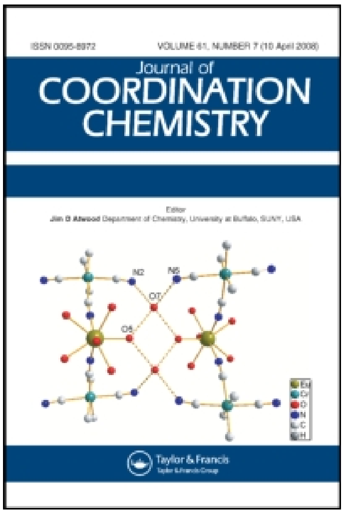

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Reactivity of 2,2-dimethylaziridine towards d^{10} transition metal halides†

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The reaction of zinc(II)bromide and zinc(II)-, cadmium(II)-, and mercury(II)iodide with 2,2-dimethylaziridine (az) yields tetrahedral mononuclear complexes of the type $(az)_2MX_2$ (M = Zn, X = Br, I; M = Hg, X = I). The reaction of CdI_2, however, with az yields the formal dimerized ligand *N*-(2-aminoisobutyl)-2,2-dimethylaziridine (aiaz) forming the ionic complex $[(aiaz)_2CdI]_2[CdI_4]$. This dimerization of two az ligands into the new bidentate aiaz ligand occurs in the coordination sphere of the metal via a metal-mediated template reaction. This may be favored by the formation of a five-membered *N*,*N*′-chelating ring. While the zinc(II) and mercury(II) complexes show tetrahedral geometries of the type $(az)_2MX_2$, the cadmium aiaz complex consists of two mono cationic trigonal bipyramidal coordinated cadmium(II) centers and one tetrahedral $[CdI_4]^{2-}$ dianion.

Keywords: Zinc; Cadmium; Mercury; Aziridine; N ligands

1. Introduction

The reactive nature of aziridine compounds is mainly due to high ring strain which was first taken into consideration by von Baeyer [1] in his strain theory. As a matter of fact, aziridines offer a great variety of synthetic applications in organic and macromolecular chemistry [2–8].

The coordination chemistry of aziridine dates back to 1956, when Jones *et al.* [9] reported the synthesis of an unstable uranium-aziridine complex. Hieber and Wiesboeck [10] introduced the aziridine ligand in organometallic chemistry by reacting it with $[Co_2(CO)_8]$ yielding $[Co(C_2H_5N)_6]^{2+}[Co(CO)_4^-]_2$. Subsequently, the coordination chemistry of aziridines has been widely explored [11–25]. As expected for secondary and tertiary amine ligands, the coordination chemistry of aziridines shows the preference for metal coordination by the N atom. Although aziridines are isolobal to oxiranes and thiiranes (C_2H_4X; X = NH, O, S), their ligand reactivity differs considerably. Oxiranes and thiiranes act as oxidizing agents towards organometallic

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†This article is dedicated to Prof. em. Dr H.C. Wolfgang Steglich on the occasion of his 75th birthday.

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compounds resulting in oxo or thio complexes via ethylene elimination [26]. Nevertheless, transition metal-mediated ring opening reactions of aziridine ligands yielding *N*,*N*′-aminoethylaziridine-complexes by dimerization [27], β-aminoacyl complexes by reaction with hydrido transition metal carbonyls [13], cyclic carbene ligands synthesized by using halogenido metal carbonyls or isocyanide complexes, and aziridine [28–30] or oxidative addition products with nickel(0) and palladium(0) complexes have been reported [31, 32]. Beck and coworkers were the first to observe metal-mediated template dimerization of aziridines forming the *N*,*N*′-chelate *N*-(2-aminoethyl)-aziridine ligand. Inspired by our recent results on the aziridine coordination chemistry [33–35], we have studied the reactivity of 2,2-dimethylaziridine towards d^{10} transition metal halides. Herein, we report the synthesis and characterization of novel 2,2-dimethylaziridine (az) and *N*-(2-aminoisobutyl)-2,2-dimethylaziridine (aiaz) complexes of $ZnBr_2$ and MI_2 (M = Zn, Cd, Hg).

2. Experimental

All manipulations were performed under a dry argon atmosphere using Schlenk techniques. 2,2-Dimethylaziridine (az) (**1**) was prepared according to literature methods, distilled from sodium and stored under argon [11, 36]. Anhydrous $ZnBr_2$, ZnI_2, CdI_2, and HgI_2 were used as received from commercial suppliers without purification. Dichloromethane was distilled from calcium hydride; *n*-pentane, *n*-hexane, and *n*-heptane were distilled from sodium and acetone (HPLC grade) was dried over 4 Å molecular sieves. All solvents were stored under dry argon and over 3 or 4 Å molecular sieves (CH_2Cl_2) or sodium (*n*-pentane, *n*-hexane, and *n*-heptane). The ^{1}H, ^{13}C and DEPT-135 ^{13}C NMR spectra were recorded using Jeol Eclipse 270 and Jeol Eclipse 400 instruments operating at 270 MHz (^{1}H), 400 MHz (^{1}H) and 68 MHz (^{13}C), 100 MHz (^{13}C). All chemical shifts are given in parts per million relative to TMS (^{1}H, ^{13}C). Mass spectra were measured using a JEOL Mstation JMS 700 in the DEI or FAB^{+} mode (NBA matrix). Multi-isotope containing fragments refer to the isotope with the highest abundance. Infrared spectra were recorded with a Bruker IFS 66v/S FT-IR and Perkin Elmer Spectrum One FT-IR spectrometer in the 4000–400 cm^{-1} range. Elemental analysis (CHNS/ICP) was provided by the Microanalytical Laboratory of the Department of Chemistry and Biochemistry, LMU Munich, using a Heraeus Elementar Vario EL and an ICP VARIAN-VISTA spectrometer.

