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*

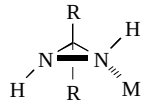
[b] *A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 117977 Moscow, Russian Federation. Fax: +7 095 135 5085; e-mail: kostya@xray.ac.ru*

DOI: 10.1070/MC2000v010n02ABEH001261

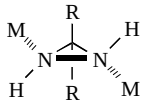
Diaziridine molecules in the title complexes 1 and 2, respectively, are bidentate ligands and form coordination polymers in which silver ions are coordinated to the *trans*-oriented nitrogen lone pairs of the ligands; complex 1 is homochiral (space group $P2_12_12_1$), whereas 2 is a pseudoracemate (space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



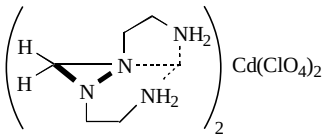
A: $R_2 = Bu^tCH(CH_2CH_2)_2$
M = RhCl(cod)
cod = cyclooctadiene
space group $P2_1/c$ ($z = 4$)



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

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

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]

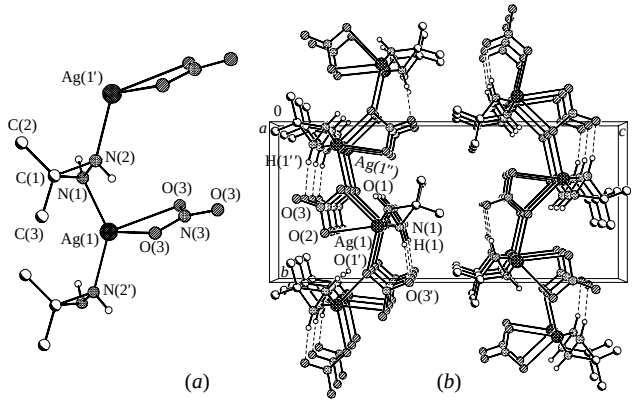


Figure 1 The crystal structure of **1**: (*a*) the Ag-coordinated homochiral polymeric chain directed along the crystallographic axis *a*; (*b*) the arrangement of chains into 'walls' laying in the crystallographic plane *ab*.

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

† **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 (λMoK 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.

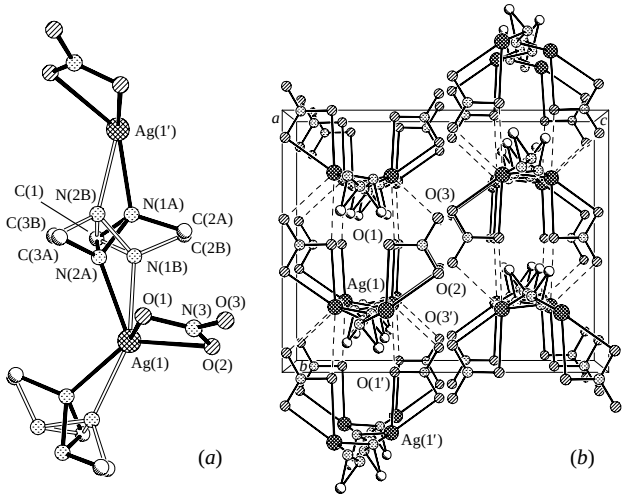


Figure 2 The crystal structure of **2**: (*a*) the superposition of enantiomers in the Ag-coordinated heterochiral polymeric chain directed along the crystallographic axis *a*; (*b*) the arrangement of chains into 'walls' laying in the crystallographic plane *ab*.

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_3SO_3Ag 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) Åand A g(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···(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···Ag distances in a chain [5.202(2) and 5.407(3) Å and between cha ins [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 compo und, 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)···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.

This work was supported by the Russian Foundation for Basic Research (grant nos. 97-03-33021 and 98-03-04119) and INTAS (project no. 157).

