Homobinuclear bis-3,6-di-*tert*-butyl-*o*-benzosemiquinone and bis-3,6-di-*tert*-butyl-*o*-catecholate complexes of Pd^{II} and Pt^{II} with bridging ligands. Molecular structure of $(3,6\text{-Cat})_2Pd_2L_2$ (L = dppm and dppy)

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Reactions of the binuclear complexes $M_2L_2Cl_2$ [M = Pt or Pd, L = bis(diphenylphosphino)methane (dppm) or 2-(diphenylphosphino)pyridine (dppy)] with thallium 3,6-di-*tert*-butyl-*o*-benzosemiquinone (3,6-SQ) in solutions have been studied. The formation of the corresponding bis(semiquinone) binuclear derivatives $M_2L_2(SQ)_2$ with retention of the metal—metal bond has been established by the ESR method. The average distances between the centers of localization of unpaired electrons, which were determined from the ESR spectral data for the complexes studied, allow conclusions about the parallel arrangement of the semiquinone ligands in skewed conformations in a square-pyramidal coordination sphere of both metal atoms. At room temperature, the biradical complexes are slowly converted to diamagnetic catecholate compounds with cleavage of the M—M bond and with retention of the bridging structure of the dppm and dppy ligands. The structures of catecholate complexes of palladium have been established by X-ray structural analysis.

Key words: ESR, biradical, semiquinone, metal—metal bond, X-ray structural analysis.

Recently, interest has substantially increased in the chemistry of homo- and heteronuclear complexes of transition metals with bridging ligands, among which bis(diphenylphosphino)methane and 2-(diphenylphosphino)pyridine are widely used.[1,2] Dihalide complexes of platinum and palladium are the most extensively studied in this field. The reactivities of these compounds are determined to a large extent by the nature of the bridging ligand and the presence of a M—M bond that links two coordinatively unsaturated metal atoms. Reactions of insertion of small molecules (CO, SO_2, RCN, and RC≡CR)[5,6] into the M—M bond are typical of complexes with a nonrigid bridging ligand (dppm), which allows the M—M distance to vary from 2.2 to 3.5 Å (see Refs. 3 and 4), whereas these reactions are untypical of compounds with 2-(diphenylphosphino)pyridine, which are characterized by a more rigid structure of the metal cycle.[2]

It is known that crystals of $(SQ)Rh(CO)_2$ that consist of one-dimensional molecular chains with Rh—Rh bonds exhibit a very interesting temperature dependence of the magnetic susceptibility.[7] The region of ferromagnetic exchange occurs for this compound at temperatures below 105 K. Apparently, the synthesis of other polynuclear polysemiquinone complexes will make it possible to reveal the nature of magnetic interactions in these compounds in more detail. In this connection, the possibility of synthesizing bis(semiquinone) complexes of the (SQ)M—M(SQ) type (where M = Pd or Pt) containing an M—M bond based on known homometal halides of the general formula $L_2M_2X_2$ is of interest.

The complexes were prepared from dihalides[8,9] by the exchange reaction with the corresponding thallium semiquinone in THF:

$$L_2M_2Cl_2 + 2(3,6\text{-SQ})Tl \xrightarrow{-2\,TlCl} L_2M_2(SQ)_2 \qquad (1)$$

1: M = Pd
2: M = Pt
L = (dppm) (**a**), (dppy) (**b**)

After completion of the reaction, TlCl was isolated, and the ESR spectra of the complexes obtained were recorded in a glassy solvent matrix at 130 K. The ESR

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 2, pp. 464—468, February, 1996.

spectra obtained are typical of biradical particles, whose zero-field splitting constants are virtually independent of the properties of the solvent (THF and toluene) (Table 1); in all cases, the half-field signal was observed that corresponds to the transition $\Delta m_s = 2$.