2.1. *Synthesis and characterization*

$ZnBr_2$ (**2**) or MI_2 (M = Zn (**3**), Cd (**4**), Hg (**5**)) was suspended in 20 mL dry CH_2Cl_2. The az (**1**) ligand was added, and the resulting colorless solutions were stirred for 12 h at ambient temperature (21°C). All remaining solid residues were removed by filtration. Subsequently, all volatiles were removed *in vacuo*. The solid residue was purified by stirring in dry *n*-hexane or *n*-heptane (20 mL) for 12 h at ambient temperature. Then the non-polar phase was removed by decantation or filtration and the solid was dried *in vacuo*. For reaction of HgI_2, all procedures were performed in the dark due to the light sensitivity of $[(az)_2HgI_2]$ (**9**) by covering reaction vessels with aluminum foil. Compound **9** is the main product obtained from the procedure described above. Nevertheless, after allowing the reaction solution to stand for two days in daylight, colorless crystals of [(aiaz)HgI_2] (**10**) were obtained due to the light induced decomposition of **9**. Spectroscopic data are given for **9**, obtained according to the method described here.

2.1.1. [Dibromido-*bis*(2,2-dimethylaziridine)-zinc(II)] (6). Compound **6** was prepared according to the method described above. Reagents: $ZnBr_2$ (**2**) (199 mg, 0.884 mmol), 2,2-dimethylaziridine (**1**) (132 mg, 168 µL, 2.1 equiv., 1.856 mmol). Colorless powder, yield: 97 mg (30%). Colorless crystals were obtained by slow isothermic diffusion of *n*-pentane into an acetone solution of **6**. Anal. Calcd for $C_8H_{18}N_2ZnBr_2$ (%): C, 26.15; H, 4.94; N, 7.62. Found: C, 26.88; H, 4.96; N, 7.82. IR (KBr, cm^{-1}) = 3258 (vs), 3120 (w), 3009 (w), 2972 (m), 2931 (w), 2868 (w), 1589 (w), 1450 (m), 1389 (m), 1352 (m), 1335 (m), 1265 (w), 1137 (m), 1124 (m), 1102 (m), 1053 (w), 1029 (w), 962 (m), 903 (m), 862 (w), 807 (s), 673 (w), 500 (w), 432 (w). ^1H NMR ($CDCl_3$): δ 2.08 (s, 4H, CH_2), 1.61–1.46 (m, 12H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 39.1 (C_q), 36.1 (CH_2), 35.2 (CH_2), 25.7 (CH_3), 22.7 (CH_3). FAB^+ mass spectrum (NBA): 287.0 $[M - Br]^+$, 216.0 $[M - Br - az]^+$.

2.1.2. [*Bis*(2,2-dimethylaziridine)-diiodido-zinc(II)] (7). Compound **7** was prepared according to the method described above. Reagents: ZnI_2 (**3**) (179 mg, 0.561 mmol), 2,2-dimethylaziridine (**1**) (84 mg, 107 µL, 2.1 equiv., 1.178 mmol). Colorless powder, yield: 202 mg (78%). Anal. Calcd for $C_8H_{18}N_2ZnI_2$ (%): C, 20.82; H, 3.93; N, 6.07. Found: C, 20.52; H, 3.81; N, 5.94. IR (KBr, cm^{-1}) = 3226 (vs), 3006 (w), 2968 (s), 2929 (m), 2872 (w), 2762 (w), 1583 (w), 1447 (m), 1387 (s), 1351 (s), 1337 (s), 1262 (m), 1192 (w), 1121 (s), 1095 (s), 1054 (w), 1031 (w), 950 (s), 907 (s), 862 (w), 805 (vs), 673 (w), 496 (m), 438 (w). ^1H NMR ($CDCl_3$): δ 3.16 (s, br, 1H, NH), 2.17 (s, br, 4H, CH_2), 1.68–1.54 (m, 12H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 40.0 (C_q), 36.4 (CH_2), 35.6 (CH_2), 26.3 (CH_3), 22.7 (CH_3). DEI mass spectrum (Acetone): 460.9 $[M + H]^+$, 333.0 $[M - I]^+$.

