Synthesis and structures of complexes of *N*-(2-aminoethyl)diaziridines with transition metal salts

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A series of complexes of *N*-(2-aminoethyl)diaziridines with transition metal salts (Zn^{2+}, Cd^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, or Fe^{2+}) were synthesized. Their structures were established by IR and NMR spectroscopy. The structure of bis[1,2-bis(2-aminoethyl)diaziridine]cadmium(II) diperchlorate was confirmed by X-ray diffraction analysis.

Key words: complex formation, *N*-(2-aminoethyl)diaziridines, bis[1,2-bis(2-aminoethyl)diaziridine]cadmium(II) diperchlorate, transition metal salts, X-ray diffraction analysis.

Studies in the field of coordination chemistry of diaziridines have been started only recently. However, the preparation of this type of structures may be of interest from different standpoints. First, complexation can be used for directed spontaneous separation of enantiomers of diaziridines.[1,2] Second, complexation can promote different reactions involving diaziridines through formation of complex intermediates, which catalyze the process, for example, carbonylation of 3,3-disubstituted diaziridines to form aza-β-lactams.[3,4] In connection with the data on potential biological activity of diaziridines,[5–7] it is of interest to study the biological activity of their complexes. In addition, the possibility of existence of stable complexes of diaziridines with transition metal salts, which are Lewis acids, is of interest in itself because it is known that diaziridines are sensitive to acids.[8] The first representatives of these complexes were synthesized by the reactions of 1,2-bis(2-aminoethyl)diaziridine (**1a**) with salts of divalent metals, *viz.*, Ni, Cu, and Cd.[9] It appeared that only Ni and Cd complexes are stable. Their structures were not unambiguously established (only the IR and UV spectra were measured).

In the present work, complexes of diaziridine **1a** and 1-(2-aminoethyl)-2-methyldiaziridine (**1b**) with transition metal salts, *viz.*, with $Ni(ClO_4)_2$, $Ni(NO_3)_2$, $Cd(ClO_4)_2$, $Mn(NO_3)_2$, $CoCl_2$, $Zn(NO_3)_2$, and $Fe(NO_3)_2$, were synthesized and their structures and properties were investigated. The salts with perchlorate and nitrate anions were chosen because the bulkiness of the anions hinders their involvement in the inner coordination sphere. In addition, perchlorates and nitrates can form crystals suitable for X-ray diffraction analysis. The starting ligands were synthesized according to known procedures.[10,11] The complexes were prepared by mixing a solution of **1a** in propan-2-ol or a solution of **1b** in methanol with solutions of the corresponding salts in the same solvents.

As shown in the scheme, complexes of the general formulas $[M(\mathbf{1a})_2]^{2+}X^{-}_2$ (**2a—f**) and $[M(\mathbf{1b})_3]^{2+}X^{-}_2$ (**3a—e**) were prepared. The structures of the complexes were established based on the data of elemental analysis for C, H, and N, quantitative analytical determination of metals and counterions, and the results of ^1H and ^{13}C NMR and IR spectroscopy. The structure of complex **2c** was also studied by X-ray diffraction analysis (Table 1—4).

The IR spectra were measured for all complexes. The NMR spectra were recorded only for complexes **2a,c,e** and **3a,b** because the remaining complexes are poorly soluble and the complex-forming metal cations exhibit paramagnetic properties resulting in substantial broadening of the signals.

The IR spectra of complexes **2** and **3** have the following characteristic absorption bands: stretching vibrations of the NH_2 group and the $N_{(ring)}$—$CH_{2(exoring)}$ bond, wagging vibrations of the NH_2 group, $CH_{2(ring)}$ rocking vibrations, and absorption bands corresponding to the anions (see Table 2). The low-frequency shifts of the stretching vibration bands of the NH_2 group by 8—145 cm^{-1} for both types of complexes compared to the analogous absorption bands of the initial diaziridines **1a,b** indicate that the metal cations are coordinated by the amino group of the 2-aminoethyl fragment (analogous shifts were observed in the study[9] and for com-

