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Powder study of poly[(μ_2-2,2-dimethylpropane-1,3-diyl diisocyanide)-μ_2-iodido-silver(I)]

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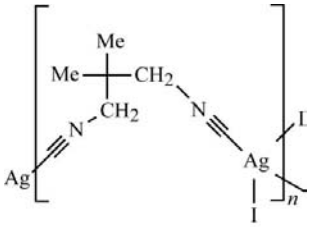
In order to explore the chemistry of the bidentate ligand 2,2-dimethylpropane-1,3-diyl diisocyanide and to investigate the effect of counter-ions on the polymeric structure of (2,2-dimethylpropane-1,3-diyl diisocyanide)silver(I) complexes, the title polymeric compound, $[AgI(C_7H_{10}N_2)]_n$, was synthesized by treatment of 2,2-dimethylpropane-1,3-diyl diisocyanide with AgI. X-ray powder diffraction studies show, as expected, a polymeric structure, similar to the very recently reported Cl^- and NO_3^- analogues $[AgX(C_7H_{10}N_2)]_n$ ($X = Cl^-$ or NO_3^-). In the title structure, the Ag^I centre is bridged to two adjacent Ag^I neighbours by bidentate 2,2-dimethylpropane-1,3-diyl diisocyanide ligands *via* the NC groups to form $[Ag\{CNCH_2C(CH_3)_2CH_2NC\}]_n$ chains. The iodide counter-ions crosslink the Ag^I centres of the chains to form a two-dimensional polymeric $\{[Ag\{CNCH_2C(CH_3)_2CH_2NC\}]I\}_n$ network. This study also shows that this bidentate ligand forms similar polymeric structures on treatment with Ag*X*, regardless of the nature of the counter-ion X^-, and also has a strong tendency to form polymeric complexes rather than dimeric or trimeric ones.

Comment

Diisocyanides have received considerable attention in coordination chemistry in recent years (Harvey, 2001; Sakata *et al.*, 2003; Espinet *et al.*, 2000; Moigno *et al.*, 2002). Some diisocyanides have been used as bidentate ligands in the synthesis of bi-, tri- and tetranuclear complexes and organometallic polymers, which have potential practical applications as new materials in areas such as hydrogen gas production (Mann *et al.*, 1977; Sigal *et al.*,1980), semi- and photoconductivity and photovoltaic cells (Fortin *et al.*, 2000). Recently, the bidentate ligand 2,2-dimethylpropane-1,3-diyl diisocyanide was used for the first time in the synthesis of the organometallic polymers $[AgX(C_7H_{10}N_2)]_n$ ($X = Cl^-$ or NO_3^-) (Al-Ktaifani *et al.*, 2008; Rukiah & Al-Ktaifani, 2008), which have been fully characterized by X-ray powder diffraction studies, IR spectroscopy and microanalysis. In both polymeric $[AgX(C_7H_{10}N_2)]_n$ structures ($X = Cl^-$ or NO_3^-), the bidentate ligand behaves only in a bis-monodentate manner to form highly insoluble polymeric compounds, rather than chelating to form dimeric or trimeric compounds. The bidentate ligands bridge the Ag^I centres to form $[Ag\{CNCH_2C(CH_3)_2CH_2NC\}]_n$ chains, while the counter-ions crosslink the Ag^I centres of the chains to form a two-dimensional polymeric network structure. It is therefore of interest to examine how changing the counter-ion or the metal centre might affect the structures and properties of the products obtained. Therefore, the syntheses of new organometallic polymers of Ag and Cu with different anions (I^-, CN^-, SO_4^{2-}, Cl^- and NO_3^-) using the bidentate ligand 2,2-dimethylpropane-1,3-diyl diisocyanide and their solid-state characterization are in progress. In this article, the synthesis of the title compound, (I), and its solid-state structure are presented.