2.1.3. Di[*bis*(*N*-(2-aminoisobutyl)-2,2-dimethylaziridine)-iodido-cadmium(II)][tetraiodido-cadmate(II)] (8). Compound **8** was prepared according to the method described above. Reagents: CdI_2 (**4**) (405 mg, 1.106 mmol), 2,2-dimethylaziridine (**1**) (393 mg, 499 µL, 5.0 equiv., 5.529 mmol). Colorless powder, yield: 1439 mg (78%). Colorless crystals were obtained by slow isothermic diffusion of *n*-pentane into a dichloromethane solution of **8**. Anal. Calcd for $C_{32}H_{72}Cd_3I_6N_8$ (%): C, 23.05; H, 4.35; N, 6.75. Found: C, 24.47; H, 4.84; N, 7.51. IR (KBr, cm^{-1}) = 3187 (s), 3121 (s), 2961 (vs), 2929 (w), 2874 (w), 1584 (w), 1456 (m), 1396 (w), 1384 (m), 1373 (w), 1340 (m), 1289 (w), 1226 (w), 1194 (w), 1153 (m), 1114 (m), 1084 (m), 1057 (m), 1017 (w), 998 (m), 950 (w), 918 (w), 861 (w), 808 (vs), 767 (w), 687 (w), 631 (w), 599 (w), 561 (w), 509 (w), 424 (w). ^1H NMR ($CDCl_3$): δ 3.48 (d, $^2J_{H,H} = 12.4$ Hz, 2H, CH_2), 3.09 (s, br, 4H, NH_2), 2.66 (s, 2H, CH_2), 1.91 (d, $^2J_{H,H} = 12.6$ Hz, 2H, CH_2), 1.42 (s, 6H, CH_3), 1.41 (s, 6H, CH_3), 1.35 (s, 6H, CH_3), 1.33 (s, 2H, CH_2), 1.26 (s, 6H, CH_3). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 62.1 (CH_2), 53.3 (C_q), 44.7 (CH_2), 38.7 (C_q), 30.4 (CH_3), 27.2 (CH_3), 27.1 (CH_3), 18.7 (CH_3). FAB^+ mass spectrum (NBA): 525.1 $[M]^+$, 383.0 $[M - aiaz]^+$.

2.1.4. [*Bis*(2,2-dimethylaziridine)-diiodido-mercury(II)] (9). Compound **9** was prepared according to the method described above. Reagents: HgI_2 (161 mg, 0.354 mmol), 2,2-dimethylaziridine (**1**) (50 mg, 64 µL, 2.0 equiv., 0.709 mmol). Colorless, light sensitive powder, yield: 128 mg (61%). Colorless crystals of **10** were obtained by slow evaporation of a dichloromethane solution of **9**. Anal. Calcd for $C_8H_{18}N_2HgI_2$ (%): Hg, 33.62. Found: Hg, 33.43. IR (KBr, cm^{-1}) = 3302 (w), 3225 (m), 3132 (w), 3048 (w), 2962 (s), 2923 (m), 2871 (w), 2734 (w), 1570 (m), 1444 (m), 1383 (s), 1372 (s), 1339 (m), 1273 (w), 1215 (w), 1190 (w), 1155 (s), 1111 (m), 1075 (w), 1043 (w), 1010 (w), 992 (m), 913 (m), 861 (w), 808 (vs), 762 (w), 688 (w), 565 (w), 506 (w), 442 (w), 414 (w). ^1H NMR ($CDCl_3$): δ 1.90 (s, 4H, CH_2), 1.38 (s, 12H, CH_3), 0.86 (s, br, 2H, NH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 36.1 (C_q), 34.9 (CH_2), 25.1 (CH_3). FAB^+ mass spectrum (NBA): 471.0 $[M-I]^+$.

2.2. *X-ray data collection and crystal structure determination*

Single crystal X-ray diffraction data were collected on a Nonius Kappa CCD using graphite-monochromated Mo-Kα radiation. The structures were solved by direct methods using SHELXS software and refined on F^2 by full-matrix least-squares with SHELXL-97 using anisotropic displacement parameters [37]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and included in the final cycle of refinement using riding models (table 1).

3. Results and discussion

3.1. *Synthesis*

2,2-Dimethylaziridine (az) (**1**) was prepared from the corresponding β-amino-alcohol [36]. The neutral *bis*(2,2-dimethylaziridine)-dihalogenido-complexes $[(az)_2MX_2]$ (**6**, **7**, and **9**) as well as the ionic complex $[(aiaz)_2CdI]_2[CdI_4]$ were prepared according to the reactions depicted in scheme 1, by suspending anhydrous $ZnBr_2$ (**2**) and MI_2 (**3**: M = Zn, **4**: M = Cd, **5**: M = Hg) in dichloromethane and adding two or four equivalents of 2,2-dimethylaziridine (**1**). Aiaz is the formal dimerization product of az and is formed in the coordination sphere of the metal center. All of the synthesized compounds are air-stable in solution and as solids. They are soluble in polar solvents such as dichloromethane or chloroform and insoluble in non-polar solvents such as *n*-hexane. Compound **9** is light sensitive and should be synthesized and stored in the dark.

