simple adduct formation as well as oxidative addition and halide abstraction.

Acknowledgment. This research was supported by a grant from the National Science Foundation (CHE-9011610). We thank M. M. Miller for experimental assistance. The Siemens R3m/E diffractometer and computing system were purchased with a grant from the National Science Foundation (CHE-8103011).

Supplementary Material Available: Figure S-1, showing the full Ag(I) ion coordination sphere, and Tables S-I–S-V, listing crystallographic data, bond distances, bond angles, anisotropic thermal parameters, and hydrogen atom coordinates and thermal parameters (4 pages); Table S-VI, listing observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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Synergism in a Transition Metal Cluster Compound. Crystal and Molecular Structure of a Polysilver Cluster Molecule with an Unusual Bridging Sulfur Atom, $Ag_{11}S(Et_2dtc)_9$

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Received October 17, 1991

One of our current research interests is to understand the synergistic effect in transition metal cluster compounds through the studies of synthetic routes, stereo- and electronic structures, and their chemical and physical properties.[1] Dialkyldithiocarbamates (R_2dtc^-) acting as either bridging or terminal ligands play an important role in modern coordination chemistry.[2–6] The dialkyldithiocarbamato molecules of the univalent coinage metals (Cu, Ag, and Au) form a class of compounds where steric restrictions strongly influence the crystal structures.[2] We had prepared the cubane-like structure compound of Mo(W)–Fe–R_2dtc and various structural types of Mo(W)–Cu–R_2dtc compounds.[3,4] In an attempt to prepare a heterometal Mo(W)–Ag cluster molecule similar to the Mo(W)–Cu–R_2dtc system, we obtained a polysilver compound whose molecular structure is completely different from that of silver(I) diethyldithiocarbamate or its β-modification.[2,5,6] Herein we report the synthesis and crystal structure of $Ag_{11}S(Et_2dtc)_9$.

Experimental Section

All operations were carried out under a pure dinitrogen atmosphere.

Preparation of $Ag_{11}S(Et_2dtc)_9$. A direct electrochemical synthetic method similar to that of Casey[7] was used to prepare the title compound. The crystal thus obtained could be used for the measurement of the crystal unit cell but was not suitable for the crystal structure determination.[8] A chemical synthetic method was then developed. A mixture of 0.34 g of $AgNO_3$ (2 mmol) and 0.45 g of $Na(Et_2dtc)\cdot 3H_2O$ (2 mmol) in 40 mL of DMF was added with $(NH_4)_2MoS_4$ (0.5 mmol) at 25 °C. After being stirred for 24 h, the dark red solution was filtered and the filtrate was diluted with 20 mL of acetone. The solution was kept at 4 °C for several days, and the orange prismlike crystals were collected,

Table I. Crystallographic Data for $Ag_{11}S(Et_2dtc)_9$

chem formula: $C_{45}H_{90}Ag_{11}N_9S_{19}$
fw = 2553.07
space group: $R3c$
a = 18.661 (6) Å
c = 43.227 (8) Å
V = 13036 Å^3
Z = 6
T = 296 K
λ = 0.71069 Å
d_{calcd} = 1.951 g cm^{-3}
μ(Mo Kα) = 28.726 cm^{-1}
R^a = 0.044
$R_w{}^b$ = 0.045

[a] $R = \sum(|F_o| - |F_c|)/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum(|F_o|)^2]^{1/2}$.

