

## Poly[( $\mu$ -2,2-dimethylpropane-1,3-diyl diisocyanide)- $\mu$ -nitrate-silver(I)]: a powder study

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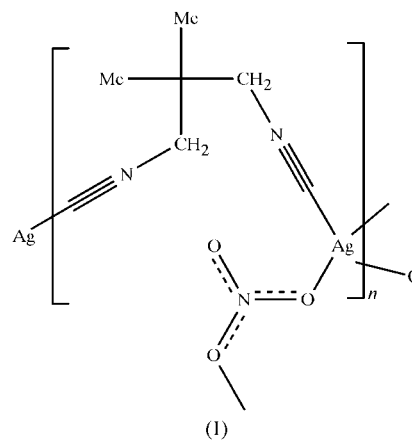
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In order to investigate the effect of counter-anions on the polymeric structure of (2,2-dimethylpropane-1,3-diyl diisocyanide)silver(I) complexes, the novel title polymeric compound,  $[\text{Ag}(\text{NO}_3)(\text{C}_7\text{H}_{10}\text{N}_2)]_n$ , has been synthesized. The crystal structure was determined by simulated annealing from X-ray powder diffraction data collected at room temperature. The current structure is similar to the recently reported structure of the analogue with chloride replacing nitrate. This study illustrates that both the chloride and nitrate complexes crystallize in the orthorhombic system in the *Pbca* space group with one monomer in the asymmetric unit, and also gives a strong indication that the counter-anion does not have a considerable effect on the polymeric structure of the complex. The Ag centre lies in a distorted tetrahedral environment and is bonded to two 2,2-dimethylpropane-1,3-diyl diisocyanide ligands to form chains. The nitrate anions crosslink the Ag centres of the chains to form a two-dimensional polymeric network structure.

### Comment

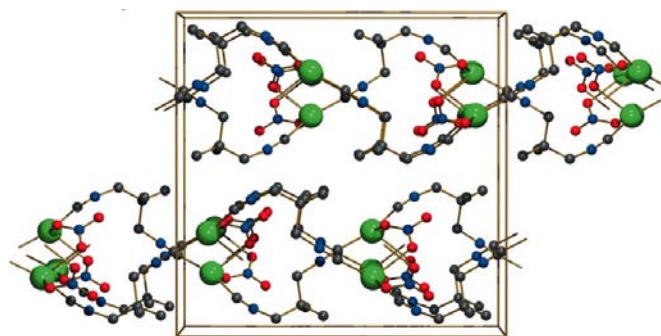
Diisocyanides are of considerable current interest as bidentate ligands in coordination chemistry (Harvey, 2001; Sakata *et al.*, 2003; Espinet *et al.*, 2000; Moigno *et al.*, 2002). Some diisocyanides have been used in the synthesis of bi-, tri- and tetranuclear complexes and organometallic polymers, which have potential practical applications as new materials in the areas of hydrogen gas production (Mann *et al.*, 1977; Sigal *et al.*, 1980) and semi- and photoconductivity (Fortin *et al.*, 2000). Very recently, we reported the synthesis and solid-state structure of the organometallic polymer  $\{[\text{Ag}\{\text{CNCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{NC}\}]\text{Cl}\}_n$  (Al-Ktaifani *et al.*, 2008), which was prepared by treatment of 2,2-dimethylpropane-1,3-diyl diisocyanide with AgCl. Since we are currently interested in the synthesis of new metal complexes using the bidentate 2,2-dimethylpropane-1,3-diyl diisocyanide ligand, it would be interesting to examine how changing the counter-anion might affect the structure and properties of the product obtained. Therefore, the title

compound, (I), which is a highly insoluble light-yellow powder, was prepared by treatment of 2,2-dimethylpropane-1,3-diyl diisocyanide. In the present work, we employed laboratory X-ray powder diffraction to solve and refine the crystal structure of this polymeric compound.



