

# A 2-D Framework Built from the Tetranuclear $\text{Ag}_4(2,2\text{-dimethylglutarate})_2$ Oligomeric Unit

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**The structure of the gel-grown coordination polymer  $\text{Ag}_4(2,2\text{-dimethylglutarate})_2$  was determined by X-ray crystallography. It crystallizes in the monoclinic space group  $P2_1/a$ , with  $a = 10.67(1)$  Å,  $b = 6.334(6)$  Å,  $c = 13.32(1)$  Å,  $\beta = 96.34(4)^\circ$ ,  $V = 895(2)$  Å<sup>3</sup>, and  $Z = 4$ . The structure is based on an unusual oligomeric unit, which was first found in silver(I) glutarate, and consists of a planar, centrosymmetric, tetranuclear silver cluster coordinated by two bridging ligands disposed at both sides of the metal plane. Additional Ag–O coordination bonds link the units together in a 2-D framework. Short metal–metal contacts in the range 2.81–3.40 Å, are observed within the layers, suggesting that  $d^{10}\text{--}d^{10}$  interactions contribute to the stabilization of the structure.**

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## INTRODUCTION

The construction of molecular-based infinite frameworks from small soluble components has been receiving an increased interest in the past years. The assembly of such supramolecular structures is usually achieved via hydrogen bonding (1), metal coordination with multifunctional ligands (2), or even weak metal–metal attractive interactions (3).

In this context, we recently examined the structure of polymers obtained through self-assembly of silver(I) cations with succinic and glutaric acids (4, 5). In the latter case, from which the present work was inspired, it was found that the oligomeric unit consists of a tetranuclear silver(I) cluster coordinated by two glutarate dianions as depicted in Scheme 1. Polymerization was achieved through "lateral" weak Ag–O interactions forming, thus, a polynuclear 2-D solid. Interestingly, "intermolecular" metal–metal distances

close or inferior to the van der Waals diameter of silver were observed within the sheets, indicating that, probably, weak  $d^{10}\text{--}d^{10}$  interactions contribute to the crystal packing.

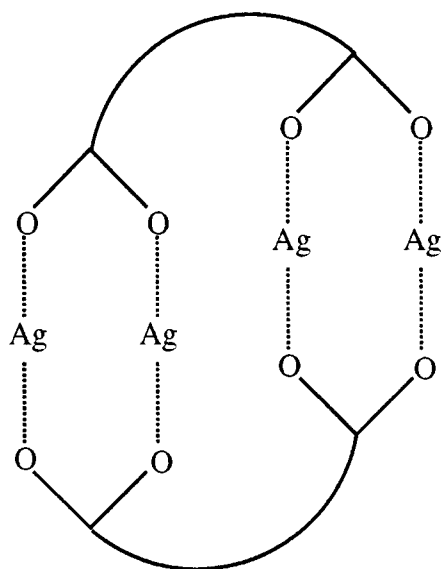
In view of these results we wondered if the aforementioned tetranuclear unit is maintained when various substituents are present in the glutarate skeleton and, if this is the case, what would be their influence on the crystal packing, especially on the metal–metal contacts. In the present work we examine the crystal structure of  $\text{Ag}_2(2,2\text{-dimethylglutarate})$ . We show that the tetranuclear oligomeric unit is indeed maintained and a 2-D solid is formed again.

## EXPERIMENTAL

Crystals suitable for X-ray crystallography were prepared by the silica gel method (6). The choice of this method was dictated by the extremely low solubility of this type of solid. A solution of 0.5 ml 1 N  $\text{HNO}_3$  was added to 10 ml of an aqueous solution of 0.1 M 2,2-dimethylglutaric acid. The resulting mixture was slowly neutralized, under vigorous stirring, by a silica gel solution ( $d = 1.06$ ) up to pH 6. The gelling solution was allowed to stand in a test tube for 4 days and then, 10 ml of an aqueous solution of 0.2 M  $\text{AgNO}_3$  was added at the top of the gel. In a few days thin crystals appeared in the gel column and were left to grow for about 1 month. Then pale yellow platelets of mean linear dimensions  $0.1 \times 0.5 \times 0.6$  mm were collected mechanically from the gel. Their examination by Weissenberg photographs showed that they were of poor quality and most of them were twinned.