As is evident from Table 1, the zero-field splitting constants in the ESR spectra of semiquinone compounds **1a** and **2a** studied in solutions are very close to the parameters of bis(semiquinone) complexes of Zn and Cd (D = 190 and 170 Oe, respectively), in which the SQ ligands are coordinated to one metal atom, and the distances between unpaired electron localized on semiquinones are ones of the shortest (5.3 and 5.5 Å).[11] Based on these data and taking into account that two SQ ligands in complexes **1a** and **2a** are bonded to different metal atoms (this is confirmed by the results of X-ray structural analysis of complexes **3a** and **3b**), it can be stated with assurance that the semiquinone fragments in these compounds are parallel to each other and perpendicular to the M—M bond. In this case, the Pd and Pt atoms have a square-pyramidal coordination with the adjacent metal atom in the axial position. If it is assumed that the M—M distance remains the same in going from halide complexes (Pd—Pd 2.70 Å; Pt—Pt 2.65 Å)[12,13] to semiquinone complexes, the torsion angle between the symmetry axes of the semiquinone fragments is approximately 120—130° for the biradical particles observed in solutions. The structural data for $(SQ)Rh(CO)_2$[7] confirm the possibility of this type of structures for binuclear *o*-semiquinone complexes of metals.

Unfortunately, we failed to isolate compounds obtained in the crystalline form because of their instability. When solutions of the complexes obtained were kept at room temperature for several hours, the biradical particle was converted to the diamagnetic dicatecholate complex with retention of the bridging structures of the ligands and with the cleavage of the M—M bond.

An attempt to obtain a more stable complex of *o*-semiquinone, namely, of phenanthrenesemiquinone, which exhibits a lower accepting ability and is less sterically hindered, was unsuccessful. The biradical phenanthrenesemiquinone complex **2a′**, which is formed in reaction (1), is not thermally stable. When the solution was kept at room temperature for one day, the intensity of the ESR signal of **2a′** went almost to zero. The distance between unpaired electrons in **2a′** (≈5.20 Å) is slightly shorter than that in the complex with (3,6-Bu^t-SQ), which is a reflection of lesser steric crowding of the compound formed.

Table 1. Zero-field splitting constants of the ESR spectra of the bis(semiquinone) complexes of Pt and Pd in THF at 130 K

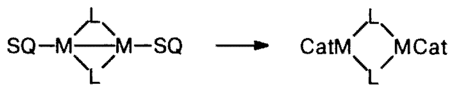
Complex	D/Oe	E/Oe	r*/Å
1a	178.8	7.1	5.35
2a	183.0	7.3	5.33
2a**	197.0	—	5.20
1b	195.0	7.6	5.22

* r is the average distance between the centers of localization of unpaired electrons (calculated by the formula[10]).

** SQ = phenanthrenesemiquinone.

The use of a more rigid bridging ligand (dppy) also did not allow us to isolate stable bis(semiquinone) binuclear complex **1b**. The parameters of the ESR spectrum of the biradical bis(semiquinone) complex recorded in a glassy solvent matrix are given in Table 1. The distance between unpaired electrons in this compound is shorter than that in **1a**, which is determined by a shortening of the M—M bond in going from the dppm to the dppy ligand.

As was mentioned above, all bis(semiquinone) bimetal complexes are unstable in solutions and are converted to diamagnetic catecholate compounds with time according to reaction (2), which is not surprising because five-coordinate 18-electron complexes of Pd and Pt are substantially less stable than the square 16-electron compounds of these metals.



(2)

3: M = Pd,
4: M = Pt
L = (dppm) (**a**), (dppy) (**b**)

A change in the initial geometry of bis(semiquinone) binuclear complexes results in an intramolecular electron transfer from metal atoms to semiquinones. In this case, the ligands are reduced to catecholates and the cleavage of the M—M bond occurs simultaneously. As a result of the reactions carried out, dicatecholate compounds **3a**, **3b**, and **4a** were isolated.

The reaction of dicatecholate complex **3a** with an equimolar amount of silver trifluoroacetate results in the oxidation of one of the catecholate ligands. The ESR spectrum of the oxidation product (triplet triplet 2.3 Oe (2 P) and 3.6 Oe (2 H_{SQ})) is similar in character and parameters to that observed upon oxidation of the mononuclear complex $(3,6\text{-Bu}^t\text{-Cat})Pd(PPh_3)_2$.[14] Introduction of an additional amount of the oxidant results in a biradical bis(semiquinone) compound, which is, apparently, associated with cleavage of the bridging structure of the complexes.