3.2. *Spectroscopic characterization*

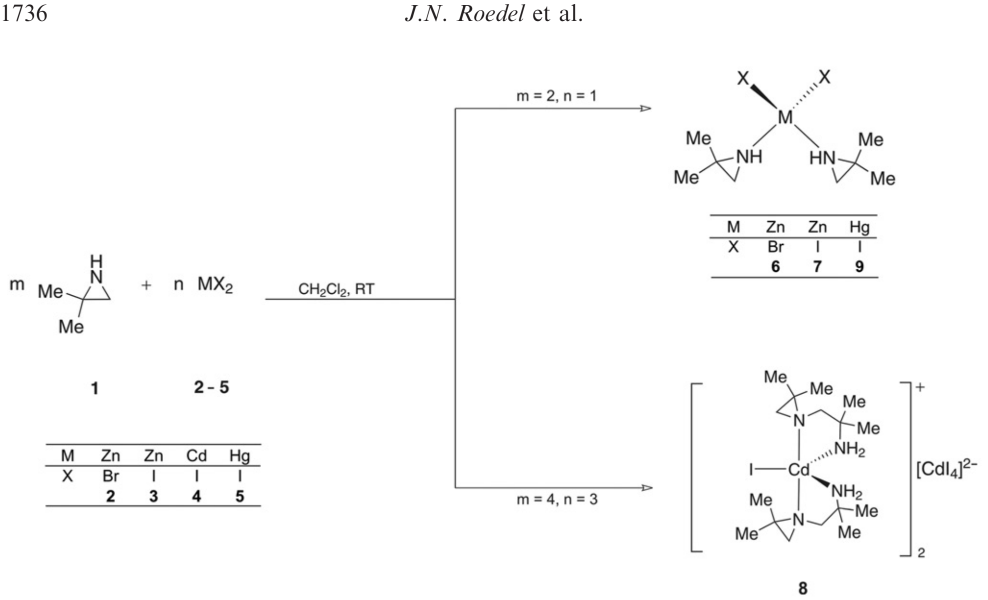
The ^1H and ^{13}C NMR spectra of **6**, **7**, and **9** show the expected aziridine signals shifted to lower field. With one exception all the ^1H signals are shifted to lower field in comparison with those observed for **1** due to coordination-induced deshielding effects. For example, the CH_2 proton signals are at 2.08 ppm (**6**), 2.17 ppm (**7**), and 1.90 ppm (**9**) and at 1.26 ppm, however, for the free aziridine **1**. The ^{13}C signal for the CH_2 fragment is shifted from 33.3 ppm for the non-coordinated aziridine **1** to

Table 1. Crystal data and details of the structure refinement for **6**, **8**, and **10**.

Compound	**6**	**8**	**10**
Formula	$C_8H_{18}Br_2N_2Zn$	$C_{34}H_{76}Cd_3Cl_4I_6N_8$	$C_8H_{18}HgI_2N_2$
Formula weight	367.43	1837.46	596.63
Temperature (K)	200(2)	200(2)	200(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/c$
Units of dimensions (Å, °)			
a	10.397(2)	11.248(2)	20.408(4)
b	6.2702(13)	16.192(3)	15.410(3)
c	20.943(4)	17.580(3)	15.397(3)
α	90	81.43(3)	90
β	101.42(3)	75.21(3)	92.83(3)
γ	90	86.04(3)	90
V (Å^3)	1338.3(5)	3059.5(9)	4836.3(16)
Z	4	2	12
ρ_{Calcd} (g cm^{-1})	1.824(9)	1.9946(6)	2.4583(8)
μ (mm^{-1})	7.772	4.264	13.350
F(000)	900	1732	3192
Crystal size (mm^3)	0.15 × 0.05 × 0.02	0.16 × 0.15 × 0.09	0.12 × 0.12 × 0.03
θ range (°)	3.40–25.37	3.21–27.46	3.14–26.04
Index range	$-12 \le h \le 12$, $-7 \le k \le 7$, $-24 \le l \le 25$	$-14 \le h \le 14$, $-20 \le k \le 20$, $-22 \le l \le 22$	$-25 \le h \le 25$, $-18 \le k \le 19$, $-18 \le l \le 18$
Reflns. collected	8346	26,138	18,335
Independent reflections	2456	13,873	9486
R_{int}	0.0443	0.0265	0.0370
Completeness to θ	99.6%	99.1%	99.4
Refinement method	Full-matrix least Squares on F^2	Full-matrix least Squares on F^2	Full-matrix least Squares on F^2
Data/restraints/parameters	2456/0/119	13,873/0/496	9486/0/365
S on F^2	1.115	1.023	1.050
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0383$, $wR_2 = 0.0933$	$R_1 = 0.0351$, $wR_2 = 0.0780$	$R_1 = 0.0457$, $wR_2 = 0.1162$
R indices (all data)	$R_1 = 0.0512$, $WR_2 = 0.1008$	$R_1 = 0.0546$, $wR_2 = 0.0868$	$R_1 = 0.0633$, $wR_2 = 0.1248$
Largest difference peak/hole (e Å^{-3})	0.920 and −0.603	1.178 and −1.288	1.552 and −1.903
CCDC number	695548	695549	695550

36.1 ppm (**6**), 36.4 ppm (**7**), and 34.9 ppm (**9**). Similar signal shifts for the C_q and CH_3 signals of **6**, **7**, and **9** are observed and are listed in the experimental section. For the two methyl groups in **6** and **7**, two singlets are slightly shifted to higher field (**6**: 22.7 ppm, **7**: 22.7 ppm) and lower field (**6**: 25.7 ppm, **7**: 26.3 ppm) compared to the non-coordinated 2,2-dimethylaziridine (**1**: 24.7 ppm) [38]. The ^1H and ^{13}C NMR spectra of **8** show clearly the signals expected for the aiaz ligands. The ethane bridge carbon atoms are detected at 62.1 ppm (CH_2) and 53.3 ppm ($C_q(CH_3)_2$) shifted to lower field compared to the ring carbon atoms at 44.7 ppm (CH_2), 38.7 ppm ($C_q(CH_3)_2$). A clear ^1H and ^{13}C NMR signal assignment of **8** was made and is listed in the experimental section.