Crystallographic data are presented in Table 1. The unit cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in the range  $11^\circ < 2\theta < 23^\circ$ . During data collection three standard reflections monitored every 97 reflections showed less

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SCHEME 1.

than 3% variation and no decay. The reflection profiles were not Gaussian due to the poor quality of the crystals. The structure was solved by direct methods using SHELXS-86 and refined by full-matrix least-squares techniques on  $F^2$  with SHELXL-93. All hydrogen atoms were introduced at calculated positions as riding on bonded atoms. All non-hydrogen atoms were refined anisotropically. The final values of  $R$ ,  $R_w$ , and GOF are in Table 1. Positional and  $U_{eq}$  thermal parameters are given in Table 2 and selected bond distances and angles in Table 3.

## RESULTS AND DISCUSSION

The crystals obtained were insoluble in water and in all common organic solvents except pyridine, which is an excellent complexing agent of silver. However, attempts to crystallize this compound by slow evaporation of pyridine were unsuccessful. This work and our previous contributions show that crystallization in a gel medium is an efficient method for the preparation of single crystals of silver(I) dicarboxylates. The advantages of this method for the growth of coordination solids have been discussed elsewhere (7). The use of ammoniacal solutions to enhance the solubility of silver(I) carboxylates is an alternative method (8,9) but ammoniac is sometimes retained in the coordination sphere of silver (9).

The X-ray crystallography study shows that the structure consists of  $\text{Ag}_4(\text{dmgl})_2$  ( $\text{dmgl} = 2,2\text{-dimethylglutarate}$ ) oligomeric units held together by weak coordination bonds. This building unit (Fig. 1), of point symmetry  $C_i$ , possesses the same topology as that encountered in silver glutarate but distances and angles present some significant differ-

**TABLE 1**  
Crystallographic Data

Crystal size (mm)	$0.10 \times 0.05 \times 0.80$
Crystal color	pale yellow
Empirical formula	$\text{C}_7\text{H}_{10}\text{O}_4\text{Ag}_2$
FW	373.89
$T$ (K)	298
$\lambda$ (Å)	0.7107
Crystal system	monoclinic
Space group	$P2_1/a$
$a$ (Å)	10.67(1)
$b$ (Å)	6.334(6)
$c$ (Å)	13.32(1)
$\beta$ (deg)	96.34(4)
$V$ (Å <sup>3</sup> )	895(2)
$Z$	4
$D_{\text{calcd}}/D_{\text{measd}}$ (g cm <sup>-3</sup> )	2.776/2.75
Abs coeff ( $\mu$ ) (mm <sup>-1</sup> )	4.354
Diffractometer used	Crystal Logic Dual Goniometer
Scan mode/scan speed (deg/min)	$\theta-2\theta/4.5$
$\theta$ range (deg)	1.54–25.01
Reflections collected	3196
Independent reflections	1590 [ $R_{\text{int}} = 0.0847$ ]
Observed reflections	1511 [ $I > 2\sigma(I)$ ]
Range of $hkl$	$0 < h < 12, -7 < k < 7, -15 < l < 15$
Refinement method	Full-matrix least squares on $F^2$
Software used for solution and refinement	SHELXS-86, SHELXL93
Weighting scheme	$w^{-1} = \sigma^2(F_0^2) + (0.0879P)^2 + 3.5623P$ , where $P = (\text{Max}(F_0^2, 0) + 2F_0^2)/3$
$F(000)$	712
$[\Delta/\sigma]_{\text{max}}$	0.222
Goodness of fit on $F^2$	1.118
$R$ indices (observed data)	$R_1 = 0.0581, wR_2 = 0.1557$
$R$ indices (all data)	$R_1 = 0.0619, wR_2 = 0.1621$

ences. The ligand adopts an approximate gauche–gauche conformation. The two dihedral angles of the carbon chain are  $\text{C1–C2–C5–C6} = -57.2(6)^\circ$  and  $\text{C2–C5–C6–C7} = 75.3(8)^\circ$ . This conformation is unusual and is certainly not the one with the lowest energy. Each glutarate dianion bridges two centrosymmetrically related metallic pairs  $\text{Ag1–Ag2}$ . The intra-unit  $\text{Ag–O}$  bond distances (Table 3) are in the range 2.160(5)–2.224(5) Å and the two  $\text{O–Ag–O}$  angles are 161.1(2) and 162.8(2) $^\circ$ . These values are comparable to those found in other silver(I) carboxylates (8, 9).

