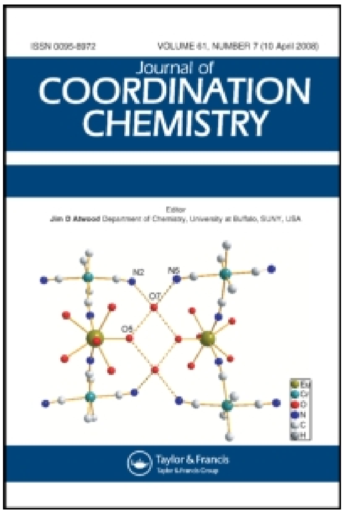

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

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To cite this Article Kurosaki, Hiromasa , Matsuda, Shu-ichi , Kawamura, Aya , Tsuruda, Nobuhiro and Goto, Masafumi(1999) 'SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF BIS (2-AMINOMETHYLAZIRIDINE)NICKEL(II) PERCHLORATE', Journal of Coordination Chemistry, 47: 4, 523 — 530

To link to this Article: DOI: 10.1080/00958979908024351

URL: http://dx.doi.org/10.1080/00958979908024351

J. Coord. Chem., 1999, Vol. 47, pp. 523–530
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SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF *BIS*(2-AMINOMETHYLAZIRIDINE)NICKEL(II) PERCHLORATE

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(Received 12 June 1998)

The structure of the *bis*(2-aminomethylaziridine = **azida**)nickel(II) complex was determined by X-ray diffraction methods. The compound, $[\mathrm{Ni(azida)_2}](\mathrm{ClO_4})_2$, crystallizes in the triclinic space group $P\bar{1}$, $Z = 1$, with $a = 7.3545(4)$, $b = 8.5235(5)$, $c = 6.2156(4)$ Å, $\alpha = 101.871(6)$, $\beta = 103.217(6)$, $\gamma = 111.283(4)$°, and $V = 335.07(5)$ Å^3. The crystal shows discrete centrosymmetrical $[\mathrm{Ni(azida)}]^{2+}$ units in which azida acts as bidentate chelating ligand through N aziridine and N amino atoms. Thus, Ni has a four-coordinate square-planar geometry with four nitrogens of azida. The aziridine ring is almost perpendicular to the coordination plane. The dihedral angle between the aziridine plane and the coordination plane is 75.28°.

Keywords: Nickel(II); 2-aminomethylaziridine; X-ray crystal structure

INTRODUCTION

Aziridine is involved in a variety of medicaments such as azinomycins A and B, which are antitumour agents and three-membered ring heterocycles have been extensively studied in cycloaddition reactions for the syntheses of precursors of biologically active compounds.[1] Recently, new platinum(II) complexes with small heterocyclic ligands were synthesized in attempt to examine their efficiencies with respect to cisplatin, *cis*-$[\mathrm{PtCl_2(NH_3)_2}]$, and to

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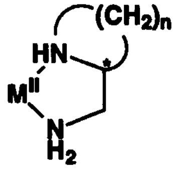
* Corresponding author.

develop more effective cisplatin analogues.[2] Some of the platinum(II) complexes of 2-aminomethylazacycloalkane derivatives have potent antitumour activity and/or are new analogues for procurement of cisplatin resistant cancer.[2] Their coordination structures, however, were only assigned on the basis of elemental analysis and detailed structural information on 2-aminomethylazacycloalkane is not available except for an X-ray structure of [(−)(*R*)-2-aminomethylpyrrolidine-1,1-cyclobutanedicarboxylatoplatinum (II)] reported by Yonei *et al.*[3] Furthermore, the chemistry of metal complexes with 2-aminomethylazacycloalkane has not been developed for 2-aminomethylaziridine (azida) and 2-aminomethylazetidine (azeda).

