# Syntheses of K[Co(tren)($NH_3$)($SO_4$)]($S_4O_6$)·2($H_2O$) and of [*cis*-α-Co(trien)($NH_3$)Cl]($S_5O_6$) – Compounds Produced by Hydrolytic Cleavage of Sulfur–Sulfur Bonds of the Tetrathionate Anion

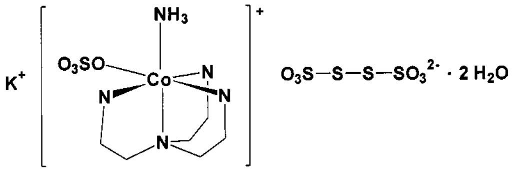
Hyungphil Chun[a] and Ivan Bernal*[a]

**Keywords:** Tetrathionates / Pentathionates / Sulfato ligands / Cobalt(III) complexes / *Thiobacillus ferrooxidans*

K[Co(tren)($NH_3$)($SO_4$)]($S_4O_6$)·2($H_2O$) (**1**) and [*cis*-α-Co(trien)($NH_3$)Cl]($S_5O_6$) (**2**) have been prepared unexpectedly while attempting to obtain crystals suitable for X-ray diffraction of [Co(tren)($NH_3$)Cl]($S_4O_6$) (**3**) and of [*cis*-Co(trien)($NH_3$)Cl]($S_4O_6$) (**4**), respectively. **1** is derived from **3** by hydrolysis of the tetrathionate anion resulting in a sulfato moiety which displaces the chloro ligand from the coordination sphere of the metal center. **2** is derived from **4** by hydrolysis of the tetrathionate anion followed by reformation into pentathionate anion and $H_2S$, as described in previous chromatographic work by Steudel. Compounds **1** and **2** have been characterized by elemental analyses and by single-crystal X-ray diffraction studies.

Some time ago, we discovered that the compound [*cis*-Co(en)$_2$($NH_3$)Br]($S_4O_6$) (**5**) crystallizes as a conglomerate, as we had hoped.[1,2] (Conglomerate crystallization is the phenomenon whereby a racemic solution produces a mechanical mixture of enantiomorphically pure single crystals of both handedness.) By a crystal structure determination, we also demonstrated that the parent compound, [*cis*-Co(en)$_2$($NH_3$)Br]$Br_2$, from which **5** was prepared was a racemate[2]. At the time, we argued that crystallization as a conglomerate was justified since both cation and anion are chiral, as one could expect for chiral recognition to occur giving rise to specificity and, indeed, that was the purpose of using the tetrathionate anion to begin with.[1] Interestingly, we found that the $S_4O_6^{2-}$ anion is hydrogen-bonded to the cations, via the $SO_3$ fragments, in exactly the same fashion as the $-SO_3$ of bromocamphorsulfonate when used as resolving agent for the same Co$^{III}$ cation.[3,4] Finally, the sodium salt of the $S_4O_6^{2-}$ anion crystallizes as a conglomerate.[5]

At the time, we indicated[1] that we planned to examine a series of polythionates of the *cis*-amminehalo cations in order to establish whether the chirality of the countercation played a role in the selection of the crystallization pathway. In this report, we detail the results of our studies using tetrathionate with two different Co$^{III}$ cations, results which produced novel and unexpected chemical products. Moreover, these results are in revealing and interesting agreement with the pioneering work of Steudel and associates,[6] who reached similar conclusions to ours using totally different sources of information.



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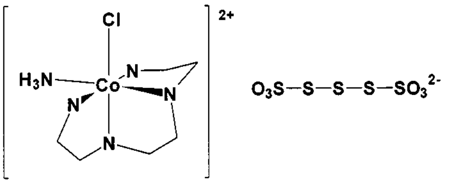

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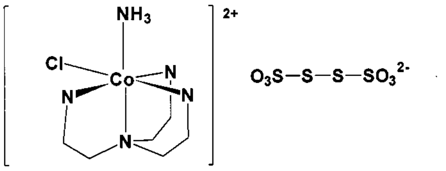

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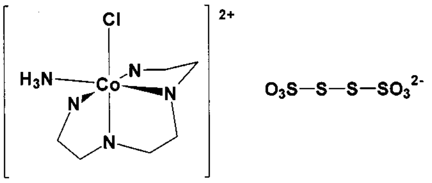

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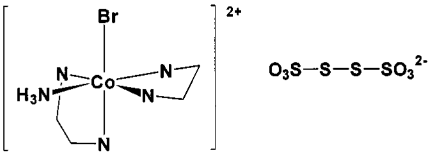

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## Results and Discussion

As indicated by the results listed in Table 3, the structures are well behaved, that of **1** being a of a little higher quality than that of **2** caused by larger number of weak data present in the crystals of the latter substance and by a small amount of disorder present in C(6) of **2**; for details of the disorder, see below.

