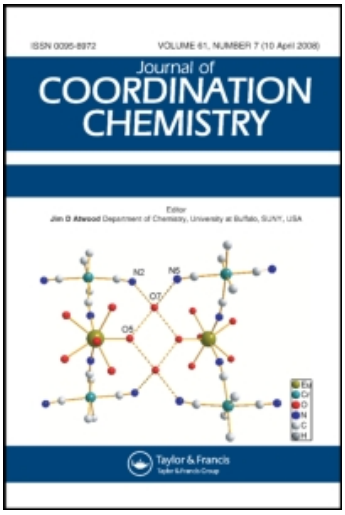

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SYNTHESIS AND CRYSTAL STRUCTURE OF A NEW ANTITUMOR AGENT: [Pt(*cis*-1,4-DIAMINOCYCLOHEXANE)(1,1-CYCLOBUTANEDICARBOXYLATE)]

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SYNTHESIS AND CRYSTAL STRUCTURE OF A NEW ANTITUMOR AGENT: [PT(*cis*-1,4-DIAMINOCYCLOHEXANE)(1,1-CYCLOBUTANEDICARBOXYLATE)]

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(Recieved December 13, 1993; in final form March 1, 1994)

The crystal structure of [Pt(*cis*-1,4-diaminocyclohexane) (1,1-cyclobutanedicarboxylate)]·1½H_2O has been determined by X-ray diffraction. The crystal is monoclinic with space group $P2_1/c$, a = 10.358(5), b = 21.887(6), c = 13.920(7)Å, β = 107.26(3)° and Z = 8. The platinum atom has slightly distorted square planar geometry, with two adjacent corners being occupied by two amino nitrogens of *cis*-1,4-diaminocyclohexane (1,4-DACH) and the remaining two positions occupied with two oxygens of 1,1-cyclobutanedicarboxylate. The DACH moiety is in a twist-boat conformation and makes a seven-membered chelating ring with platinum. The strain in bidentate 1,4-DACH binding with platinum is evidenced by the expansion of average N-Pt-N and Pt-N-C angles to 98.2° and 123.4°, respectively. The cyclobutane ring is nonplanar. There are two crystallographically independent molecules in the asymmetric unit surrounding the three water molecules. The equatorial planes of the two molecules are titled at 32° to each other. The near edges are directly hydrogen-bonded, while the open side is hydrogen bonded through the water molecules.

KEYWORDS: platinum, *cis*-1,4-diaminocyclohexane, synthesis, X-ray

INTRODUCTION

Since discovery of cisplatin[1] as an effective anticancer drug, new platinum drugs with higher or equal antitumor activity but lower toxicity have been sougth.[2–6] Though cisplatin is the most active antitumor agent in clinical use today,[7] its clinical effectiveness is limited by dose toxicities such as renal failure, nausea, and vomiting.[8–10] Consequently, efforts were directed towards altering the pharmacokinetics of cisplatin, and this was achieved by replacing the labile chloro ligands with other leaving groups and extending the stable amine ligands to a series of either cyclic or acyclic alkyl amines. Such second-generation platinum drugs, like carboplatin[11,12] and iproplatin,[13,14] then came into clinical use. A number of third-generation drugs with different stable amine ligands and different leaving groups are in active clinical trials.[15] The interest in the diaminocyclohexane (DACH) carrier ligand has been increasing in recent years, because compounds

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having this ligand retain activity against L-1210 leukemia made resistant to cisplatin.[16]

We have, therefore, been developing platinum complexes of various 1,2-DACH isomers, some of which have shown promising antitumor activity.[17–20] A liposomal preparation of one of these drugs *cis*-bis(neodecanoato)(*trans*-1R,2R-diamino-cyclohexane) platinum (L-NDDP), is currently undergoing clinical trials at M.D. Anderson Cancer Center.[21] Here we report the synthesis and crystal structure of a new antitumor platinum complex with *cis*-1,4-DACH as carrier ligand, [Pt(*cis*-1,4-DACH) (1,1-cyclobutanedicarboxylate)]·1½H_2O. Preliminary data, to be published later, suggest this drug has excellent antitumor activity.