X-ray structural studies confirmed the fact that two PdCat fragments in **3a** and **3b** are linked *via* two dppm and three dppy bridges in **3a** and **3b**, respectively, to form the binuclear complexes (Figs. 1 and 2). In these complexes, the planes of the Cat ligands are not parallel to each other: the dihedral angles between the average planes of the Cat—Pd(1)—P(1)—P(4), Cat—Pd(2)—P(2)—P(3) and Cat—Pd(1)—P(1)—N(2), Cat—Pd(2)—N(1)—P(2) fragments are 88.4 and 80.1° in **3a** and **3b**, respectively. Large values of the Pd—Pd distances (4.421(4) and 4.368(2) Å in **3a** and **3b**, respectively) are

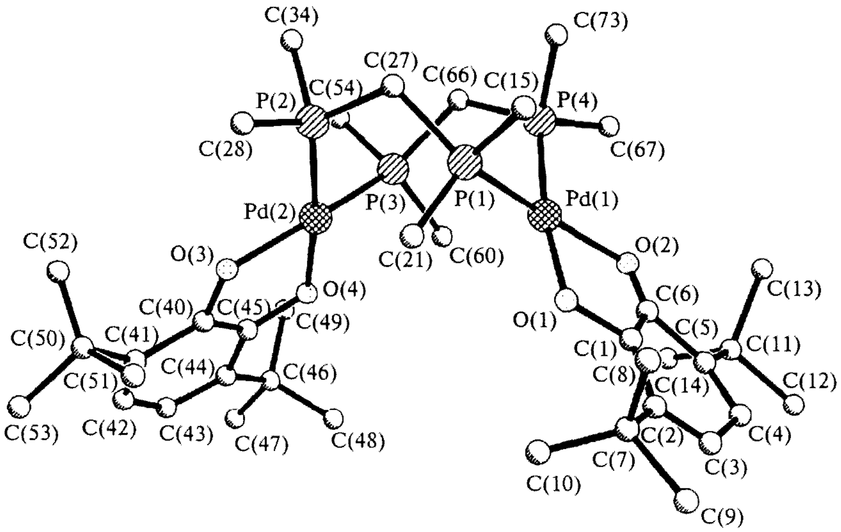


Fig. 1. Overall view of molecule **3a**. In the bridging ligands, only carbon atoms of the phenyl rings bonded to phosphorus atoms are shown.

indicative of the absence of direct bonding between Pd atoms.

The Pd atoms in compounds **3a** and **3b** have a distorted planar-square coordination. The planes of the P(1)—Pd(1)—P(4) and P(2)—Pd(2)—P(3) fragments in **3a** and P(1)—Pd(1)—N(2) and P(2)—Pd(2)—N(1) fragments in **3b** deviate only slightly from the planes of the O—Pd—O fragments at the corresponding Pd atoms. The dihedral angles between these planes are 12.8°, 12.6° and 9.5°, 10.0°, respectively.

The Pd—P distances (2.235(9)—2.258(9) Å in **3a** and 2.265(3) and 2.270(3) Å in **3b**) coincide with those for