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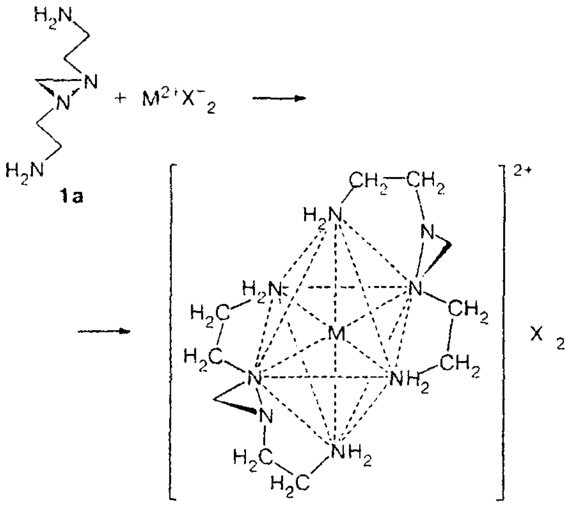
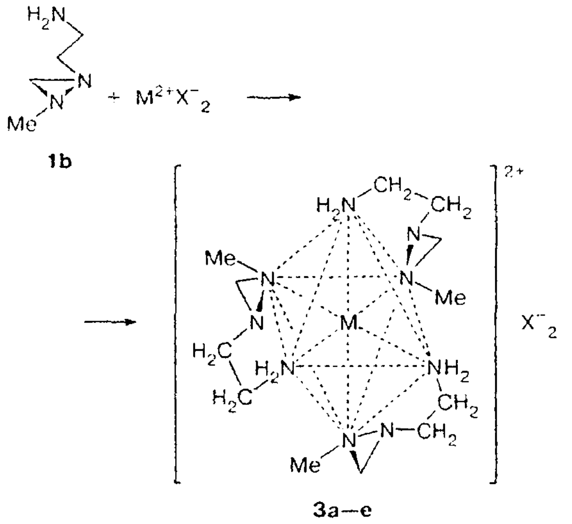


2a—f
(ML_2X_2, L = **1a**)

2	**a**	**b**	**c**	**d**	**e**	**f**
M	Ni	Ni	Cd	Mn	Zn	Co
X	ClO_4	NO_3	ClO_4	NO_3	NO_3	Cl



3a—e
(ML_3X_2, L = **1b**)

3	**a**	**b**	**c**	**d**	**e**
M	Cd	Zn	Co	Mn	Fe
X	ClO_4	NO_3	Cl	NO_3	NO_3

plexes with ethylenediamine[12]). The involvement of the amino groups in coordination is also evidenced by the noticeable high-frequency shifts of the wagging vibration bands of the NH_2 group in both types of the complexes (the bands are shifted from 905 and 908 cm^{-1} to the region of 1130—1182 cm^{-1}).

Apparently, splitting of the band at 1025 cm^{-1} belonging to stretching vibrations of the $N_{(ring)}$—$CH_{2(exoring)}$ bond in the spectra of complexes **2** simultaneously with the low-frequency shift of one of these bands is associated with the nonequivalence of the nitrogen atoms of the ring due to coordination only through one of them. In the IR spectra of complexes **3**, the band of the N—CH_3 group is slightly shifted to the high-frequency region (by 13—22 cm^{-1}) compared to the analogous absorption band of the initial compound, while the position of the band of the $N_{(ring)}$—$CH_{2(exoring)}$ bond changes insignificantly. Apparently, the difference in the direction of the shift of the $N_{(ring)}$—$CH_{2(exoring)}$ band in complexes **2** and of the shift of the $N_{(ring)}$—CH_3 band in complexes **3** is associated with the larger strength of the bond between the M^{2+} ion and the nitrogen atom involved in the $N_{(ring)}$—CH_3 bond due to the higher electron density on this nitrogen atom owing to the electron-donating effect of the methyl group. Based on these data, it can be suggested that the nitrogen atom bound to the methyl group serves as the second coordination center for the metal cation in complexes **3**. The shift of the rocking vibration bands of the cyclic CH_2 group to the low-frequency region by 4—55 cm^{-1} may be indicative of the formation of the bond between the metal cation and the nitrogen atom of the ring in both types of the complexes. The IR spectra of all perchlorate complexes have absorption bands at 1080 and 610—645 cm^{-1}, which are typical of the ClO_4^- ion, whereas the IR spectra of the nitrate complexes have intense absorption bands at 1350 cm^{-1} belonging to the NO_3^- anion.