EXPERIMENTAL

cis-1,4-DACH was purchased from CTC organics, Atlanta, GA. Dimethylsulfoxide (DMSO) and 1,1-cyclobutanedicarboxylic acid (CBDCA) were obtained from Aldrich Chemical Co. Milwaukee, WI, and potassium tetrachloroplatinate(II) was purchased from Johnson Matthey, Seabrook, NH.

Typical Procedure for the Preparation of [Pt(cis-1,4-DACH) (CBDCA)]

Potassium tetrachloroplatinate(2-) (6.25 g; 15 mM) was dissolved in 100 ml of water. DMSO (2.43 g; 30 mM) in 10 ml of water was added to the solution. The reaction mixture was kept at room temperature for two days. Pale yellow needles of *cis*-[$Pt(DMSO)_2Cl_2$] were obtained, filtered, washed with cold water, and dried *in vacuo*. Yield: 75%. *cis*-[$Pt(DMSO)_2Cl_2$] (5.1 g; 12 mM) was dissolved in 250 ml of warm water. To this solution was added a suspension of the disilver salt of CBDCA (4.2 g; 11.64 mM). The reaction mixture, protected from light, was kept stirring for 24 h at room temperature. The solution was filtered, and the yellow filtrate was evaporated to 50 ml under reduced pressure at 35°C and kept in ice. The white crystalline [$Pt(DMSO)_2$(CBDCA)] was isolated, washed with cold water, and dried under vacuum. Yield: 70%. To a hot solution of *cis*-[$Pt(DMSO)_2$(CBDCA)] (2.47 g; 5 mM) in 150 ml of water was added a solution of *cis*-1,4-DACH (0.57 g; 5 mM) in 10 ml of water. The mixture was stirred at 90°C for 1.5 h. Completion of reaction was monitored by high pressure liquid chromatography. The solution was filtered while hot, cooled, and then evaporated to a minimum volume under reduced pressure at 35°C and kept in ice. An off-white compound was precipitated, filtered and recrystallized from water. A white compound was obtained. Yield 50%. Fifty milligrams of this compound was dissolved in 20 ml of water and kept for slow evaporation. After a few days, colorless crystals were obtained. *Anal.* Calcd. (%): C, 30.68; H, 4.73; N, 5.97. Found: C, 30.98; H, 5.05%; and N, 5.98.

Crystallographic Measurements

A colorless block having approximate dimensions 0.22 × 0.28 × 0.44 mm was cut from a very long square column and mounted in a random orientation on a Nicolet R3m/V automatic diffractometer. The sample was rapidly transferred to the goniometer and placed in a stream of dry nitrogen gas at − 50°C. The radiation used was Mo Kα monochromatized by a highly ordered graphite crystal. Final cell

constants, as well as other information pertinent to data collection and refinement, are listed in Table 1. The Laue symmetry was determined to be 2/m, and from the systematic absences noted, the space group was shown unambiguously to be $P2_1/c$. Intensities were measured using the omega scan technique, with the scan rate depending on the count obtained in rapid pre-scans of each reflection. Two standard reflections were monitored after every 2 hours or after 100 data points were collected, and these showed no significant variation. It was noted, however, that the sample turned on amber color after exposure to X-rays. During data reduction, Lorentz and polarization corrections were applied, as well as a semi-empirical absorption correction based on psi scans of 10 reflections having *chi* values between 70° and 90°.

The structure was solved by interpretation of the Patterson map, which revealed the positions of the Pt atoms in the asymmetric unit, consisting of two independent molecules. The remaining nonhydrogen atoms were found in subsequent difference Fourier syntheses. The usual sequence of isotropic and anisotropic refinement was followed, after which all hydrogens were entered in ideal calculated positions and constrained to riding motion, with a single variable isotropic temperature factor for all of them. Three water molecules of solvation were also found. However, their hydrogens could not be located. After all shift/esd ratios were less than 0.1, convergence was reached at the agreement factors listed in Table 1. No unusually high correlations were noted between any of the variables in the last cycle on full-matrix least squares refinement, and the final difference density map showed a maximum peak of about 2 $e/Å^3$, located close to Pt. All calculations were made using Nicolet's SHELXTL PLUS (1987) series of crystallographic programs.