The lack of structural information prompted us to synthesize a series of metal complexes with 2-aminomethylazacycloalkanes and characterize the structure of their metal complexes in both solution and solid state. In this paper, the synthesis and characterization of *bis*(2-aminomethylaziridine)-nickel(II), [Ni(azida)$_2$](ClO$_4$)$_2$, is described.



n	**ligand**
1	**azida : 2-aminomethylaziridine**
2	**azeda : 2-aminomethylazetidine**
3	**pyrda : 2-aminomethylpyrrolidine**
4	**pipda : 2-aminomethylpiperidine**

EXPERIMENTAL

Reagents

Ni(ClO$_4$)$_2$ · 6H$_2$O was purchased from Kishida Kagaku Co., Japan, and was used without further purification. Azida was prepared according to the literature method.[4]

Preparation of [Ni(azida)$_2$](ClO$_4$)$_2$

A solution of Ni(ClO$_4$)$_2$ · 6H$_2$O (550 mg, 1.5 mmol) in ethanol (5 cm^3) was added dropwise to a solution of azida (216 mg, 3 mmol) in ethanol (1 cm^3) at room temperature with mild stirring. The mixture was allowed to stand for 20 h at room temperature. The resulting orange precipitates were collected on a filter, washed with ethanol and ether, and dried. Yield, 255 mg (21%). *Anal.* Calcd. for [Ni(C$_3$H$_8$N$_2$)$_2$](ClO$_4$)$_2$ (%): C, 17.94; H, 4.01; N, 13.94. Found: C, 17.66; H, 3.98; N, 13.84.

Warning: This Ni(II) complex is potentially explosive!

TABLE I Crystallographic data for $[Ni(azida)_2](ClO_4)_2$

Formula	$C_6H_{16}N_4O_8Cl_2Ni$
fw	401.82
Cryst syst	triclinic
Space group	$P\bar{1}$
a, Å	7.3545(4)
b, Å	8.5235(5)
c, Å	6.2156(4)
α, deg	101.871(6)
β, deg	103.217(6)
γ, deg	111.283(4)
V, Å^3	335.07(5)
Z	1
T, K	293
Cryst size, mm	0.45 × 0.35 × 0.10
d_{calc}, $g \cdot cm^{-3}$	1.991
Radiation	MoKα ($\lambda = 0.71069$ Å)
μ(MoKα), cm^{-1}	18.93
Diffractometer	Rigaku AFC 7R
Scan method	ω–2θ
Scan speed, deg min^{-1}	16.0
$2\theta_{max}$, deg	55.0
No. of data collected	1653
No. of unique reflection	1534
No. of data used in refinement	1414 ($I > 3\alpha(I_0)$)
R	0.022
R_w	0.026

X-ray Crystal Analysis of $[Ni(azida)_2](ClO_4)_2$

Single crystals of $[Ni(azida)_2](ClO_4)_2$ were grown by slow evaporation of an aqueous solution of the compound. X-ray data (Table I) were collected on a Rigaku AFC 7R diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.71069$ Å) at 20 ± 1°C. The cell parameters were determined from 25 reflections in the 2θ range $39.39° \leq 2\theta \leq 39.95°$. For the intensity data collections, the $\omega - 2\theta$ scan mode was used at the scan rate of 16° min^{-1} with a scan width of $(1.57 + 0.30 \tan\theta)°$ in ω. Standard reflections were observed in every 150 reflections. A correction was made for Lorentz and polarization effects. Decay correction was applied. A total of 1414 reflections with $I > 3\sigma(I_0)$ were used for the structure determination. The chosen space group $P\bar{1}$ was confirmed by the successful structure solution. The structure was solved by direct methods. The nickel was placed at the origin. Successive refinements by using the full-matrix least-squares method revealed the locations of all the non-hydrogen atoms. In the last refinement cycles, anisotropic thermal parameters were used for all the non-hydrogen atoms. The hydrogen atoms were clearly located in the final difference

TABLE II Positional parameters and thermal parameters (Å^2) of non-hydrogen atoms of $[Ni(azida)_2](ClO_4)_2$ with e.s.d.'s in parentheses