References

1 M. Fujita, N. Fujita, K. Ogura and K. Yamaguchi, *Nature*, 1999, **400**, 52.
2 D. Whang and K. Kim, *J. Am. Chem. Soc*., 1997, **119**, 451.
3 C. Piguet, G. Bemardinelli and G. Hopgartner, *Chem. Rev.*, 1997, **97**, 2005.
4 D. Philp and J. F. Stoddart, *Angew. Chem., Int. Ed. Engl*., 1996, **35**, 1154.
5 A. K. Ghosh, P. Mathivanan and J. Cappiello, *Tetrahedron Asymm*., 1998, **9**, 1.
6 D. A. Evans, E. J. Olhava, J. S. Johnson and J. M. Janey, *Angew. Chem., Int. Ed. Engl*., 1998, **37**, 3372.
7 C. B. Aakeröy, *Acta Crystallogr*., 1997, **B53**, 569.
8 A. Williams, *Chem. Eur. J*., 1997, **3**, 15.
9 T. L. Hennigar, D. C. MacQuarrir, P. Losier, R. D. Rogers and M. J. Zaworotko, *Angew. Chem., Int. Ed. Engl*., 1997, **36**, 972.
10 P. Klüfe rs and J. Schuhmacher, *Angew. Chem., Int. Ed. Engl*., 1994, **33**, 1742.
11 D. A. Evans, K. A. Woerpel and M. J. Scott, *Angew. Chem., Int. Ed. Engl*., 1992, **31**, 430.
12 R. G. Kostyanovsky, R. Murugan and M. Sutharchanadevi, in *Comprehensive Heterocyclic Chemistry*, ed. A. Padwa, Pergamon Press, Oxford, 1996, vol. 1A, ch. 1.11, p. 347.
13 R. G. Kostyanovsky, G. V. Shustov, V. V. Starovoitov and I. I. Chervin, *Mendeleev Commun*., 1998, 113.
14 (*a*) R. G. Kostyanovsky, A. E. Polyakov and V. I. Markov, *Izv. Akad. Nauk SSSR, Ser. Khim*., 1974, 1671 (in Russian); (*b*) R. G. Kostyanovsky, A. E. Polyakov and V. I. Markov, *Izv. Akad. Nauk SSSR, Ser. Khim*., 1975, 198 (in Russian); (*c*) R. G. Kostyanovsky, A. E. Polyakov, G. V. Shustov, K. S. Zakharov and V. I. Markov, *Dokl. Akad. Nauk SSSR*, 1974, **219**, 873 [*Dokl. Chem.* (*Engl. Transl.*), 1974, **219**, 831].
15 R. G. Kostyanovsky, A. E. Polyakov and G. V. Shustov, *Tetrahedron Lett*., 1976, 2059.
16 R. G. Kostyanovsky and G. V. Shustov, *Dokl. Akad. Nauk SSSR*, 1977, **232**, 1081 [*Dokl. Chem.* (*Engl. Transl.*), 1977, **232**, 71].
17 R. G. Kostyanovsky, G. V. Shustov and N. L. Zaichenko, *Tetrahedron*, 1982, **38**, 949.
18 G. V. Shustov, G. K. Kadorkina, R. G. Kostyanovsky and A. Rauk, *J. Am. Chem. Soc*., 1988, **110**, 1719.
19 G. V. Shustov, S. N. Denisenko, M. A. Shochen and R. G. Kostyanovsky, *Izv. Akad. Nauk SSSR, Ser. Khim*., 1988, 1862 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37**, 1665).
20 S. V. Konovalikhin, A. B. Zolotoi, L. O. Atovmyan, G. V. Shustov, S. N. Denisenko and R. G. Kostyanovsky, *Izv. Akad. Nauk, Ser. Khim*., 1995, 500 (*Russ. Chem. Bull.*, 1995, **44**, 483).
21 V. A. Korneev, G. V. Shustov, I. I. Chervin and R. G. Kostyanovsky, *Izv. Akad. Nauk, Ser. Khim*., 1995, 1396 (*Russ. Chem. Bull*., 1995, **44**, 1346).
22 A. Adedapo, S. A. Benyunes, P. A. Chaloner, C. Claver, P. B. Hitchcock, A. Ruiz and N. Ruiz, *J. Organomet. Chem*., 1993, **443**, 241.
23 A. Adedapo, A. G. Avent, D. Carmichael, P. A. Chaloner, P. B. Hitchcock and A. Wagnenaar, *J. Chem. Soc., Chem. Commun*., 1993, 186.
24 A. V. Shevtsov, V. Yu. Petukhova, S. A. Kutepov, V. V. Kuznetsov, N. N. Makhova, N. E. Kuzmina and G. G. Alexandrov, *Izv. Akad. Nauk, Ser. Khim*., submitted for publication.
25 G. V. Shustov, A. B. Zolotoi, S. V. Konovalikhin, L. O. Atovmyan and R. G. Kostyanovsky, *Mendeleev Commun*., 1995, 218.
26 J. Jacques, A. Collet and S. H. Willen, *Enantiomers, Racemates, and Resolution*, Krieger Publ. Co., Malabar, Florida, 1994, pp. 5, 104.
27 L. Carlucci, G. Ciani, D. M. Proserpio and A. Sironi, *Angew. Chem., Int. Ed. Engl*., 1995, **34**, 1895.
28 J. F. Modder, K. Vrieze, A. L. Spek and G. van Koten, *J. Org. Chem*., 1991, **56**, 5606.

29 R. G. Kostyanovsky, V. A. Korneev, I. I. Chervin, V. N. Voznesensky, Yu. V. Puzanov and P. Rademacher, *Mendeleev Commun*., 1996, 106.
30 H. D. Flack, *Acta Crystallogr.*, 1983, **A39**, 876.

Received: 30th December 1999; Com. 99/1587