Table 1 Data collection and processing parameters

Space group	$P2_1/c$ (monoclinic)
Cell constants	a = 10.358(5)Å
	b = 21.887(6)
	c = 13.920(7)
	β = 107.26(3)°
	V = 3014Å^3
Molecular formula	$C_{12}H_{20}N_2O_4Pt \cdot 1\frac{1}{2}H_2O$
Formula weight	478.46
Formula units per cell	Z = 8
Density	ρ = 2.11 g-cm^{-3}
Absorption coefficient	μ = 94.31 cm^{-1}
Temperature	T = − 50°C
Radiation (Mo Kα)	λ = 0.71073Å
Collection range	$4° \leq 2\Theta \leq 45°$
Scan width	$\Delta\Theta$ = 1.35 + (Kα_2 − Kα_1)°
Scan speed range	1.5 to 15.0°-min^{-1}
Total data collected	4286
Independent data, $I > 3\sigma(I)$	3281
Total variables	371
$R = \Sigma\|\|F_O\| - \|F_C\|\|/\Sigma\|F_O\|$	0.036
$R_w = [\Sigma w(\|F_O\| - \|F_C\|)^2/\Sigma w\|F_O\|^2]^{1/2}$	0.038
Weights	$w = \sigma(F)^{-2}$

RESULTS AND DISCUSSION

The synthesis of the title compound is summarized in Scheme 1. *cis*-$[Pt(DMSO)_2Cl_2]$[22] and $[Pt(DMSO)_2(CBDCA)]$[23] were prepared as described previously. The required compound [Pt(*cis*-1,4-DACH)(CBDCA)] was obtained in 50% yield by keeping the reaction mixture at 90°C for 1.5 h. If the reaction is kept at 100°C for 6 h as described in the procedure for the synthesis of [Pt(*trans*-(-)-1,2-DACH)(CBDCA)][23], slow decomposition starts, and the whole reaction mixture turns black with yield of only 5%.

$$K_2[PtCl_4] + 2\ DMSO \longrightarrow cis\text{-}[Pt(DMSO)_2Cl_2] + 2\ KCl \quad (1)$$

$$cis\text{-}[Pt(DMSO)_2Cl_2] + Ag_2CBDCA \longrightarrow [Pt(DMSO)_2(CBDCA)] + 2AgCl \quad (2)$$

$$[Pt(DMSO)_2(CBDCA)] + cis\text{-}1,4\text{-}DACH \xrightarrow[1\frac{1}{2}\ h]{90^\circ C} [Pt(cis\text{-}1,4\text{-}DACH)(CBDCA)] + 2\ DMSO \quad (3)$$

Scheme 1

Figure 1 shows a perspective view of the molecule with the numbering scheme adopted. Bond lengths and bond angles are given in Tables 2 and 3, respectively.

The platinum atom has slightly distorted square planar geometry with two adjacent corners being occupied by the two nitrogens of *cis*-1,4-DACH, with the remaining two *cis* positions occupied by two oxygens of CBDCA. The DACH moiety is in a twist-boat configuration. Platinum bonding with the amino nitrogens at positions 1 and 4 is considerably strained, resulting in expansion of the N1-Pt-N8 bond angle to 98.2°, in contrast to the bond angles 83.5° and 94.8° reported in the literature for 1,2-DACH[23,24] and 1,3-DACH[25] complexes, respectively. Expansion of N-Pt-N angle is quite obvious, as the positions of the amino groups in the DACH change from 1,2 to 1,4, because 1,2-DACH forms a five-membered chelating ring with platinum, and 1,3-DACH and 1,4-DACH form six- and seven-membered chelating rings, respectively. In compensation, the N1-Pt-O18 bond angle in the

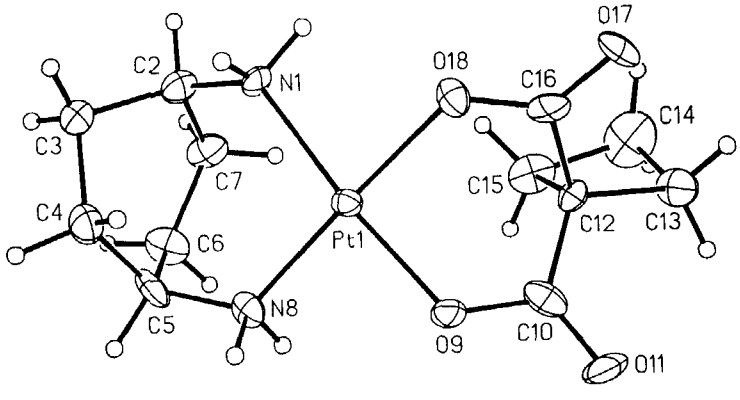

Figure 1 View of one molecule showing the atom numbering scheme. Thermal ellipsoids are 50% equiprobability envelopes, with hydrogens as spheres of arbitrary diameter. To get labels for the other molecule, add 1 to Pt and 18 to the other values shown.