IR spectroscopic investigations of **6**–**9** show sharp absorptions for the NH and NH_2 stretching vibrations of the az and aiaz ligands in the range 3258–2961 cm^{-1}. In addition, typical σ- and δ-ring vibrations in the fingerprint region of coordinated



Scheme 1. Synthesis of the aziridine complexes (**6–9**) by reaction of MX_2 (**2–5**) with 2,2-dimethylaziridine (**1**).

az and aiaz from 1589 cm^{-1} (**6**) to 1570 cm^{-1} (**9**) were observed [35]. As expected, the $\nu(C-H)$ absorptions for **6–9** were observed in the region 3000 cm^{-1}. The aiaz ligands coordinated to Cd(II) in **8** show the characteristic $\delta(NH_2)$ vibration at 1584 cm^{-1}.

Mass spectrometry was also used to investigate the complexes using DEI and FAB^+ mode in a *m*-nitrobenzylalcohol (NBA) matrix. The mass spectra obtained for the Zn(II) and Hg(II) complexes **6**, **7**, and **9** show the $[M-X]^+$ ($X=Br, I$) peak and a peak corresponding to the successive loss of one az ligand (**6**). The Cd(II) complex **8** shows the parent $[M^+]$ peak at $m/z=525.1$ corresponding to the $[(C_8H_{18}N_2)_2CdI]^+$ cation and a peak corresponding to the $[M-\text{aiaz}]^+$ fragment at $m/z=383.0$.

3.3. *X-ray structure analyses*

The molecular structures of **6**, **8**, and **10** were determined using single crystal X-ray diffraction. Single crystals suitable for X-ray diffraction were obtained by allowing *n*-pentane to slowly diffuse into dichloromethane or acetone solutions of **6** or **8**, respectively. Crystals of **10** were obtained by allowing a saturated solution of **9** to stand for 2 days in daylight resulting in the partial formation of the $[(\text{aiaz})HgI_2]$ complex (**10**) due to light induced decomposition and an isomerization reaction of **9**. The ligand release results in the partial formation of **10** due to excess az present in the reaction solution. This was verified by ^{13}C NMR spectroscopy. A considerably less intense signal set which could be assigned to the coordinated aiaz ligand was observed. After two days, colorless crystals of **10** suitable for X-ray diffraction were formed.

The X-ray structure determination revealed formation of tetrahedral (**6** and **10**) and trigonal bipyramidal (**8**) geometries. The zinc(II) center in **6** is coordinated by two bromido ligands and the nitrogens of two aziridines resulting in a slightly distorted tetrahedral geometry. Selected bond angles and bond lengths of **6** together with the molecular structure are given in figure 1 and table 2. C–C and C–N bond lengths and

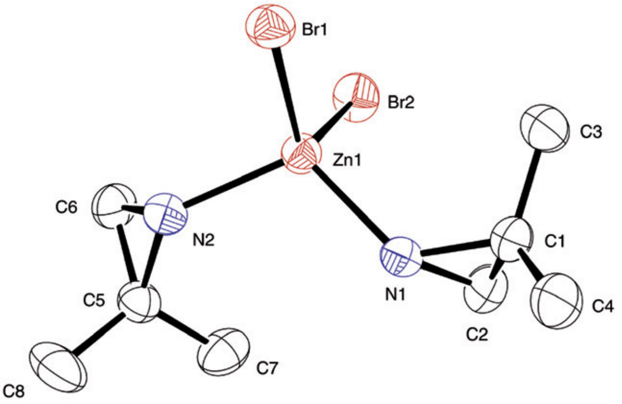


Figure 1. Molecular structure of **6**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°) for **6**.

Bond lengths (Å)				Bond angles (°)			
Zn(1)–N(1)	2.018(4)	C(1)–C(4)	1.497(7)	N(1)–Zn(1)–N(2)	110.47(16)	C(1)–N(1)–Zn(1)	127.0(3)
Zn(1)–N(2)	2.019(4)	N(1)–C(1)	1.500(6)	N(1)–Zn(1)–Br(1)	108.52(11)	C(2)–N(1)–Zn(1)	122.6(3)
Zn(1)–Br(1)	2.4192(8)	N(1)–C(2)	1.497(6)	N(1)–Zn(1)–Br(2)	108.13(11)	C(2)–C(1)–N(1)	60.8(3)
Zn(1)–Br(2)	2.3717(9)	–	–	N(2)–Zn(1)–Br(1)	100.94(12)	C(1)–C(2)–N(1)	61.0(3)
C(1)–C(2)	1.455(7)	–	–	N(2)–Zn(1)–Br(2)	110.93(11)	C(2)–N(1)–C(1)	58.1(3)
C(1)–C(3)	1.514(7)	–	–	Br(1)–Zn(1)–Br(2)	117.65(3)	–	–

angles differ slightly from those of the free aziridine **1** in the solid state [39] and only marginally from those found for other 3-D transition metal coordinated aziridines [20–22]. Both Zn–N and Zn–Br bond lengths of 2.018(4) and 2.019(4) or 2.3717(9) and 2.4192(8) observed in **6** are in good agreement with the bond lengths described for comparable zinc(II)-*sec*.-amine compounds [40]. The Br–Zn–Br angle (117.65(3)° (**6**)) is larger than the N–Zn–N angle (110.47(16)° (**6**)) due to steric repulsion of both halogenido ligands. Additionally, the C–N–Zn angles of 127.0(3)° and 128.5(3)° in **6** prove the distorted tetrahedral configuration of the aziridine nitrogen atoms. An estimate of the degree of distortion from idealized tetrahedral geometry for four coordinated complexes has been calculated according to the metric parameter τ_4 introduced by Yang *et al.* [41]. The value of τ_4 for **6** is 0.93, indicating a geometry closest to a distorted tetrahedron. The solid state structure of **6** also contains intermolecular hydrogen bridges between the bromido ligand Br1 and the nitrogen atoms N1 and N2 of adjacent aziridine ligands (d(N–Br) = 3.547 Å, 3.582 Å; N–H–Br angles = 156.20°, 152.54°).

