The Interaction between Amminehalocobalt(III) Cations and Polythionate Anions: Hydrogen-Bonding Patterns and S–S Bond Cleavage Reactions

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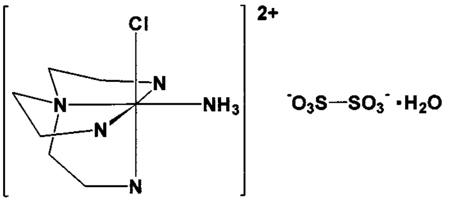
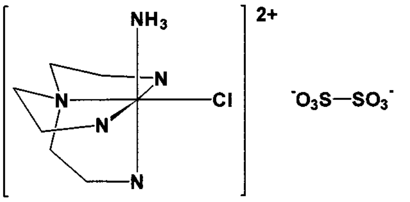
Crystal structures of amminehalocobalt(III) compounds with di- or trithionate anions have been determined in order to know whether they interact to adopt specific molecular packing patterns and whether di- and trithionate anions undergo the S–S bond cleavage reactions as has been found for the $S_4O_6^{2-}$ ion. In the structures of *p*-[Co(tren)(NH_3)Cl]S_2O_6•H_2O (**1**) and *t*-[Co(tren)(NH_3)Cl]S_2O_6 (**2**), the configurational differences in the cations dictate the hydrogen-bonding pattern with the dithionate anion to lead to racemic structures. *cis*-[Co(en)$_2$(NH_3)Br]S_3O_6 (**3**) also crystallizes in a racemic space group $P2_1/c$ in which the ions form a macrocyclic hydrogen-bonded network. Aqueous solutions of $S_3O_6^{2-}$ and *p*-[Co(tren)(NH_3)Cl]$^{2+}$ produce *p*-[Co(tren)(NH_3)(OSO_3)]ClO_4 (**4**) which is believed to be derived from the hydrolytic cleavage of S–S bond in the trithionate anion. These results reinforce our previous observation of the S–S cleavage reactions for the tetrathionate anion.

In the course of investigating crystallization behavior of Werner-type cobalt(III) compounds, Bernal et al. reported that the *cis*-[Co(en)$_2$(NH_3)Br]$^{2+}$ cation spontaneously resolves into its optical antipodes when crystallized with the $S_4O_6^{2-}$ ion.[1] And, in a recent study, we reported that when the $S_4O_6^{2-}$ ion was used to crystallize the *cis*-α-[Co(trien)(NH_3)Cl]$^{2+}$ ion, an unexpected cleavage at a S−S bond, followed by a disproportionation, occurs to give *cis*-α-[Co(trien)(NH_3)Cl]S_5O_6.[2] Also reported in that paper was the crystal structure of K[Co(tren)(NH_3)(OSO_3)]S_4O_6·$2H_2O$ produced by the same cleavage reaction of $S_4O_6^{2-}$ ion. These observations led us to further investigate the hydrogen-bonding modes of amminehalocobalt(III) cations with polythionate anions and the specificity of S−S bond cleavage reactions.

In this study, we discuss the crystal structures of *p*-[Co(tren)(NH_3)Cl]S_2O_6·H_2O (**1**), *t*-[Co(tren)(NH_3)Cl]S_2O_6 (**2**), *cis*-[Co(en)$_2$(NH_3)Br]S_3O_6 (**3**) and *p*-[Co(tren)(NH_3)(OSO_3)]ClO_4 (**4**). Although the cations of **1** and **2** differ only in the position of the NH_3 ligand with respect to the tertiary nitrogen atom of the tren ligand, their molecular packing structures show totally different hydrogen-bonding patterns leading to the racemic structures. The crystal structure of **3** is interesting in that the cation crystallizes as a conglomerate with a tetrathionate anion[1] but as a racemate with two bromide ions and two water molecules of crystallization.[3] Compound **3** also is interesting when viewed against the fact that the $S_3O_6^{2-}$ ion underwent a hydrolytic cleavage reaction while the chloro ligand of the *p*-[Co(tren)(NH_3)Cl]$^{2+}$ ion was replaced to produce compound **4**.