(I)

Compound (I) was prepared by the treatment of AgI with two equivalents of 2,2-dimethylpropane-1,3-diyl diisocyanide in dry EtOH. The product is a highly insoluble white powder, even in polar or coordinate solvents. This is an indication that (I) has a polymeric structure. The FT–IR spectrum of the powder of (I) shows a characteristic sharp absorption at 2196.3 cm^{-1}, which is readily assigned to the N≡C stretching mode. The slight increase of the N≡C stretching frequency in the present Ag complex (2196.3 cm^{-1}) compared with the free diisocyanide ligand (2148.3 cm^{-1}) is consistent with the coordination of the NC groups of the ligands to the Ag^I centres. This is quite in accord with the propensity of the N≡C group to be a good donor and relatively weak back-bonding group (Mathieson *et al.*, 2001).

An X-ray powder diffraction study was carried out to solve and refine the crystal structure of the powder compound. As expected, the study reveals a polymeric structure, which is very similar to the analogous Cl^- and NO_3^- polymers, in which the Ag^I centres are bridged to each of two adjacent Ag^I neighbours by the bidentate $CNCH_2C(CH_3)_2CH_2NC$ ligand *via* the NC groups, at Ag—C distances of 2.078 (11) and 2.043 (12) Å, to form $[Ag\{CNCH_2C(CH_3)_2CH_2NC\}]_n$ chains. The I^- counter-ions crosslink the Ag^I centres of the chains at Ag—I distances of 2.956 (2) and 2.892 (2) Å to form a polymeric two-dimensional network, $\{[Ag\{CNCH_2C(CH_3)_2CH_2NC\}]I\}_n$ (Fig. 1). As observed in the polymeric structures of the Cl^- and NO_3^- analogues, the $CNCH_2C(CH_3)_2CH_2NC$ ligand in complex (I) acts in a bis-monodentate manner, and chelating behaviour is completely absent. This is undoubtedly expected for steric reasons, as the distance between the two isocyanide groups in the $CNCH_2C(CH_3)_2CH_2NC$ molecule is

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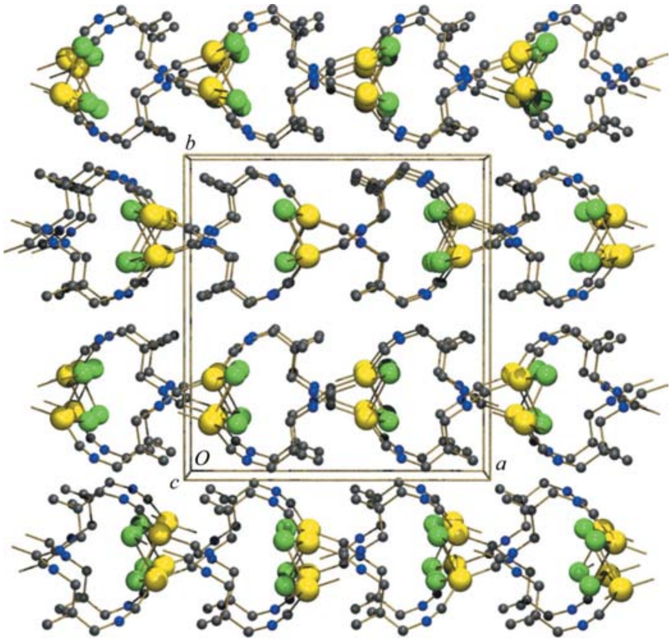

Figure 1
A view, along the *a* axis, of the crystal structure of compound (I). H atoms have been omitted.

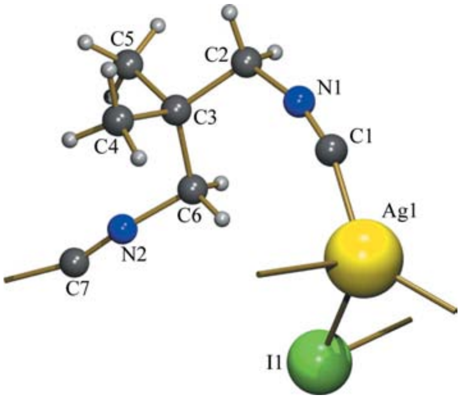

Figure 2
The asymmetric unit of (I), showing the atom-numbering scheme.