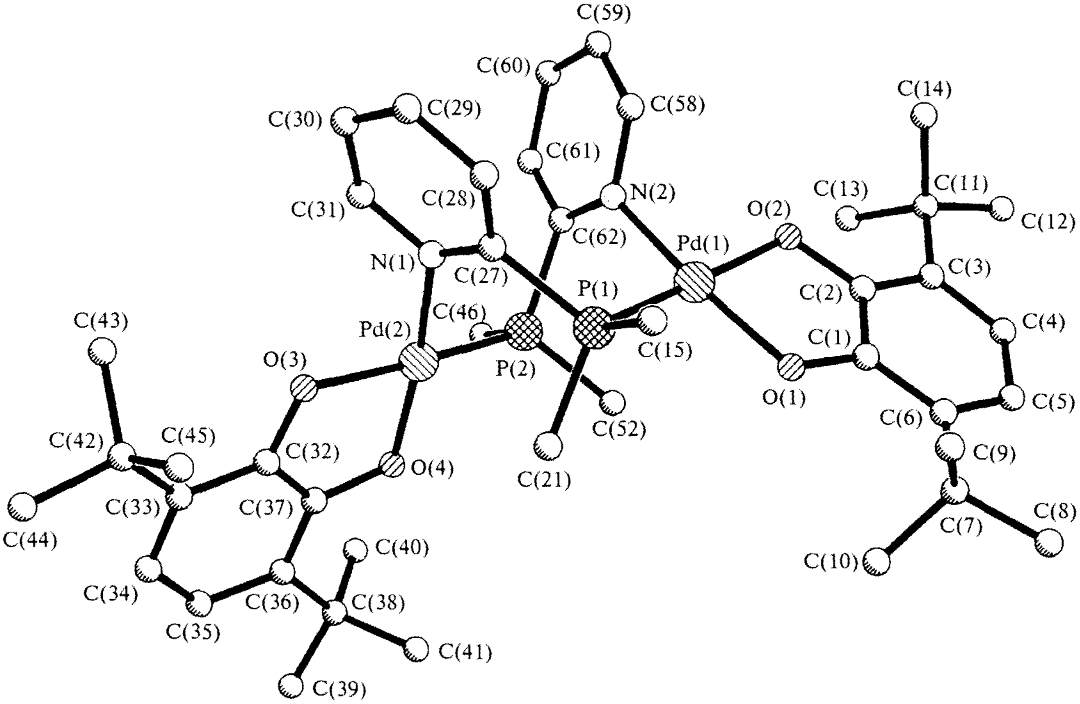


Fig. 2. Overall view of molecule **3b**. In the bridging ligands, only carbon atoms of the phenyl rings bonded to phosphorus atoms are shown.

analogous bonds with the terminal PPh_3 groups in the catecholate complexes of Pd studied previously (2.281 and 2.292 Å in $(PPh_3)_2Pd(o\text{-}Cl_4Cat)$[14]), but they are substantially smaller than the sum of covalent radii of Pd and P atoms (2.46 Å).[15] The Pd—N distances (2.030(6) and 2.060(6) Å) in **3b** are close to the sum of covalent radii of Pd and N atoms (2.10 Å).[15] Catecholate ligands are planar within 0.044 Å and 0.014 Å in **3a** and **3b**, respectively. The average values of the observed O—C and C—C distances (1.31 and 1.39 Å in **3a** and 1.36 and 1.40 Å in **3b**) in the five-membered metal cycles of the coordinated Cat ligands are close to the corresponding values typical of benzoquinone ligands in the catecholate form (1.32—1.58 Å and 1.358—1.415 Å for the C—O and C—C bonds, respectively).[16] The average values of the Pd—O distances in **3a** and **3b** (2.013 and 1.970 Å, respectively) are close to each other, but they are slightly smaller than the analogous distances in the (3,6-DTBSQ)Pd($C_9H_{15}O$) complex (2.051 and 2.139 Å).[17]

Two palladium atoms and bridging ligands, which link palladium atoms together, form eight-membered cycles Pd(1)—P(1)—C(27)—P(2)—Pd(2)—P(3)—C(66)—P(4) in **3a** (see Fig. 1) and Pd(1)—P(1)—C(27)—N(1)—Pd(2)—P(2)—C(62)—N(2) in **3b** (see Fig. 2), which have a boat conformation in both structures.

Experimental

The ESR spectra were recorded on an ER-200D-SRC instrument. The starting compounds were prepared according to known procedures.[2,6,8,9] Synthesis and studies of the reactivities were carried out in evacuated ampules.

Preparation of bis(μ-diphenylphosphinomethane)bis(3,6-di-*tert*-butylpyrocatechol)dipalladium(II). A solution of (3,6-SQ)Tl in THF prepared from 3,6-Q (0.5 mmol) and 3,6-$CatTl_2$ (0.5 mmol) was added to a solution of $Pd_2(dppm)_2Cl_2$ (0.527 g, 0.5 mmol) in 30 mL of THF. The ESR spectrum of the radical pair was recorded at low temperature. The reaction mixture was filtered off from TlCl at room temperature. Green crystals were isolated from the solution obtained; these crystals readily disintegrate in air because of the loss of crystallization water. Found (%): C, 65.49; H, 6.49; P, 8.04; Pd, 13.27, which corresponds to $Pd_2(dppm)_2(3,6\text{-Cat})_2 \cdot 2.5$ THF. $C_{88}H_{104}O_{6.5}P_4Pd_2$. Calculated (%): C, 65.98; H, 6.55; P, 7.74; Pd, 13.23.