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[a] Chemistry Department, University of Houston,
Houston, Texas 77204-5641, USA

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Upon solving the structures of the two compounds, we realized that marked changes from the expected compounds had occurred. This is evident from Figures 1, 2 (see also Tables 1, 2) which, to our great surprise, show the true molecular and stereochemical nature of the two compounds − a fact that was later verified by elemental analyses.

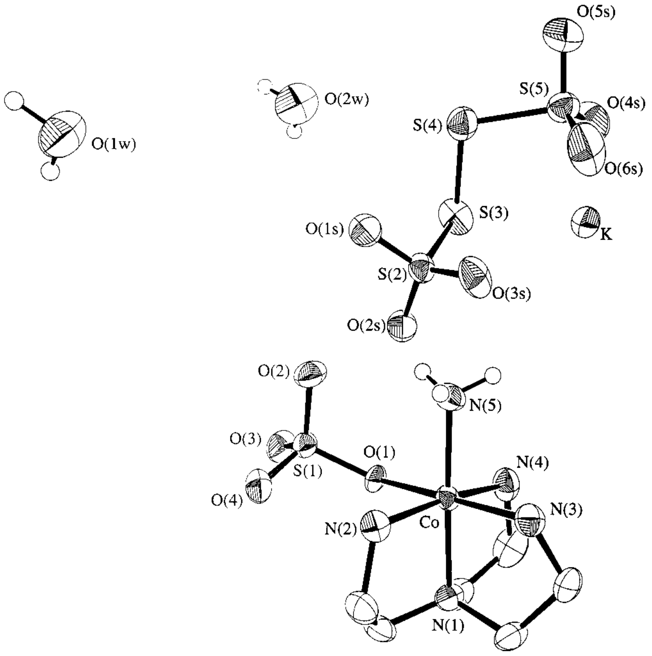

Figure 1. A view of the cations, anion and waters of crystallization of **1**; note the hydrogen bonds of the $-NH_3$ ligand to the oxygen atoms of S(2); those are the closest hydrogen bonds present in the molecule; also note the bonds between the potassium ion and the oxygen atoms of S(5)

Table 1. Selected bond lengths [Å] and angles [°] for **1**

| | | | |
|---|---|---|---|
| Co−N(1) | 1.955(3) | N(5)−Co−N(1) | 177.6(2) |
| Co−N(2) | 1.951(4) | N(2)−Co−N(4) | 170.3(2) |
| Co−N(3) | 1.924(4) | N(1)−Co−O(1) | 91.75(13) |
| Co−N(4) | 1.957(4) | N(2)−Co−O(1) | 92.5(2) |
| Co−N(5) | 1.952(4) | N(3)−Co−O(1) | 175.1(2) |
| Co−O(1) | 1.978(3) | N(4)−Co−O(1) | 82.4(2) |
| S(1)−O(1) | 1.540(3) | N(5)−Co−O(1) | 90.6(2) |
| S(1)−O(2) | 1.451(3) | N(2)−Co−N(1) | 86.5(2) |
| S(1)−O(3) | 1.468(3) | N(3)−Co−N(1) | 86.3(2) |
| S(1)−O(4) | 1.464(3) | N(4)−Co−N(1) | 85.4(2) |
| S(2)−S(3) | 2.109(2) | S(1)−O(1)−Co | 129.5(2) |
| S(3)−S(4) | 2.009(2) | S(2)−S(3)−S(4) | 103.06(8) |
| S(4)−S(5) | 2.121(2) | S(3)−S(4)−S(5) | 104.68(8) |
| S(2)−O(1S) | 1.448(3) | O(1S)−S(2)−S(3) | 106.5(2) |
| S(2)−O(2S) | 1.452(3) | O(2S)−S(2)−S(3) | 99.2(2) |
| S(2)−O(3S) | 1.438(3) | O(3S)−S(2)−S(3) | 108.8(2) |
| S(5)−O(4S) | 1.421(4) | O(4S)−S(5)−S(4) | 106.4(2) |
| S(5)−O(5S) | 1.435(4) | O(5S)−S(5)−S(4) | 98.4(2) |
| S(5)−O(6S) | 1.418(4) | O(6S)−S(5)−S(4) | 107.8(2) |
| H(2N)−O(4) | 2.111 (0.054) | | |
| H(3N)−O(2W)_$1 | 1.988 (0.055) | $: 1 −*x*, −*y* + 1, −*z* + 1 | |
| H(5N)−O(1W)_$1 | 2.192 (0.054) | | |
| H(7N)−O(3)_$2 | 2.205 (0.072) | $: 2 *x* − 1, *y*, *z* | |
| H(8N)−O(1S)_$1 | 2.277 (0.071) | | |
| H(9N)−O(2) | 2.268 (0.061) | | |
| H(1W)−O(2S)_$4 | 1.826 (0.086) | $: 4 *x*, *y* + 1, *z* | |
| H(3W)−O(5S)_$7 | 2.080 (0.035) | $: 7 − *x*, −*y* + 1, −*z* + 2 | |
| H(4W)−O(5S)_$6 | 2.280 (0.070) | $: 6 *x* + 1, *y*, *z* | |

