

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

A head-to-tail isomer of bis[μ -2-(*N*'-methyl-4,4'-bipyridinium-1-yl)-acetamidato]bis[*cis*-diammineplatinum(II)] hexaperchlorate dihydrate

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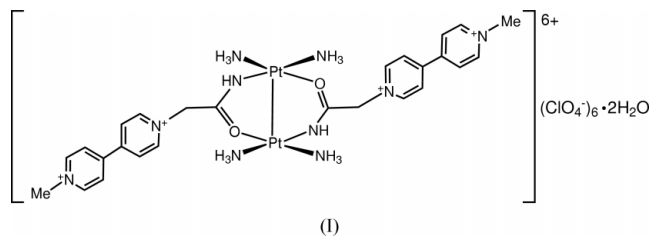
Key indicators

Single-crystal X-ray study
T = 296 K
Mean $\sigma(\text{C}-\text{C}) = 0.039 \text{ \AA}$
H-atom completeness 91%
Disorder in solvent or counterion
R factor = 0.062
wR factor = 0.108
Data-to-parameter ratio = 11.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.A head-to-tail isomer of bis[μ -2-(*N'*-methyl-4,4'-bipyridinium-1-yl)acetamidato]bis[*cis*-diammineplatinum(II)] hexaperchlorate dihydrate

In the title compound, $[\text{Pt}_2(\mu\text{-C}_{13}\text{H}_{14}\text{N}_3\text{O})_2(\text{NH}_3)_4](\text{ClO}_4)_6 \cdot 2\text{H}_2\text{O}$, the dinuclear Pt^{II} cation is found to be a head-to-tail isomer having pseudo- C_2 symmetry. Two positively charged viologen moieties tethered to the diplatinum unit are located at the farthest position to minimize the electrostatic repulsion between the moieties, and also serve as relatively strong electron-withdrawing groups, giving rise to a very long intradimer $\text{Pt} \cdots \text{Pt}$ distance [$3.0852(13) \text{ \AA}$] which is the longest distance among those reported for amidate-bridged *cis*-diammineplatinum(II) dimers to date.

Comment

A photochemical system made up of $\text{Ru}(\text{bpy})_3^{2+}$ (bpy = 2,2'-bipyridine) and methylviologen (usually, *N,N'*-dimethyl-4,4'-bipyridinium dichloride) has been thought of as one of the promising candidates to achieve artificial photosynthetic devices (Borgarello *et al.*, 1981). More than a decade ago, we discovered that amidate-bridged *cis*-diammineplatinum(II) dimers, $[\text{Pt}_2(\text{NH}_3)_4(\mu\text{-amidato})_2]^{2+}$ (amidate = acetamidate, α -pyrrolidinonate, α -pyridonate, *etc.*), are generally active as H_2 -evolving catalysts in the above photosystem (Sakai & Matsumoto, 1990; Sakai *et al.*, 1993). Since then, efforts have been made to develop photosynthetic molecular devices which enable visible-light-induced reduction of water into molecular hydrogen in a sophisticated manner. In order to confirm the validity of our approach, efforts have also been made to prepare and to evaluate the amidate-bridged platinum dimers tethered to the methylviologen derivatives.



We now report, for the first time, the crystal structure of such a dimer, *viz.* HT- $[\text{Pt}_2(\text{NH}_3)_4(\mu\text{-bridge})_2](\text{ClO}_4)_6 \cdot 2\text{H}_2\text{O}$, (I), where bridge = 2-(*N'*-methyl-4,4'-bipyridinium-1-yl)-acetamidate and HT is a prefix denoting that this is a head-to-tail dimer, at least in the solid state. Note that two geometrical isomers, head-to-head (HH) and head-to-tail (HT), are possible for this class of doubly bridged dimers, because of the asymmetric feature of amidate N—C—O units. It should also be noted that the compound rapidly isomerizes, upon dissolution to aqueous media, to give a mixture of the HH and HT isomers; this has been confirmed thus far by using ^{195}Pt NMR

