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Synthesis and Structural Characterization of a Novel S-Bridged $Co^{III}Ni^{II}Co^{III}$ Complex, $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ (aet = 2-Aminoethanethiolate; en = Ethylenediamine): Ligand Transfer from the Nickel(II) to the Cobalt(III) Coordination Sphere

It has been recognized that the bridging ability of coordinated thiolato sulfur atoms allows *fac*(*S*)-$[M(aet)_3]$ or *fac*(*S*)-$[M(\text{L-cys-}N,S)_3]^{3-}$ (aet = 2-aminoethanethiolate; L-cys = L-cysteinate; M = Co(III), Rh(III), or Ir(III)) to function as a terdentate ligand to a variety of metal ions, forming linear-type[1,2] or cage-type[3] S-bridged polynuclear structures. For example, the reactions of *fac*(*S*)-$[Co(\text{aet or L-cys-}N,S)_3]^{0\text{ or }3-}$ with Co(II) or Co(III) have produced S-bridged trinuclear complexes $[Co^{III}\{Co(\text{aet or L-cys-}N,S)_3\}_2]^{3+\text{ or }3-}$[1a,2a,e] and those with $[CoCl_3(\text{triamine})]$ gave S-bridged dinuclear complexes $[Co\{Co(\text{aet or L-cys-}N,S)_3\}(\text{triamine})]^{3+\text{ or }0}$.[2g] On the other hand, $[M'(aet)_2]$ (M′ = Ni(II) or Pd(II)) has been shown to function as a bidentate ligand to M″ = Ni(II), Pd(II), and Pt(II), forming S-bridged trinuclear complexes $[M''\{M'(aet)_2\}_2]^{2+}$.[4] These facts seem to indicate that an S-bridged dinuclear complex $[Co\{Ni(aet)_2\}(en)_2]^{3+}$ is possibly formed by the reaction of $[Ni(aet)_2]$ with $[CoCl_2(en)_2]^+$. However, this reaction gave a novel S-bridged $Co^{III}Ni^{II}Co^{III}$ trinuclear complex (**1**), in which the bidentate-*N*,*S* ligand aet does not chelate to Ni(II), but to Co(III). In this paper we describe the synthesis, characterization, and properties of **1**.

To a green suspension of $[Ni(aet)_2]$[4a] (1.0 g, 4.7 mmol) in water was added *trans*-$[CoCl_2(en)_2]Cl$ (2.7 g, 9.4 mmol). After the mixture had been stirred at room temperature for 2 h, the resulting red-brown complex (**1**) (0.42 g) was collected by filtration. Recrystallization of **1** from water gave dark red crystals,[5] one of which was used for X-ray structural analysis. **1** was also obtained using *cis*-$[CoCl_2(en)_2]Cl$ instead of *trans*-$[CoCl_2(en)_2]Cl$.

X-ray structural analysis of **1** revealed the presence of a discrete tetravalent complex cation, four chloride anions, and water molecules.[6] As shown in Figure 1, the complex cation consists of two octahedral *cis*(*S*)-$[Co(aet)_2(en)]^+$ subunits and one nickel atom. The nickel atom is coordinated by four thiolato sulfur atoms from the two terminal *cis*(*S*)-$[Co(aet)_2(en)]^+$ subunits, forming the linear-type S-bridged trinuclear structure. The central NiS_4 sphere is markedly distorted from square-planar to tetrahedral geometry, in which the NiS1S1′ and NiS2S2′ planes intersect to form dihedral angle of 16.2°. This is inconsistent with the square-planar geometry of the central NiS_4 sphere observed in the related S-bridged trinuclear complex $[Ni\{Ni(aet)_2\}_2]^{2+}$.[4c] Molecular model examinations reveal that this distortion decreases the cross-plane interaction between the aet chelate rings of the two C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ subunits. The S–Ni–S "bite" angles (86.86 (4) and 86.80 (5)°) are larger than those found in $[Ni\{Ni(aet)_2\}_2]^{2+}$ (81.4 (2)°) and more close to the S–Ni–S "bite" angles of 90–92° observed in the mononuclear $[Ni^{II}(\text{thiolato})_4]^{2-}$ complexes.[7d,g] The Ni–S bond lengths (2.208 (1) and 2.199 (1) Å) are within the range of 2.16–2.23 Å normally observed for the four-coordinated Ni(II) complexes.[4c,7]

Of 10 isomers possible for $[Ni\{Co(aet)_2(en)\}_2]^{4+}$,[8] crystal **1** consists of the $\Delta(C_2\text{-}cis(S))\text{–}\Delta(C_2\text{-}cis(S))$ isomer and its enantiomer $\Lambda(C_2\text{-}cis(S)\text{–}\Lambda(C_2\text{-}cis(S))$, which combine to form the racemic compound (Figure 1). This is in agreement with the fact that **1** was optically resolved with use of $[Sb_2(d\text{-tart})_2]^{2-}$ as the