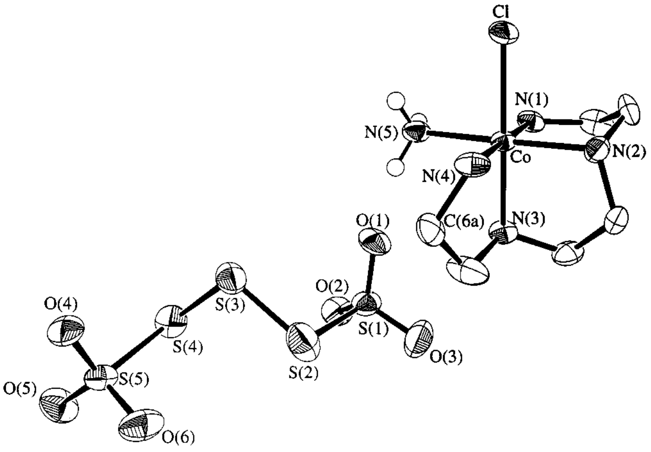

Figure 2. A view of the cation and anion of compound **2**; the anion is located at the position at which it forms the shortest hydrogen bonds to the cation, which are those with the $-NH_3$ hydrogen atoms; the carbon atom C(6a) is depicted as ordered in the position which poduces the lowest energy conformation of its ring, in this case λ

Table 2. Selected bond lengths [Å] and angles [°] for **2**

| | | | |
|---|---|---|---|
| Co−N(1) | 1.975(7) | N(5)−Co−N(2) | 174.9(3) |
| Co−N(2) | 1.958(7) | N(4)−Co−N(1) | 179.1(3) |
| Co−N(3) | 1.950(6) | N(3)−Co−Cl | 174.2(2) |
| Co−N(4) | 1.949(7) | N(1)−Co−Cl | 90.6(2) |
| Co−N(5) | 1.951(7) | N(2)−Co−Cl | 91.7(2) |
| Co−Cl | 2.266(2) | N(4)−Co−Cl | 89.6(2) |
| C(5)−C(6A) | 1.46(2) | N(5)−Co−Cl | 88.4(2) |
| C(5)−C(6B) | 1.44(2) | C(6A)−C(5)−N(3) | 115.1(4) |
| C(6A)−N(4) | 1.491(11) | C(6B)−C(5)−N(3) | 111.1(9) |
| C(6B)−N(4) | 1.51(2) | C(5)−C(6A)−N(4) | 107.0(4) |
| S(1)−S(2) | 2.102(4) | C(5)−C(6B)−N(4) | 107.1(13) |
| S(2)−S(3) | 2.053(4) | S(1)−S(2)−S(3) | 98.7(2) |
| S(3)−S(4) | 2.018(4) | S(2)−S(3)−S(4) | 106.2(2) |
| S(4)−S(5) | 2.122(3) | S(3)−S(4)−S(5) | 100.4(2) |
| S(1)−O(1) | 1.418(6) | O(1)−S(1)−S(2) | 105.3(3) |
| S(1)−O(2) | 1.444(6) | O(2)−S(1)−S(2) | 105.5(4) |
| S(1)−O(3) | 1.427(7) | O(3)−S(1)−S(2) | 101.7(4) |
| S(5)−O(4) | 1.434(6) | O(4)−S(5)−S(4) | 105.8(3) |
| S(5)−O(5) | 1.431(7) | O(5)−S(5)−S(4) | 99.9(3) |
| S(5)−O(6) | 1.441(6) | O(6)−S(5)−S(4) | 106.2(3) |
| H(1C)−O(4)_$1 | 2.044(0.009) | $1: *x* − 1, *y*, *z* | |
| H(1D)−O(6)_$2 | 2.191(0.010) | $2: *x* − 1, 1/2 − *y*, *z* − 1/2 | |
| H(2C)−O(2)_$3 | 2.048(0.009) | $3: 2 − *x*, *y* − 1/2, 1/2 − *z* | |
| H(5G)−O(1) | 2.201(0.009) | | |
| H(4C)−O(2)_$3 | 2.239(0.010) | | |

