A Novel *trans*-1,2-Dimethyldiaziridine–Silver Nitrate Complex: Synthesis and Molecular and Crystal Structure

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trans-1,2-Dimethyldiaziridine **1** reacts with $AgNO_3$ yielding a stable complex **2** (1:1 ratio); according to X-ray analysis silver ions are coordinated on the lone pairs of the diaziridine nitrogen atoms, and together with molecules of **1** of the opposite configuration form polymer chains.

The organometallic chemistry of diaziridines has been actively developing recently. The synthesis of diaziridines by the reaction of Fisher's carbenes with diazo compounds has been successfully carried out.[1–3] New and interesting regiospecific transformations of diaziridines under the action of cobalt and platinum complexes have been found.[4,5] Complexes of 1,2,3-trialkyldiaziridines with $Fe(CN)_2$,[6] 1,2-bis(β-aminoethyl)diaziridine[7] $[M^{+2}L_2]X_2^-$, where M = Ni, Cu, Cd; X = NO_3, ClO_4 as well as rhodium,[8] palladium[9] and platinum[10,11] complexes of diaziridines have been obtained. The structure of the monocoordinated rhodium complex of 1,3,3-trialkyldiaziridine,[8] as well as one mono- and two dimetallated platinum complexes of 3,3-dialkyldiaziridines[11] have been studied by X-ray methods.

A few stable diaziridine salts such as oxalates[12] and picrates are known, the latter having been studied by X-ray methods.[13]

By treating 1,2-dimethyldiaziridine[14] **1** with $AgNO_3$ in MeCN we have obtained for the first time the stable diaziridine–silver complex **2** which crystallized out from the reaction solution in analytically pure form.[†] According to elemental analysis the composition of **2** corresponds to the ratio **1**:$AgNO_3$ = 1:1. As is evident from the X-ray data[‡] silver ions in the crystal **2** associate molecules **1** of *opposite configuration* into continuous polymer chains which are parallel to the *c* axis of the elementary cell. Nitrate ions are located at the chain periphery. The molecule of **1** bound with $AgNO_3$ is a unit cell (Table 1) with a centrally symmetric spatial group. Multiplication of the unit cell is accompanied both by misalignment and turning by 180° along the chain axis with the result that, for example, N(2)–C(3) and N(2)*–C(3)* bonds are directed to different sides (Figure 1). Adjacent chains are bound by contacts of Ag...O(1)′ = 2.88(2) and Ag...O(2)′ = 2.72(2) Å which correspond to the sum of the ionic radii of Ag and O (2.88 Å).[15]

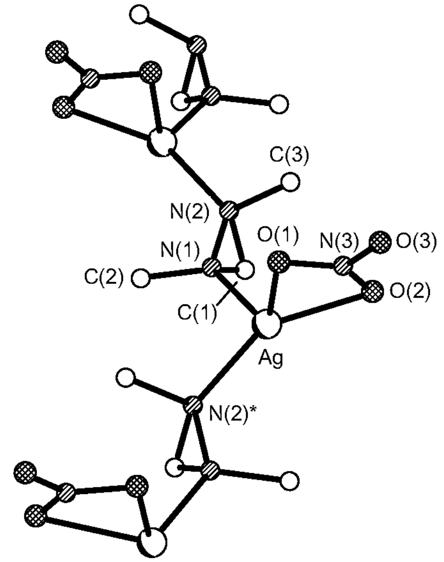

Figure 1 Structure of complex **2**. Basic bonds lengths/Å and valent angles/°: N(1)–N(2) 1.38(3); N(1)–C(1) 1.46(2); N(2)–C(1) 1.44(2); N(1)–C(2) 1.50(3); N(2)–C(3) 1.60(3); Ag–N(1) 2.30(2); Ag–N(2) 2.34(2); Ag–O(1) 2.59(2); Ag–O(2) 2.50(2); N(3)–O(1) 1.20(2); N(3)–O(2) 1.25(2); N(3)–O(3) 1.23(2); N(1)C(1)N(2) 57(1); N(1)N(2)C(1) 62(1); N(2)N(1)C(1) 61(1); C(1)N(1)C(2) 115(2); C(1)N(2)C(3) 111(2); N(2)N(1)C(2) 109(1); N(1)N(2)C(3) 108(1); AgN(1)N(2) 129(2); AgN(1)C(1) 115(1); AgN(1)C(2) 117(1); O(1)N(3)O(2) 118(1); O(2)N(3)O(3) 122(1); O(1)N(3)O(3) 120(1); O(1)AgO(2) 48.3(6).