1



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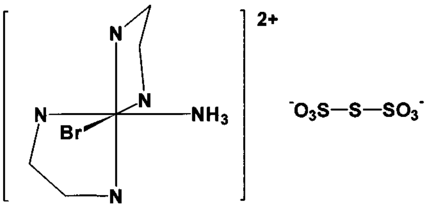

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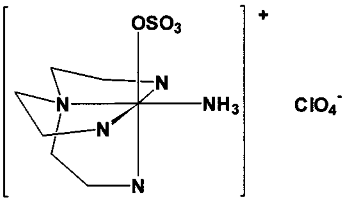

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Although both *p* and *t* isomers of the [Co(tren)(NH_3)Cl]$^{2+}$ ion and their related compounds have been studied extensively by Buckingham and co-workers,[4−6] their crystal

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structures have not been reported in the CSD[7] except for a few compounds with an *N*-methylated tren ligand.[8] Also it is noted that Asakura et al. reported a chiral autocatalysis reaction leading to the preparation of an optically pure form of the cation of **3** as a bromide salt without water molecules of crystallization.[9]

Results and Discussion

As described by Buckingham and co-workers,[4] the red compound *p*-$[Co(tren)(NH_3)Cl]Cl{\cdot}ClO_4$ was prepared by ligand substitutions of four ammine groups with the tren ligand followed by acidic cleavage (HCl) of the peroxo bridge of $[Co(NH_3)_5(O_2)(NH_3)_5Co](NO_3)4{\cdot}2H2O$ and then converted into a dithionate salt to give compound **1**. Its molecular structure is shown in Figure 1.

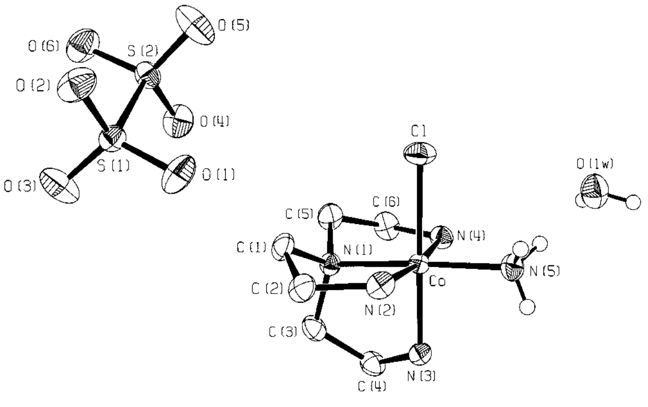

Figure 1. ORTEP diagram of **1** drawn at 50% probability level; hydrogen atoms of the tren ligand have been omitted for clarity; selected bond lengths and angles: Co−N(1) 1.964(2), Co−N(2) 1.967(2), Co−N(3) 1.930(2), Co−N(4) 1.963(2), Co−N(5) 1.959(2), Co−Cl 2.2783(9), S(1)−S(2) 2.1357(9) Å; N(1)−Co−N(5) 177.33(10), N(2)−Co−N(4) 171.32(9), N(3)−Co−Cl 178.70(7)°

In the geometry of the cobalt cation, the largest deviation from a regular octahedron is the angle N(2)−Co−N(4) [171.32(9)°]and N(5)−Co−Cl [87.21(8)°]. The former is a consequence of the geometrical features of the tren ligand and the latter is attributed to the weak the internal hydrogen bonds between Cl and hydrogen of the ammine ligand. For the anion, two S−O bond lengths, S(1)−O(1), 1.435(2) Å and S(2)−O(5), 1.436(2) Å, are significantly shorter than the other four [average 1.452(2) Å] and the two oxygen atoms do not participate in any hydrogen bond shorter than 2.5 Å.