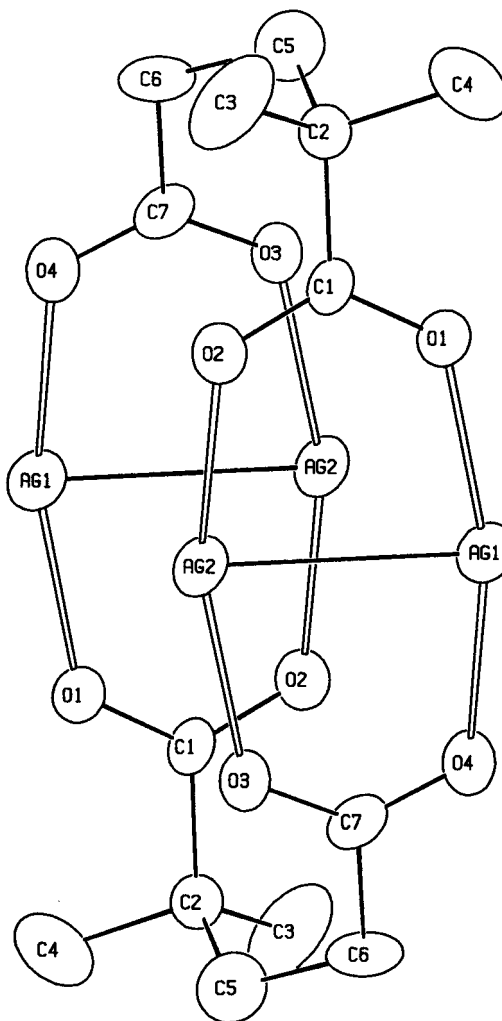
The four silver cations are organized around an inversion center situated at the intersection of the two diagonals of the metallic cluster. The metal–metal distance in each  $\text{Ag1–Ag2}$  pair is 2.818(2) Å, quite inferior to the distance in metallic silver (2.89 Å). The  $\text{Ag1–Ag2}$  and  $\text{Ag2–Ag2}$  distances between the pairs are 3.306(3) and 3.079(3) Å, respectively. These contacts are well below the van der Waals diameter of silver (3.44 Å) (10).

**TABLE 2**  
Positional ( $\times 10^4$ ) and Equivalent Thermal Parameters ( $\times 10^3$ )<sup>a</sup>  
of the Non-H Atoms (esd's in Parentheses)

Atom	x	y	z	$U_{eq}$
Ag1	4006(1)	1978(1)	1048(1)	41(1)
Ag2	4018(1)	6764(1)	60(1)	38(1)
O1	5139(5)	3598(9)	2254(4)	40(1)
O2	1861(4)	873(8)	1474(4)	32(1)
O3	5256(5)	8176(7)	1302(4)	33(1)
O4	3087(4)	1175(9)	-471(4)	36(1)
C1	6242(6)	4248(9)	2236(5)	27(1)
C2	6894(6)	5259(11)	3195(5)	31(1)
C3	8252(10)	4549(20)	3415(9)	76(3)
C4	6215(11)	4527(23)	4111(7)	74(3)
C5	6757(9)	7644(15)	3150(7)	51(2)
C6	7247(8)	8808(13)	2257(5)	40(2)
C7	6396(6)	8567(10)	1272(5)	29(1)

$$^a U_{eq} = 1/3(U_{11} + U_{22} + U_{33}).$$

Each oligomeric unit interacts with four neighboring ones related by the operation of the screw axes  $2_1$  through weak metal-carboxylate interactions (Fig. 2), thus generating  $Ag_2O_2$  units of the type D structure, according to the classification proposed by Mak *et al.* (11). The corresponding Ag-O distances, 2.517(5) and 2.399(5) Å, are in the range of the usually observed distances in silver(I) carboxylates. The shortest inter-unit Ag-Ag distances are 3.398(3) and



**FIG. 1.** ORTEP view of the structure of the oligomeric unit. Thermal ellipsoids are shown at the 50% probability level.