Atom	*x/a*	*y/b*	*z/c*	B_{eq}
Ni(1)	0	0	0	1.655(8)
Cl(1)	0.20015(8)	−0.22677(7)	0.39580(8)	2.17(1)
O(1)	0.0258(3)	−0.3966(2)	0.2820(3)	3.37(4)
O(2)	0.3106(3)	−0.2234(2)	0.6220(3)	3.67(4)
O(3)	0.1315(3)	−0.0886(2)	0.4280(3)	3.59(4)
O(4)	0.3325(3)	−0.1987(2)	0.2569(3)	4.10(5)
N(1)	0.0773(3)	0.2400(2)	0.1634(3)	1.93(3)
N(2)	0.2770(3)	0.0806(2)	−0.0099(3)	2.04(4)
C(1)	0.2780(3)	0.3640(3)	0.1581(4)	2.11(4)
C(2)	0.2628(3)	0.3293(3)	0.3773(4)	2.29(4)
C(3)	0.3614(3)	0.2704(3)	0.0035(4)	2.26(4)

Fourier map and were included but not refined. Reliability factors were defined as $R=\sum||F_0|-|F_c||/\sum|F_0|$ and $R_w=[\sum w(|F_0|-|F_c|)^2/\sum w|F_0|^2]^{1/2}$, where the weights were taken as $w=1/\sigma^2(|F_0|)$. The atomic scattering factors were taken from Ref. 5. All the computations were performed with teXsan crystallographic software package on an Iris Indigo workstation from Silicon Graphics.[6] The final positional parameters of non-hydrogen atoms with their estimated standard deviations are listed in Table II.

RESULTS AND DISCUSSION

Preparation of the Nickel(II) Complex

The reaction of $Ni(ClO_4)_2 \cdot 6H_2O$ with 2 equiv of azida afforded the orange nickel(II) complex $[Ni(azida)_2](ClO_4)_2$ in 21% yield. The infrared spectrum of $[Ni(azida)_2](ClO_4)_2$ exhibits a characteristic $\nu(ClO_4)$ stretching vibration at 1110 cm^{-1}, indicating the presence of ClO_4^- as the counter anion. When this complex was dissolved in acetonitrile–nitromethane (1 : 9), the colour of the mixture quickly changed to violet showing two visible absorption maxima at 552 nm ($\varepsilon = 7\,M^{-1}\,cm^{-1}$) and at 885 nm ($\varepsilon = 6\,M^{-1}\,cm^{-1}$), indicating the formation of high-spin octahedral geometry with two acetonitrile molecules occupying axial positions.[7]

Crystallography

Crystal data and positional parameters are presented in Tables I and II, respectively. An ORTEP drawing of the cation $[Ni(azida)_2]^{2+}$ with the