When $[Co(tren)Cl_2]Cl$ is stirred in a warm methanolic ammonia solution, the other isomer *t*-$[Co(tren)(NH_3)Cl]Cl_2$ is isolated as a reddish purple microcrystalline precipitate with a reasonable yield (> 50%) and then converted into a dithionate salt to give compound **2**. In the structure shown in Figure 2, the crystallographic asymmetric unit contains the cobalt cation and two $-SO_3$ fragments of a dithionate anion in different positions.

The fragment generates the other half when an inversion symmetry operation is performed. The structural parameters for the cation and anion show the same trends as those of **1** described above. **3** was prepared by adding an aqueous solution of $K_2S_3O_6$ to a saturated solution of *cis*-$[Co(en)_2(NH_3)Br]Br_2$ and its molecular structure is shown in Figure 3.

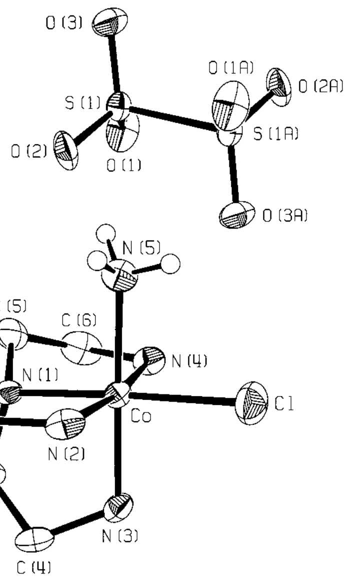

Figure 2. Molecular structure of **2**; hydrogen atoms of the tren ligand have been omitted for clarity; selected bond lengths and angles: Co−N(1) 1.949(4), Co−N(2) 1.959(5), Co−N(3) 1.939(5), Co−N(4) 1.946(5), Co−N(5) 1.976(5), Co−Cl 2.247(2), S(1)−S(1A) 2.114(3) Å; N(2)−Co−N(4) 171.5(2), N(3)−Co−N(5) 178.3(2), N(1)−Co−Cl 176.56(13)°

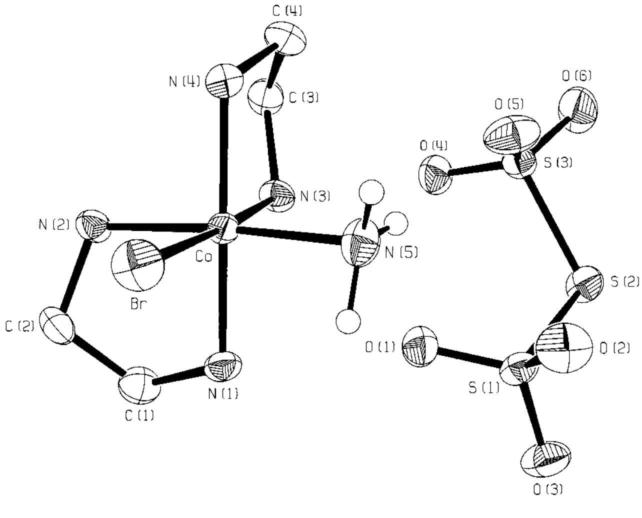

Figure 3. Molecular structure of **3**; hydrogen atoms of the en ligands have been omitted for clarity; selected bond lengths and angles: Co−N(1) 1.945(3), Co−N(2) 1.958(3), Co−N(3) 1.961(3), Co−N(4) 1.962(3), Co−N(5) 1.960(4), Co−Br 2.3915(10), S(1)−S(2) 2.1120(13), S(2)−S(3) 2.092(2) Å; N(1)−Co−N(4) 176.81(14), N(2)−Co−N(5) 174.7(2), N(3)−Co−Br 176.42(11), S(1)−S(2)−S(3) 102.71(7)°

In the structure, the two S−S bonds of the trithionate anion are not equal in distances [2.1120(13) and 2.092(2) Å] and the six S−O lengths fall within their 3σ ranges with the average of 1.443(3) Å.