The present study reveals a polymeric structure, in which the Ag centres are bridged to each of the two adjacent Ag neighbours by bidentate 2,2-dimethylpropane-1,3-diyl diisocyanide ligands *via* the NC groups, at distances of 2.092 (8) and 2.104 (8) Å, to form  $\{\text{Ag}(\text{CNCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{NC})\}_n$  chains. The  $\text{NO}_3$  counter-anions crosslink the Ag centres of the chains, each *via* two O atoms at distances of 2.597 (4) and 2.538 (5) Å, to form a polymeric two-dimensional  $\{[\text{Ag}\{\text{CNCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{NC}\}]\text{NO}_3\}_n$  network (Fig. 1). The distances between the Ag centre and both the isocyanide C atom of the ligand and the nitrate O atom were restrained in the Rietveld refinement. The polymeric structure of (I) shows that the 2,2-dimethylpropane-1,3-diyl diisocyanide ligand in the complex behaves only in a bis-monodentate manner, while chelate behaviour is completely absent. This is undoubtedly expected for steric reasons, as the distance between the two isocyanide groups in the 2,2-dimethylpropane-1,3-diyl diisocyanide molecule is too short to allow chelate complexing (Chemin *et al.*, 1996) (Fig. 2).

In the title complex, the C—C bond distances are 1.566 (11), 1.496 (12), 1.487 (11) and 1.574 (11) Å (average 1.531 Å). The  $\text{C}\equiv\text{N}$  [1.136 (11) and 1.134 (10) Å] and N—C [1.452 (10) and

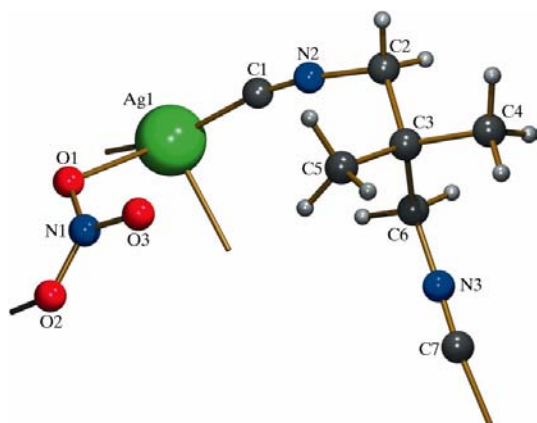


**Figure 1**

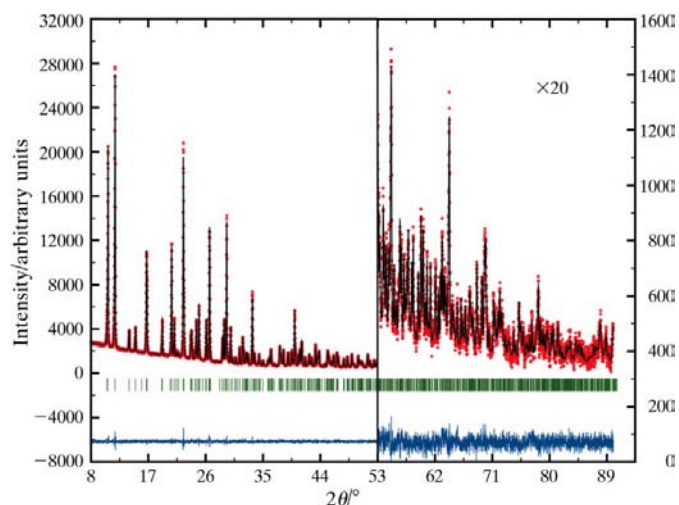
The crystal structure of polymer (I), viewed parallel to the *a* axis. H atoms have been omitted.

1.457 (10) Å] bond lengths are in their normal ranges (Allen *et al.*, 1987) and comparable with their counterparts in the reported polymeric structures of {[Ag{CNCH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>NC}]Cl}<sub>n</sub> (Al-Ktaifani *et al.*, 2008) and {[Ag(dmb)<sub>2</sub>]NO<sub>3</sub>·0.7H<sub>2</sub>O}<sub>n</sub> (dmb is 1,8-diisocyan-*p*-menthan; Fortin *et al.*, 1997), and the dinuclear complexes Ag(dmb)<sub>2</sub>X<sub>2</sub> (X = Cl, Br or I; Perreault *et al.*, 1993). These distances were restrained to their normal values in the Rietveld refinement. In each Ag[CNCH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>NC]Ag unit of the polymer, the two Ag—C≡N angles are almost linear [169.3 (7) and 174.6 (7)°]. Excluding H··H contacts, four short contacts (less than the sum of the van der Waals radii) exist: C4··N3 [2.913 (12) Å], C5··N3 [2.960 (2) Å], C5··N2 [3.000 (14) Å] and C6··N2 [2.928 (10) Å]. Two short contacts are also observed between neighbouring monomers: C1··O2(*x*,  $\frac{1}{2}$  - *y*,  $\frac{1}{2}$  + *z*) [2.988 (6) Å] and Ag1··O1(*x*,  $\frac{1}{2}$  - *y*,  $\frac{1}{2}$  + *z*) [3.047 (10) Å].