Received 7 August 2003
Accepted 11 August 2003
Online 23 August 2003

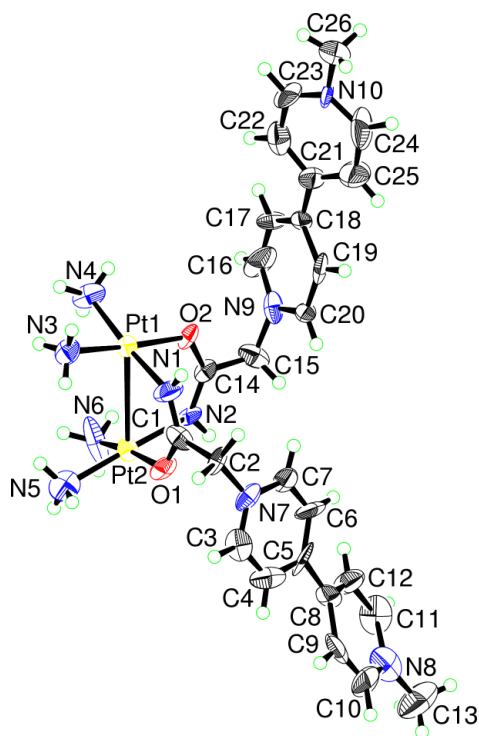


Figure 1
The structure of the complex cation in (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

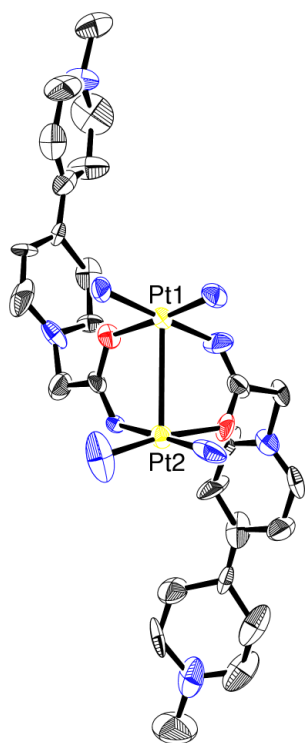


Figure 2
The structure of the cationic part of (I), showing that the complex has pseudo- C_2 symmetry.

(the details will appear in our future publications). The catalytic activity of (I) has been confirmed to be comparable to that of the acetamidate-bridged analog reported in our earlier

paper (Sakai *et al.*, 1993). An attractive feature of (I) is that the photolysis of a solution containing (I), together with edta (sacrificial electron donor) and $\text{Ru}(\text{bpy})_3^{2+}$ (photosensitizer), in the absence of methylviologen, also results in the evolution of H_2 in a relatively high quantum efficiency. Details of the photocatalytic function of (I) will also appear in future publications.

The asymmetric unit of (I) involves a dinuclear Pt^{II} cation, six perchlorate anions and two water molecules. As previously reported on an analogous dimer doubly bridged by *N*-methylisonicotinamidates, $\text{HH}[\text{Pt}_2(\text{NH}_3)_4(\mu\text{-}N\text{-methylisonicotinamidato})_2](\text{ClO}_4)_4$ [abbreviated as (II); Sakai, Shiomi *et al.*, 2003], it is often possible to determine the binding directions of two bridging amidates in a rational way (see *Experimental*). The experiments reveal that the reported dimer adopts the head-to-tail isomeric form in the crystal structure. As discussed above, the compound behaves as a mixture of both the HH and HT isomers in solution (based on ^{195}Pt NMR; unpublished results). As shown in Fig. 2, the complex cation in (I) possesses pseudo- C_2 symmetry, in which the conformations of the two bridges roughly resemble one another [$\text{O1}-\text{C1}-\text{C2}-\text{N7} = 38(3)^\circ$, $\text{N1}-\text{C1}-\text{C2}-\text{N7} = -140(2)^\circ$, $\text{O2}-\text{C14}-\text{C15}-\text{N9} = 9(3)^\circ$ and $\text{N2}-\text{C14}-\text{C15}-\text{N9} = -165(2)^\circ$]. The most remarkable feature is an amazingly long intradimer $\text{Pt}\cdots\text{Pt}$ distance [$3.0852(13)\text{ \AA}$]; the values reported for analogous dimers having the *cis*- $\text{Pt}(\text{NH}_3)_2$ units have been in the range $2.88\text{--}3.06\text{ \AA}$ (Sakai & Takahashi, 2003; Sakai, Shiomi *et al.*, 2003). As described in these reports, the observed long $\text{Pt}\cdots\text{Pt}$ distance in (I) reflects the relatively weak $\text{Pt}^{\text{II}}-\text{Pt}^{\text{II}}$ bond. Obviously, the positively charged bipyridinium moieties in (I) play roles as electron-withdrawing groups to diminish the electron density at the Pt^{II} centers, leading to the weakening of the ‘mutual dative bonds’ within the diplatinum cation [two Pt^{II} centers in a close contact are considered to form dative $\text{Pt}(5d_{z^2}) \rightarrow \text{Pt}(6p \text{ or } 6s)$ bonds with one another; Connick *et al.*, 1997]. It must be also noted that the long intradimer $\text{Pt}\cdots\text{Pt}$ distance is, in part, due to the HT structure, which tends to give a longer intradimer $\text{Pt}\cdots\text{Pt}$ distance compared to the HH one (Sakai, Tanaka *et al.*, 1998).