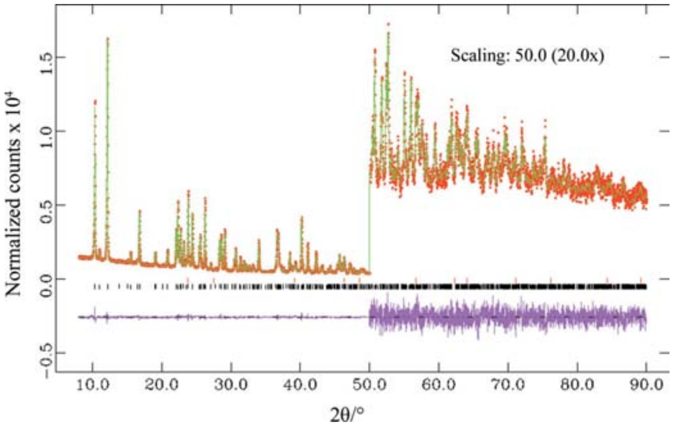

Figure 3
Final observed (points), calculated (line) and difference profiles for the Rietveld refinement of (I).

too short to allow chelate complexing (Chemin *et al.*, 1996) (Fig. 2).

In complex (I), the average bond distances and angles of $\{[Ag^I\{CNCH_2C(CH_3)_2CH_2NC\}]I\}_n$ are comparable with their analogues in $\{[Ag^I\{CNCH_2C(CH_3)_2CH_2NC\}]Cl\}_n$, and the conformation of the bidentate $CNCH_2C(CH_3)_2CH_2NC$ ligand in both polymeric structures is almost the same. Hence it can be concluded that both molecular structures are very similar. Thus, the counter-ion (NO_3^-, Cl^- or I^-) plays no effective role in changing the polymeric structure of the complex. The C—C, C≡N and N—C bond lengths were restrained to their normal values during the Rietveld refinement and are in their normal ranges (Allen *et al.*, 1987) and comparable with their counterparts in the reported polymeric structures $\{[Ag\{CNCH_2C(CH_3)_2CH_2NC\}]X\}_n$ ($X = Cl^-$ or NO_3^-; Al-Ktaifani *et al.*, 2008; Rukiah & Al-Ktaifani, 2008), in $\{[Ag(dmb)_2]NO_3\cdot0.7H_2O\}_n$ (dmb is 1,8-diisocyano-*p*-menthane; Fortin *et al.*, 1997), and in the dinuclear complexes $Ag_2(dmb)_2X_2$ ($X = Cl^-$, Br^- or I^-; Perreault *et al.*, 1993). In complex (I), the two Ag—C≡N angles (Table 1) in the Ag–$\{CNCH_2C(CH_3)_2CH_2NC\}$–Ag unit of the polymer are comparable with their counterparts in $\{[Ag\{CNCH_2C(CH_3)_2CH_2NC\}]X\}_n$ ($X = Cl^-$ or NO_3^-). Excluding H⋯H contacts, four short intraligand contacts (less than the sum of the van der Waals radii) exist, namely C4⋯N2 = 2.941 (13) Å, C5⋯N1 = 3.086 (11) Å, C5⋯N2 = 2.784 (13) Å and C6⋯N1 = 3.052 (13) Å.

In summary, the synthesis of organometallic polymers using the bidentate ligand 2,2-dimethylpropane-1,3-diyl diisocyanide, giving the title complex (I) as well as the previously reported polymers $\{[Ag^I\{CNCH_2C(CH_3)_2CH_2NC\}]X\}_n$ ($X = Cl^-$ and NO_3^-), has been shown to give similar polymeric structures regardless of the counter-ions. It is also noteworthy that the bidentate ligand exhibits a very strong tendency to form polymeric complexes rather than dimeric or trimeric ones, suggesting that it is a potential bidentate ligand in the synthesis of organometallic polymers of different transition metals.