For compound **4**, a solution mixture of *p*-$[Co(tren)(NH_3)Cl]Cl{\cdot}ClO_4$ and $K_2S_3O_6$ did not yield any crystalline product, unlike the compounds **1** and **2**, which began to crystallize almost immediately after mixing the two reactants. Instead, a white powdery precipitate was slowly deposited on the bottom of the beaker as the solvent evaporated. When the solution was concentrated, it was divided into four portions. Three of them were used for liquid diffusion with acetone, ethanol and acetonitrile and from the fourth the solvent was allowed to evaporate slowly. Only the one with ethanol produced a small amount of red crystals after standing for several weeks. A suspicion for the integrity of the trithionate thus entered our mind and was later proved to be true when we solved the structure. The structure and geometrical parameters of the cation shown in Figure 4 are very similar to the one produced by hydrolytic cleavage of the $S_4O_6^{2-}$ anion.[2]

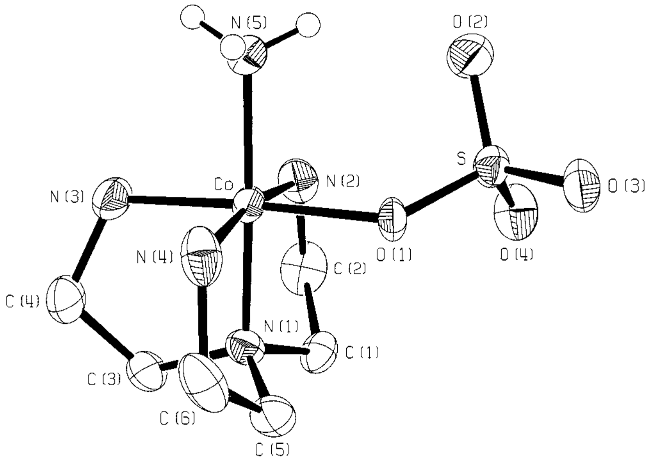

Figure 4. View of the cation of **4**; hydrogen atoms of the tren ligand have been omitted for clarity; selected bond lengths and angles: Co–N(1) 1.962(4), Co–N(2) 1.935(5), Co–N(3) 1.926(5), Co–N(4) 1.974(5), Co–N(5) 1.955(5), Co–O(1) 1.958(3), S–O(1) 1.510(4), S–O(2) 1.460(4), S–O(3) 1.464(4), S–O(4) 1.476(4) Å; N(1)–Co–N(5) 178.1(2), N(2)–Co–N(4) 170.8(2), N(3)–Co–O(1) 175.1(2), Co–O(1)–S 131.3(2)°

In the packing structure of **1**, shown in Figure 5, a dithionate anion displays hydrogen bonds with a cation in a side-on fashion.

Such one-to-one side-on contacts are possible because the ammine ligand is *cis* to all three hydrogen-bearing nitrogen atoms of the tren ligand. That is, the so-called *p* configuration of the cation allows the hydrogen atoms of N-donor atoms to be arranged around two trigonal faces of an octahedron. The closest hydrogen bond found was between the oxygen atom of a water molecule and a hydrogen atom of the ammine ligand [2.005(42) Å].

The apparently complicated packing structure of **2**, shown in Figure 6, can be best understood by realizing that the three hydrogen-bearing nitrogen atoms of the tren and the NH_3 ligands are lying on the same plane.

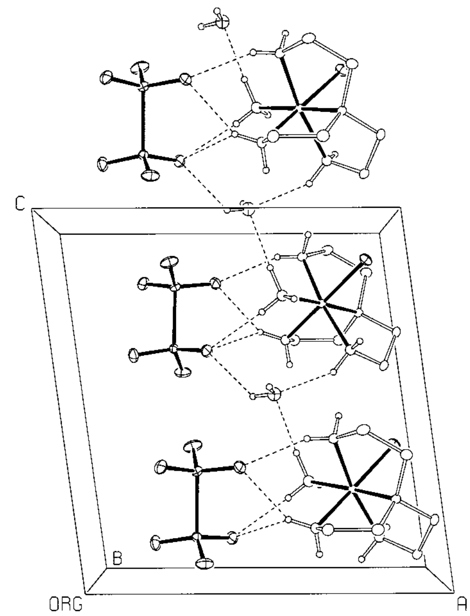

Figure 5. Packing of ions and water molecules of crystallization of **1**; the molecules shown are related by *c*-glide plane symmetry; hydrogen bonds shorter than 2.5 Å are shown as dotted lines