Comparing the average C—C (1.531 Å), Ag—C (2.098 Å), N≡C (1.135 Å) and N—C (1.455 Å) bond distances and the average Ag—C—N (172.0°) and C—Ag—C (159.9°) bond angles of {[Ag{CNCH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>NC}]NO<sub>3</sub>]<sub>n</sub> with their



**Figure 2**  
The asymmetric unit of (I), showing the atom-labelling scheme.



**Figure 3**  
Final observed (points), calculated (line) and difference profiles for the Rietveld refinement of (I).

analogous bond distances [average C—C (1.548 Å), Ag—C (2.116 Å), N≡C (1.160 Å), N—C (1.480 Å)] and angles [average Ag—C—N (164.0°) and C—Ag—C (159.9°)] in {[Ag{CNCH<sub>2</sub>C(CH<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>NC}]Cl}<sub>n</sub>, although the conformations of the bidentate 2,2-dimethylpropane-1,3-diyl diisocyanide ligand in both polymeric structures are almost alike, it can be concluded that both molecular structures are very similar. Thus, the counter-anion (NO<sub>3</sub> or Cl) plays no effective role in changing the polymeric structure of the complex.

## Experimental

All reactions and manipulations were carried out under an inert atmosphere using a twofold vacuum line and Schlenk techniques. Solvents were dried and distilled over sodium wire. Glassware was dried and flamed before use. AgNO<sub>3</sub> was a commercial sample (Merck) and was used as received. To a suspension of AgNO<sub>3</sub> (0.12 g, 0.71 mmol) in dry EtOH (15 ml) at room temperature was added dropwise a solution of 2,2-dimethylpropane-1,3-diyl diisocyanide (0.17 g, 1.39 mmol) in EtOH (10 ml) with rapid stirring. The resulting solution was stirred for 1 h, filtered and the volatiles removed *in vacuo*. The resulting product was washed with ether to afford a light-yellow powder [yield 0.24 g, 90%; m.p. 441 K (starts to decompose)]. Analysis found for C<sub>7</sub>H<sub>10</sub>AgN<sub>3</sub>O<sub>3</sub>: C 28.60, H 3.77, N 14.62%; required: C 28.78, H 3.45, N 14.38%. IR (KBr)  $\nu$  cm<sup>-1</sup>: 2200.3 (N≡C).

## Crystal data

[Ag(NO<sub>3</sub>)(C<sub>7</sub>H<sub>10</sub>N<sub>2</sub>)]  
M<sub>r</sub> = 292  
Orthorhombic, *Pbca*  
*a* = 16.8649 (8) Å  
*b* = 16.5864 (9) Å  
*c* = 7.4838 (4) Å  
*V* = 2093.43 (19) Å<sup>3</sup>  
*Z* = 8  
Cu K $\alpha$ <sub>1</sub> radiation

Wavelength of incident radiation:  
1.54060 Å  
 $\mu$  = 15.39 mm<sup>-1</sup>  
*T* = 295 K  
Specimen shape: flat sheet  
7.00 × 7.00 × 0.04 mm  
Specimen prepared at 101.3 kPa  
Specimen prepared at 295 K  
Particle morphology: fine powder  
(visual estimate), light yellow

## Data collection

Stoe STADI P transmission  
diffractometer  
Specimen mounting: drifted powder  
between two Mylar foils  
Specimen mounted in transmission  
mode  
Scan method: step

Absorption correction: for a  
cylinder mounted on the  $\varphi$  axis  
*T*<sub>min</sub> = 0.370, *T*<sub>max</sub> = 0.400  
(*JANA2000*; Petříček *et al.*, 2000)  
 $2\theta_{\min}$  = 8.0,  $2\theta_{\max}$  = 89.0°  
Increment in  $2\theta$  = 0.01°

## Refinement

*R*<sub>p</sub> = 0.028  
*R*<sub>wp</sub> = 0.036  
*R*<sub>exp</sub> = 0.029  
*R*<sub>B</sub> = 0.025  
*S* = 1.27  
Excluded region(s): none  
Profile function: pseudo-Voigt

846 reflections  
92 parameters  
18 restraints  
H-atom parameters constrained  
Preferred orientation correction:  
none