Preparation of bis(μ-diphenylphosphinomethane)bis(3,6-di-*tert*-butylpyrocatechol)diplatinum(II). A solution of (3,6-SQ)Tl (0.5 mmol) in THF was added to a solution of $Pt_2(dppm)_2Cl_2$ (0.31 g, 0.25 mmol) in 20 mL of THF. After filtration and removal of the solvent, the residue was recrystallized from toluene. Orange crystals of $Pt_2(dppm)_2(3,6Cat)_2 \cdot 3CH_3C_6H_5$ were obtained. Found (%): C, 63.09; H, 5.82; P, 6.44; Pt, 19.56. $C_{99}H_{108}O_4P_4Pt_2$. Calculated (%): C, 63.37; H, 5.81; P, 6.61; Pt, 20.80.

Preparation of bis[μ-2-(diphenylphosphino)pyridine]bis(3,6-di-*tert*-butylpyrocatechol)dipalladium(II). A solution of 3,6-SQTl (0.6 mmol) in THF was added to a solution of $Pd_2(dppy)_2Cl_2$ (0.24 g, 0.3 mmol) in 20 mL CH_2Cl_2. The reaction mixture was filtered off, and then the filtrate was evaporated. The residue was recrystallized from pentane. Dark-brown crystals of $Pd_2(dppy)_2(3,6\text{-Cat})_2 \cdot C_5H_{10}$ were obtained.

X-ray structural studies of compounds **3a** and **3b** were carried out on a Siemens P3-PC diffractometer at room temperature (Mo-Kα radiation, graphite monochromator). Crystals of **3a** $\{C_{78}H_{84}O_4P_4Pd_2 \cdot (C_7H_8)_{2.5}\}$ and **3b** $\{C_{62}H_{68}O_4N_2P_2Pd_2 \cdot C_5H_{12}\}$ are monoclinic, a = 17.734(4) and 20.513(2) Å, b = 24.730(5) and 14.138(3) Å, c = 19.998(4) and 22.480(4) Å, β = 101.24(3) and 114.01(2)°, V = 8602(6) and 5955(4) Å^3, Z = 4 for both crystals, d_{calc} = 1.276 and 1.380

Table 2. Principal bond lengths (d) in molecules **3a** and **3b**

Bond	d/Å	Bond	d/Å
Molecule **3a**		Molecule **3b**	
Pd(1)—P(1)	2.255(9)	Pd(1)—O(1)	1.973(5)
Pd(1)—O(1)	1.99(2)	Pd(1)—P(1)	2.265(3)
Pd(2)—P(3)	2.235(9)	Pd(2)—O(3)	1.980(6)
Pd(2)—O(4)	2.00(2)	Pd(2)—P(2)	2.270(3)
Pd(1)—P(4)	2.258(9)	Pd(1)—O(2)	1.976(6)
Pd(1)—O(2)	2.05(3)	Pd(1)—N(2)	2.030(6)
Pd(2)—P(2)	2.257(9)	Pd(2)—O(4)	1.952(5)
Pd(2)—O(3)	2.01(2)	Pd(2)—N(1)	2.060(6)