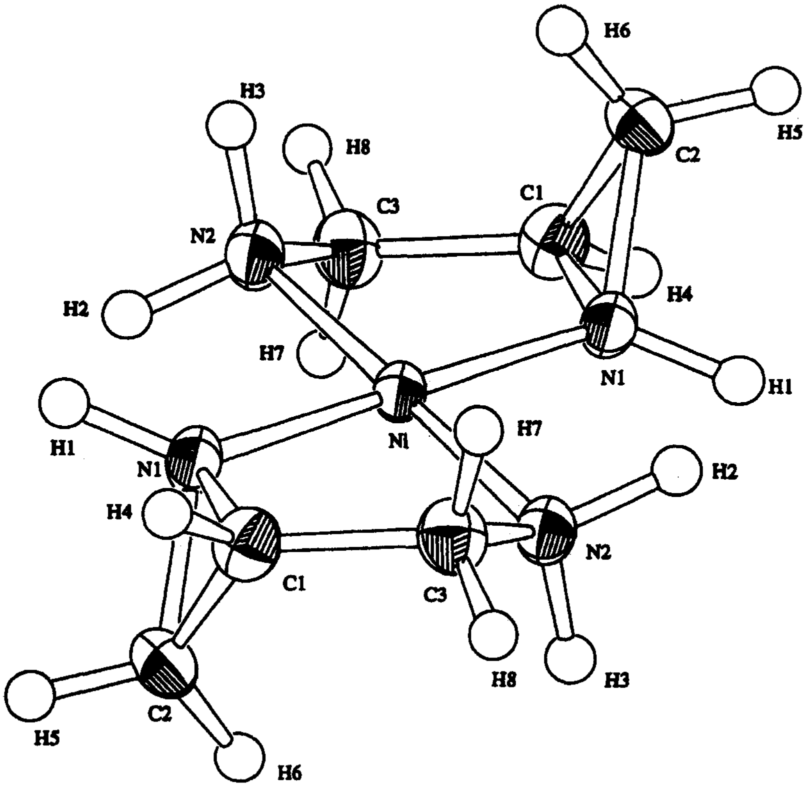


FIGURE 1 ORTEP diagram for $[Ni(azida)_2]^{2+}$ showing the atom numbering scheme.

atom-labelling scheme is shown in Figure 1. Bond distances and angles are given in Table III. This complex cation possesses a crystallographically imposed centre of symmetry. The crystal structure consists of discrete ions of $[Ni(azida)]^{2+}$ with respective ClO_4^- counter ions. The Ni(II) complex has a square-planar *trans* configuration with bidentate azida (sum of four angles around nickel is 360°). The Ni–N bond lengths (Ni–N(1) = 1.891(2) and Ni–N(2) = 1.919(2) Å) are shorter than those of dibromo[α-(*tert*-butyl-1-aziridinyl-2)benzylamine]zinc(II), (2.071(5) and 2.061(6) Å),[8] and shorter than those found for *trans*-$[Ni(ethanediamine)_2](NO_3)_2$ (2.115 Å).[9] The N(1)–Ni–N(2) angle of 85.83(7)° is larger than those of 84.4° for $[ZnBr_2(C_{13}H_{20}N_2)]$[8] and 82.3° for $[Ni(en)_2]^{2+}$.[9] The mode of fusion between the three-membered aziridine ring and the five-membered chelate ring is *cis* to each ring. The conformation of the five-membered chelate ring is the

TABLE III Bond lengths (Å) and angles (deg) in $[Ni(azida)_2](ClO_4)_2$

Bond lengths			
Ni–N(1)	1.891(2)	Ni–N(2)	1.919(2)
Cl(1)–O(1)	1.434(2)	Cl(1)–O(2)	1.443(2)
Cl(1)–O(3)	1.436(2)	Cl(1)–O(4)	1.432(2)
N(1)–C(1)	1.484(3)	N(1)–C(2)	1.486(3)
N(2)–C(3)	1.484(3)	C(1)–C(2)	1.473(3)
C(1)–C(3)	1.501(4)		
Bond angles			
N(1)–Ni–N(2)	85.83(7)	O(1)–Cl(1)–O(2)	108.9(1)
O(1)–Cl(1)–O(3)	110.1(1)	O(1)–Cl(1)–O(4)	109.3(1)
O(2)–Cl(1)–O(3)	108.4(1)	O(2)–Cl(1)–O(4)	110.2(2)
O(3)–Cl(1)–O(4)	109.9(1)	Ni–N(1)–C(1)	113.3(1)
Ni–N(1)–C(2)	117.7(1)	C(1)–N(1)–C(2)	59.4(1)
Ni–N(2)–C(3)	110.5(1)	N(1)–C(1)–C(2)	60.4(1)
N(1)–C(1)–C(3)	111.6(1)	C(2)–C(1)–C(3)	121.7(2)
N(1)–C(2)–C(1)	60.2(1)	N(2)–C(3)–C(1)	108.7(2)