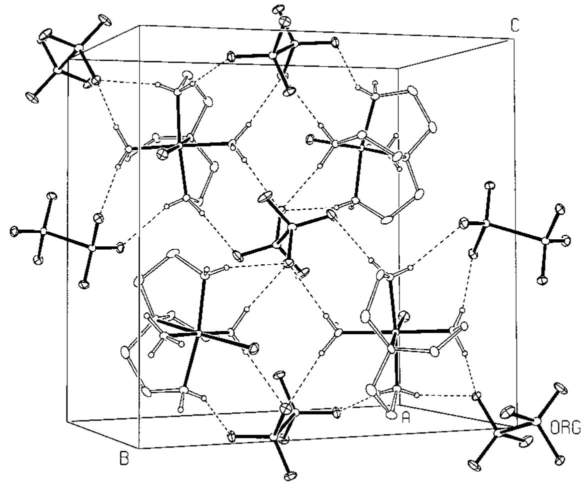

Figure 6. Packing diagram of **2** showing hydrogen-bonded interactions; note that dithionate anions are positioned on crystallographic inversion centers.

As a consequence, four dithionate anions are arranged around a tetragonal basal plane of an octahedron to form hydrogen bonds with hydrogen atoms of tren and of the NH_3 ligand. Since the anions are positioned on crystallographic inversion centers, as mentioned above, the two cobalt cations connected to $-SO_3$ ends of a dithionate anion by hydrogen bonds are a racemic pair.

Figure 7 depicts the packing of *cis*-$[Co(en)_2(NH_3)Br]^{2+}$ ions with trithionate anions in **3**.

In the structure, an $-SO_3$ end of a trithionate ion bridges two neighboring cations to form a macrocyclic hydrogen-bonded network made of four molecules. Meanwhile, the $-SO_3$ moieties, which are not involved in forming the network, have contacts with other cations located along the *a* axis of the unit cell, and those cations form the macrocyclic networks again.

Trithionate ($S_3O_6^{2-}$) has been known to thermally decompose to produce SO_4^{2-}, SO_2 and S in aqueous solution.[10] And as the preparation and structure of **3** implies, the divalent anion is perfectly stable in aqueous solutions

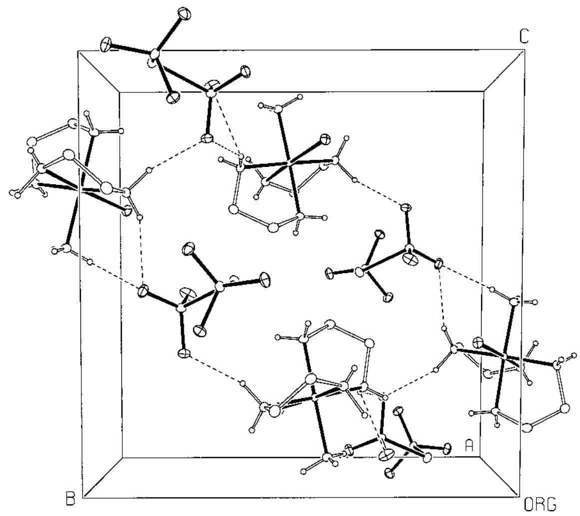

Figure 7. Macrocyclic hydrogen-bonded network structure of **3**; dotted lines represent hydrogen bonds shorter than 2.5 Å

at room temperature for the relatively short period of time required for crystallization. However, the production of compound **4**, in conjunction with our previous report,[2] might suggest the ability of $[CoN_4(NH_3)X]^{n+}$ ions [where N_4 is tren or trien, but not $(en)_2$] to apparently promote the cleavage reactions of S−S bonds in a series of polythionates. Dithionate, which has no reduced form of sulfur atoms, however, does not readily cleave its single S−S bond (although it does in strong acid, albeit slowly).