The powder sample was ground lightly in a mortar, loaded between two Mylar foils and fixed in the sample holder with a mask of suitable internal diameter. Data were collected at room temperature and pressure in transmission geometry employing Cu K $\alpha$ <sub>1</sub> radiation. The pattern was indexed using the program *DICVOL04* (Boultif & Louër, 2004). An orthorhombic unit cell of reasonable volume (assuming *Z* = 8) gave indexing figures of merit *M*<sub>20</sub> = 30.9 and *F*<sub>20</sub> = 79.0 (0.0054, 47). The best estimated space group in the orthorhombic system was *Pbca*, which was determined with the help of the program

**Table 1**  
Selected geometric parameters (Å, °).

Ag1—C1	2.092 (8)	C1—N2	1.136 (11)
Ag1—C7 <sup>i</sup>	2.104 (8)	N2—C2	1.452 (10)
Ag1—O1	2.597 (4)	C6—N3	1.457 (10)
Ag1—O2 <sup>ii</sup>	2.538 (5)	N3—C7	1.134 (10)
C1—Ag1—C7 <sup>i</sup>	159.9 (3)	O1—Ag1—O2 <sup>ii</sup>	83.6 (2)
C1—Ag1—O1	102.1 (2)	Ag1—C1—N2	169.3 (7)
C1—Ag1—O2 <sup>ii</sup>	81.7 (3)	C1—N2—C2	170.3 (9)
C7 <sup>i</sup> —Ag1—O1	93.2 (2)	C6—N3—C7	178.7 (8)
C7 <sup>i</sup> —Ag1—O2 <sup>ii</sup>	113.3 (3)	Ag1 <sup>iii</sup> —C7—N3	174.6 (7)
N2—C2—C3—C4	177.8 (7)	C2—C3—C6—N3	176.5 (6)
N2—C2—C3—C5	−56.5 (10)	C4—C3—C6—N3	62.7 (8)
N2—C2—C3—C6	63.7 (8)	C5—C3—C6—N3	−61.6 (9)

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

**CHEKCELL** (Laugier & Bochu, 2001). The program **FOX** (Favre-Nicolin & Černý, 2002) was employed for structure solution. The powder pattern was truncated to  $35.3^\circ$  in  $2\theta$  (Cu  $K\alpha_1$ ), corresponding to a real-space resolution of 2.54 Å. Monte Carlo simulated annealing (parallel tempering algorithm) was used to solve the crystal structure of (I) from the powder pattern in direct space. One molecule of the 2,2-dimethylpropane-1,3-diyl diisocyanide ligand, one nitrate anion and one free Ag atom were introduced randomly in the orthorhombic cell calculated by Le Bail refinement. During the parallel tempering calculations, the ligand was allowed to translate, rotate around its centre of mass and modify its torsion angles, the nitrate anion was only allowed to translate, and the Ag atom was allowed to modify its position in the unit cell. The model found by **FOX** was introduced into the program **JANA2000** (Petříček *et al.*, 2000) for Rietveld refinement. The effect of the asymmetry of some low-order peaks was corrected using a pseudo-Voigt description of the peak shape which allows for angle-dependent asymmetry with axial divergence (Finger *et al.*, 1994), restricted by the equation  $H/L = S/L$  (where  $L$  is the diffractometer radius, and  $H$  and  $S$  are the sample and detector heights). Geometric soft restraints were applied to restrain the Ag—C, Ag—O, C≡N, N—C and C—C distances and O—N—O angles to their normal values. H atoms were introduced in their theoretical positions, with CH<sub>3</sub> and CH<sub>2</sub> distances constrained to be 0.97 and 0.98 Å, respectively. They were refined as riding on their carrier atoms. The C and N atoms were assigned isotropic displacement parameters. The final refinement cycles were performed using anisotropic displacement parameters for Ag and O atoms. H atoms were assigned constant isotropic displacement parameters of 1.2

times those of their carrier atoms. No preferred orientation was applied to the final refinement. The observed and calculated diffraction patterns for the refined crystal structure are shown in Fig. 3 ( $\chi^2 = 1.61$ ,  $R_{\text{exp}} = 0.029$ ,  $R_p = 0.028$  and  $R_{\text{wp}} = 0.036$ ).

Data collection: **WinXpow** (Stoe & Cie, 1999); cell refinement: **JANA2000** (Petříček *et al.*, 2000); data reduction: **WinXpow**; program(s) used to solve structure: **FOX** (Favre-Nicolin & Černý, 2002); program(s) used to refine structure: **JANA2000**; molecular graphics: **PLATON** (Spek, 2003); software used to prepare material for publication: **JANA2000**.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3191). Services for accessing these data are described at the back of the journal.

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