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. AgI was obtained commercially and used as received. IR and electronic spectra were recorded on an FT–IR Jasco 300 E spectrometer and a Shimadzu UV-3100 spectrophotometer, respectively. Microanalysis was performed using a EURO EA analyzer.

To a suspension of AgI (0.28 g, 1.19 mmol) in dry EtOH (15 ml) was added dropwise a solution of $CNCH_2C(CH_3)_2CH_2NC$ (0.30 g, 2.45 mmol) in EtOH with rapid stirring at room temperature. The resulting solution was stirred overnight and then filtered, and the volatiles removed *in vacuo*. The resulting product was washed with ether to afford a white powder, (I) [yield: 0.35 g, 85%; m.p. 440 K (starts to decompose)]. Analysis found for $C_7H_{10}AgIN_2$: C 24.47, H 3.01, N 7.41%; required: C 23.55, H 2.82, N 7.84%. IR (KBr, ν, cm^{-1}): 2196.3 (N≡C).

Crystal data

$[AgI(C_7H_{10}N_2)]$
M_r = 356.94
Orthorhombic, *Pbca*
a = 16.1168 (2) Å
b = 17.1119 (2) Å
c = 7.68115 (7) Å
V = 2118.38 (6) Å^3
Z = 8
Cu $K\alpha_1$ radiation
Wavelength of incident radiation: 1.54060 Å
μ = 37.72 mm^{-1}
T = 298 K
Specimen shape: flat sheet
7.0 × 7.0 × 0.02 mm
Specimen prepared at 101.3 kPa
Specimen prepared at 298 K
Particle morphology: fine powder (visual estimate), white

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 φ axis as implemented and documented in *GSAS* (Larsen & Von Dreele, 2004)
T_{min} = 0.209, T_{max} = 0.258
$2\theta_{min}$ = 8.00, $2\theta_{max}$ = 89.99°
Increment in 2θ = 0.01°

Refinement

R_p = 0.035
R_{wp} = 0.045
R_{exp} = 0.037
R_B = 0.046
S = 1.24
Excluded region(s): none
Profile function: pseudo-Voigt (Thompson *et al.*, 1987) with asymmetry correction (Finger *et al.*, 1994)
876 reflections
96 parameters
40 restraints
H-atom parameters constrained
Preferred orientation correction: spherical harmonics function

Table 1
Selected geometric parameters (Å, °).

Ag1—I1	2.956 (2)	Ag1—C7^{ii}	2.043 (12)
Ag1—I1^{i}	2.892 (2)	C1—N1	1.159 (6)
Ag1—C1	2.078 (11)	C7—N2	1.158 (6)
I1—Ag1—I1^{i}	107.07 (9)	Ag1—C1—N1	165 (2)
I1—Ag1—C1	97.1 (6)	C3—C2—N1	113.0 (7)
I1—Ag1—C7^{iii}	100.3 (6)	C3—C6—N2	110.8 (6)
I1^{i}—Ag1—C1	102.8 (6)	Ag1^{v}—C7—N2	161 (2)
I1^{i}—Ag1—C7^{iii}	106.5 (6)	C1—N1—C2	163 (2)
C1—Ag1—C7^{iii}	139.5 (9)	C6—N2—C7	168.5 (17)
Ag1—I1—Ag1^{iv}	96.87 (8)		
N1—C2—C3—C4	177.7 (7)	C2—C3—C6—N2	176.9 (5)
N1—C2—C3—C5	67.5 (6)	C4—C3—C6—N2	−57.3 (5)
N1—C2—C3—C6	−55.3 (6)	C5—C3—C6—N2	51.4 (5)

Symmetry codes: (i) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; (ii) $x+\frac{1}{2}, -y+\frac{3}{2}, -z+2$; (iii) $x+\frac{3}{2}, -y+\frac{5}{2}, -z+2$; (iv) $x, -y+\frac{3}{2}, z-\frac{1}{2}$; (v) $x+\frac{1}{2}, -y+\frac{5}{2}, -z+2$.