The cadmium(II) centers of $[(C_8H_{18}N_2)_2CdI]^+{}_2\ [CdI_4]^{2-}$ (**8**) show a distorted tetrahedral geometry for the $[CdI_4]^{2-}$ anion and an ambiguous geometry in both $[(C_8H_{18}N_2)_2CdI]^+$ cations [42]. A metal-mediated dimerization reaction of the 2,2-dimethylaziridine yielding the chelating *N*-(2-aminoisobutyl)-2,2-dimethylaziridine (aiaz) is observed. The mechanism of this metal-mediated template reaction has

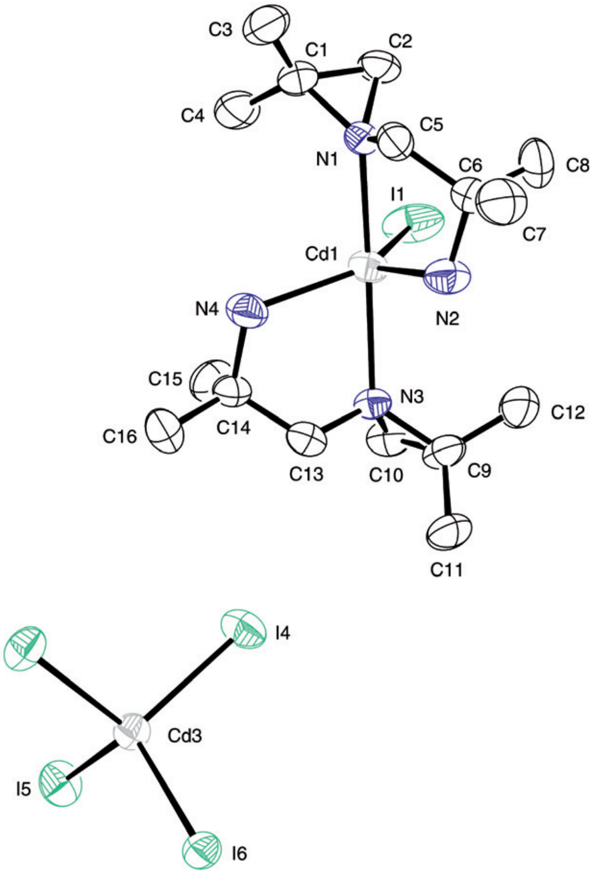


Figure 2. Molecular structure of **8**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms, two dichloromethane molecules and a $[(C_8H_{18}N_2)_2CdI]^+$ cation are omitted for clarity.

been discussed in the other literature [12]. The geometry of the $[(C_8H_{18}N_2)_2CdI]^+$ cations exhibits a borderline case between trigonal bipyramidal and square pyramidal. Two bidentate aiaz ligands and an iodido ligand are coordinated to the Cd(II) center. The metric parameter τ_5 introduced by Addison *et al.* [43] is used to determine the degree of trigonality. Both cations of **8** have a mean τ_5 of 0.60 which confirms the borderline case stated above. The tendency towards a trigonal bipyramidal geometry with an ideal τ_5 of 1 is obvious. The value of τ_4 for the tetrahedral $[CdI_4]$-dianion of **8** is 0.96 and confirms the observed tetrahedral geometry. Selected bond lengths and angles as well as the molecular structure of one cation of **8** are given in figure 2 and table 3. Again, the C–C and C–N bond lengths and angles of the bidentate aziridine ligands differ only slightly from those observed for the free aziridine **1** in the solid state [39]. The $Cd{-}NH_2R$ bond lengths of 2.292(4) and 2.294(4) Å and the $Cd{-}NR_3$ bond lengths of 2.393(4) and 2.403(4) Å observed in **8** are in good agreement with those reported for cadmium(II)-amine complexes [44]. The N–C bond lengths within the aziridine ring lie in the expected range between 1.509(6) Å (az), 1.487(6) Å (az) and 1.496(6) Å in the $H_2N{-}Cq{-}CH_2{-}NR_2$ bridge, whereas the C–C

Table 3. Selected bond lengths (Å) and angles (°) for **8**.