Table II. Atomic Coordinates and Thermal Parameters for $Ag_{11}S(S_2CNEt_2)_9$

atom	x	y	z	B,[a] Å^2
Ag(1)	0.02181 (8)	0.1512 (1)	0.0628 (0)	5.37 (4)
Ag(2)	−0.12086 (8)	0.03507 (8)	0.10469 (4)	5.00 (3)
Ag(3)	−0.1383 (1)	0.02824 (9)	0.03268 (4)	6.33 (4)
Ag(4)	0.0000 (0)	0.0000 (0)	0.13348 (7)	4.91 (5)
Ag(5)	0.0000 (0)	0.0000 (0)	0.01196 (7)	7.21 (6)
S(1)	0.0000 (0)	0.0000 (0)	0.0698 (2)	4.1 (1)
S(11)	0.1087 (3)	0.2255 (2)	0.1116 (1)	3.7 (1)
S(12)	−0.0286 (2)	0.1092 (2)	0.1548 (1)	3.6 (1)
S(21)	−0.0869 (3)	0.1759 (3)	0.0358 (1)	4.7 (1)
S(22)	−0.1854 (3)	0.1222 (3)	0.0954 (1)	5.5 (2)
S(31)	0.1459 (3)	0.2591 (3)	0.0268 (1)	6.0 (1)
S(32)	−0.1312 (3)	−0.0440 (3)	−0.0234 (1)	6.5 (1)
N(10)	0.0194 (7)	0.2689 (7)	0.1467 (3)	3.9 (3)
N(20)	−0.1647 (8)	0.2461 (7)	0.0597 (4)	4.8 (4)
N(30)	0.091 (1)	0.285 (1)	−0.0251 (4)	11.2 (6)
C(10)	0.0310 (8)	0.2049 (8)	0.1385 (3)	3.1 (3)
C(11)	−0.051 (1)	0.258 (1)	0.1647 (4)	6.6 (6)
C(12)	−0.028 (1)	0.271 (1)	0.1981 (5)	7.8 (8)
C(13)	0.072 (1)	0.3534 (8)	0.1353 (4)	4.0 (4)
C(14)	0.040 (1)	0.367 (1)	0.1046 (5)	6.1 (6)
C(20)	−0.1483 (9)	0.1850 (8)	0.0643 (4)	3.7 (4)
C(21)	−0.146 (1)	0.294 (1)	0.0301 (4)	5.8 (5)
C(22)	−0.060 (2)	0.372 (1)	0.0333 (6)	8.2 (8)
C(23)	−0.209 (1)	0.270 (1)	0.0846 (5)	7.4 (7)
C(24)	−0.295 (1)	0.237 (2)	0.0812 (7)	9.5 (9)
C(30)	−0.224 (1)	−0.124 (1)	−0.0095 (4)	8.0 (6)
C(31)	0.057 (2)	0.271 (3)	−0.0599 (8)	17 (2)
C(32)	−0.028 (2)	0.219 (3)	−0.0604 (9)	22 (2)
C(33)	0.098 (2)	0.358 (1)	−0.0157 (9)	17.9 (9)
C(34)	0.187 (2)	0.420 (2)	−0.026 (1)	23 (1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as (4/3) $[a^2(B(1,1)) + b^2(B(2,2)) + c^2(B(3,3)) + ab(\cos\gamma)(B(1,2)) + ac(\cos\beta)(B(1,3)) + bc(\cos\alpha)(B(2,3))]$.

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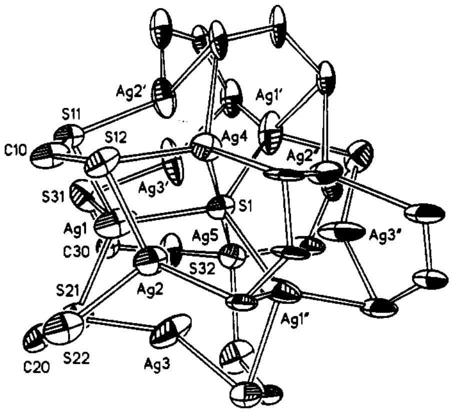

Figure 1. Perspective view of the inner coordination sphere of $Ag_{11}S(Et_2dtc)_9$, omitting NEt_2 groups for clarity. Thermal ellipsoids are drawn at the 30% probability level.

washed with acetone, and dried in vacuo to afford 0.20 g (44%) of the title compound. The IR spectrum (KBr) shows characteristic Ag–S absorptions (555, 405, 430, and 390 cm^{-1}) which differ from those of $Ag(Et_2dtc)$.[9] Anal. Calcd for $C_{45}H_{90}Ag_{11}N_9S_{19}$: C, 21.17; H, 3.55; N, 4.94; S, 23.86. Found: C, 21.75; H, 3.68; N, 4.86; S, 23.55. Elemental analyses were performed by the Analytical Chemistry Group of this institute.

