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Key indicators

Single-crystal X-ray study
 $T = 273\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$
 R factor = 0.021
 wR factor = 0.048
Data-to-parameter ratio = 19.2For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Bis(μ - N,N -diethyldithiocarbamato- $\kappa^3S,S':S'$)bis(μ - N,N -diethyldithiocarbamato- κ^2S,S')silver(II)

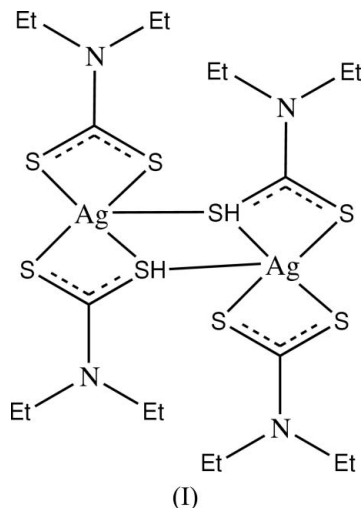
The title Ag^{II} complex, $[\text{Ag}_2(\text{C}_5\text{H}_{10}\text{NS}_2)_4]$, has been obtained by the reaction of AgNO_3 and $\text{Na}(\text{detc})$ with a 1:2 molar ratio in a methanol solution at 353 K (detc = N,N -diethyldithiocarbamate). In the crystal structure of the complex, two detc anions chelate to an Ag^{II} ion in an S,S' -bidentate manner, and an S atom of the detc anion bridges to the neighboring Ag^{II} ion to form the centrosymmetric dinuclear molecule.

Received 7 June 2006

Accepted 15 August 2006

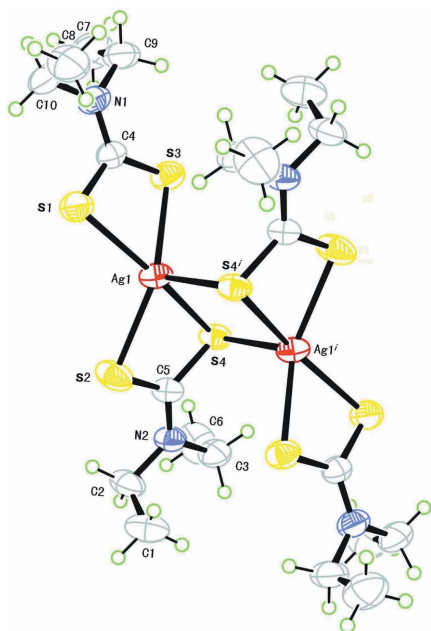
Comment

Ag^{I} compounds incorporating dialkyldithiocarbamate have been widely studied (Yamaguchi *et al.*, 1976; Hesse & Nilson, 1969). The partial oxidation product $[\text{Ag}_6(\text{detc})_4(\text{SCN})_4]$ (detc = N,N -diethyldithiocarbamate) was prepared by the reaction of the Ag^{I} compound $[\text{Ag}(\text{detc})]_6$ and $(\text{SCN})_2$ at room temperature (Calabro *et al.*, 1981). Recently, we obtained the title detc complex of Ag^{II} , (I), in a solvent-thermal reaction. We report here the X-ray crystal structure of (I).

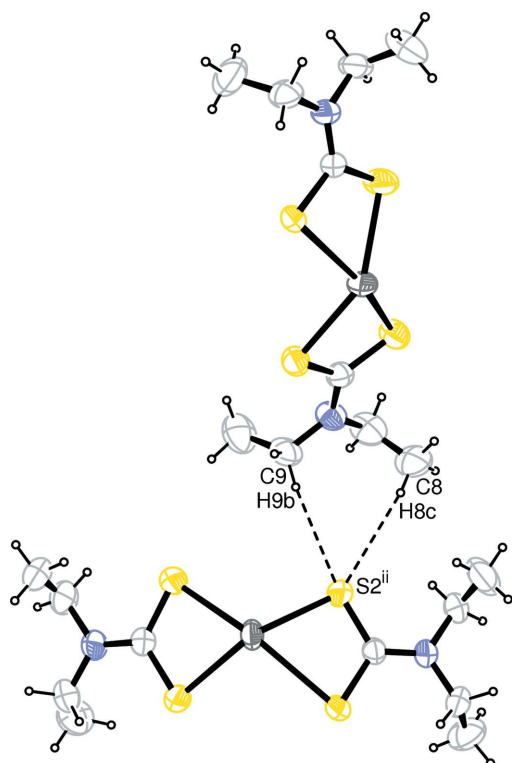


The dinuclear molecular structure of (I) is shown in Fig. 1. While two detc anions chelate to the Ag^{II} atom, the S4 atom of the C5-detc anion bridges the Ag^{II} atom to form the centrosymmetric dinuclear molecule [symmetry code: (i) $1 - x, 1 - y, -z$]. Atom Ag^{II} is coordinated by five S atoms with a distorted trigonal-bipyramidal geometry. The $\text{Ag}-\text{S}$ bonds involving the bridging atom (S4) are significantly longer than other $\text{Ag}-\text{S}$ bonds (Table 1). This is consistent with what is found in $[\text{M}(\text{detc})_2]_2$ ($M = \text{Zn}, \text{Cd}, \text{Hg}$; Tiekink, 2003).