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(5) Anal. Calcd for $[Ni\{Co(NH_2CH_2CH_2S)_2(NH_2CH_2CH_2NH_2)\}_2]Cl_4\cdot 6H_2O$: C, 16.93; H, 6.16; N, 13.16; Co, 13.85; Ni, 6.89. Found: C, 16.93; H, 6.15; N, 12.97; Co, 13.54; Ni, 6.56. Visible–UV spectrum, H_2O solvent [ν_{max}, 10^3 cm^{-1} (log ϵ; ϵ in mol^{-1} dm^3 cm^{-1})]: 21.1 (3.27 sh), 24.1 (3.69 sh), 27.78 (4.31), 37.31 (4.33), 42.02 (4.52). The sh label denotes a shoulder. NMR (500 MHz, D_2O, ppm from DSS): ^1H NMR, δ 1.78 (td, J = 14 and 5 Hz, $-CH_2S$), 2.50 (dd, J = 14 and 4 Hz, $-CH_2S$), 2.54 (d, J = 9 Hz, $-CH_2N$ of en), 2.77 (d, J = 9 Hz, $-CH_2N$ of en), 3.67 (dd, J = 13 and 4 Hz, $-CH_2N$), 4.31 (td, J = 13 and 4 Hz, $-CH_2N$); ^{13}C NMR, δ 34.70 ($-CH_2S$), 46.58 ($-CH_2NH_2$ of en), and 55.76 ($-CH_2NH_2$).

(6) Crystal data for $[Ni\{Co(C_2H_6NS)_2(C_2H_8N_2)\}_2]Cl_4\cdot 6H_2O = C_{12}H_{52}N_8O_6S_4Cl_4Co_2Ni$ at 293 K: M_r = 851.2, 0.23 × 0.20 × 0.15 mm, monoclinic, $C2/c$, a = 14.987 (4) Å, b = 19.480 (3) Å, c = 12.916 (4) Å, β = 113.67 (1)°, V = 3454 (1) $Å^3$, Z = 4, D_{calcd} = 1.64 g cm^{-3}, λ(Mo Kα) = 0.71069 Å, μ(Mo Kα) = 20.75 cm^{-1}, R (R_w) = 0.046 (0.065) for 2875 independent reflections with $F_o > 3\sigma(F_o)$ ($2\theta < 50°$). The position of the nickel atom was obtained from a three-dimensional Patterson function. Difference Fourier maps, based on the nickel position, revealed all the non-hydrogen atoms. The Co1, Ni, and Co2 atoms were constrained to the special positions of point symmetry 2 (0, *y*, 0.25) with a site occupancy factor of 0.5. Two of three water oxygen atoms (OW2 and OW3) exhibited positional disorder and were best modeled with two positions for each atom. The structure was refined by full-matrix least-squares methods using anisotropic thermal parameters for non-hydrogen atoms. All calculations were performed with use of the programs of SHELX-76. Selected bond lengths (Å) and angles (deg) are as follows: Ni–S1, 2.208 (1); Ni–S2, 2.199 (1); Co–S1, 2.233 (1); Co–S2, 2.242 (1), Co1–N11, 1.969 (3); Co1–N12, 1.987 (3); Co2–N21, 1.987 (3); Co2–N22, 2.003 (3); S1–Ni–S1′, 86.86 (4); S1–Ni–S2, 94.24 (4); S2–Ni–S2′, 86.80 (5); S1–Co1–S1′, 85.64 (5); S1–Co1–N11, 87.7 (1); S1–Co1–N12, 94.8 (1); N11–Co1–N12, 91.5 (1); N12–Co1–N12′, 85.0 (2); S2–Co2–S2′, 84.74 (4); S2–Co2–N21, 87.5 (1); S2–Co2–N22, 95.0 (1); N21–Co2–N22, 91.9 (1); N22–Co2–N22′, 85.4 (2).