Instrumentation. Proton NMR spectra were recorded on a Varian FT-80A spectrometer. DMSO-d_6 was used as solvent and TMS as internal standard, with positive values given to downfield shifts. IR spectra were recorded on a Digilab 20E/D spectrophotometer.

Structure Determination. Diffraction data for the title compound were collected at room temperature on a Rigaku AFC5R diffractometer using graphite-monochromatized Mo Kα radiation (λ = 0.71069 Å). An empirical absorption correction (ψ scan) and DIFABS were applied. After data reduction (including correction for Lorentz and polarization effects), the remaining 1784 unique reflections with $I > 3\sigma(I)$ were used for the subsequent structure solution and refinement. Calculations were performed on a VAX 11/785 computer with the SDP program package. The structure was solved by direct methods. Full-matrix least-squares refinement with anisotropic thermal parameters for all non-hydrogen atoms led to convergence with R = 0.044. Crystallographic data appear in Table I, and the atomic coordinates and average thermal parameters are listed in Table II. The structure of the title compound is depicted in Figure 1.

Results and Discussion

At a mild reaction temperature in DMF solvent and with similar stoichiometric amounts of reactants, $FeCl_2$ reacts with MoS_4^{2-} and R_2dtc^- to form a single-cubane compound,[3] while CuCl forms a double-defect cubane-like compound.[4] However, in a similar reaction, $AgNO_3$ reacts with MoS_4^{2-} and R_2dtc^- to form a chainlike complex similar to other Ag–R_2dtc compounds.[2,5] The unusual "central" sulfur atom may come from the hydrolysis of MoS_4^{2-}

$$MoS_4^{2-} + H_2O \rightarrow MoS_3O^{2-} + H_2S$$

Using WS_4^{2-} in place of MoS_4^{2-}, the title compound was also obtained in a similar reaction.

Table III. Selected Atomic Distances (Å) and Bond Angles (deg) for $Ag_{11}S(Et_2dtc)_9$

Ag(1)–Ag(2)	3.048 (2)	Ag(2)–S(12)	2.681 (5)
Ag(1)–Ag(3)	3.006 (3)	Ag(2)–S(22)	2.493 (6)
Ag(2)–Ag(3)	3.126 (3)	Ag(3)–S(1)	3.299 (5)
Ag(2)–Ag(4)	2.922 (2)	Ag(3)–S(21)	2.428 (6)
Ag(3)–Ag(5)	3.017 (2)	Ag(3)–S(31)'	2.484 (6)
Ag(1)–S(1)	2.659 (2)	Ag(3)–S(32)'	2.810 (6)
Ag(1)–S(11)	2.600 (6)	Ag(4)–S(1)	2.751 (9)
Ag(1)–S(21)	2.575 (6)	Ag(4)–S(12)'	2.524 (5)
Ag(1)–S(31)	2.679 (7)	Ag(5)–S(1)	2.502 (9)
Ag(2)–S(1)	3.043 (5)	Ag(5)–S(32)	2.644 (7)
Ag(2)–S(11)'	2.530 (5)		
S–C[a]	1.73 ± 0.02	N–C(C)[a]	1.49 ± 0.08
(S)C–N[a]	1.37 ± 0.02	C–C[a]	1.48 ± 0.06
Ag(4)–S(1)–Ag(5)	180.01 (2)	S(11)'–Ag(2)–S(12)	114.8 (2)
S(1)–Ag(1)–S(11)	101.4 (2)	S(11)'–Ag(2)–S(22)	113.3 (2)
S(1)–Ag(1)–S(21)	121.7 (2)	S(12)–Ag(2)–S(22)	100.9 (2)
S(1)–Ag(1)–S(31)	118.7 (2)	S(21)–Ag(3)–S(31)'	147.8 (2)
S(11)–Ag(1)–S(21)	127.5 (2)	Ag(1)–Ag(2)–Ag(3)	58.25 (6)
S(11)–Ag(1)–S(31)	89.8 (2)	Ag(1)–Ag(3)–Ag(2)	59.60 (5)
S(21)–Ag(1)–S(31)	93.7 (2)	Ag(2)–Ag(1)–Ag(3)	62.16 (6)

[a] Average distances with standard deviations.