The trien and especially the tren complexes are slow to hydrolyze by the spontaneous pathway, but are very base-sensitive, and base-catalyzed hydrolysis of bound Cl^- or Br^- is the major contribution to the hydrolysis rate even at pH = 7−8. Certainly, color changes consistent with formation of $[CoN_4(NH_3)(OH_2)]^{3+}$ are observed for solutions of these ions in water, in the presence or absence of polythionates, over periods of hours. Thus, for tren and trien complexes where the time scale for the crystallization are long (days to weeks), sulfato complexes are formed, and sulfur, free sulfate and polythionates of different stoichiometry are also formed by hydrolysis and disproportionation of the original polythionate (be it $S_4O_6^{2-}$ or $S_3O_6^{2-}$). Slow anation of the aquametal complex by sulfate logically accounts for the formation of the sulfato complex, and it preferentially crystallizes from solution simply because it is less soluble than the other components. We also note that the crystalline potassium polythionate salts have a finite shelf life, $K_2S_4O_6$, $K_2S_5O_6$ and $K_2S_6O_6$ in particular, such that fresh solutions of aged salts (months to years) can lead to the immediate crystallization of unexpected polythionates. Moreover, we note that the published syntheses[11] of the penta- and hexathionates are not particularly reproducible.

Activation to hydrolysis through metal ion coordination of amino acid esters and peptides have long been known and well documented,[12,13] and a similar mechanism for $S_nO_6^{2-}$ merits consideration. For example, polythionate complexes $[Co(N)_4(NH_3)O_3S(S)_nSO_3]^+$ might be formed

Table 1. Summary of data collection and refinements

	1	**2**	**3**	**4**
Empirical formula	$C_6H_{23}ClCoN_5O_7S_2$	$C_6H_{21}ClCoN_5O_6S_2$	$C_4H_{19}BrCoN_5O_6S_3$	$C_6H_{21}ClCoN_5O_8S$
Molecular mass	435.79	417.78	468.26	417.72
λ [Å]	0.71073	0.71073	0.71073	0.71073
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$	$P2_1/c$
a [Å]	11.310(2)	8.640(2)	8.207(1)	12.875(4)
b [Å]	11.602(6)	13.356(4)	13.366(2)	8.675(4)
c [Å]	11.958(2)	13.103(4)	13.543(1)	14.234(5)
β [°]	97.96(2)	91.88(3)	93.54(9)	111.51(3)
V [Å^3]	1553.9(9)	1511.2(8)	1482.8(3)	1479.2(9)
Z	4	4	4	4
$D_{calcd.}$ [g/cm^3]	1.863	1.836	2.098	1.876
μ [mm^{-1}]	1.586	1.622	4.305	1.531
F(000)	904	864	944	864
Crystal size [mm]	0.48 × 0.46 × 0.23	0.50 × 0.12 × 0.11	irregular fragment	0.64 × 0.47 × 0.35
θ_{max} [°]	25.00	24.97	27.56	25.98
Index ranges (h,k,l)	±13, +12, +14	±10, +15, +15	±10, +17, +17	±15, +10, +17
Total reflections	2803	2761	3570	3025
Independent (R_{int})	2668 (0.0274)	2647 (0.0337)	3436 (0.0534)	2900 (0.0352)
Observed [$I > 2\sigma(I)$]	2165	1407	2509	1405
Absorption correction	ψ scans	ψ scans	ψ scans	ψ scans
T_{max}/T_{min}	0.9950/0.8277	0.9730/0.9111	0.9996/0.5920	0.9991/0.8898
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/parameters	2668/291	2647/274	3436/257	2900/202
GOF on F^2	1.072	0.958	0.981	0.981
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0264 wR_2 = 0.0707	R_1 = 0.0404 wR_2 = 0.0801	R_1 = 0.0393 wR_2 = 0.1035	R_1 = 0.0454 wR_2 = 0.1205
R indices (all data)	R_1 = 0.0380 wR_2 = 0.0741	R_1 = 0.1223 wR_2 = 0.0924	R_1 = 0.0626 wR_2 = 0.1117	R_1 = 0.1380 wR_2 = 0.1388
Largest diff. peak and hole [e/Å^3]	0.375 and −0.403	0.500 and −0.410	1.314 and −0.911	0.546 and −0.419