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(8) Considering two absolute configurations (Δ and Λ) and two geometries (C_1-*cis*(*S*) and C_2-*cis*(*S*)) for the two *cis*(*S*)-$[Co(aet)_2(en)]^+$ subunits, the possible isomers are $\Delta(C_1\text{-}cis(S))\text{–}\Delta(C_1\text{-}cis(S))$, $\Delta(C_1\text{-}cis(S))\text{–}\Delta(C_2\text{-}cis(S))$, $\Delta(C_2\text{-}cis(S))\text{–}\Delta(C_2\text{-}cis(S))$, $\Delta(C_1\text{-}cis(S))\text{–}\Lambda(C_1\text{-}cis(S))$, $\Delta(C_1\text{-}cis(S))\text{–}\Lambda(C_2\text{-}cis(S))$, $\Delta(C_2\text{-}cis(S))\text{–}\Lambda(C_1\text{-}cis(S))$, $\Delta(C_2\text{-}cis(S))\text{–}\Lambda(C_2\text{-}cis(S))$, $\Lambda(C_1\text{-}cis(S))\text{–}\Lambda(C_1\text{-}cis(S))$, $\Lambda(C_1\text{-}cis(S))\text{–}\Lambda(C_2\text{-}cis(S))$, $\Lambda(C_2\text{-}cis(S))\text{–}\Lambda(C_2\text{-}cis(S))$. The prefixes C_1 and C_2 denote that the *cis*(*S*)-$[Co(aet)_2(en)]^+$ subunit has a C_1 or C_2 axis.

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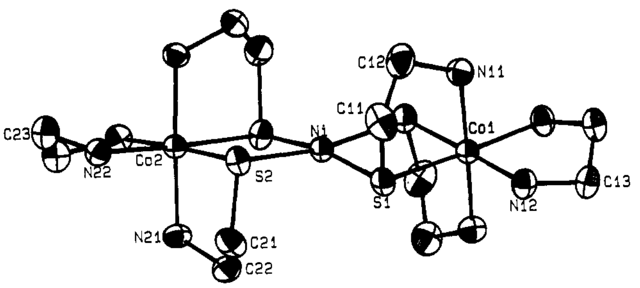

Figure 1. Perspective view of the complex cation of **1** ($[Ni\{Co(aet)_2(en)\}_2]^{4+}$) with the atomic labeling scheme. Unlabeled atoms are related to labeled atoms by the 2-fold axis through the Co1, Ni, and Co2 atoms. Ellipsoids represent 50% probability.

resolving agent, showing CD extrema with opposite signs at 516 and 463 nm. All the aet and en chelate rings possess a distinct gauche form with the λ conformation for the $\Delta\Delta$ isomer and the δ one for the $\Lambda\Lambda$ isomer, and furthermore all four bridging sulfur atoms are fixed to the *S* configuration for the $\Delta\Delta$ isomer and the *R* one for the $\Lambda\Lambda$ isomer. The ^{13}C NMR spectrum of **1** in D_2O gives only two signals due to methylene carbons of the four aet ligands and one signal due to methylene carbons of the two en ligands.[5] In the 500-MHz ^1H NMR spectrum methylene protons of the four aet ligands appear as two sets of double doublets and two sets of triple doublets and those of the two en ligands appear as two sets of doublets.[5] These NMR spectral behavior demonstrate that the geometry around the two C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ subunits observed in the crystal is retained in solution, having a D_2 symmetrical structure.

The electronic absorption spectrum of **1** in water[5] is characterized by the three intense absorption bands at 27.78 × 10^3, 37.31 × 10^3, and 42.02 × 10^3 cm^{-1}. Treatment of **1** (0.1 g) with 10% H_2O_2 (2.5 cm^3) in water, followed by the addition of 15% HBr (1 cm^3), led the solution color change from red-brown to yellow, from which the yellow complex (**2**) was isolated in 81% yield.[9] The absorption spectrum of **2** is quite similar to those of *cis*-(*S*)-$[Co(sulfinato\text{-}S)_2(amine)_4]^+$ type complexes over the whole region.[10] In the ^{13}C NMR spectrum **2** gives two sharp signals at δ 40.83 and 64.16 and a signal which splits into two at δ 46.57 and 46.68.[9] From these facts and elemental analysis, **2** can be confidently assigned the C_2-*cis*(*S*)-$[Co(NH_2CH_2CH_2SO_2\text{-}N,S)_2(en)]Br$ formula; that is, the H_2O_2 oxidation of **1** causes the cleavage of Ni–S bonds to form the mononuclear sulfinato Co(III) complex, retaining the C_2-*cis*(*S*) geometry of the $[Co(aet)_2(en)]^+$ subunits.

In the present work, the reaction of $[Ni(aet)_2]$ and $[CoCl_2(en)_2]^+$ under a moderate condition gave the S-bridged $Co^{III}Ni^{II}Co^{III}$ complex **1** containing C_2-*cis*(*S*)-$[Co(aet)_2(en)]^+$ subunits, and furthermore the mononuclear sulfinato complex **2** was derived from **1** with retention of the C_2-*cis*(*S*) geometry. This result obviously implies that the bidentate-*N,S* ligand aet readily transfers from Ni(II) to Co(III) coordination sphere. It is noted that the mononuclear $[Co(aet)_2(en)]^+$ has not been prepared to date; the direct reaction of Co^{2+}, 2-aminoethanethiol, cystamine, and ethylenediamine results in the formation of $[Co(aet)(en)_2]^{2+}$, $[Co(aet)_3]$, and $[Co\{Co(aet)_3\}_2]^{3+}$.[11] In addition, the analogous $[Co(\text{L-cys-}N,S)_2(en)]^-$, which is formed by the reaction of Co^{2+}, L-cysteine, L-cystine, and ethylenediamine, is not stable enough to be isolated, converting into polymeric structures in water.[11,12] Taking these facts into consideration, it is assumed that the *cis*(*S*)-$[Co(aet)_2(en)]$ arrangement in $[Ni\{Co(aet)_2(en)\}_2]^{4+}$ is stabilized by the S-bridged structure with the central Ni(II).