Bond lengths (Å)				Bond angles (°)			
Cd(1)–N(1)	2.393(4)	Cd(2)–I(2)	2.762(10)	N(1)–Cd(1)–I(1)	98.61(9)	N(4)–Cd(1)–I(1)	128.39(12)
Cd(1)–N(2)	2.292(4)	Cd(3)–I(3)	2.7694(9)	N(1)–Cd(1)–N(3)	163.98(12)	C(1)–N(1)–C(2)	59.3(3)
Cd(1)–N(3)	2.403(4)	C(1)–C(2)	1.481(7)	N(2)–Cd(1)–N(1)	75.17(14)	C(1)–C(2)–N(1)	61.1(3)
Cd(1)–N(4)	2.294(4)	C(1)–C(3)	1.507(8)	N(2)–Cd(1)–N(3)	92.43(14)	C(2)–C(1)–N(1)	59.6(3)
Cd(1)–I(1)	2.752(12)	N(1)–C(1)	1.509(6)	N(2)–Cd(1)–N(4)	104.39(16)	N(1)–C(5)–C(6)	111.6(4)
Cd(2)–N(5)	2.384(4)	N(1)–C(2)	1.487(6)	N(2)–Cd(1)–I(1)	127.12(12)	N(2)–C(6)–C(5)	107.7(4)
Cd(2)–N(6)	2.292(4)	C(5)–N(1)	1.477(6)	N(3)–Cd(1)–I(1)	96.97(9)	C(6)–N(2)–Cd(1)	112.3(3)
Cd(2)–N(7)	2.435(4)	C(5)–C(6)	1.530(7)	N(1)–Cd(1)–N(4)	97.29(13)	C(5)–N(1)–Cd(1)	108.3(3)
Cd(2)–N(8)	2.285(4)	C(6)–N(2)	1.496(6)	N(3)–Cd(1)–N(4)	75.69(14)	I(3)–Cd(3)–I(5)	109.53(3)

bond length of 1.481(7) Å (az) is shortened compared to that of 1.530(7) Å within the five-membered ring of the *N*,*N*′-chelate ligand.

The $H_2RN-Cd-NH_2R$ angles of 104.39(16) and 114.94(16) as well as the $H_2RN-Cd-I$ angles of 128.39(12) and 125.13(12)° together with the R_3N–Cd–NR_3 angles of 163.98(12) and 161.13(14)° are more consistent with the distorted trigonal bipyramidal geometry discussed above. Furthermore, the angles enclosed by the N atoms of aiaz and the cadmium(II) center within the five-membered ring of 75.17(14) and 75.69(14)° are much smaller compared to the $H_2RN-Cd-NR_3$ angles of 92.43(14) and 97.29(13)° between the two vicinal aiaz ligands. The main reason for this is the constraint of the five-membered ring formed by the chelating aiaz ligand which does not allow opening up to 90°. The aiaz chelate ligands are arranged in a *twist* conformation with torsion angles H_2N–Cq–CH_2–NR_2 of 56.76, 60.10, 56.57, and 59.85°. Furthermore, intermolecular hydrogen bridges between the iodido ligands of the tetraiodidocadmate anion and the NH_2 groups of the aiaz ligands of solid **8** are formed (lengths: 3.678–3.833 Å, angles: 144.02–170.51°). Figure 3 illustrates the hydrogen bonds of **8** connecting the $[CdI_4]^{2-}$ anion and the primary amino groups of the $[(C_8H_{18}N_2)_2CdI]^+$ cations.

The mercury(II) center in $[(aiaz)HgI_2]$ (**10**) is coordinated by the two nitrogens of an aiaz ligand and two iodido ligands, resulting in a slightly distorted tetrahedral geometry. Selected bond lengths and angles and the molecular structure of one $[(aiaz)HgI_2]$ are given in figure 4 and table 4. Again, a metal-mediated dimerization reaction of the 2,2-dimethylaziridine ligand is observed when a saturated solution of **9** is allowed to stand for several days in daylight. Due to the excess az released in the reaction solution by light induced decomposition of **9**, nucleophilic attack on the az ligands of **9** occurs yielding formation of the $[(aiaz)HgI_2]$ complex. C–C and C–N bond lengths and angles differ only marginally from those found for other transition metal coordinated aiaz ligands [20–22]. $Hg-NH_2R$, $Hg-NR_3$ and Hg–I bond lengths of 2.387(6) Å, 2.346(7) Å and 2.7139(9) Å, 2.6683(10) Å observed for **10** are comparable with the bond lengths described for similar 1,2-diaminoethane-mercury(II)iodide complexes, but compared to **8** the difference between the Hg–NR_3 and the $Hg-NH_2R$ bond lengths is smaller [45]. The I–Hg–I angle of 123.58(3)° is larger than the $H_2RN-Hg-NR_3$ angle of 75.2(2)° because of the bite angle of the five-membered chelate ring system. The N–C bond lengths of 1.464(11) and 1.483(10) Å are slightly shortened compared to those in **8** (1.509(6) Å, 1.487(6) Å). The C–C bond length of 1.494(13) Å within the aziridine ring is slightly enlarged