The values of the exocyclic valence angles of AgN(1)N(2), AgN(1)C(1) and AgN(1)C(2) evidence that Ag ions are coordinated in the direction of the maximal electron density of the HOMO ligand *i.e.* to the top of the nitrogen pyramid. The N atoms of the ligand are strongly pyramidal: the sum of the valence angles is 282° at the N(1) atom and 281° at the N(2) atom, and the dihedral angle C(2)N(1)N(2)C(3) is 149°. The lengths of the Ag–N bonds are similar and approximately the same as in complexes of AgI_2 with piperidine (2.34 Å)[16] and with piperazine (2.32 Å).[17] Usually such Ag–N bonds are much shorter than the sum of the covalent radii of Ag and N atoms (2.48 Å).[15] In the silver triaziridine (N_3H_3) complex the Ag–N bond is appreciably extended (2.59 Å).[18] On the basis of the data obtained and within the limits of experimental accuracy both nitrogen atoms are assumed to participate equally in coordination with silver(I) ions in the crystal.

The length of the N–N bond in 1,2-*trans*-diaziridines in the free state changes within the limits 1.44–1.51 Å[19,20] and depends on destabilizing the interaction of the n_N-orbitals forming the HOMO.[21,22] The electron withdrawal from the

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[†] 1,2-Dimethyldiaziridine–silver nitrate complex **2**.

1,2-Dimethyldiaziridine[6] (1.80 g, 25 mmol) was added to a solution of $AgNO_3$ (3.40 g, 20 mmol) in absolute MeCN (30 ml) and kept in the dark at 20 °C. After 2 h the precipitated white crystals were filtered off, washed with absolute MeCN, ether and then dried in vacuum to obtain complex **2** (3.29 g, 68%), m.p. 135–136 °C. (Found: C, 14.96; H, 3.48; N, 13.40. Calc. for $C_3H_8N_3O_3Ag$: C, 14.86; H, 3.33; N, 13.36%). ^1H NMR (60 MHz, $[^2H_6]$DMSO): δ 2.39 (6H, MeN), 2.56 (2H, CH_2). The product darkens slightly in the light and does not change at 0 °C in the dark during lengthy storage.

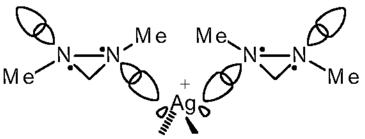
[‡] Basic crystallographic data: $C_3H_8N_3O_3Ag$, $M = 242.0$; $a = 10.784(3)$, $b = 13.433(6)$, $c = 10.234(3)$ Å, $V = 1482.5(9)$ Å^3, $d_{calc} = 2.18$ g cm^{-3}. Space group P_{bca}, $z = 4$. Intensities of 802 reflections with $I > 3\sigma(I)$ were measured on an automatic diffractometer DAR-UM. The structure was determined by a direct method and also by a series of consequent Fourier syntheses by the program 'Rentgen-75'.[24] Hydrogen atoms are not localized. The structure was refined by a least-squares procedure using an isotropic approximation for all atoms down to $R = 0.093$. Full lists of 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.*, 1995, issue 1.

Table 1 Atomic coordinates ($\times 10^4$) for the unit cell of polymer chain **2**.

Atom	*x*	*y*	*z*
Ag	2462(1)	3296(1)	7139(1)
N(1)	2671(19)	2765(18)	3943(19)
N(2)	2975(16)	2508(16)	5214(18)
N(3)	135(11)	4322(9)	7835(11)
O(1)	126(11)	3432(8)	7719(13)
O(2)	1107(13)	4769(10)	7589(16)
O(3)	−83(12)	4764(11)	8177(15)
C(1)	3892(12)	3022(11)	4413(15)
C(2)	3200(17)	1407(11)	5268(17)
C(3)	1758(16)	3698(12)	4010(18)

HOMO of the diaziridine ligand in complex **2** results in appreciable shortening of the N–N bond (Figure 1).

Thus, in complex **2** the silver(I) ion is coordinated in the direction of maximal electron density of the HOMO of the diaziridine ligand, which is a C_2-symmetrical combination of non-bonding (n_N) orbitals of the nitrogen atoms.[21] Two lowest unoccupied sp^3-hybridized orbitals of the silver ion participate in formation of the bond.



The Ag, O(1), O(2) and N(3) atoms form a planar four-membered ring and deviation of the atoms from the central plane does not exceed 0.05 Å. The bonds Ag–O(1) and Ag–O(2) are slightly extended in comparison with the sum of the covalent radii of these atoms (2.40 Å).[15] The silver atom has a tetrahedral configuration but due to ionic interchain contacts it possesses the configuration of a distorted octahedron, so its coordination number increases up to 6.