The C4-S1 and C4-S3 bond distances are almost identical, which implies that the C4-containing thiocarboxyl group should be a deprotonated group. Atom S2 is involved in two


Figure 1

The molecular structure of (I) with 50% probability displacement ellipsoids (arbitrary spheres for H atoms) [symmetry code: (i) $1 - x, 1 - y, -z$].


Figure 2

The weak $C-H \cdots S$ hydrogen bonding (dashed lines) between complexes [symmetry code: (ii) $\frac{1}{2} + x, \frac{1}{2} - y, \frac{1}{2} + z$].

weak intermolecular $C-H \cdots S$ hydrogen bonds (Fig. 2 and Table 2), suggesting that there is no H atom bonded to the S2 atom. Although the difference of 0.037 (3) Å between the C5–S4 and C5–S2 bonds is significant, it is considered to be due to bridging of atom S4. This means that the C5-thio-

carboxyl group is also a deprotonated one. These facts clearly suggest that the title compound is an Ag^{II} complex, which agrees with that cited above (Calabro *et al.*, 1981).

The weak $C-H \cdots S$ interactions occur between complexes (Table 2), helping to stabilize the crystal structure of (I).

Experimental

$AgNO_3$ (0.046 g, 1 mmol) was added to a methanol solution (10 ml) of $NaS_2CN(C_2H_5)_2$ (0.342 g, 2 mmol). The mixture was put in an autoclave at 353 K for 10 h and gradually cooled to room temperature. Yellow single crystals of (I) were obtained in 45% yield.

Crystal data

$[Ag_2(C_5H_{10}NS_2)_4]$
 $M_r = 808.78$
 Monoclinic, $P2_1/n$
 $a = 10.0453$ (4) Å
 $b = 10.7601$ (4) Å
 $c = 16.0064$ (6) Å
 $\beta = 103.931$ (2)°
 $V = 1679.22$ (11) Å³

$Z = 2$
 $D_x = 1.600$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 1.68$ mm⁻¹
 $T = 273$ (2) K
 Block, yellow
 $0.40 \times 0.35 \times 0.30$ mm

Data collection

Bruker APEX-II diffractometer
 φ and ω scans
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 2002)
 $T_{min} = 0.518, T_{max} = 0.612$

12005 measured reflections
 3029 independent reflections
 2594 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.024$
 $\theta_{max} = 25.2^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.021$
 $wR(F^2) = 0.048$
 $S = 1.02$
 3029 reflections
 158 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0211P)^2 + 0.4069P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.19$ e Å⁻³
 $\Delta\rho_{min} = -0.45$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Ag1–S1	2.5927 (6)	S1–C4	1.722 (2)
Ag1–S2	2.5403 (6)	S2–C5	1.714 (2)
Ag1–S3	2.5544 (6)	S3–C4	1.730 (2)
Ag1–S4 ⁱ	2.6256 (6)	S4–C5	1.751 (2)
Ag1–S4	2.8107 (6)		
S2–Ag1–S3	145.16 (3)	S1–Ag1–S4 ⁱ	103.00 (2)
S2–Ag1–S1	110.42 (2)	S2–Ag1–S4	67.255 (18)
S3–Ag1–S1	70.801 (19)	S3–Ag1–S4	99.088 (17)
S2–Ag1–S4 ⁱ	106.06 (2)	S1–Ag1–S4	159.28 (2)
S3–Ag1–S4 ⁱ	107.437 (19)	S4 ⁱ –Ag1–S4	97.250 (16)

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

Table 2

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
C8–H8C \cdots S2 ⁱⁱ	0.96	2.98	3.892 (3)	159
C9–H9B \cdots S2 ⁱⁱ	0.97	2.92	3.825 (3)	156

Symmetry code: (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$.

Methyl H atoms were placed in calculated positions with $C-H = 0.96$ Å and torsion angles were refined to fit the electron density; $U_{iso}(H) = 1.5U_{eq}(C)$. Methylene H atoms were placed in calculated

positions with C—H = 0.97 Å and refined in riding mode, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINTE* (Bruker, 1999); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

This work was supported by the Natural Science Foundation of Guangdong Province (990463) and the National Natural Science Foundation of China (29561002).

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