem. Soc.* **2000**, *122*, 8299−8300.

[6] [6a] L. Heinrich, Y. Li, J. Vaisssermann, J. C. Chottard, *Eur. J. Inorg. Chem.* **2001**, 1407−1409. [6b] L. Heinrich, A. Mary-Verla, Y. Li, J. Vaisssermann, J. C. Chottard, *Eur. J. Inorg. Chem.* **2001**, 2203−2206.

[7] M. Rat, R. Alves de Sousa, J. Vaissermann, P. Leduc, D. Mansuy, I. Artaud, *J. Inorg. Biochem.* **2001**, *84*, 207−213.

[8] S. Chatel, M. Rat, S. Dijols, P. Leduc, J. P. Tuchagues, D. Mansuy, I. Artaud, *J. Inorg. Biochem.* **2000**, *80*, 239−246.

[9] L. Heinrich, Y. Li, K. Provost, A. Michalowicz, J. Vaissermann, J. C. Chottard, *Inorg. Chim. Acta* **2001**, *318*, 117−126.

[10] S. Dutta, U. Beckmann, E. Bill, T. Weyhermüller, K. Wieghardt, *Inorg. Chem.* **2000**, *39*, 3355−3364.

[11] L. A. Tyler, M. M. Olmstead, P. K. Mascharak, *Inorg. Chim. Acta* **2001**, *321*, 135−141.

[12] R. D. Shannon, *Acta Crystallogr., Sect. A* **1976**, *32*, 751−767.

[13] F. H. Allen, O. Kennard, 3D Search and Reasearch Using the Cambridge Data Base, Chemical Design Automation News, **1993**, *8*, 31−37.

[14] [14a] D. A. House, V. McKee, P. Steel, *Inorg. Chem.* **1986**, *25*, 4884−4889. [14b] C. Fukuhara, E. Asato, T. Shimoji, K. Katsura, M. Mori, K. Matsumoto, S. Ooi, *J. Chem. Soc., Dalton Trans.* **1987**, 1305−1311. [14c] A. Golobic, B. Stefane, S. Polanc, *Polyhedron* **1999**, *18*, 36661−3668.

[15] B. N. Figgis, *Nature (London)* **1958**, 182, 1568−1570.

[16] L. Banci, A. Bencini, C. Benelli, D. Gatteschi, C. Zanchini, *Struct. Bonding (Berlin)* **1982**, *52*, 37−67.

[17] A. Bencini, C. Benelli, D. Gatteschi, C. Zanchini, *Inorg. Chem.* **1983**, *22*, 2123−2126.

[18] Stoe and Cie (1996) IPDS Manual. Version 2.75. Stoe and Cie, Darmstadt, Germany.

[19] G. M. Sheldrick, *SHELXS−97, Program for Crystal structure solution*, University of Göttingen, Germany, **1997**.

[20] G. M. Sheldrick, *SHELXL-97, Program for Crystal structure refinement*, University of Göttingen, Germany, **1997**.

[21] C. K. Johnson, *ORTEPII*, Report ORNL-5138, Oak Ridge National Laboratory, TN, **1976.**

Received July 18, 2002
[I02398]