In the ^1H NMR spectra of compounds **1a,b**, the CH_2 group bound to the diaziridine ring is manifested as an

Table 1. Yields and selected characteristics of the compounds[a]

Complex	Yield (%)	T_{decomp} /°C	Found/Calculated (%)				
			X[b]	M[b]	C	H	N
2d	83	136	29.04 28.28	12.41 12.51	27.32 27.35	6.48 6.38	31.99 31.90
2e	92	158	27.33 27.59	14.52 14.61	26.76 26.70	6.28 6.25	31.33 31.15
2f	87	187	14.11 14.26	11.70 11.83	30.92 30.72	7.28 7.16	28.77 28.66
3a	66	280	11.36 11.55	18.32 18.29	23.27 23.44	5.26 5.37	20.45 20.51
3b	31	210	25.20 25.18	12.98 13.28	29.63 29.25	6.56 6.70	31.36 31.27
3c	38	180	25.52 24.01	14.25 13.63	32.45 32.25	7.84 7.62	29.36 29.03
3d	20	220	25.73 25.71	11.68 11.41	29.57 29.87	6.69 6.85	31.65 31.95
3c	30	202	25.69 23.26	13.48 13.99	35.82 36.11	7.93 8.27	17.49 17.59

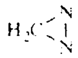
[a] The synthesis and IR spectra of complexes **2a—c** were reported previously.[9]
[b] X is the anion and M is the metal atom.

Table 2. Selected vibration frequencies (ν/cm^{-1}) and their assignment in the IR spectra of 1,2-bis(2-aminoethyl)diaziridine (**1a**), 1-(2-aminoethyl)-2-methyldiaziridine (**1b**), and their complexes **2** and **3**

Compound	$\nu(NH_2)$	$\omega(NH_2)$	$\nu(N_{ring}-CH_{2(exoring)})$	$\nu(N_{ring}-CH_3)$	$\rho(CH_{2(ring)})$	$\nu(M^{2+}-N)$
1a	3370 s, 3290 s, 3190 sh	908 s	1025 sh	—	796 sh	—
2d	3323 s, 3240 sh, 3182 sh	1178 sh	1040 sh, 1017 sh	—	790 s	608 m, 513 w, 467 m, 432 m
2e	3327 s, 3260 sh, 3203 sh	1182 m	1045 sh, 1022 w	—	789 m	623 m, 525 m, 478 m, 437 m, 426 sh
2f	3303 s, 3187 s	1180 m	1028 m, 1011 m	—	792 s	623 m, 532 s, 486 m, 447 m
1b	3365 s, 3290 s, 3190 sh	905 s	1045 sh	1055 s	875 s	—
3a	3269 s, 3148 m	1130 m	1043 m	—	820 m	520 m, 376 m, 304 w
3b	3267 s, 3145 m	1135 m	1050 m	1071 m	825 m	415 m, 336 m
3c	3268 s, 3152 s	1133 m	1046 m	1068 m	830 m	530 m, 457 m, 394 m
3d	3272 s, 3151 m	1145 s	1048 m	1077 m	835 m	568 m, 336 m
3e	3270 s, 3150 m	1140 s	1040 m	1075 m	835 w	464 m

Note: ν, stretching vibrations; ω, wagging vibrations; ρ, rocking vibrations; s, strong band; m, medium band; w, weak band; sh, shoulder.

Table 3. The ^{1}H and ^{13}C NMR spectra of 1,2-bis(2-aminoethyl)diaziridine (**1a**), 1-(2-aminoethyl)-2-methyldiaziridine (**1b**), and their complexes **2** and **3** in D_2O

Compound	δ (*J*/Hz)							
			N—C̲H̲$_2$—C		C—C̲H̲$_2$—NH$_2$		N—Me	
	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C	^{1}H	^{13}C
1a	2.75 s	55.18 t	2.35 m, 2.65 m	60.68 t	2.82 m	38.62 t		
1b*	2.63 (AB, ^2J = 5.4)	57.11 t	2.76 m	41.02 t	2.30 m, 2.60 m	63.39 t	2.41 s	47.65 q
2a	2.75 br.s		2.25 m, 3.16 m		2.66 m			
2s	3.21 br.s	55.51 t	2.25 br.m, 3.48 br.m	60.52 t	3.32 br.s	39.54 t		
2e	3.24 br.s	56.25 t	2.39 m, 3.27 m	59.14 t	3.10 m	39.96 t		
3a*	2.84 (AB, ^2J = 4.8)	57.21 t	3.20 m	40.11 t	2.51 m, 2.92 m	60.17 t	2.52 s	47.74 q
3b	2.95 (AB, ^2J = 5.5)		3.42 m		2.65 m, 3.10 m		2.65 s	
3s*		57.45 t		39.23 t		57.19 t		47.57 q

* ^{13}C NMR spectra in DMSO-d_6.