What those results demonstrate is that a $S-SO_3$ bond had been broken and that the terminal sulfur atom had been oxidized to $S^{6+}$ creating a sulfato moiety. At the same time the chloro ligand, initially present in the $Co^{III}$ substrate, has been eliminated and a sulfato ligand has replaced it using a single oxygen atom to coordinate the metal center. At a later time, the solubility limit of **1** was reached and crystals began to be deposited. A check of the literature revealed the following facts:

(a) the Cambridge Structural Database (CSD)[7] lists no mononuclear 3-d metal complex in the 3+ charge state containing a monodentate sulfato ligand. There are some 3-d metal complexes carrying such ligands; however, they are all 2+ complexes. Among them, the majority are $Cu^{2+}$ complexes, some $Zn^{2+}$ and three $Co^{2+}$ examples. A large number of sulfato complexes are known in which the ligand bridges two or more metal centers or acts as a bidentate ligand to a single metal center. We also examined the Inorganic Crystal Sturucture Database(ICSD)[8] which does not list a single example of a trivalent metal center bearing a monodentate sulfato ligand. These facts make compound **1** an interesting rarity.

(b) A check in the literature revealed the presence of a seminal paper by Steudel and colleagues[6] detailing their chromatographic separation experiments during the equilibration of polythionates in carefully controlled media. They reported detecting $S_nO_6^{2-}$ species, where $n = 2...22$. Two equations of the equilibria they proposed are particularly relevant to the results we are reporting. They are:

$$S_4O_6^{2-} + H_2O \rightarrow HS_2SO_3^- + HSO_4^- \quad (1)$$

$$2\,HS_2SO_3^- \rightleftharpoons S_5O_6^{2-} + H_2S \quad (2)$$

All those species were detected in their chromatographic work and, now, we have trapped the sulfate as a ligand to the metal center in **1** and the pentathionate in Equation 2 is the counteranion to the metal center in compound **2**. Thus, the two studies are mutually reinforcing and it is specially pleasing that we were able to obtain the structures of the relevant moieties proposed by Steudel, et al.[6]

## The Stereochemistry of 1 and 2

As shown in Figure 1, the cation of **1** consists of a Co$^{III}$ cation surrounded by the four nitrogen atoms of the ligand tren [tris(2-aminoethyl)amine]. The ammine ligand is *trans* to the central nitrogen atom of tren (so-called *p*-mode of binding) and the sulfato ligand is *cis* to the ammine and bound to the metal center by a single oxygen atom. There are two waters of crystallization which are hydrogen-bonded to terminal $-NH_2$. The potassium cation is bonded to oxygen atoms of a terminal $-SO_3$ fragment of the tetrathionate anion (see Figure 4 for further details); finally, the $-SO_3$ fragment at the opposite end of the tetrathionate anion is hydrogen-bonded to the $-NH_3$ hydrogen atoms, as shown in Figure 1.

An interesting stereochemical result is that the S−O bond of the metal-bound sulfate is noticeably longer than those of the other three oxygen atoms which is to be expected since the bound oxygen atom is donating its electron density to the Co$^{III}$ ion. The average value of the S−O distances in the tetrathionate anion is 1.435(4) Å which is significantly shorter than those in the bound sulfato ligand. Finally, the S−S distances within the tetrathionate differ in that the central S−S bond is significantly shorter than the outer two. This result is in close agreement with the values published earlier for compound **5**[1] where the central S−S bond was found to be 2.019(2) Å and the outer ones were 2.111(2) and 2.133(2) Å. The remaining stereochemistry of this molecule is normal and it does not require further comment. Its main importance is the fact that the postulated formation of the sulfate anion has been verified by the accident of trapping it into the cation of **1**.