**TABLE 3**  
Selected Bond Lengths (Å) and Angles (deg)

Ag1-O1	2.160(5)	Ag2-O3	2.191(5)
Ag1-O4	2.209(5)	Ag2-O2 <sup>b</sup>	2.224(5)
Ag1-O2	2.517(5)	Ag2-O4 <sup>b</sup>	2.399(5)
Ag1-Ag2 <sup>a</sup>	2.818(2)	Ag2-Ag2 <sup>a</sup>	3.079(3)
Ag1-Ag2	3.306(3)		
Ag2 <sup>a</sup> -Ag1-Ag2	59.7(1)	Ag2 <sup>a</sup> -Ag2-Ag1	52.2(1)
Ag1 <sup>a</sup> -Ag2-Ag2 <sup>a</sup>	68.0(1)	Ag1 <sup>a</sup> -Ag2-Ag1	120.3(1)
Ag2 <sup>a</sup> -Ag1-Ag2 <sup>c</sup>	120.8(1)	Ag1-Ag2 <sup>c</sup> -Ag1 <sup>c</sup>	99.5(1)
Ag1-Ag2 <sup>c</sup> -Ag1 <sup>d</sup>	119.3(1)	Ag1-Ag2 <sup>c</sup> -Ag1 <sup>b</sup>	94.7(1)
Ag2-Ag1 <sup>b</sup> -Ag2 <sup>c</sup>	81.0(1)	Ag2-Ag1 <sup>b</sup> -Ag2 <sup>b</sup>	84.8(1)
O1-Ag1-O2	114.3(2)	O3-Ag2-O2 <sup>b</sup>	162.8(2)
O4-Ag1-O2	79.6(2)	O3-Ag2-O4 <sup>b</sup>	113.1(2)
O1-Ag1-Ag2 <sup>a</sup>	82.3(2)	O2 <sup>b</sup> -Ag2-O4 <sup>b</sup>	82.0(2)
O4-Ag1-Ag2 <sup>a</sup>	82.4(1)	O3-Ag2-Ag1 <sup>a</sup>	81.8(2)
O1-Ag1-Ag2	80.5(2)	O2 <sup>b</sup> -Ag2-Ag1 <sup>a</sup>	81.6(1)
O4-Ag1-Ag2	82.3(2)	O4 <sup>b</sup> -Ag2-Ag1 <sup>a</sup>	159.5(1)
O2-Ag1-Ag2	112.8(1)	O1-Ag1-O4	161.1(2)

Notes. Symmetry transformations used to generate equivalent atoms: <sup>a</sup> -x + 1, -y + 1, -z; <sup>b</sup> -x + 1/2, y + 1/2, -z; <sup>c</sup> -x + 1/2, y - 1/2, -z; <sup>d</sup> x - 1/2, -y + 1/2, z; <sup>e</sup> x - 1/2, -y + 3/2, z.

3.555(3) Å (Fig. 3). In this way, polymeric layers parallel to the *ab* plane are formed. These layers are stacked by weak van der Waals interactions in the direction of the *c* axis (Fig. 4). The mean distance between the layers (13.24 Å) is substantially longer than the corresponding distance in silver glutarate (10.36 Å). This is well reflected by the corresponding density decrease from 3.42 to 2.77 g cm<sup>-3</sup>.

The intra- and inter-aggregate Ag-Ag distances of all known structures of silver(I) with simple (no complexing groups on the carbon chain) aliphatic dicarboxylic acids are summarized in Table 4. It is obvious that there is a net tendency for cluster formation with long-chain dicarboxylic acids. The intra-unit metal-metal distances in  $Ag_4(dmgl)_2$  have been reduced significantly compared to those observed in silver glutarate. Their value indicates in this case, too, the possibility of  $d^{10}-d^{10}$  interactions, which might account for the adoption of the relatively high-energy conformation of