The formation of complexes such as **2** is assumed to be one of the stages in the oxidation of 1,2*H*-diaziridines to diazirines under the action of Ag_2O.[6]

As determined in the present work, complex **2** is a centrally symmetric entity. Therefore, the action of a calculated amount of $AgNO_3$ on non-racemic diaziridine **1** with a known enantiomeric excess can be used for enhancement of this excess as is achieved for 1,3,3-trialkyldiaziridines under the action of chloral.[23]

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References

1 M. Tasi, A. K. Powell and H. Vahrenkamp, *Chem. Ber.*, 1991, **124**, 1549.
2 C. T. Maxey and L. McElwee-White, *Organometallics*, 1991, **10**, 1913.
3 C. T. Maxey, H. F. Sleiman, S. T. Massey and L. McElwee-White, *J. Am. Chem. Soc.*, 1992, **114**, 5153.
4 R. Dominique and A. Howard, *J. Chem. Soc., Chem. Commun.*, 1987, 212.
5 A. Howard, D. Daniele, K. Masayuki and R. Dominique, *Organometallics*, 1990, **9**, 762.
6 E. Schmitz, *Dreiringe mit Zwei Heteroatomen*, Springer-Verlag, Berlin, 1967 (in German).
7 V. P. Sinditskii, M. D. Dutov, A. E. Fogel'zang and V. V. Kuznetsov, *Zh. Neorg. Khim.*, 1991, **36**, 944 (*Russ. J. Inorg. Chem.*, 1991, 535).
8 A. Adedapo, S. A. Benyunes, P. A. Chaloner, C. Claver, P. B. Hitchcock, A. Ruiz and N. Ruiz, *J. Organomet. Chem.*, 1993, **443**, 241.
9 P. F. dos Santos Filho and H. de O. Pastore, *J. Chem. Res. S.*, 1989, 326.
10 G. Sosnovsky and J. Lukszo, *J. Cancer Res. Clin. Oncol.*, 1984, **107**, 217.
11 A. Adedapo, A. G. Avent, D. Carmichael, P. A. Chaloner, P. B. Hitchcock and A. Wagenaar, *J. Chem. Soc., Chem. Commun.*, 1993, 186.
12 E. Schmitz and D. Habisch, *Chem. Ber.*, 1962, **95**, 680.
13 B. Carboni, L. Toupet and R. Carrie, *Tetrahedron*, 1987, **43**, 2293.
14 R. Ohme, E. Schmitz and P. Dolge, *Chem. Ber.*, 1966, **99**, 2104.
15 S. S. Batsanov, *Zh. Neorg. Khim.*, 1991, **36**, 3015 (*Russ. J. Inorg. Chem.*, 1991, 1694).
16 G. B. Ansell, L. A. Burkardt and W. G. Finnegan, *J. Chem. Soc., Chem. Commun.*, 1969, 459.
17 G. B. Ansell and W. G. Finnegan, *J. Chem. Soc., Chem. Commun.*, 1969, 1300.
18 Y. Kim, J. W. Gilje and K. Seff, *J. Am. Chem. Soc.*, 1977, **99**, 7057.
19 V. S. Mastryukov, O. V. Dorofeeva, L. V. Vilkov and A. V. Golubinskii, *J. Mol. Struct.*, 1976, **32**, 161.
20 G. V. Shustov, A. B. Zolotoi, N. L. Zaichenko, O. A. Dyachenko, L. O. Atovmyan and R. G. Kostyanovsky, *Tetrahedron*, 1984, **40**, 2151.
21 G. V. Shustov, S. N. Denisenko, I. L. Asfandiarov, L. R. Khusnutdinova and R. G. Kostyanovsky, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1986, 1824 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1986, **35**, 1655).
22 G. V. Shustov, A. Yu. Shibaev, Yu. V. Puzanov and R. G. Kostyanovsky, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1988, 1869 (*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1988, **37**, 1671).
23 R. G. Kostyanovsky, A. E. Polyakov, G. V. Shustov, I. S. Zakharov and V. I. Markov, *Dokl. Akad. Nauk SSSR*, 1974, **219**, 873 [*Dokl. Chem. (Engl. Transl.)*, 1974, 831].
24 V. I. Andrianov, Z. Sh. Saphina and B. L. Tarnopolskii, *'Rentgen-75'. Computer program for the solution of crystal structures*, Chernogolovka, 1975.

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