Homochiral and pseudoracemic 3,3- and 1,2-dimethyldiaziridine–silver nitrate complexes

Remir G. Kostyanovsky,*[a] Konstantin A. Lyssenko[b] and Vasily R. Kostyanovsky[a]

[a] *N. N. Semenov Institute of Chemical Physics, Russian Academy of Sciences, 117977 Moscow, Russian Federation.*
Fax: +7 095 938 2156; e-mail: kost@center.chph.ras.ru
[b] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 117977 Moscow, Russian Federation.*
Fax: +7 095 135 5085; e-mail: kostya@xray.ac.ru

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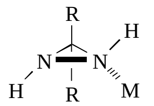
Diaziridine molecules in the title complexes **1** and **2**, respectively, are bidentate ligands and form coordination polymers in which silver ions are coordinated to the *trans*-oriented nitrogen lone pairs of the ligands; complex **1** is homochiral (space group $P2_12_12_1$), whereas **2** is a pseudoracemate (space group *Pbca*) in which the alternation of ligands with opposite configurations is statistically disordered.

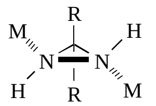
Molecular assembling by metal coordination and, in particular, by coordination polymerisation is an important tool in supramolecular chemistry[1–4] and crystal engineering.[5–11] Diaziridines (see ref. 12 for a recent review) are bidentate ligands suitable for coordination polymerisation because the *trans*-oriented lone pairs of nitrogen cannot be coordinated to the same metal ion. All monocyclic diaziridines are chiral (with the exception of *cis*-1,2-dimethyl-3-*tert*-butyldiaziridine[13]); we resolved them into enantiomers for the first time;[14–21] however, there is no data concerning their spontaneous resolution.

The data on coordinated complexes are limited (see refs. 22–25 and references therein). According to the X-ray diffraction analysis of mixed complexes such as **A**[22] and **B**–**D**[23] and of complex **E**,[24] they do not form coordinated polymers in crystals. It should be emphasised that complex **C** is homochiral.[23]



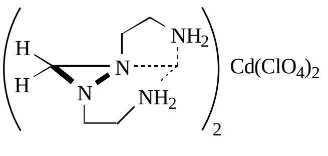
A: R_2 = Bu^{t}CH(CH_2CH_2)$_2$
M = RhCl(cod)
cod = cyclooctadiene
space group $P2_1/c$ (z = 4)

B: R_2C = 2,2-adamantylidene
M = $PtCl_2(Et_3P)$
space group *Pbca* (z = 8)



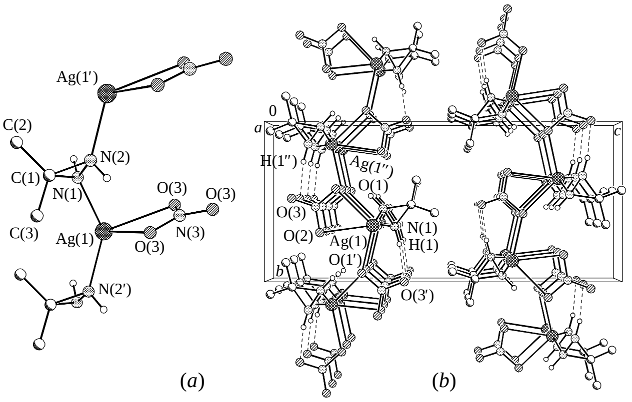
C: R_2 = $(CH_2)_5$
M = $PtCl_2(Et_3P)$
space group $P2_1$ (z = 2)

D: R_2C = 2,2-adamantylidene
M = $PtCl_2(Et_3P)$
Space group $P2_1/n$ (z = 4)



E: space group $Pbc2_1$ (z = 4)

In this work, we synthesised[†] complex **1** of 3,3-dimethyldiaziridine with $AgNO_3$ for the first time and found by X-ray diffraction analysis of a single crystal[‡] that **1** is a homochiral (space group $P2_12_12_1$) coordinated polymer (Figure 1). Complex **2** of 1,2-dimethyldiaziridine with $AgNO_3$ was prepared earlier; however, the relevant structural data reported were inadequate.[25]



(*a*) (*b*)

Figure 1 The crystal structure of **1**: (*a*) the Ag-coordinated homochiral polymeric chain directed along the crystallographic axis *a*; (*b*) the arrangement of chains into ‘walls’ laying in the crystallographic plane *ab*.