The stereochemistry of **2** is shown in Figure 2 in which the trien (1,4,7,10-tetraazadecane) ligand is in the *cis*-α configuration. Figure 3 shows that C(6) is disordered (50:50) into its two alternate positions, making that ring either λ or δ, the former being the lowest energy conformation and it is the one shown in Figure 2.

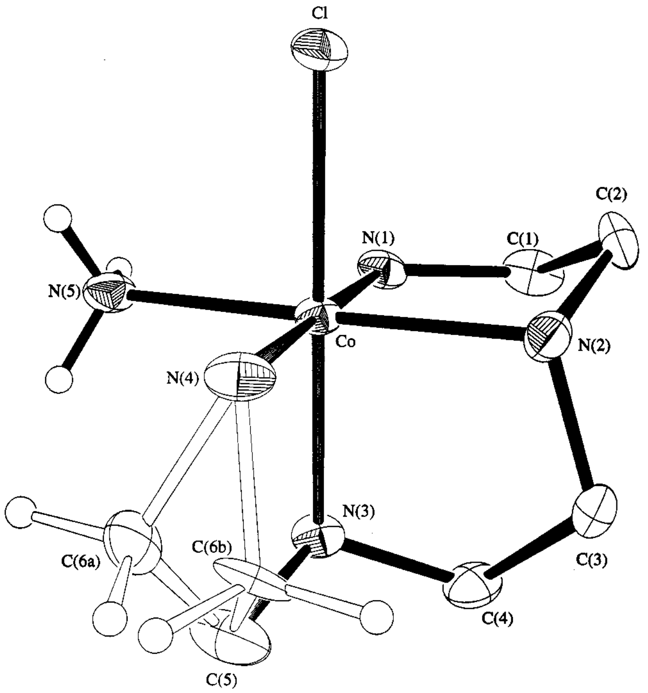

Figure 3. A view of the cation of **2** showing the disorder of the ring containing C(6)

This disorder contributes to the somewhat higher *R* factors listed in Table 3 since occupancy factors and anisotropic thermal parameters are correlated, as is widely known. Also, the partial disorder at C(6) is probably the result of steric hindrance with O(1) which is held in that position by hydrogen bonding to the $-NH_3$ hydrogen atoms, as is clear from Figures 2 and 5. The O(1)−C(6a) contact is 3.804 Å and the O(1)−H(6a2) is 3.282 Å while the hydrogen bond O(1)−H(5g) is 2.201 Å and these contacts are the likely source of the disorder we discovered. We also note that the $-NH_3$ hydrogen atoms were readily found in the structural analysis and were located at very reasonable positions indicating that the disorder problem is strictly localized at C(6). Figure 5 depicts the association of pentathionate anions with the cations in the crystal structure. Its S−O distances are fairly uniform, the longest being 1.444(6) Å and the shortest 1.418(6) Å, with an average of 1.433(7) Å. The small differences are probably due to differences in extents of hydrogen bonding of the two ends of the anion.

## Mechanism of the Reactions Observed in 1 and 2

First, let us emphasize the fact that not every *cis*-amminehalo compound of a (polyamine)cobalt complex causes the fragmentation of the tetrathionate anion since we deter-

