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Synthesis and Structure of Iridium Complexes $[Ph_3PR][trans\text{-}IrCl_4(DMSO)_2]$

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Abstract—The reaction of sodium chloroiridate with acetonyl-, cyanomethyl-, and 2-butenyltriphenylphosphonium chloride in dimethyl sulfoxide was used to synthesize ionic iridium complexes $[Ph_3PR][trans\text{-}IrCl_4(DMSO)_2]$ (R = $CH_2C(O)Me$, CH_2CN, $CH_2CH{=}CHMe$). The phosphorus atoms in the $[Ph_3RP]^+$ cations have a slightly distorted tetrahedral coordination. The dimethyl sulfoxide ligand in the octahedral anions $[trans\text{-}IrCl_4(DMSO)_2]$ is coordinated to metal via sulfur atoms.

Keywords: ionic iridium complexes, dimethyl sulfoxide, X-ray diffraction analysis

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Ionic complexes of iridium(III) with the $[IrCl_4(DMSO)_2]^-$ anion where the dimethyl sulfoxide ligands are in the *trans* position are mentioned in the literature by only one complex $[H\text{-(Nicotine)}]^+[trans\text{-}IrCl_4(DMSO)_2]^-$. Its synthesis, structure, and properties are described in [1].

We synthesized and structurally characterized acetonyl-, cyanomethyl-, and 2-butenyltriphenyl-phosphonium *trans*-tetrachlorobis(dimethyl sulfoxide) iridates (complexes **I–III**, respectively). The complexes were prepared from sodium hexachloroiridate(III) and acetonyl-, cyanomethyl-, and 2-butenyltriphenylphosphonium chlorides in water and then recrystallized from dimethyl sulfoxide (Scheme 1).

On mixing equimolar amounts of the starting salts in water no changes in the color of the solution were observed. The finely dispersed residue after evaporation of water was dissolved in DMSO. Complexes **I–III** precipitated as yellow crystals at a slow evaporation of the solvent.

According to X-ray diffraction data the crystals of complexes **II** and **III** contain two types of crystallographically independent anions, and the crystal of complex **III**, contains in addition solvate DMSO molecules. The principal crystal data and results of structure refinement are listed in Table 1, and the principal bond lengths and angles, in Table 2.

The phosphorus atoms in the cations have a distorted tetrahedral coordination, the CPC bond angles span a narrow range and are close to the normal values of 104.80(12)°–113.50(13)° (Figs. 1–3). The $P–C_{Ph}$ bond lengths in complexes **I** and **II** [1.793(3)–1.800(3) and 1.789(5)–1.791(5) Å, respectively] are almost coincident with the $P–C_{Alk}$ bond lengths [1.803(3) and 1.804(4) Å], whereas the $P–C_{Alk}$ bond in complex **III** is longer than $P–C_{Ph}$ [1.821(5) and 1.790(4)–1.797(5) Å, respectively] (Table 2).

The *trans* DMSO molecules in the $[trans\text{-}IrCl_4(DMSO)_2]^-$ anion are coordinated to metal by the sulfur atoms. The SIrS and *trans*-ClIrCl angles

Scheme 1.

$$[Ph_3RP]Cl + Na_3[IrCl_6] \xrightarrow[(2)\ Me_2SO]{(1)\ H_2O} \underset{\textbf{I–III}}{[Ph_3RP]^+[IrCl_4(DMSO)_2\text{-}trans]^-} + 3NaBr,$$

R = $CH_2C(O)CH_3$ (**I**), CH_2CN (**II**), $CH_2CH{=}CHCH_3$ (**III**).

Table 1. Crystal data and details of the experiment and structure refinement for complexes **I–III**

