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meso-Tetrakis(ethylenediamine)-1κ^4N,N';3κ^4N,N'-di-μ-sulfidoacetato-1:2κ^3O,S:S;2:3κ^3S:S,O-dicobalt(III)-silver(I) triperchlorate

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In the crystal structure of the title compound, $[AgCo_2(C_2H_4O_2S)_2(C_2H_8N_2)_4](ClO_4)_3$, the Ag^I atom is located on an inversion center and is linearly coordinated by two sulfide S atoms from Δ- and Λ-$[Co^{III}(C_2H_4O_2S)(C_2H_8N_2)_2]^+$ octahedral units, forming a *meso* configurational S-bridged Co^{III}–Ag^I–Co^{III} trinuclear structure.

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Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.006 Å
Disorder in solvent or counterion
R factor = 0.032
wR factor = 0.085
Data-to-parameter ratio = 14.0

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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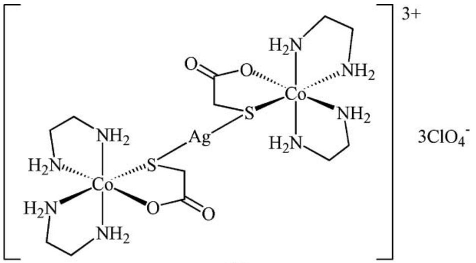
Comment

Thiolato groups coordinated to a metal center possess a relatively strong Lewis basicity, which allows them to bind with a second metal center (Konno, 2004). Heeg *et al.* (1980) reported that the thiolato group in $[Co^{III}(tga)(en)_2](ClO_4)$ (tga = mercaptoacetate, en = ethylenediamine) binds with an Ag^I ion to afford an S-bridged Co^{III}–Ag^I–Co^{III} trinuclear complex, *racemic*-$[Ag\{Co(tga)(en)_2\}_2](ClO_4)_3$, (II). In (II), the two $[Co^{III}(tga)(en)_2]^+$ units have the same chiral configuration (Δ or Λ) to form a *racemic* (ΔΔ/ΛΛ) compound. In this paper, we report the structure of the *meso* (ΔΛ) compound of $[Ag\{Co(tga)(en)_2\}_2](ClO_4)_3$, (I).



(I)

The asymmetric unit of (I) contains half a centrosymmetric complex cation, an ordered perchlorate anion, and half a centrosymmetrically disordered perchlorate anion. The entire complex cation is composed of two approximately octahedral $[Co^{III}(tga)(en)_2]^+$ units that are linked by an Ag^I atom through Ag—S bonds, forming a linear-type S-bridged Co^{III}–Ag^I–Co^{III} trinuclear structure in $[Ag\{Co(tga)(en)_2\}_2]^{3+}$ (Fig. 1). The two $[Co(tga)(en)_2]^+$ units in (I) have the opposite chiral configurations (Δ and Λ) to give a *meso* compound (ΔΛ), which is distinct from the structure of (II) (Heeg *et al.*, 1980). In (I), the Ag atom is located on a crystallographic inversion center and thus adopts a strictly linear coordination geometry, while compound (II) contains an angular Ag^I atom [S—Ag—S = 169.34 (9)°]. In addition, the Ag—S bonds in (I) [Ag1—S1 = 2.3954 (10) Å] are appreciably longer than those in (II) [Ag—S = 2.370 (1) Å]. This could be ascribed to the contact of perchlorate anions with the Ag^I center [Ag···O = 3.090 (5) and 3.124 (7) Å] in (I) (Konno *et al.*, 2002). The other bond

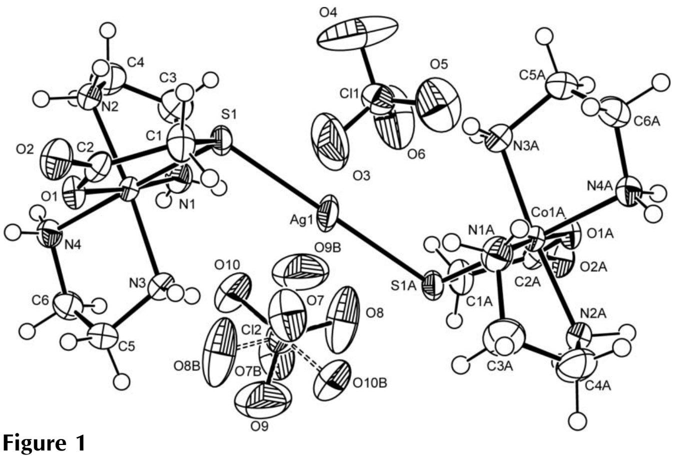


Figure 1
A view of the molecular structure of (I), showing the atom-numbering scheme and 50% probability displacement ellipsoids. Both the disordered components of ClO_4^- anions are shown. The suffixes A and B correspond to symmetry codes $(1 - x, 1 - y, 1 - z)$ and $(1 - x, -y, 1 - z)$, respectively.