distorted *gauche* form with a torsion angle of −25.5(3)° for N(1)–C(1)–C(3)–N(2); both carbon atoms, C(1) and C(3) are found on the same side of the least-squares plane defined by NiN_4, opposite to the aziridine ring, with displacements from the NiN_4 plane of 0.27 and 0.62 Å, respectively. The aziridine ring extends from this chelate ring to an axial orientation. Bond angles Ni–N(1)–C(1), N(1)–C(1)–C(3), C(1)–C(3)–N(2), and Ni–N(2)–C(3) are 113.3(1), 111.6(2), 108.7(2), and 110.5(1)°, respectively. The aziridine ring takes a nearly regular triangular structure with bond angles of 59.4(1), 60.4(1), and 60.2(1)° for C(1)–N(1)–C(2), N(1)–C(1)–C(2) and N(1)–C(2)–C(1). Bond distances in the aziridine ring are N(1)–C(1), 1.484(3) Å, N(1)–C(2), 1.486(3) Å, and C(1)–C(2), 1.473(3) Å, showing a characteristic three-membered ring contraction.

The complex molecule lies almost parallel to the *ab* plane and the perchlorate anion locates in the centre of the space formed by four complex cations. Hydrogen bonds (NH···O bonding) between the complex cation and the perchlorate anion are shown in Figure 2 as solid lines. Hydrogen bond parameters are given in Table IV.

Supplementary Material

Tables of bond lengths and angles, anisotropic temperature factors, atomic coordinates and temperature factors, hydrogen atom coordinates and temperature factors, and observed and calculated structure factors are available from the authors on request.

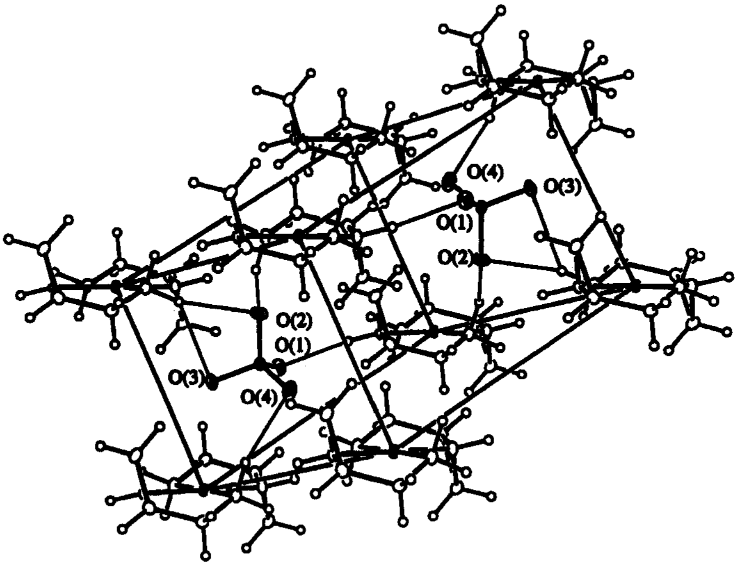


FIGURE 2 Unit cell diagram for $[Ni(azida)_2](ClO_4)_2$ showing the hydrogen-bonding interactions.

TABLE IV Distances (Å) and angles (°) for hydrogen bonding in $[Ni(azida)_2](ClO_4)_2$[a] with e.s.d's in parentheses

N	*H*	*O*	*N–H* (Å)	*H···O* (Å)	*N···O* (Å)	*N–H···O* (°)
N(1)	H(1)	O(1)[b]	0.96	2.44	3.213(2)	136.79
N(2)	H(2)	O(2)[e]	1.01	2.23	3.208(2)	161.30
N(2)	H(2)	O(3)[e]	1.01	2.43	3.244(3)	136.96
N(2)	H(3)	O(2)[d]	0.97	2.25	3.044(2)	137.23
N(2)	H(3)	O(4)[c]	0.97	2.54	3.256(3)	130.66

[a] Symmetry operation: [b] $(x, y+1, z)$, [c] (x, y, z), [d] $(x-1, -y, -z-1)$, [e] $(x, y, z-1)$.

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