The dihedral angle between the two Pt coordination planes within the dimeric unit (τ), and their average torsional twist about the $\text{Pt}-\text{Pt}$ axis (ω) are estimated as $\tau = 40.8(5)^\circ$ and $\omega = 5(1)^\circ$ (see also Table 1), where $\omega = 0^\circ$ denotes that the two Pt coordination planes stack in an eclipsed fashion. The small ω value is characteristic of dimers bridged by chain amidate ligands (Sakai, Tanaka *et al.*, 1998; Matsumoto & Sakai, 1999; Sakai, Shiomi *et al.*, 2003), indicating that the intradimer $\text{Pt}-\text{Pt}$ distance and the ω value are strongly correlated with one another. On the other hand, atoms Pt1 and Pt2 are respectively displaced from their coordination planes by $0.063(8)$ and $0.085(8)\text{ \AA}$ in such a manner that they have an attractive interaction with one another.

The pyridinium plane directly attached to the acetamidate unit is inclined with respect to the bridging $\text{O}-\text{C}-\text{N}$ unit by $89(3)^\circ$ for $\text{N9}/\text{C16}-\text{C20}$ and $84(1)^\circ$ for $\text{N7}/\text{C3}-\text{C7}$. These are comparable to that reported for the uncoordinated ligand [$79.1(2)^\circ$; Sakai *et al.*, 1997]. The twist angles of the two

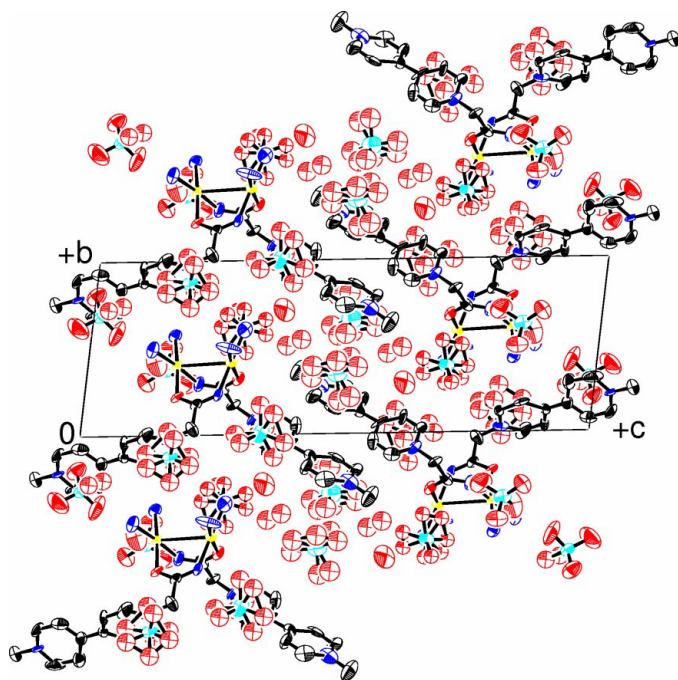


Figure 3
The crystal packing of (I), viewed down the *a* axis. H atoms have been omitted for clarity.

pyridinium planes within the individual bipyridinium moieties are 28.4 (8)° for the bipyridinium involving N9 and N10, and 25.6 (12)° for that involving N7 and N8. These values are both effectively larger than that observed for the uncoordinated ligand [6.1 (2)°; Sakai *et al.*, 1997]. This might reflect that the π^* (bipyridinium) orbitals accept part of the electron density shifted from the Pt centers, leading to the decrease in aromaticity at the central C—C bonds of the bipyridinium units.