The repeated X-ray determination of the structure of **2** confirmed that the complex is a heterochiral coordination polymer (space group *Pbca*). However, in contrast to data,[25] we found

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[†] **1** was prepared by the procedure given below. 3,3-Dimethyldiaziridine was purified by freezing from *n*-hexane, mp 40 °C. ^{1}H NMR (CD_3CN) δ: 1.31 (s, 6H, Me_2C), 2.26 (br. s, 2H, 2HN). A mixture of 0.2 g of 3,3-dimethyldiaziridine and 0.4 g of $AgNO_3$ in 5 ml of absolute MeOH was kept at 4 °C for 10 h; the precipitate (0.5 g, 88%) was separated and crystallised from absolute MeCN to give 0.3 g of colourless transparent bright crystals in 52.6% yield, mp 137 °C. ^{1}H NMR (CD_3CN) δ: 1.44 (s, 6H, Me_2C), 3.26 (br. s, 2H, 2HN). Found (%): N, 17.46. Calc. for $C_3H_8N_3O_3Ag$ (%): N, 17.37.

2 was prepared by the known method,[25] mp 136 °C (MeCN). The product with $[\alpha]_D^{20}$ = 27.9° (c 2.5, MeCN) was obtained from partly enriched (+)-1,2-dimethyldiaziridine,[29] $[\alpha]_D^{20}$ = 9.5° (c 2.2, MeCN) after the treatment with a half-mole quantity of $AgNO_3$ in MeCN, the separation of **2** and the distillation of the mother liquor into a cold trap (–80 °C).

[‡] *Crystallographic data for* **1** *and* **2**: at –80 °C, crystals of $C_3H_8AgN_3O_3$ **1** are orthorhombic, space group $P2_12_12_1$, a = 5.2023(9), b = 7.921(1), c = = 17.653(3) Å, V = 726.7(2) Å^3, Z = 4, d_{calc} = 2.212 g cm^{-3}, μ = 2.778 mm^{-1}, M = 241.99, $F(000)$ = 472; crystals of $C_3H_8AgN_3O_3$ **2** are orthorhombic, space group *Pbca*, a = 10.192(3), b = 10.678(4), c = 13.339(4) Å, V = = 1451.6(9) Å^3, Z = 8, d_{calc} = 2.215 g cm^{-3}, μ = 2.731 mm^{-1}, M = 241.99, $F(000)$ = 944. The intensities of 1498 reflections for **1** and 2143 reflections for **2** were measured on a Syntex P2$_1$ diffractometer at –80 °C (λMoKα radiation, $\theta/2\theta$-scan technique, $2\theta_{max}$ < 60° and 70° for **1** and **2**, respectively). The structures were solved by a direct method and refined by a full-matrix least squares technique against F^2 in the anisotropic–isotropic approximation. The positions of hydrogen atoms were calculated from the geometrical point of view with the exception of the nitrogen atoms in **1**, which were located from the difference Fourier synthesis and refined in the isotropic approximation. An analysis of difference electron density syntheses in the structure of **2** revealed additional electron density maxima which were interpreted as the disorder of diaziridine molecules. The refinement of the occupancies for two positions of nitrogen atoms resulted in the 1:1 ratio. The absolute *S*-configurations for the N(1) and N(2) atoms in **1** were confirmed by estimating the Flack absolute structure parameter x,[30] is equal to zero with a rather small *esd* [–0.00(11)] in the case of the *S*-configuration for N(1) and N(2). The refinement converged to wR_2 = 0.1668 and COF = 1.133 for 1396 reflections [R_1 = 0.0699 was calculated against F for the 1308 observed reflections with $I > 2\sigma(I)$] for the structure of **1** and to wR_2 = = 0.1892 and COF = 1.10 for all independent reflections [R_1 = 0.0689 was calculated against F for the 1852 observed reflections with $I > 2\sigma(I)$] for the structure of **2**. All calculations were performed using the SHELXTL PLUS 5.0 program on an IBM PC/AT. Atomic coordinates, bond lengths, bond angles and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see ‘Notice to Authors’, *Mendeleev Commun.*, Issue 1, 2000. Any request to the CCDC for data should quote the full literature citation and the reference number 1135/62.