from the aqua complex by anation, and cleaved at the S−S bond nearest the polarizing Co^{III} center by activated hydrolysis, thereby providing the sulfato complex. We have as yet not performed the appropriate control experiments to either support or discount this mechanism, but note that the synthesis of even the simplest polythionate complex, $[Co(NH_3)_5O_3SSO_3]^+$, has so far eluded us. Chelated polythionates are likely to be more viable, and we are presently investigating potential 5- and 6-membered ring systems derived from $S_2O_6^{2-}$ and $S_3O_6^{2-}$, respectively, in the *cis*-$[Co(en)_2X_2]^+$ system.

In summary, di- and trithionate anions do not show a specific hydrogen-bonding pattern with amminehalocobalt(III) cations; according to the geometrical arrangement of hydrogen atoms around the coordination sphere, they show a one-to-one side-on pattern or play end-on bridging roles. Sulfur−sulfur bonds in polythionates other than $S_2O_6^{2-}$ seem to be prone to slow hydrolytic cleavage reactions at room temperature.

Experimental Section

General: *p*-$[Co(tren)(NH_3)Cl]Cl\cdot ClO_4$ and *t*-$[Co(tren)(NH_3)Cl]Cl_2$ were prepared by known methods[4] except for chromatographic procedures. *cis*-$[Co(en)_2(NH_3)Br]Br_2$ was prepared by the method reported earlier.[3] $Na_2S_2O_6\cdot 2H_2O$ (Fisher Scientific Company) was used as received. Elemental analyses were carried out by the Galbraith laboratories.[14]

$K_2S_3O_6$: Each of the two methods described in Brauer's book[11] was used. A set of X-ray data was collected for a single crystal to confirm its structure. The structure is known[15]: orthorhombic, *Pmnb*, $a = 5.751(6)$, $b = 9.810(1)$, $c = 13.700(3)$, $Z = 4$ and $R = 0.0381$ for 672 observed reflections [$> 2\sigma(I)$]. − $K_2S_3O_6$ (270.37): calcd. S 35.57; found S 35.73.

p-$[Co(tren)(NH_3)Cl]S_2O_6\cdot H_2O$ (1): A solution of partly dissolved *p*-$[Co(tren)(NH_3)Cl]Cl\cdot ClO_4$ (1.97 g, 5 mmol) in 40 mL of water was filtered directly into a 50-mL aqueous solution containing $Na_2S_2O_6\cdot 2H_2O$ (7.27 g, 30 mmol) so that the two solutions formed layers. Dark red crystals began to grow within 30 min. − $C_6H_{23}ClCoN_5O_7S_2$ (435.79): calcd. C 16.54, H 5.33, Cl 8.13, Co 13.52, N 16.08, S 14.71; found C 16.24, H 5.52, Cl 8.20, Co 14.03, N 15.79, S 15.10.

***trans*-$[Co(tren)(NH_3)Cl]S_2O_6$ (2):** 0.40 g(1.2 mmol) of *t*-$[Co(tren)(NH_3)Cl]Cl_2$ was dissolved in 5 mL of water and added to a 10-mL aqueous solution of 0.50 g (2.1 mmol) of $Na_2S_2O_6\cdot 2H_2O$. Purple crystals were formed immediately and collected the next day (0.21 g, 41%). − $C_6H_{21}ClCoN_5O_6S_2$ (417.77): calcd. C 17.25, H 5.07, N 16.76; found C 17.31, H 5.08, N 16.35.