Fig. 3 shows a crystal packing view of (I). The shortest Pt···Pt distance is determined as Pt1···Pt2(*x* + 1, *y*, *z*) = 9.0380 (14) Å (see Table 1), confirming the lack of any intermolecular Pt—Pt interaction in the crystal structure. The crystal packing is stabilized both by the electrostatic interactions between the complex cations and perchlorate anions and also by hydrogen bonds formed between the amines and the O atoms of perchlorates (Tables 2 and 3).

Experimental

N-(Carbamoylmethyl)-*N'*-methyl-4,4'-bipyridinium diperchlorate hydrate was prepared as previously described (Sakai *et al.*, 1997). Compound (I) was prepared as follows: to an aqueous solution of *cis*-[Pt(NH₃)₂(OH)₂](ClO₄)₂ (0.2 mmol Pt/2 ml H₂O), prepared as previously described (Sakai, Takeshita *et al.*, 1998), was added *N*-(carbamoylmethyl)-*N'*-methyl-4,4'-bipyridinium diperchlorate hydrate (0.32 mmol). The solution was heated at 323 K for 2 d. Letting the filtrate stand at room temperature for a few days afforded (I) as yellow plates (yield: 6%). Analysis calculated for

C₂₆H₄₄Cl₆N₁₀O₂₈Pt₂: C 20.18, H 2.87, N 9.05%; found: C 19.85, H 2.57, N 8.82%. ¹H NMR (D₂O, 296 K): δ 4.52 (*s*, 6H); 5.52–5.65 (*m*, 4H); 8.55–8.61 (*m*, 8H); 9.01–9.07 p.p.m. (*m*, 8H).

Crystal data

[Pt₂(C₁₃H₁₄N₃O)₂(NH₃)₄]
(ClO₄)₆·2H₂O
M_r = 1547.59
Triclinic, *P* $\bar{1}$
a = 9.7641 (8) Å
b = 10.4448 (8) Å
c = 27.245 (2) Å
 α = 80.396 (4)°
 β = 83.548 (3)°
 γ = 63.566 (3)°
V = 2450.9 (3) Å³

Z = 2
D_x = 2.097 Mg m⁻³
Mo *K*α radiation
Cell parameters from 801 reflections
 θ = 2.4–16.6°
 μ = 6.13 mm⁻¹
T = 296 (2) K
Plate, yellow
0.42 × 0.28 × 0.06 mm

Data collection

Bruker SMART APEX CCD-detector diffractometer
 ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
*T*_{min} = 0.233, *T*_{max} = 0.692
14 233 measured reflections

7033 independent reflections
2548 reflections with *I* > 2σ(*I*)
*R*_{int} = 0.164
 θ _{max} = 23.3°
h = -10 → 9
k = -11 → 11
l = -30 → 30

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.062
wR(*F*²) = 0.108
S = 0.70
7033 reflections
613 parameters

H-atom parameters constrained
w = 1/[σ²(*F_o*²)]
(Δ/σ)_{max} < 0.001
Δρ_{max} = 0.89 e Å⁻³
Δρ_{min} = -0.89 e Å⁻³

Table 1

Selected geometric parameters (Å, °).