The molecule of the title compound consists of 3-fold axis through Ag(4)–S–Ag(5) and three equivalent units of $Ag_3(Et_2dtc)_3$ (U3). It is interesting to see that the central sulfur atom is weakly coordinated by five silver atoms: 3 Ag(1), Ag(4), and Ag(5) (Ag–S distances vary from 2.502 to 2.751 Å). Ag(4) and Ag(5) coordination polyhedra are trigonal pyramids, elongated and compressed along the molecular 3-fold axis Ag(4)–S–Ag(5), respectively. Within a U3 unit, the three Ag atoms and the three Et_2dtc bridging ligands are geometrically different from one another. The Ag(1) coordination environment is a highly distorted tetrahedron, while Ag(2) is coordinated by three sulfur atoms and Ag(3) essentially by two, S(21) and S(31), if the atomic distance of Ag–S > 2.8 Å is considered noncoordinating. All sulfur atoms except S(22) and S(32) of the dithiocarbamato ligands act as bridging atoms connecting two silver atoms, but their geometric environments are all different, as indicated in Table III. The three Et_2dtc ligands attach to the molecule at various "degrees of tightness"; for example, ligand 3 coordinates loosely to the molecule, as S–Ag distances of this group are all longer than 2.60 Å except Ag(3)–S(31) (2.484 Å). Therefore, it would be understood that the thermal parameters of N(30) and C(31)–(34) are quite large.

Only one set of proton NMR signals of $CH_3CH_2^-$ was observed: a triplet at 1.34 and a quintet at 4.01 ppm with fwhm of 5 Hz in DMSO-d_6 solution. This fact confirms that the molecule is diamagnetic, as expected from the valence state of the silver atoms, and that the geometrical differences of the sulfur atoms have little influence on the chemical shielding at the other end of the diethyldithiocarbamato ligands. Similar proton NMR spectra were observed for $[M_2Cu_5S_6O_2(Et_2dtc)_3]^{2-}$ (M = Mo, W) and for free the ligand Et_2dtc^-.[4g]

In conclusion, the title compound is paramagnetic and its valence electrons are localized, so that there is no synergistic effect in the molecule. The synergistic character appears in the synthetic routes: at a mild reaction temperature in DMF solvent and similar stoichiometric amounts of reactants, the compound formed by $AgNO_3$ is very different from that formed by CuCl or $FeCl_2$.[3,4]

Acknowledgment. This work was partly supported by the National Natural Science Foundation.

Supplementary Material Available: A listing of the crystal data and experimental parameters (Table S1), a table of anisotropic thermal parameters (Table S2), and extended lists of interatomic distances and bond angles (Tables S3 and S4) (5 pages); a list of observed and calculated structure factor amplitudes (21 pages). Ordering information is given on any current masthead page.

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(8) A mixture of $(Et_4N)_2MoS_4$ (0.25 mmol) and $(Et_2NCS_2)_2$ (0.67 mmol) in 50 mL of acetone with $(Et_4N)PF_6$ (0.1 mmol) as supporting electrolyte was stirred for 30 min. An Ag plate anode (surface area 2 cm^2) and a Pt cathode were then immersed in the solution. The quantity of the electric charge (0.62 mF) that flowed through the solution agrees well with the weight of the Ag anode lost (65 mg), if Ag from the anode dissolved into the solution is oxidized to Ag(I). Crystal data giving a = 18.637 Å, c = 42.91 Å, and the preliminary positions of nine Ag atoms determined by the direct methods using 1443 reflections with $I > 2\sigma(I)$ were in good agreement with those given in the main text.

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