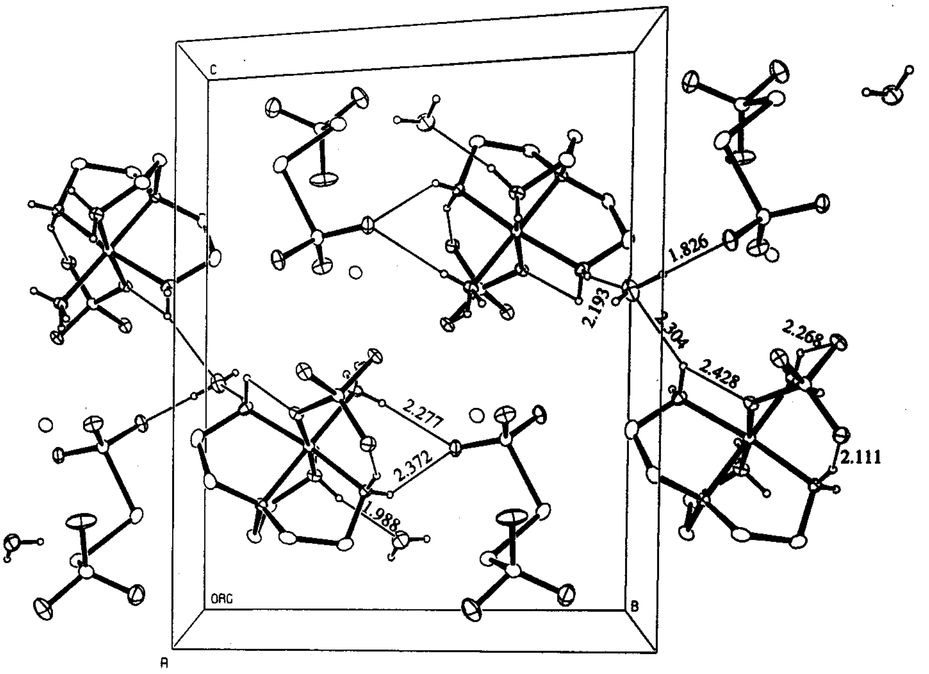

Figure 4. The packing of the ions and waters of crystallization of compound **1**; note the hydrogen bonds holding the pieces together; only the shortest ones are drawn (light lines) and their distances are given; the tetrathionate anions are bonded by a single oxygen atom to only two hydrogen atoms of a cation; in those cases of conglomerate crystallization (see ref.[1]) there were strong hydrogen bonds of the three oxygen atoms of one $-SO_3$ moiety to three hydrogen atoms of a *fac* face of its cation

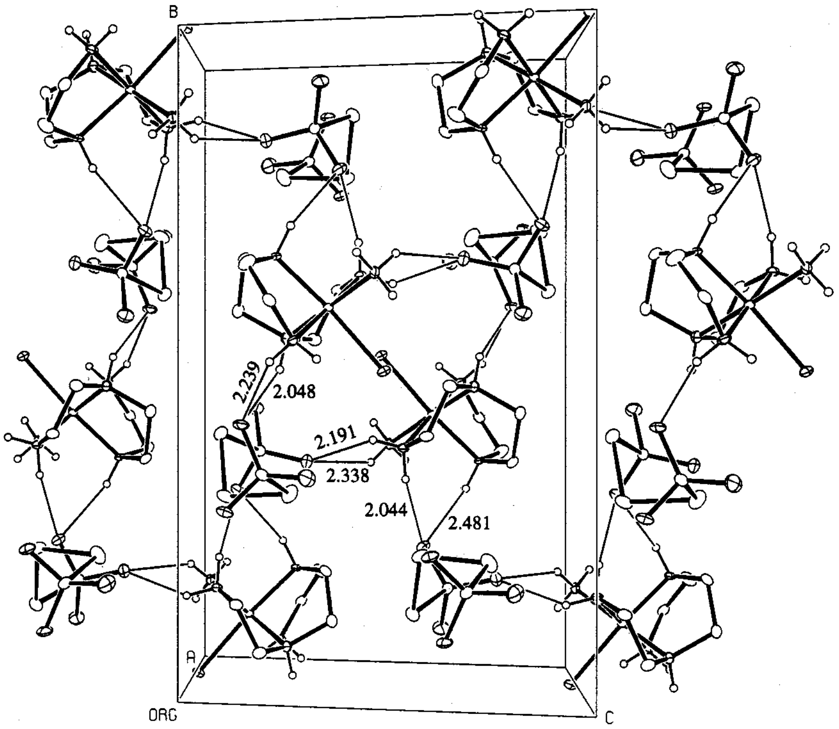

Figure 5. The packing of the ions of compound **2**; only the shortest hydrogen bonds are drawn (light lines) and their distances are given; note that the pentathionate anions are also bonded by two oxygen atoms to two hydrogen atoms of a pair of adjacent cations