Table 3. Principal bond angles (ω) in molecules **3a** and **3b**

Angle	ω/deg	Angle	ω/deg
Molecule **3a**		Molecule **3b**	
P(1)—Pd(1)—P(4)	94.1(3)	O(1)—Pd(1)—O(2)	84.5(2)
P(4)—Pd(1)—O(1)	171.2(9)	O(2)—Pd(1)—P(1)	169.8(1)
P(4)—Pd(1)—O(2)	93.1(9)	O(2)—Pd(1)—N(2)	85.9(2)
P(2)—Pd(2)—P(3)	94.7(3)	O(3)—Pd(2)—O(4)	84.3(2)
P(3)—Pd(2)—O(3)	164.1(6)	O(4)—Pd(2)—P(2)	89.7(2)
P(3)—Pd(2)—O(4)	87.5(6)	O(4)—Pd(2)—N(1)	169.5(3)
P(2)—P(2)—C(27)	126.0(11)	Pd(1)—O(1)—C(1)	109.6(4)
P(1)—C(27)—P(2)	115.3(16)	Pd(2)—O(3)—C(32)	110.1(4)
Pd(1)—P(4)—C(66)	122.2(11)	Pd(1)—P(1)—C(15)	109.4(3)
Pd(1)—P(4)—C(66)	122.2(11)	C(15)—P(1)—C(21)	102.8(4)
P(3)—C(66)—P(4)	120.0(18)	C(15)—P(1)—C(27)	104.8(3)
P(1)—Pd(1)—O(1)	88.7(9)	Pd(2)—P(2)—C(46)	110.4(3)
P(1)—Pd(1)—O(2)	167.2(8)	C(46)—P(2)—C(52)	102.4(3)
O(1)—Pd(1)—O(2)	82.7(12)	C(46)—P(2)—C(62)	103.6(4)
P(2)—Pd(2)—O(3)	96.0(6)	Pd(2)—N(1)—C(27)	126.7(4)
O(3)—Pd(2)—O(4)	173.2(7)	Pd(1)—N(2)—C(62)	124.7(5)
O(3)—Pd(2)—O(4)	80.7(8)	P(1)—C(27)—N(1)	117.7(4)
Pd(1)—P(1)—C(27)	124.9(9)	O(1)—Pd(1)—P(1)	91.5(2)
Pd(2)—P(3)—C(66)	125.1(9)	O(1)—Pd(1)—N(2)	169.9(2)
Pd(1)—O(2)—C(6)	108.1(31)	P(1)—Pd(1)—N(2)	98.4(2)
Pd(2)—O(4)—C(45)	112.0(19)	O(3)—Pd(2)—P(2)	168.4(1)
Pd(1)—O(1)—C(1)	106.4(24)	O(3)—Pd(2)—N(1)	85.6(2)
Pd(2)—O(3)—C(40)	113.2(20)	P(2)—Pd(2)—N(1)	100.7(2)
		Pd(1)—O(2)—C(2)	110.3(5)
		Pd(2)—O(4)—C(37)	111.4(4)
		Pd(1)—P(1)—C(21)	120.3(2)
		Pd(1)—P(1)—C(27)	111.7(3)
		C(21)—P(1)—C(27)	106.4(4)
		Pd(2)—P(2)—C(52)	117.8(3)
		Pd(2)—P(2)—C(62)	111.0(3)
		C(52)—P(2)—C(62)	110.4(4)
		Pd(2)—N(1)—C(31)	113.5(5)
		Pd(1)—N(2)—C(58)	116.0(5)
		P(2)—C(62)—N(2)	118.2(6)

g cm^{-3}, μ(Mo-Kα) = 5.40 and 7.40 cm^{-1} for **3a** and **3b**, respectively, the space group is $P2_1/n$ for both crystals. Intensities of 7742 and 10276 reflections were measured using the $\theta/2\theta$ scanning technique ($2 < 2\theta < 45°$ and $2 < 2\theta < 53°$) of which 3507 and 5545 independent reflections with $I > 2\sigma(I)$ and $I > 3\sigma(I)$ for **3a** and **3b**, respectively, were used in calculations. The structures were solved by the direct method and refined by the block-diagonal least-squares method with anisotropic thermal parameters for nonhydrogen atoms. In both structures, H atoms were refined using the riding model with fixed thermal parameters for **3a** (U_{iso} = 0.08 Å^2) and with variable thermal parameters for **3b**. In the crystal of **3a**, in addition to the basic molecule, three solvate toluene molecules were found. Two of them occupy general sites, in one of these groups the Me groups are statistically disordered at two sites that differ by the rotation by 180°. The third toluene molecule is located on a center of symmetry. The Me groups of this molecule are disordered at two sites that differ by rotation by 180°. In the crystal of **3b**, one solvate pentane molecule was found, which is also disordered at two sites related by a center of symmetry. The disordered solvent molecules in **3a** and **3b** were refined with one-half occupancies of these positions. Absorption corrections were applied using the DIFABS program.[18] The final values of the R and R_w factors were 0.114 and 0.107 for **3a** and 0.049 and 0.052 for **3b**. High values of the R factors in **3a** were determined by the presence of a great number of solvate solvent molecules. All calculations were carried out using the SHELXTL PLUS program package.[19] Atomic coordinates and selected bond lengths and bond angles for **3a** and **3b** are given in Tables 2—3.

This work was financially supported by the Russian Foundation for Basic Research (Project No. 95-03-09455a). X-ray structural studies were supported by the International Science Foundation (Grant M04 300).

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Received July 28, 1995