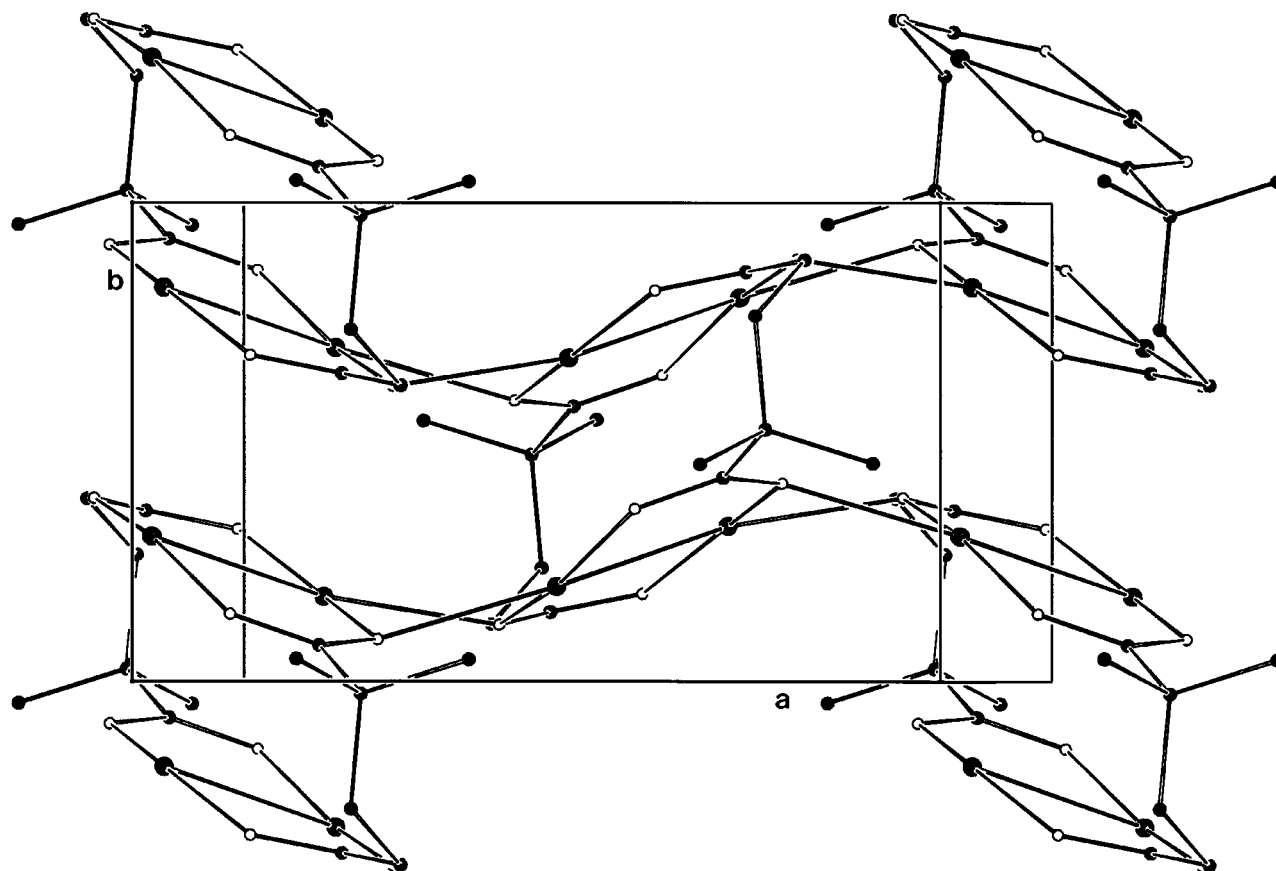


FIG. 2. View of the structure down the *c* axis. The weak coordination bonds between the oligomeric units are indicated. The Ag cations and the carbon atoms are represented by the large and the small filled circles, respectively. Open circles represent oxygen atoms.

the 2,2-dimethylglutarate dianion. The longer inter-unit Ag–Ag distance (3.555 Å) seems to exclude any significant metal–metal interaction. We should emphasize, however, that the Van der Waals diameter (3.44 Å) must not be taken as an absolute criterion. Silver–silver interactions at distances as long as 3.60 Å have recently been detected by Raman spectroscopy (13) but there are also examples with distances well below 3.44 Å presenting no interaction (14). It is clear

that we need more structural results, coupled with luminescence experiments or electrical conductivity studies, to obtain more precise interpretations.

In conclusion, the tetranuclear unit Ag<sub>4</sub>(diacid)<sub>2</sub> can be used as a design element for the construction of 2-D polynuclear molecular-based solids. The formation of this unusual oligomeric unit seems to be related to the existence of weak metal–metal interactions. Furthermore, the

TABLE 4  
Metal–Metal Distances (Å) in Various Silver(I) Dicarboxylates

Compound	Type of metal aggregate	Intra-aggregate Ag–Ag distance <sup>a</sup>	Inter-aggregate Ag–Ag distance	Reference
Ag <sub>2</sub> (oxalate)	Dinuclear	2.94	3.46	12
Ag <sub>2</sub> (malonate)	Dinuclear	2.85		8
Ag <sub>2</sub> (succinate)	Tetranuclear	2.94, 3.10	3.67	4
Ag <sub>4</sub> (glutarate) <sub>2</sub>	Tetranuclear	2.80, 3.20, 3.42	3.14, 3.43	5
Ag <sub>4</sub> (2,2-dimethylglutarate) <sub>2</sub>	Tetranuclear	2.81, 3.08, 3.31	3.40	This work

<sup>a</sup>Only distances below the van der Waals diameter of silver are shown.