Supplementary Material Available: Tables A–C, listing atomic coordinates and equivalent isotropic thermal parameters, bond distances and angles, and anisotropic thermal parameters for **1** (3 pages); Table D, listing observed and calculated structure factors for **1** (11 pages). Ordering information is given on any current masthead page.

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[9] Anal. Calcd for $[Co(NH_2CH_2CH_2SO_2)_2(NH_2CH_2CH_2NH_2)]Br$: C, 17.36; H, 4.86; N, 13.32. Found: C, 17.30; H, 4.94; N, 13.32. Visible–UV spectrum, H_2O solvent [ν_{max}, 10^3 cm^{-1} (log ϵ; ϵ in mol^{-1} dm^3 cm^{-1})]: 23.20 (2.45), 32.89 (4.17), 34.70 (4.19). NMR (500 MHz, D_2O, ppm from DSS): ^1H NMR δ 2.75 (td, *J* = 13 and 5 Hz, $-CH_2S$), 2.90 (br, $-CH_2N$ of en), 2.91 (dt, *J* = 13 and 5 Hz, $-CH_2S$), 3.00 (br, $-CH_2N$ of en), 3.14 (dt, *J* = 12 and 5 Hz, $-CH_2N$), and 3.78 (td, *J* = 12 and 5 Hz, $-CH_2N$); ^{13}C NMR, δ 40.83 ($-CH_2N$), 46.57 and 46.68 ($-CH_2N$ of en), and 64.16 ($-CH_2S$). The H_2O_2 oxidation of the $(-)^{CD}_{516}$ isomer of **1** gave the optical isomer of **2**, which shows a major negative CD band at 439 nm.

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An Unusual Species Containing the Mixed-Valence $\{V^{III}(\mu\text{-}N)V^{IV}\}^{4+}$ Core Obtained by Reductive Decomposition of Me_3SiN_3: $[VBr_2(N_3)(dmpe)(\mu\text{-}N)VBr(dmpe)_2]$

One approach to gaining an understanding of nitrogen fixation involves the preparation and study of plausible intermediates in the process, such as nitride complexes. While a reasonably large number of nitride complexes of second- and third-row transition elements have been structurally characterized, there exist by comparison relatively few first-row examples.[1] Recently we have focused some attention on obtaining vanadium nitride complexes from the reaction between low-valent vanadium complexes and azides. Herein are reported the synthesis, structure, and some physical properties of a relatively low-valent asymmetric nitride-bridged divanadium complex, $[VBr_2(N_3)(dmpe)(\mu\text{-}N)VBr(dmpe)_2]$ (**1**), which was produced using the aforementioned reaction type under mild conditions. Compound **1** is a trapped mixed-valence $V^{III}V^{IV}$ complex and is quite distinct from the few high-valent vanadium nitride complexes which have been reported previously.[2-4]

The vanadium(II) phosphine complex *trans*-$[VBr_2(dmpe)_2]$[5] (dmpe = 1,2-bis(dimethylphosphino)ethane) was generated in solution by mixing 0.250 g (0.443 mmol) of *trans*-$[VBr_2(tht)_4]$[6] (tht = tetrahydrothiophene) and 0.133 g (0.887 mmol) of dmpe in 10 mL of tetrahydrofuran (thf). After the pink reaction mixture was stirred at room temperature for 1 h, 0.130 g (0.887 mmol) of Me_3SiN_3 was added. Within 1 h a green precipitate[7] appeared and the solution color had changed to orange. The green precipitate was filtered away and the fitrate was evaporated to dryness. The residue was redissolved in 10 mL of toluene, and 5 mL of hexane were carefully layered on top of the toluene solution. Crystallization was allowed to proceed for 1 week at −35 °C. Using this procedure a 34% yield (0.130 g) of compound **1** as red-orange crystals[8] suitable for X-ray diffraction studies[9]

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[7] This green product has recently been identified as *trans*-$[V(NSiMe_3)Br(dmpe)_2](Br)$ and will be the subject of a future report.

[8] Satisfactory element analyses (CHN) were obtained for compound **1**.

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