Pt1—N1	1.996 (17)	Pt1···Pt2 ⁱ	9.0380 (14)
Pt1—N3	2.012 (13)	Pt2—N2	1.974 (15)
Pt1—O2	2.034 (12)	Pt2—N6	1.991 (17)
Pt1—N4	2.082 (14)	Pt2—N5	2.044 (16)
Pt1···Pt2	3.0852 (13)	Pt2—O1	2.048 (14)
N1—Pt1—N3	91.2 (6)	N2—Pt2—N6	89.7 (7)
N1—Pt1—O2	89.6 (6)	N2—Pt2—N5	178.5 (6)
N3—Pt1—O2	176.2 (6)	N6—Pt2—N5	90.8 (6)
N1—Pt1—N4	175.4 (7)	N2—Pt2—O1	90.8 (6)
N3—Pt1—N4	91.8 (6)	N6—Pt2—O1	171.7 (7)
O2—Pt1—N4	87.2 (5)	N5—Pt2—O1	88.4 (6)
N1—Pt1—Pt2	75.4 (6)	N2—Pt2—Pt1	76.4 (5)
N3—Pt1—Pt2	103.5 (4)	N6—Pt2—Pt1	108.8 (6)
O2—Pt1—Pt2	80.3 (4)	N5—Pt2—Pt1	104.8 (4)
N4—Pt1—Pt2	107.3 (5)	O1—Pt2—Pt1	79.4 (4)
O2—Pt1—Pt2—N2	5.0 (6)	N3—Pt1—Pt2—N5	4.1 (7)
N4—Pt1—Pt2—N6	3.9 (7)	N1—Pt1—Pt2—O1	6.3 (6)

Symmetry code: (i) 1 + *x*, *y*, *z*.

Table 2

Contact distances (Å).

O11B···O28B	2.91 (5)	O27···O14B ⁱⁱⁱ	3.06 (4)
O27···O28B ⁱ	2.72 (4)	O27···O9B ⁱⁱ	3.18 (3)
O27···O10A ⁱⁱ	2.81 (5)	O28A···O11A ^{iv}	2.80 (7)
O27···O28A ⁱ	2.87 (5)	O28B···O27 ^v	2.72 (4)
O27···O13A ⁱⁱⁱ	3.06 (4)	O28B···O13B ^{iv}	3.12 (6)

Symmetry codes: (i) *x* - 1, *y*, *z*; (ii) *x*, 1 + *y*, *z*; (iii) -*x*, 1 - *y*, 1 - *z*; (iv) 1 - *x*, 1 - *y*, 1 - *z*; (v) 1 + *x*, *y*, *z*; (vi) -*x*, 1 - *y*, -*z*.

Table 3
Hydrogen-bonding geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N3–H3A···O4	0.89	2.22	2.96 (2)	141
N3–H3B···O15B	0.89	2.30	3.16 (3)	161
N3–H3B···O16A	0.89	1.90	2.79 (2)	179
N3–H3A···O25	0.89	2.57	3.10 (2)	118
N3–H3C···O21A ⁱⁱ	0.89	2.38	3.05 (2)	133
N4–H4A···O24A	0.89	2.25	3.12 (4)	165
N4–H4B···O6 ⁱ	0.89	2.16	3.01 (2)	159
N4–H4A···O20A ⁱⁱ	0.89	2.75	3.19 (2)	113
N4–H4B···O20B ⁱⁱ	0.89	2.58	3.16 (6)	124
N4–H4C···O23 ^{vi}	0.89	2.15	2.99 (3)	156
N5–H5A···O27	0.89	1.96	2.84 (2)	173
N5–H5C···O15B	0.89	2.43	2.89 (3)	112
N5–H5B···O19B ⁱⁱ	0.89	2.32	3.16 (5)	157
N6–H6A···O20B ⁱⁱ	0.89	2.26	3.04 (5)	145
N6–H6B···O17A ⁱ	0.89	2.53	3.05 (3)	118
N6–H6C···O17B ⁱ	0.89	2.71	3.12 (3)	109
N6–H6A···O18A ⁱ	0.89	2.74	3.09 (3)	105

Symmetry codes: (i) $x-1, y, z$; (ii) $x, 1+y, z$; (iii) $-x, 1-y, 1-z$; (iv) $1-x, 1-y, 1-z$; (v) $1+x, y, z$; (vi) $-x, 1-y, -z$.