mined[1] the crystal structure of [*cis*-$Co(en)_2(NH_3)Br](S_4O_6)$ (**5**; conglomerate) and of pre-resolved $(+)_{589}$[*cis*-Λ(δλ)-$Co(en)_2(NH_3)Br](S_4O_6)$ (**6**); we saw no evidence of the formation of either sulfate or of pentathionate with those compounds. These observations are the more interesting when viewed against the fact that the spectrochemical series classifies a chloro ligand as being stronger than a bromo ligand. Consequently, if sulfate were formed by cleavage of $S-SO_3$ in **5** and **6** it should more readily displace the bromo ligand from the coordination sphere of the cobalt center in those cations; however, this is not the experimental result. Therefore, the suggestion is that only specific combinations of polythionates and *cis*-ammine(halo)cobalt cations are capable of giving rise to S−S cleavage reactions. As a matter of fact, we have recently determined the structure of [*cis*-Co(en)$_2$($NH_3$)Br]($S_3O_6$) and observed no evidence of S−S bond fragmentation, either.[9]

The $-NH_3$ ligands of **1** and **2** have remained bound to their cobalt centers and we note that in the latter the chloro ligand has also remained bound to its metal atom. This is a puzzling result in view of the fact that Equation 1 of the mechanism proposed by Steudel, et al.[6] requires the formation of $HS_2SO_3^-$ + $HSO_4^-$ in order to use the former for the creation of the pentathionate found on **2**. This suggests that the first stage of the reaction (Equation 1; sulfate formation) happens without chloride elimination, concerted or otherwise. The suggestion is, then, that after the formation of the sulfate anion, the chloro ligand of **1** is replaced by a sulfato ligand which loses then its proton − an example of highly charged metal induction of proton elimination, as in the classical case of:

$$[M(H_2O)_6]^{3+} \rightarrow [M(H_2O)_5(OH)]^{2+} + H^+$$

We observed experimentally that such a process of halide elimination and sulfato substitution does not occur in the case of **2**. What could be the possible reason it does not do so?

First, we note that the chloro ligand in **1** is *trans* to a primary (terminal) $-NH_2$ ligand whereas in **2** it is *trans* to a secondary −NH− ligand, the latter being a better Lewis base; and, thus, a better σ donor to the metal center. It is fair to assume that in both compounds the chloro ligand is an equally good σ donor and π acceptor and is not the root of any differences in bonding. However, if more σ-electron density is donated to the metal center of **2**, one would expect a stronger (shorter) Co−Cl bond in the case of **2**. The structures of three different salts of $[Co(tren)(NH_3)Cl]^{2+}$ (the parent cation for **1**) were precisely determined by Buckingham et al.[10] who found Co−Cl bonds of 2.301(2), 2.288(2) and 2.291(4) Å. In compound **2**, the Co−Cl bond length is 2.266(2) Å, the difference from the average value of Buckingham′s results [2.293(3) Å] is 0.027 Å, which is greater than ca. 10 times the esds given. Thus, the difference is significant and may be the reason why the chloro ligand was not expelled by sulfato in the case of **2**.

## The Connection with *Thiobacillus ferrooxidans* (*T. f.*)

It was pointed out by Steudel et al.[6] that *T. f.* is "a chemolithotrophic bacterium which participates in the sulfur cycle in nature and plays an important role in the bacterial leaching of mineral ores." $Fe^{2+}$ is present in these bacterial cultures and the energy driving these systems is the oxidation of $Fe^{2+}$ to $Fe^{3+}$ and/or the oxidation of low-valent sulfur compounds to sulfate. Since we generated, and trapped, sulfate in the case of **1** and, presumably, we also formed sulfate in the case of **2** (see above arguments), our compounds may have some value as bio-inorganic models for such reactions, despite the fact that they are Co$^{III}$ derivatives.

## Experimental Section

Pure samples of $K_2S_4O_6$ and $Na_2S_4O_6 \cdot 2H_2O$ were purchased from SIGMA Chemical Company. [Co(tren)($NH_3$)Cl]Cl($ClO_4$) was prepared by a literature method[11] and [Co(trien)($NH_3$)Cl]$Cl_2$ was prepared by the same method using trien instead of tren. The elemental analyses described were performed by Galbraith Laboratories.[12]

**Synthesis of K[Co(tren)($NH_3$)($OSO_3$)]($S_4O_6$)·2($H_2O$) (1):** A solution of partially dissolved [Co(tren)($NH_3$)Cl]Cl($ClO_4$) (1.46 g, 3.72 mmol) in 30mL of water was filtered and added slowly to 30 mL of an aqueous solution containing $K_2S_4O_6$ (1.35 g, 4.46 mmol). A small amount (35 mg) of single crystals suitable for X-ray diffraction study was obtained by liquid diffusion with acetone. − $C_6H_{25}CoKN_5O_{12}S_5$ (617.64): calcd. C 11.67, H 4.09, Co 9.54, N 11.34; found C 11.33, H 3.62, Co 9.26, N 11.06.