***cis*-$[Co(en)_2(NH_3)Br]S_3O_6$ (3):** To a saturated solution of *cis*-$[Co(en)_2(NH_3)Br]Br_2$ in water was added an aqueous solution of $K_2S_3O_6$. Crystals suitable for X-ray work were grown from water by the same method but using more dilute solutions. − $C_4H_{19}BrCoN_5O_6S_3$ (468.24): calcd. C 10.29, H 4.09, N 14.96; found C 10.28, H 4.16, N 14.85.

p-$[Co(tren)(NH_3)(OSO_3)]ClO_4$ (4): This compound was prepared by the same method used for **1** except for using $K_2S_3O_6$ instead of $Na_2S_2O_6\cdot 2H_2O$. The solution was frequently filtered off in order to remove a white powdery precipitate, most likely S and $KClO_4$. A small amount of single crystals were obtained by liquid diffusion with ethanol after 2 months.

Crystallography: For all four compounds, the intensity data were collected with an Enraf−Nonius CAD-4 diffractometer at room temperature and SHELXS-86[16] and SHELXL-93[17] were used to solve and refine the structures. All the hydrogen atoms of **1**, **2** and **3** were located from difference maps and refined isotropically; those of **4** were placed in their geometrically ideal positions with isotropic temperature factors 1.2 times those of the attached non-hydrogen atoms. In the refinement of **3**, relatively large residual electron densities found in the final difference map were ignored since they are too close to cobalt and bromide (< 1 Å). The structures of **2** and **4**, for which many weak reflections were collected, yielded *R* factors a little higher than the other two. Parameters for data collection and structure refinements are summarized in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre[7] as supplementary publication no. CCDC-118583 to -118586. 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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[1] I. Bernal, J. Cetrullo, W. G. Jackson, *Inorg. Chem.* **1993**, *32*, 4098.

[2] H. Chun, I. Bernal, *Eur. J. Inorg. Chem.* **1999**, 717.

[3] I. Bernal, J. Cetrullo, W. G. Jackson, *J. Coord. Chem.* **1993**, *28*, 89.

[4] D. A. Buckingham, P. J. Creswell, A. M. Sargeson, *Inorg. Chem.* **1975**, *14*, 1485.

[5] M. J. Gaudin, C. R. Clark, D. A. Buckingham, *Inorg. Chem.* **1986**, *25*, 2569.

[6] D. A. Buckingham, C. R. Clark, W. S. Webley, *Aust. J. Chem.* **1980**, *33*, 263.

[7] Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

[8] D. A. Buckingham, J. D. Edwards, G. M. McLaughlin, *Inorg. Chem.* **1982**, *21*, 2770.

[9] K. Asakura, K. Kobayashi, Y. Mizusawa, T. Ozawa, S. Osami, S. Yoshikawa, *Physica D* **1995**, *84*, 72.

[10] W. G. Palmer, *Experimental Inorganic Chemistry*, Cambridge University Press, **1954**, p. 372.

[11] F. Fehér in *Handbook of Preparative Inorganic Chemistry*, 2nd ed. (Ed.:G. Brauer), Academic Press, New York, **1967**, vol. 1, p. 398.

[12] R. W. Hay, P. J. Morris in *Metal Ions in Biological Systems* (Ed.: H. Sigel), vol. 5, Basel, New York, **1976**, p. 224.

[13] P. A. Sutton, D. A. Buckingham, *Acc. Chem. Res.* **1987**, *20*, 357.

[14] Galbraith Laboratories, Inc., P. O. Box 51610, Knoxville, TN, 37950−1610, USA.

[15] J. M. Stewart, J. T. Szymanski, *Acta Crystallogr.* **1979**, *B35*, 1967.

[16] G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467.

[17] G. M. Sheldrick, *SHELXL-93, A program for crystal structure determination*, University of Göttingen, **1993**.

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