The binding directions of O and NH for the bridging amidates were rationally determined, as follows, by the least-squares calculations performed for two possible arrangements for each ligand. A wrong combination gave an asymmetric feature with regard to the equivalent displacement parameters of the assumed O and N atoms, while an appropriate combination gave a moderate balance in these values. For O1 and N1, $U_{eq}(O1) = 0.044(5) \text{ \AA}^2$ and $U_{eq}(N1) = 0.054(6) \text{ \AA}^2$ were judged to be correct; the reverse selection gave values of $U_{eq}(N \text{ instead of } O1) = 0.019(4) \text{ \AA}^2$ and $U_{eq}(O \text{ instead of } N1) = 0.088(8) \text{ \AA}^2$. For O2 and N2, $U_{eq}(O2) = 0.037(4) \text{ \AA}^2$ and $U_{eq}(N2) = 0.033(5) \text{ \AA}^2$ were judged to be correct; the reverse selection gave values of $U_{eq}(N \text{ instead of } O2) = 0.014(4) \text{ \AA}^2$ and $U_{eq}(O \text{ instead of } N2) = 0.061(5) \text{ \AA}^2$. It must be also noted that the equivalent displacement parameters of the two Pt ions [$U_{eq}(Pt1) = 0.0327(3) \text{ \AA}^2$ and $U_{eq}(Pt2) = 0.0355(3) \text{ \AA}^2$] deny the coexistence of two isomers in a certain disorder model (Sakai, Shiomi *et al.*, 2003).

Four of six ClO_4^- anions show orientational disorder. Around each Cl atom there are two sets of possible positions as follows: O7A/O8A/O9A/O10A and O7B/O8B/O9B/O10B around Cl2; O11A/O12A/O13A/O14A and O11B/O12B/O13B/O14B around Cl3; O15A/O16A/O17A/O18A and O15B/O16B/O17B/O18B around Cl4; and O19A/O20A/O21A/O22A and O19B/O20B/O21B/O22B around Cl5. It was assumed that the disordered O atoms around each Cl atom have the same isotropic displacement parameter. Furthermore, Cl–O distances were restrained at 1.43 (3) Å and six O···O distances within each perchlorate anion were restrained as equal. The occupation factors of site A and B (sof_A and sof_B) around each Cl converged at values as follows: $\text{sof}_A(\text{Cl2}) = 26(2)\%$ and $\text{sof}_B(\text{Cl2}) = 74(2)\%$; $\text{sof}_A(\text{Cl3}) = 50(2)\%$ and $\text{sof}_B(\text{Cl3}) = 50(2)\%$; $\text{sof}_A(\text{Cl4}) = 54(2)\%$ and $\text{sof}_B(\text{Cl4}) = 46(2)\%$; $\text{sof}_A(\text{Cl5}) = 78(1)\%$ and $\text{sof}_B(\text{Cl5}) = 22(1)\%$. One of the remaining ClO_4^- ions was also judged to be partially disordered, in which only one of the four O atoms was

assumed to be disordered over two sites (O24A and O24B). The occupation factors of these atoms were refined to converge at 42 (3) and 58 (3)%, respectively. A water molecule was also assumed to be disordered over two sites (O28A and O28B). These were assumed to have the same isotropic displacement parameter. The occupation factors of site A and B converged at 45 (7) and 55 (7)%, respectively.

All H atoms, except for those of water molecules, were located at their idealized positions [$\text{C–H}(\text{methyl}) = 0.96 \text{ \AA}$, $\text{C–H}(\text{aromatic}) = 0.93 \text{ \AA}$, $\text{N–H}(\text{amine}) = 0.89 \text{ \AA}$ and $\text{N–H}(\text{amidate}) = 0.86 \text{ \AA}$], and included in the refinement in riding-motion approximation, with $U_{iso}(\text{methyl H}) = 1.5U_{eq}(\text{bonded C})$, $U_{iso}(\text{aromatic H}) = 1.2U_{eq}(\text{bonded C})$, $U_{iso}(\text{amine H}) = 1.5U_{eq}(\text{bonded N})$ and $U_{iso}(\text{amidate H}) = 1.2U_{eq}(\text{bonded N})$. The water H atoms were not located. The highest peak was located 1.65 Å from Pt2, while the deepest hole was located 1.17 Å from Pt2.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: KENX (Sakai, 2002); software used to prepare material for publication: SHELXL97, TEXSAN (Molecular Structure Corporation, 2001), KENX and ORTEPII (Johnson, 1976).

This work was partly supported by a Grant-in-Aid for Scientific Research (No. 14340223) from the Ministry of Education, Science, Sports, and Culture of Japan.

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