**Synthesis of [*cis*-α-Co(trien)($NH_3$)Cl]($S_5O_6$) (2):** 1.0 g (3.21 mmol) of [Co(trien)($NH_3$)Cl]$Cl_2$ was dissolved in 15 mL of water and was filtered directly into 10 mL of an aqueous solution of 1.0 g (3.27 mmol) of $Na_2S_4O_6 \cdot 2H_2O$. Red crystalline products were formed and collected after 6 d (90 mg). − $C_6H_{21}ClCoN_5O_6S_5$ (513.96): calcd. C 14.02, H 4.12, N 13.63; found C 14.07, H 4.27, N 13.63.

**Crystallography:** Crystals of **1** and **2** were obtained directly from the reaction media and were mounted onto a goniometer head and

Table 3. Crystal data and structure refinement for K[Co(tren)-($NH_3$)($OSO_3$)]($S_4O_6$)·2($H_2O$) (**1**) and [*cis*-α-Co(trien)($NH_3$)Cl]-($S_5O_6$) (**2**)

| | **1** | **2** |
|---|---|---|
| Empirical formula | $C_6H_{25}CoKN_5O_{12}S_5$ | $C_6H_{21}ClCoN_5O_6S_5$ |
| Molecular mass | 617.64 | 513.96 |
| Crystal system | triclinic | monoclinic |
| Space group | *P*−1 | *P*2$_1$/*c* |
| *Z* | 2 | 4 |
| *a* [Å] | 7.260(3) | 9.720(2) |
| *b* [Å] | 11.202(4) | 17.829(3) |
| *c* [Å] | 13.914(7) | 11.096(3) |
| α [°] | 86.97(3) | 90 |
| β [°] | 87.46(4) | 104.16(2) |
| γ [°] | 75.33(4) | 90 |
| *V* [Å$^3$] | 1092.6(8) | 1864.6(7) |
| *D*(calcd.) [g/cm$^3$] | 1.877 | 1.831 |
| μ [mm$^{-1}$] | 1.518 | 1.657 |
| Crystal size [mm] | 0.66 × 0.44 × 0.41 | 0.14 × 0.25 × 0.58 |
| 2θ range [°] | 4.00−48.00 | 4.00−50.00 |
| Index ranges | ±8, ±12, +15 | ±11, +21, +13 |
| Collected reflections | 3416 | 3438 |
| Independent reflections | 3416 ($R_{int}$ = 0.0000) | 3269 ($R_{int}$ = 0.0550) |
| Obsd. with $I > 2\sigma(I)$ | 2912 | 1662 |
| Data/restraints/ parameters | 3416/2/371 | 3269/0/224 |
| Goodness-of-fit on $F^2$ | 1.044 | 0.952 |
| $R_1$ [$I > 2\sigma(I)$] | 0.0378 | 0.0652 |
| $R_1$ (all data) | 0.0470 | 0.1444 |
| Largest diff. peak/hole [e/Å$^3$] | 1.716/−0.685 | 1.546/−0.671 |

transferred to an Enraf-Nonius CAD4 diffractometer. For both compounds the intensity data were collected with the Enraf-Nonius data-collection package for PC-driven diffractometers.[13] The crystals were centered with data in the range 14° ≤ 2θ ≤ 36° and examination of the cell constants, systematic absences, and Niggli matrix[14] showed **1** to crystallize in the space group $P\bar{1}$ (no. 2) while **2** crystallizes in the space group $P2_1/c$ (no. 14). The intensity data were corrected for absorption using empirical curves derived from φ scans of suitable reflections. The solutions and refinements of the structures were carried out using SHELXS-86[15a] and SHELXL-93.[15b] The scattering curves were taken from Cromer and Waber's compilation.[16] During data collection three intensity and orientation standards were monitored and showed no significant deviations from the initial values. A summary of data collection and refinements for both compounds is given in Table 3. Selected bond lengths and angles for **1** and **2** are given in Tables 1 and 2, respectively. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1018665 and -101866. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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