Table 2 Bond lengths (Å)

Pt(1)–N(1)	2.043 (8)	Pt(1)–N(8)	2.052 (11)
Pt(1)–O(9)	2.021 (7)	Pt(1)–O(18)	2.034 (9)
N(1)–C(2)	1.507 (16)	C(2)–C(3)	1.552 (19)
C(2)–C(7)	1.540 (18)	C(3)–C(4)	1.564 (16)
C(4)–C(5)	1.546 (17)	C(5)–C(6)	1.561 (18)
C(5)–N(8)	1.465 (16)	C(6)–C(7)	1.509 (20)
O(9)–C(10)	1.332 (16)	C(10)–O(11)	1.211 (15)
C(10)–C(12)	1.545 (18)	C(12)–C(13)	1.569 (19)
C(12)–C(15)	1.546 (18)	C(12)–C(16)	1.530 (17)
C(13)–C(14)	1.511 (19)	C(14)–C(15)	1.563 (22)
C(16)–O(17)	1.219 (18)	C(16)–O(18)	1.272 (15)
Pt(2)–N(19)	2.048 (11)	Pt(2)–N(26)	2.029 (8)
Pt(2)–O(27)	2.030 (9)	Pt(2)–O(36)	2.019 (7)
N(19)–C(20)	1.492 (16)	C(20)–C(21)	1.503 (19)
C(20)–C(25)	1.538 (19)	C(21)–C(22)	1.517 (19)
C(22)–C(23)	1.564 (21)	C(23)–C(24)	1.523 (18)
C(23)–N(26)	1.493 (17)	C(24)–C(25)	1.520 (18)
O(27)–C(28)	1.274 (15)	C(28)–O(29)	1.218 (17)
C(28)–C(30)	1.505 (17)	C(30)–C(31)	1.548 (18)
C(30)–C(33)	1.550 (16)	C(30)–C(34)	1.558 (16)
C(31)–C(32)	1.513 (18)	C(32)–C(33)	1.526 (23)
C(34)–O(35)	1.217 (14)	C(34)–O(36)	1.295 (17)

Table 3 Bond angles (°)