Table 4. Principal bond lengths (*d*) and bond angles (ω) in bis[1,2-bis(2-aminoethyl)diaziridine]cadmium(II) diperchlorate (**2c**)

Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
Cd(1)—N(1)	2.390(8)	N(2)—C(4)	1.49(1)	N(4)—H(13)	0.62
Cd(1)—N(2)	2.364(6)	N(3)—C(3)	1.47(1)	N(4)—H(14)	0.89
Cd(1)—N(3)	2.350(7)	N(4)—C(5)	1.46(1)	N(7)—H(21)	0.92
Cd(1)—N(4)	2.459(9)	N(5)—C(6)	1.39(2)	N(7)—H(22)	0.83
Cd(1)—N(5)	2.337(6)	N(5)—C(7)	1.52(1)	N(8)—H(27)	0.99
Cd(1)—N(6)	2.402(6)	N(6)—C(6)	1.46(1)	N(8)—H(28)	0.79
N(1)—N(2)	1.46(1)	N(6)—C(9)	1.51(1)	C(2)—C(3)	1.49(2)
N(5)—N(6)	1.41(1)	N(7)—C(8)	1.46(1)	C(4)—C(5)	1.47(1)
N(1)—C(1)	1.46(1)	N(8)—C(10)	1.43(1)	C(7)—C(8)	1.50(2)
N(1)—C(2)	1.52(1)	N(3)—H(7)	0.94	C(9)—C(10)	1.50(2)
N(2)—C(1)	1.42(1)	N(3)—H(8)	0.98		

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
N(1)—Cd(1)—N(4)	86.6(3)	N(2)—N(1)—C(1)	58.2(5)	N(1)—C(2)—C(3)	108.3(8)
N(1)—Cd(1)—N(8)	104.0(3)	N(2)—N(1)—C(2)	107.3(6)	N(2)—C(4)—C(5)	111.1(7)
N(3)—Cd(1)—N(4)	89.2(3)	N(5)—N(6)—C(6)	57.9(7)	N(3)—C(3)—C(2)	112.1(8)
N(3)—Cd(1)—N(8)	88.2(2)	N(5)—N(6)—C(9)	109.0(7)	N(4)—C(5)—C(4)	112.3(7)
N(4)—Cd(1)—N(5)	89.5(3)	N(6)—N(5)—C(6)	62.9(7)	N(5)—C(7)—C(8)	109.3(9)
N(4)—Cd(1)—N(7)	97.8(3)	N(6)—N(5)—C(7)	109.1(8)	N(6)—C(9)—C(10)	109.3(7)
N(4)—Cd(1)—N(8)	167.9(2)	C(1)—N(1)—C(2)	112.7(7)	N(7)—C(8)—C(7)	110.0(8)
N(5)—Cd(1)—N(8)	81.0(3)	C(1)—N(2)—C(4)	114.0(5)	N(8)—C(10)—C(9)	113.1(8)
N(7)—Cd(1)—N(8)	86.7(2)	C(6)—N(5)—C(7)	111.8(9)	N(1)—C(1)—N(2)	61.1(5)
N(1)—N(2)—C(1)	60.7(5)	C(6)—N(6)—C(9)	112.6(8)	N(5)—C(6)—N(6)	59.1(7)

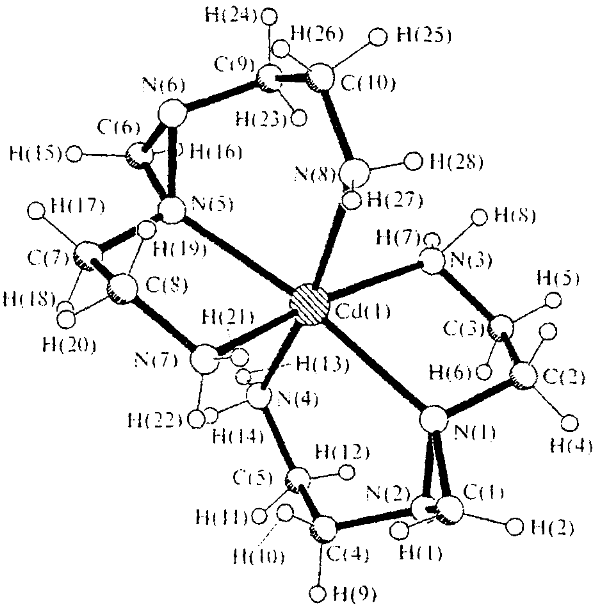


Fig. 1. Overall view of the molecule of bis[1,2-bis(2-aminoethyl)diaziridine]cadmium(II) diperchlorate (**2c**)

ABX_2 system.[10,11] In the ^1H and ^{13}C NMR spectra of complexes **2** and **3** with these ligands (solutions in D_2O or DMSO-d_6), all signals are noticeably shifted, which is indicative of complexation. Taking into account that the metal cation in complexes **2** is coordinated by two amino groups and one nitrogen atom of the ring, which was assumed based on analysis of the IR spectra, two ABX_2 systems would be expected to appear due to the nonequivalence of the nitrogen atoms of the ring. However, this situation was not actually observed. Evidently, the equilibrium coordination of the nitrogen atoms of the diaziridine ring to the metal cation exists in solution.