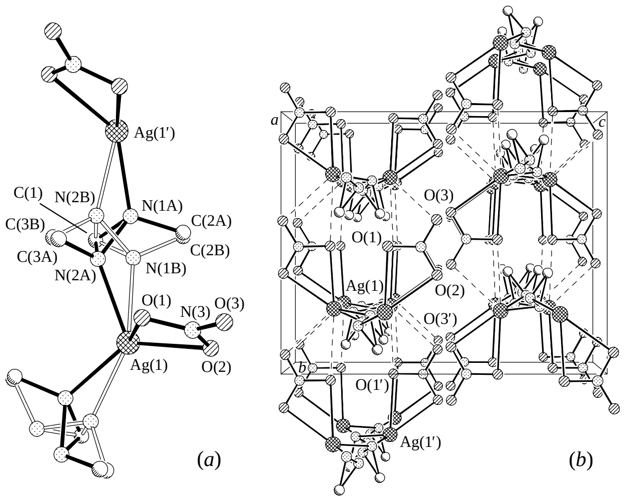

Figure 2 The crystal structure of **2**: (*a*) the superposition of enantiomers in the Ag-coordinated heterochiral polymeric chain directed along the crystallographic axis *a*; (*b*) the arrangement of chains into ‘walls’ laying in the crystallographic plane *ab*.

that diaziridine ligands are statistically disordered (each ligand position is randomly occupied by the opposite enantiomers) leading to a chain-type structure containing AgNO$_3$ with the superposition of diaziridine enantiomers [Figure 2(*a*)]. Thus, complex **2** is a rare example of a pseudoracemate.[26]

The Ag–N bond lengths in complexes **1** and **2** are slightly different and equal to 2.228(6)–2.238(6) and 2.279(8)–2.336(5) Å, respectively. For comparison, the Ag–N bond lengths in the polymeric complexes of AgBF$_4$ and AgSbF$_6$ with pyrazine[27] and of CF$_3$SO$_3$Ag with a methionine derivative[28] are 2.459(9)–2.519(8) and 2.219(4)–2.378(5) Å, respectively.

In both structures, within the above chain directed along the crystallographic axis *a*, NO$_3$ acts as a bidentate ligand with some shortening of the Ag–O bond lengths in the case of **2** [2.508(3), 2.590(3) Å], as compared with **1** [2.622(4), 2.643(6) Å]. Additional chain-to-chain interactions between Ag and NO$_3$ in **1** and **2** are different. In complex **1**, NO$_3$ acting as a monodentate ligand links adjacent chains to ‘walls’ laying along the crystallographic plane *ab* [Ag(1)–O(1′) ($x - 1$, $y - 1/2$, $z - 1/2$) 2.528(6) Å] [Figure 1(*b*)]. The additional interaction of the O(1) atom with two silver atoms results in elongation of the N(3)–O(1) bond [1.264(6) Å], as compared with the N(3)–O(2) bond [1.243(6) Å]. At the same time, the formation of similar ‘walls’ (also laying in the crystallographic plane *ab*) in **2** is accomplished by weak interactions of NO$_3$, which acts as a bidentate ligand [Ag(1)–O(1′) ($3/2 - x$, $1/2 + y$, z) 2.853(4) Å and Ag(1)–O(2′) ($3/2 - x$, $1/2 + y$, z) 2.733(4) Å] [Figure 2(*b*)].

Thus, both of the structures are build up from the chains assembled into ‘walls’ by means of the Ag$\cdots$(NO$_3$) interactions. Note that the ‘walls’ in complex **1** are more compact because of the above chain-to-chain interactions. This can be illustrated by a comparison between the Ag$\cdots$Ag distances in a chain [5.202(2) and 5.407(3) Å] and between chains [4.534(2) and 5.531(2) Å] in complexes **1** and **2**, respectively. The higher density of **2** can be explained by more tightly packed ‘walls’ in this compound, as compared with **1**.

The observed difference in the layer architecture of complexes **1** and **2** is probably due to the presence of a bulky substituent at nitrogen in **2**. In addition, the homochiral crystal packing in complex **1** is stabilised by the formation of hydrogen bonds [N(1)–H(1)$\cdots$O(3) distances of 3.01(1) and 2.13 Å] between the diaziridine molecule of a chain and the NO$_3$ ligand of the adjacent chain. Thus, favourable steric conditions of the ligand and hydrogen bonding probably lead to the formation of conglomerate **1**.

As was presumed earlier,[25] the formation of racemic complex **2** can be used for increasing the optical purity of partially enriched (+)-1,2-dimethyldiaziridine. The treatment with a half-mole quantity of AgNO$_3$ resulted in an increase in the optical purity by a factor of about three.† Similarly, we used chloral for increasing the optical purity of 1-methyl-3,3-pentamethylenediaziridine, which forms a racemic adduct with this compound.[14(c)]

The attempts to separate an optically active NH-diaziridine from homochiral complex **1** (and also perhaps from compound **C**[23]) were unsuccessful because of the easy racemization due to proton exchange. Thus, we attempt to prepare homochiral complexes of AgNO$_3$ with 1,3-dimethyl- and 1,3,3-trimethyldiaziridines.

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