N(1)-Pt(1)-N(8)	98.8(4)	N(1)-Pt(1)-O(9)	174.7(4)
N(8)-Pt(1)-O(9)	86.5(3)	N(1)-Pt(1)-O(18)	85.5(3)
N(8)-Pt(1)-O(18)	174.0(3)	O(9)-Pt(1)-O(18)	89.2(3)
Pt(1)-N(1)-C(2)	122.3(7)	N(1)-C(2)-C(3)	110.9(10)
N(1)-C(2)-C(7)	112.6(9)	C(3)-C(2)-C(7)	110.4(11)
C(2)-C(3)-C(4)	108.7(9)	C(3)-C(4)-C(5)	112.1(10)
C(4)-C(5)-C(6)	113.3(9)	C(4)-C(5)-N(8)	110.7(11)
C(6)-C(5)-N(8)	110.3(10)	C(5)-C(6)-C(7)	113.0(12)
C(2)-C(7)-C(6)	113.9(10)	Pt(1)-N(8)-C(5)	123.1(7)
Pt(1)-O(9)-C(10)	121.5(7)	O(9)-C(10)-O(11)	120.3(12)
O(9)-C(10)-C(12)	116.6(10)	O(11)-C(10)-C(12)	123.1(13)
C(10)-C(12)-C(13)	114.9(9)	C(10)-C(12)-C(15)	115.5(12)
C(13)-C(12)-C(15)	89.2(10)	C(10)-C(12)-C(16)	112.5(10)
C(13)-C(12)-C(16)	112.5(11)	C(15)-C(12)-C(16)	110.2(9)
C(12)-C(13)-C(14)	88.2(10)	C(13)-C(14)-C(15)	90.8(11)
C(12)-C(15)-C(14)	87.2(11)	C(12)-C(16)-O(17)	119.6(11)
C(12)-C(16)-O(18)	115.8(12)	O(17)-C(16)-O(18)	124.5(11)
Pt(1)-O(18)-C(16)	123.8(8)	N(19)-Pt(2)-N(26)	97.6(4)
N(19)-Pt(2)-O(27)	176.2(3)	N(26)-Pt(2)-O(27)	86.0(4)
N(19)-Pt(2)-O(36)	86.7(4)	N(26)-Pt(2)-O(36)	175.0(4)
O(27)-Pt(2)-O(36)	89.8(3)	Pt(2)-N(19)-C(20)	123.1(7)
N(19)-C(20)-C(21)	110.6(10)	N(19)-C(20)-C(25)	109.7(12)
C(21)-C(20)-C(25)	109.6(10)	C(20)-C(21)-C(22)	113.0(13)
C(21)-C(22)-C(23)	112.9(10)	C(22)-C(23)-C(24)	111.5(12)
C(22)-C(23)-N(26)	111.7(9)	C(24)-C(23)-N(26)	109.6(11)
C(23)-C(24)-C(25)	113.9(10)	C(20)-C(25)-C(24)	114.7(11)
Pt(2)-N(26)-C(23)	123.7(8)	Pt(2)-O(27)-C(28)	120.7(8)
O(27)-C(28)-O(29)	121.4(11)	O(27)-C(28)-C(30)	117.9(12)
O(29)-C(28)-C(30)	120.7(12)	C(28)-C(30)-C(31)	113.7(11)
C(28)-C(30)-C(33)	112.3(9)	C(31)-C(30)-C(33)	88.6(9)
C(28)-C(30)-C(34)	109.0(9)	C(31)-C(30)-C(34)	115.6(9)
C(33)-C(30)-C(34)	116.5(11)	C(30)-C(31)-C(32)	88.9(10)
C(31)-C(32)-C(33)	90.7(11)	C(30)-C(33)-C(32)	88.3(10)
C(30)-C(34)-O(35)	121.0(12)	C(30)-C(34)-O(36)	116.1(9)
O(35)-C(34)-O(36)	122.8(11)	Pt(2)-O(36)-C(34)	120.6(7)

platinum square plane is reduced to 85.5°, compared with analogous angles of 93.8° and 94.4° in [Pt(*trans*-(-)-1,2-DACH)(CBDCA)][23] and [Pt(1R,2R-DACH)(NMIDA)],[24] respectively. The strain in binding of 1,4-DACH to platinum is also shown in the expansion of the mean Pt-N-C angle to 123.4°, as compared with the 1,2-DACH complexes like [Pt(*trans*-(-)-1,2-DACH)(CBDCA)] (110.5°)[23], [Pt(*trans*-1R,2R-DACH) (oxalate)] (105.5°) and [Pt(*trans*-(-)-1,2-DACH) (malonate)] (108°).[26] The Pt-N mean bond length of 2.05 Å agrees well with the Pt-N bond lengths of other cyclic diamine platinum complexes.[23-26] The cyclohexane ring lies at a right angle to the coordination plane of the metal ion.

The structural features of CBDCA include an average Pt-O bond length of 2.03Å which is slightly longer than the Pt-O length in [Pt(*trans*-(-)-1,2-DACH)(CBDCA) (2.006 Å).[23] This bond length is consistent with those found for other carboxylate-containing complexes such as [Pt(1R,2R-DACH)(oxalate)] and [Pt(1R,2R-DACH)(malonate)] (2.02 Å)[26] and carboplatin (2.03 Å).[27] It forms a six-membered chelating ring with platinum and adopts a boat conformation as in the other complexes containing CBDCA.[23-28] The O-Pt-O angle of 89.2° within the chelating ring is normal as compared with the values observed in [Pt-(*trans*-(-)-1,2-DACH)(CBDCA)][23] and other complexes containing CBDCA ligand, which were close to 90°. The cyclobutane ring in the drug reported here is decidedly nonplanar and makes a right angle with the plane of metal coordination sphere. In most of the other compounds reported in the literature however, the cyclobutane ring is planar.[27]