The structures of the complexes of type **2** were confirmed by X-ray diffraction study of bis[1,2-bis(2-aminoethyl)diaziridine]cadmium(II) diperchlorate (**2c**). In the crystal structure of compound **2c**, the structural units are the complex cation $[Cd(N_4C_5H_{14})_2]^{2+}$ and two crystallographically nonequivalent ClO_4^- anions (Fig. 1). According to the X-ray diffraction data, the Cd^{2+} ion in complex **2c** is coordinated by two nitrogen atoms of the NH_2 groups and two nitrogen atoms of the diaziridine rings of two different 1,2-bis(2-aminoethyl)diaziridine molecules. The CdN_6 coordination polyhedron is a distorted octahedron (the average deviation of the N(1), N(3), N(5), N(7), and Cd(1) atoms from the plane is 0.10 Å; the axial N(4)N(8) line is inclined to the equatorial plane at an angle of 86°). In the 1,2-bis(2-aminoethyl)diaziridine molecules, the 2-aminoethyl substituents are *trans*-oriented with respect to the plane of the heterocycle (the C(2)N(1)N(2)C(4) and C(7)N(5)N(6)C(9) torsion angles are −146.8 and 149.4°, respectively). The geometric parameters of the 2-aminoethyl substituents and the ClO_4^- anions are close to the standard values. The principal bond lengths and bond angles are given in Table 4.

Based on the similarity of the spectral characteristics of all complexes studied in the present work, it can be assumed that the complex cations in all compounds in the crystalline state have octahedral structures identical to that established by X-ray diffraction analysis of the cadmium perchlorate complex.

Experimental

The IR spectra were recorded on a UR-20 spectrometer in KBr pellets. The ^1H and ^{13}C NMR spectra were measured on Bruker WM-250 (250 MHz) and Bruker AM-300 (75.5 MHz) spectrometers, respectively, with $MeSi_4$ as the internal standard. TLC was carried out on Silufol UV-254 plates; spots were visualized with I_2 vapor and independently by spraying the TLC plates with a solution of diphenylamine in acetone followed by heating of the plates ($MeOH-H_2O-NH_3$ as the eluent; 93 : 5 : 2 v/v). The decomposition temperatures of the complexes were determined on a Boetius PHMK 05 instrument.

Synthesis of complexes 2 and 3 (general procedure). A solution of the corresponding salt (0.02 mol for **1a** or 0.03 mol for **1b**) in 10 mL of propan-2-ol (for **1a**) or methanol (for **1b**) was added to a solution of the corresponding (2-aminoethyl)diaziridine **1a,b** (0.01 mol) in the same solvent (10 mL). The reaction mixture was stirred at 20 °C for 10—15 min. The precipitate that formed was filtered off, washed with the corresponding solvent, and dried in air.

X-ray diffraction study of bis[1,2-bis(2-aminoethyl)diaziridine]cadmium(II) diperchlorate (2c). X-ray diffraction data were collected on an automated Enraf-Nonius CAD-4 diffractometer (λ(Mo-Kα) radiation, graphite monochromator, θ/2θ scanning technique, θ_{max} = 30°). A total of 3416 reflections were measured of which 2883 independent reflections were with $I > 3\sigma$. The crystals are orthorhombic: a = 9.238(5), b = 16.494(7), c = 14.319(7) Å, V = 2181.7(9) Å^3, molecular weight 571.7, space group $Pbc2_1$, Z = 4, d_{calc} = 1.74 g cm^{-3}, $F(000)$ = 1160, μ = 1.29 cm^{-1}.

The structure was solved by the direct method and refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms. The positions of the H atoms of the amino groups were located from the difference electron density synthesis. The positions of the remaining H atoms were calculated from crystal-chemical considerations. All H atoms were included in the refinement with fixed thermal and positional parameters. The final R factor was 0.0401, wR = 0.113, and GOOF = 1.057. All calculations were performed on an IBM Pentium computer with the use of the SHELXTL93 program package.[13] The complete tables of the atomic coordinates and the geometric parameters were deposited with the Cambridge Structural Database.

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