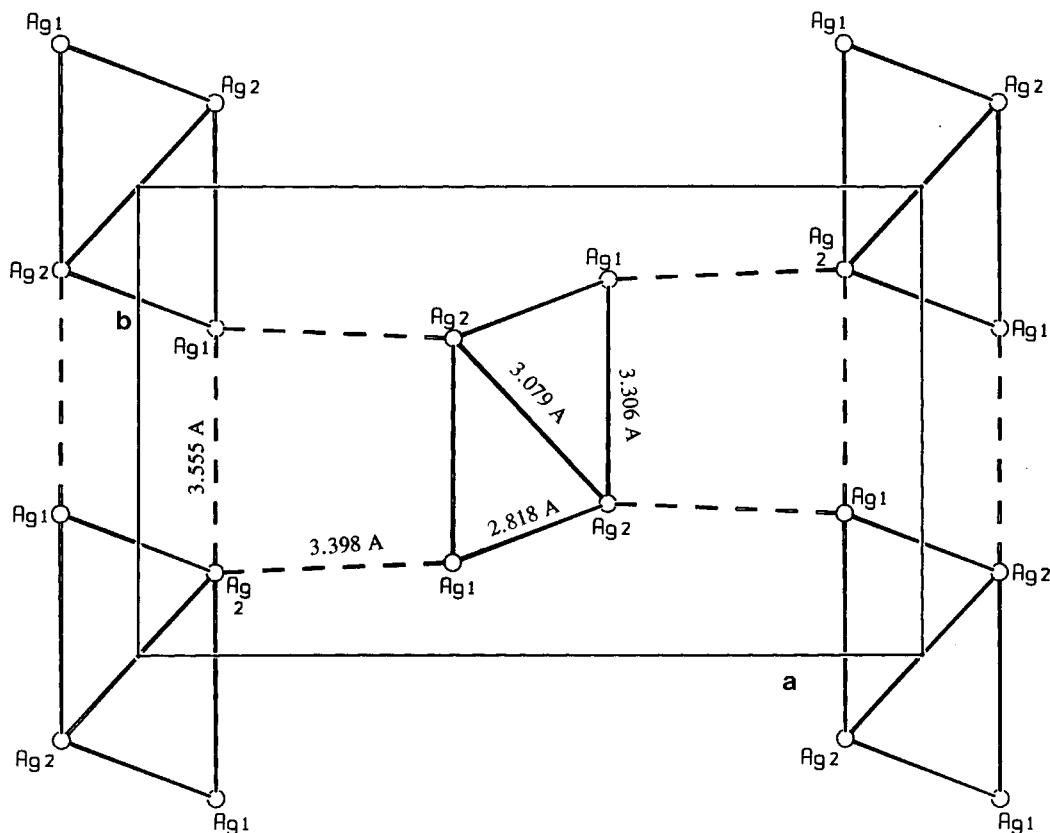


FIG. 3. View of the structure down the  $c$  axis. Organic units are omitted for clarity. Dashed lines indicate interunit distances.

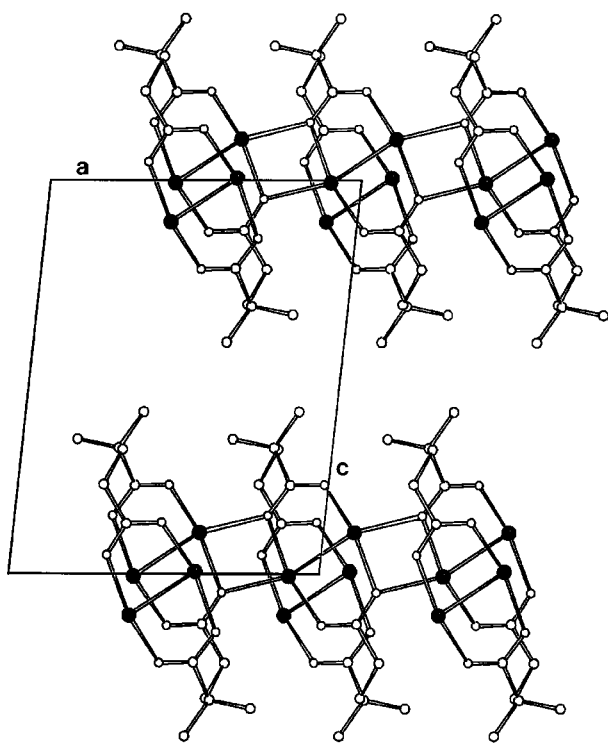


FIG. 4. View of the structure down the  $b$  axis.

clusters observed in this structure do not belong either to the family of discrete molecular clusters or to purely inorganic compounds with extended metal aggregation but might constitute a link between them.

#### ACKNOWLEDGMENTS

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