Figure 2 shows a view of the asymmetric unit and hydrogen bonding between two molecules. The interesting geometric features in the hydrogen-bonding are that there are two crystallographically independent molecules in the 'local block'

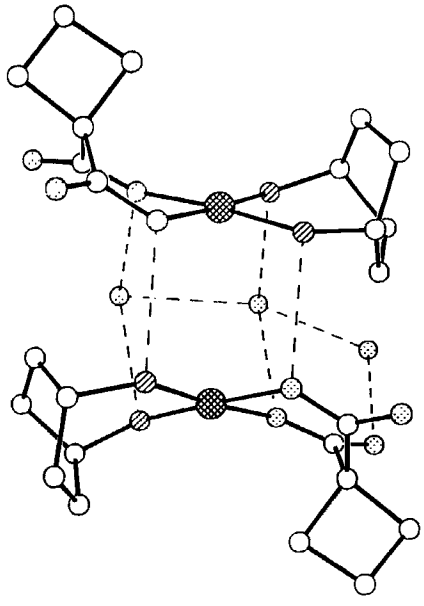

Figure 2 View of the asymmetric unit, showing the hydrogen bonding between the molecules.

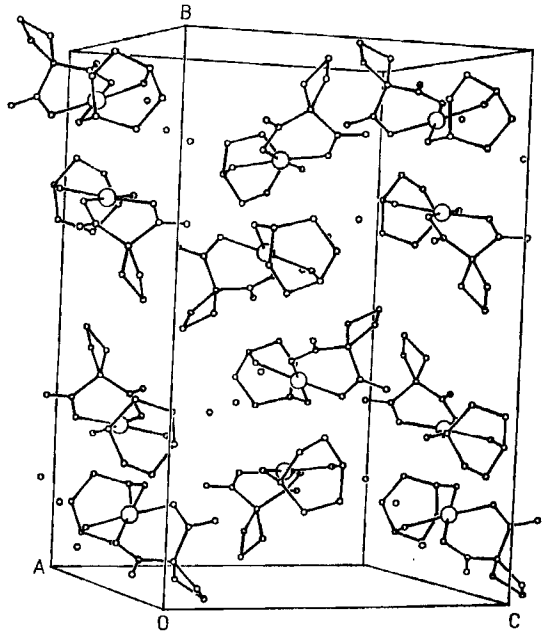

Figure 3 Packing in the unit cell, as viewed along the *a* axis.

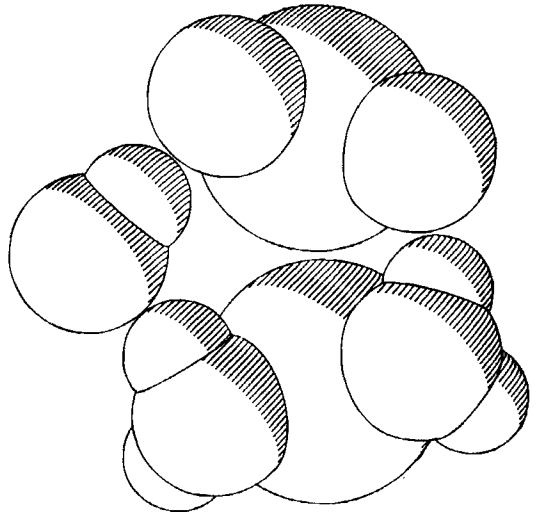

Figure 4 Cutaway space-filling view of the relationship between the square planes of the two mutually hydrogen bonded molecules. A hydrogen has been artificially added to the bridging water molecule.

surrounding the three water molecules. Both have virtually identical configurations, but the equatorial planes of the two molecules are tilted at 32° to each other. The near edges, *i.e.*, N8 and O9 of one molecule and N19 and O27 of the other molecule, are directly hydrogen bonded, while the open side is hydrogen bonded through the water molecules.

Figure 3 shows a stereoscopic view of the molecular packing in the unit cell along the *a* axis.

Supplementary Material

Observed and calculated structure factors, as well as anisotropic thermal factors and hydrogen atomic coordinates, can be obtained from the authors on request.

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