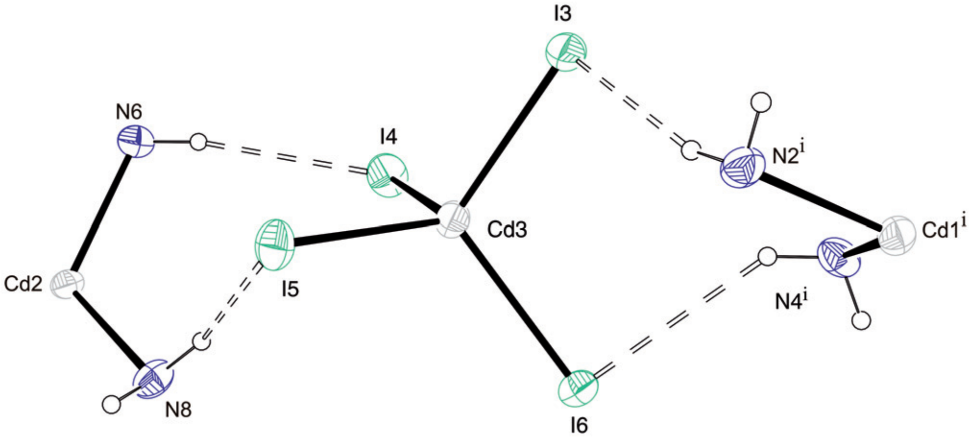


Figure 3. Hydrogen bonds (dashed lines) between the $[(C_8H_{18}N_2)_2CdI]^+$ cations and the $[CdI_4]^{2-}$ anion of **8**. Thermal ellipsoids are drawn at the 30% probability level. The remaining parts of **8** and two dichloromethane molecules are omitted for clarity (symmetry transformation i = [$-x+1$, $-y$, $-z+1$]).

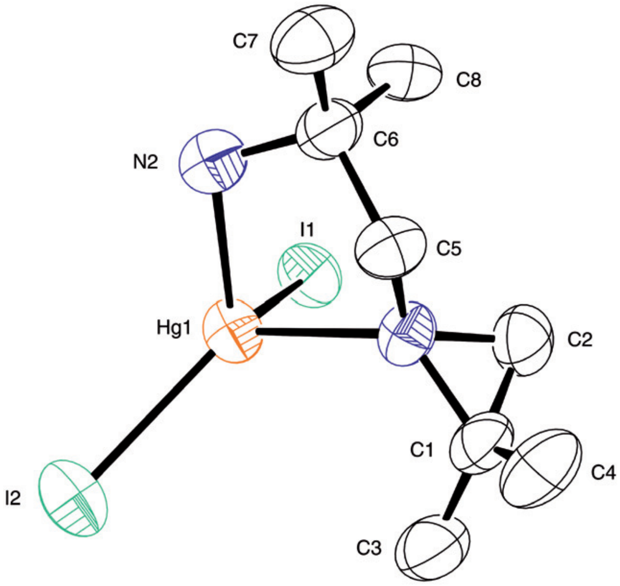


Figure 4. Molecular structure of **10**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity.

compared to **8** (1.481(7) Å). The five-membered ring formed by the aiaz ligands and the Hg(II) center in **10** shows the analogous *twist* conformation as in cationic **8** with torsion angles $NH_2R{-}C_q{-}CH_2{-}NR_3$ of 54.92 to 61.31°. The τ_4 value of **10** is 0.85, indicating a geometry closest to a slightly distorted tetrahedron.

Similar to the previously discussed compounds, **10** exhibits intermolecular hydrogen bonding in the solid state between the primary amino groups of the aiaz ligands and the iodido ligands (3.814 to 4.012 Å and 126.90° to 156.54°).

Table 4. Selected bond lengths (Å) and angles (°) for **10**.

Bond lengths (Å)				Bond angles (°)			
Hg(1)–N(1)	2.387(6)	N(1)–C(1)	1.483(10)	N(1)–Hg(1)–N(2)	75.2(2)	C(2)–N(1)–C(1)	60.9(6)
Hg(1)–N(2)	2.346(7)	N(1)–C(2)	1.464(11)	N(1)–Hg(1)–I(1)	104.48(16)	N(1)–C(2)–C(1)	60.2(6)
Hg(1)–I(1)	2.7139(9)	N(1)–C(5)	1.474(10)	N(1)–Hg(1)–I(2)	117.07(16)	N(1)–C(1)–C(2)	58.9(5)
Hg(1)–I(2)	2.6683(10)	C(5)–C(6)	1.546(11)	I(1)–Hg(1)–I(2)	123.58(3)	N(1)–C(1)–C(3)	112.9(7)
C(1)–C(2)	1.494(13)	N(2)–C(6)	1.465(11)	N(2)–Hg(1)–I(1)	111.45(19)	N(1)–C(5)–C(6)	111.4(7)
C(1)–C(3)	1.501(13)	C(6)–C(7)	1.533(12)	N(2)–Hg(1)–I(2)	114.69(18)	N(2)–C(6)–C(5)	108.4(7)

4. Conclusion

Studies on the coordination chemistry of the monodentate ligand 2,2-dimethylaziridine **1** (az) with d^{10} transition metal halides like MX_2 (M = Zn, Cd, Hg, X = Br, I) (**2**–**5**) show for $ZnBr_2$ and ZnI_2 as well as HgI_2 formation of the expected tetrahedral $[(az)_2MX_2]$ complexes **6**, **7** and **9** with two az ligands. In the case of CdI_2, however, metal-mediated dimerization of two az ligands in the coordination sphere of the Cd(II) center is observed forming the bidentate *N*-(2-aminoisobutyl)-2,2-dimethylaziridine (aiaz) in the complex $[(aiaz)_2CdI]_2[CdI_4]$ (**8**). Moreover, a rarely observed five-coordinate, distorted trigonal bipyramidal Cd(II) cation is formed. The same aiaz ligand is obtained by isomerization of $[(az)_2HgI_2]$ (**9**) to $[(aiaz)HgI_2]$ (**10**). The connectivity within the complexes was deduced by single crystal X-ray crystallography, IR and NMR spectroscopy.

Supplementary data

The CCDC numbers listed in table 1 contain the supplementary crystallographic data of the crystal structure determinations published in this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif. ORTEP-3 plots are shown with thermal ellipsoids at the given probability level.

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