The powder sample was ground slightly 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 $K\alpha_1$ radiation. Indexing was performed using the program *DICVOL04* (Boultif & Louër, 2004) with standard options. Confidence figures of merit M_{20} = 28.8 and F_{20} = 64.8 (0.0049, 63) were obtained for an orthorhombic unit cell of reasonable volume (assuming Z = 8). Cell parameters were a = 17.098 (3) Å, b = 16.113 (3) Å, c = 7.677 (1) Å and V = 2115.1 Å^3. These unit-cell parameters were allowed to vary during the Rietveld refinement. The most probable space group was *Pcab*, which was obtained using the program *CHECK-GROUP* interfaced by *WINPLOTR* (Roisnel & Rodriguez-Carvajal, 2001). The parameters a and b were interchanged for working with the standard space group *Pbca*. The program *FOX* (Favre-Nicolin & Černý, 2002) was employed for structure solution. The powder pattern was truncated to 45.3° in 2θ (Cu $K\alpha_1$), corresponding to a real-space resolution of 2.00 Å. Monte Carlo simulated annealing (parallel tempering algorithm) was used to solve the crystal structure of compound (I) in direct space. One molecule of 2,2-dimethylpropane-1,3-diyl diisocyanide and two free atoms of Ag and I were introduced randomly in the orthorhombic cell obtained by the program *DICVOL04*. The H atoms were not introduced during the structure solution process. During the parallel tempering calculations, the ligand had the possibility of translating, rotating around its centre of mass and modifying its torsion angles. The Ag and I atoms had the possibility of modifying their positions in the unit cell. The model obtained by *FOX* was used as the starting point for Rietveld refinements in the program *GSAS* (Larsen & Von Dreele, 2004), interfaced by *EXPGUI* (Toby, 2001). The profile function used was a pseudo-Voigt function convoluted with an axial divergence asymmetry function (Finger *et al.*, 1994), and with *S*/*L* and *D*/*L* both fixed at 0.0225.

H atoms were included in calculated positions and treated in the subsequent refinement as riding atoms, with CH_2 and CH_3 C—H distances constrained to be 0.98 and 0.97 Å, respectively. Geometric soft restraints were applied to the C≡N, N—C and C—C distances to guide them towards their normal values, but no restraints were imposed on the Ag—C and Ag—I distances. Likewise, no restraints were imposed on bond angles.

The background was refined using a shifted Chebyshev polynomial with 15 coefficients, whereas the preferred orientation was modelled using a spherical-harmonics description (Von Dreele, 1997). One isotropic atomic displacement parameter for C, N and H atoms was used, and this was fixed at 0.035 Å^2 for C and N, and at 0.05 Å^2 for H atoms. The final refinement cycles were performed using anisotropic atomic displacement parameters for Ag and I atoms. A joint refinement strategy was implemented, in which the structure of AgI was included to take account of the impurity peaks arising from the presence of a small amount (estimated at less than 1%) of this compound in the sample. In the course of the refinement, the AgI unit-cell parameters were allowed to vary, whilst all other parameters were fixed. The observed and calculated diffraction patterns for the refined crystal structure are shown in Fig. 3.

Data collection: *WinXPOW* (Stoe & Cie, 1999); cell refinement: *GSAS* (Larsen & Von Dreele, 2004); data reduction: *WinXPOW*; program(s) used to solve structure: *FOX* (Favre-Nicolin & Černý, 2002); program(s) used to refine structure: *GSAS*; molecular graphics: *PLATON* (Spek, 2009); software used to prepare material for publication: *GSAS*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GT3002). Services for accessing these data are described at the back of the journal.

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