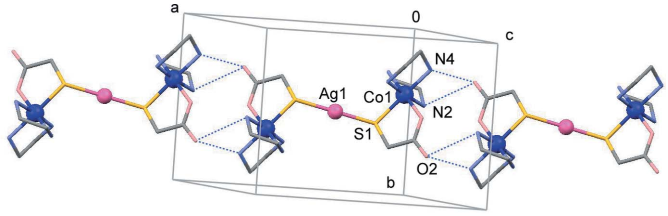


Figure 2
A view of the one-dimensional chain structure formed along the *a* axis in (I). Dashed lines indicate N—H···O hydrogen bonds. H atoms have been omitted for clarity.

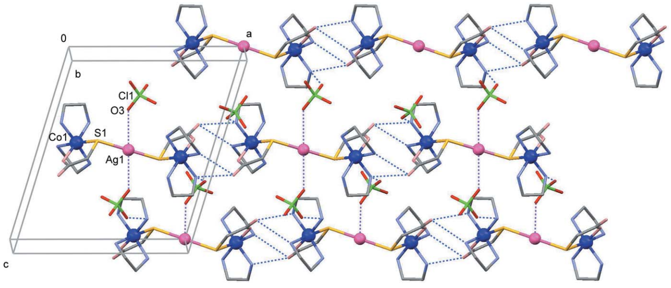


Figure 3
Packing diagram of (I). Dashed lines indicate N–H···O hydrogen bonds (blue) and Ag···O interactions (purple). H atoms and the minor components of disordered ClO_4^- anions have been omitted for clarity.

distances and angles in (I) are similar to those in (II) (Table 1). In each $[Co^{III}(tga)(en)_2]^+$ unit of (I), the tga *O*,*S*-chelate ring is almost planar, while the two en *N*,*N*′-chelate rings have a *gauche* conformation with *lel* (λ for Δ and δ for Λ) and *ob* (δ for Δ and λ for Λ) forms. This conformational feature is the same as that in (II).

The crystal structure of (I) is stabilized by several intermolecular N—H···O hydrogen-bonding interactions (Table 2). It is noteworthy that each complex cation is connected with two adjacent cations through eight N—H···O=C hydrogen bonds to construct a one-dimensional chain structure (Fig. 2). The one-dimensional chains are further bridged by ordered perchlorate anions through N—H···O hydrogen bonds besides the Ag···O bonding interaction (Fig. 3).

Experimental

$[Ag\{Co(tga)(en)_2\}_2](ClO_4)_3$ was prepared by a method described in the literature (Heeg *et al.*, 1980), and crystals of the *meso* compound (I) were grown from aqueous $NaClO_4$, instead of the use of aqueous $HClO_4$.

Crystal data

$[AgCo_2(C_2H_4O_2S)_2(C_2H_8N_2)_4](ClO_4)_3$
$M_r = 944.69$
Monoclinic, $P2_1/n$
$a = 12.486$ (3) Å
$b = 8.974$ (2) Å
$c = 14.410$ (2) Å
$\beta = 106.857$ (14)°
$V = 1545.2$ (6) Å^3
$Z = 2$
$D_x = 2.030$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 2.16$ mm^{-1}
$T = 296$ (2) K
Prism, red
0.35 × 0.35 × 0.25 mm

Data collection

Rigaku AFC-7S diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.492$, $T_{max} = 0.583$
3700 measured reflections
3542 independent reflections
2788 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 27.5°$
3 standard reflections every 150 reflections intensity decay: 0.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.085$
$S = 1.03$
3542 reflections
253 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0367P)^2 + 1.5353P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.59$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ag1—S1	2.3954 (10)	Co1—N2	1.952 (3)
Ag1—O3	3.090 (5)	Co1—N3	1.965 (3)
Ag1—O7	3.124 (7)	Co1—N4	1.983 (3)
Co1—O1	1.897 (2)	Co1—S1	2.2458 (10)
Co1—N1	1.957 (3)		
S1—Ag1—S1^{i}	180.0	O1—Co1—N1	175.06 (12)
N4—Co1—S1	176.16 (10)	N2—Co1—N3	175.04 (13)

Symmetry code: (i) $-x + 1, -y + 1, -z + 1$.

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H4···O2^{ii}	0.92 (5)	2.27 (5)	3.053 (4)	143 (4)
N4—H8···O2^{ii}	0.87 (4)	2.53 (4)	3.004 (4)	115 (3)
N1—H2···O4^{iii}	0.78 (5)	2.34 (5)	3.057 (6)	152 (5)
N2—H3···O6^{iv}	0.81 (4)	2.26 (4)	2.993 (5)	151 (3)

Symmetry codes: (ii) $-x, -y + 1, -z + 1$; (iii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$; (iv) $-x + \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.

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H atoms bound to C atoms were placed at calculated positions (C—H = 0.97 Å) and refined as riding, with $U_{iso}(H) = 1.2U_{eq}(C)$. H atoms bound to N atoms were refined freely, giving N—H = 0.78 (5)–0.92 (5) Å. Atoms O7, O8, O9 and O10, disordered about the inversion center at atom Cl2, were refined with a fixed occupancy of 0.5.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: Crystal structure (Rigaku/MSC, 2004); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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