Parameter	**I**	**II**	**III**
Formula	$C_{25}H_{32}Cl_4IrO_3PS_2$	$C_{24}H_{28}Cl_4IrNO_2PS_2$	$C_{28}H_{40}Cl_4IrO_3PS_3$
M	809.60	791.56	885.75
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$
a, Å	13.6473(5)	10.6683(4)	9.0051(3)
b, Å	8.0522(3)	15.5482(5)	15.1360(5)
c, Å	27.6065(10)	17.8507(7)	25.9840(9)
α, deg	90.00	90.00	90.00
β, deg	98.4960(10)	102.4620(10)	90.00
γ, deg	90.00	90.00	90.00
V, Å^3	3000.41(19)	2891.18(18)	3541.7(2)
Z	4	4	4
D_{calc}, g/cm^3	1.792	1.819	1.661
μ, mm^{-1}	5.025	5.211	4.321
F(000)	1592.0	1548.0	1760.0
Crystal dimensions, mm	0.49×0.35×0.22	0.36×0.24×0.13	0.50×0.30×0.20
θ range for data collection, deg	5.88°–53.04°	6.02°–52.86°	6.12°–52.8°
Reflection index ranges	$-17 \le h \le 17$, $-10 \le k \le 9$, $-34 \le l \le 34$	$-13 \le h \le 13$, $-19 \le k \le 19$, $-22 \le l \le 22$	$-11 \le h \le 11$, $-18 \le k \le 18$, $-32 \le l \le 32$
Measured reflections	49830	59024	31348
Unique reflections	6173	5943	5286
R_{int}	0.0200	0.0260	0.0236
Refinement variables	330	323	371
GOOF	1.179	1.120	1.141
R-Factors for $F^2 > 2\sigma(F^2)$	R_1 0.0190, wR_2 0.0427	R_1 0.0293, wR_2 0.0540	R_1 0.0317, wR_2 0.0649
R-Factors for all reflections	R_1 0.0215, wR_2 0.0440	R_1 0.0451, wR_2 0.0628	R_1 0.0445, wR_2 0.0698
Residual electron density (min/max), *e*/Å^3	0.93/–0.80	1.12/–0.68	1.00/–0.70

[178.20(2)°–180° and 176.48(3)°–180.0°] point to an almost ideal octahedral configuration. The Ir–Cl and Ir–S bond lengths [2.3394(7)–2.3674(7) and 2.3054(12)–2.3241(7) Å, respectively] are close to those in the complex [H-(Nicotine)]$^+$[*trans*-$IrCl_4(DMSO)_2$] with the same anion [2.340(2), 2.368(3), and 2.314(3), 2.325(3) Å] [1].

Note that the bond angles of the DMSO sulfur atom in complex **III** are close to those in a free DMSO molecule within experimental error [99.4(3)°–108.8(5)° and 100.1(6)°–108.6(5)°, respectively], and, therewith, the S–O bond in the free molecule is longer than the respective bonds in the ligands [1.472(6), 1.459(5), and 1.462(3) Å].

Table 2. Bond lengths and bond angles in complexes **I–III**

Bond	*d*, Å	Angle	ω, deg	Bond	*d*, Å	Angle	ω, deg
			I				
$Ir^1–Cl^1$	2.3564(7)	$Cl^1Ir^1Cl^4$	90.76(3)	$S^2–O^3$	1.460(2)	$S^1Ir^1Cl^4$	90.64(3)
$Ir^1–Cl^2$	2.3492(8)	$Cl^2Ir^1Cl^1$	176.48(3)	$S^2–C^{36}$	1.785(4)	$S^1Ir^1S^2$	178.20(2)
$Ir^1–Cl^3$	2.3394(7)	$Cl^2Ir^1Cl^4$	92.44(4)	$S^2–C^{37}$	1.764(3)	$S^2Ir^1Cl^1$	88.22(3)
$Ir^1–Cl^4$	2.3674(7)	$Cl^3Ir^1Cl^1$	88.14(3)	$P^1–C^1$	1.800(3)	$S^2Ir^1Cl^2$	93.35(3)
$Ir^1–S^1$	2.3157(6)	$Cl^3Ir^1Cl^2$	88.69(4)	$P^1–C^{11}$	1.796(3)	$S^2Ir^1Cl^3$	91.24(3)
$Ir^1–S^2$	2.3241(7)	$Cl^3Ir^1Cl^4$	178.59(3)	$P^1–C^{21}$	1.793(3)	$S^2Ir^1Cl^4$	87.85(3)
$S^1–O^2$	1.466(2)	$S^1Ir^1Cl^1$	92.78(2)	$P^1–C^{31}$	1.803(3)	$O^2S^1Ir^1$	118.07(9)
$S^1–C^{34}$	1.769(3)	$S^1Ir^1Cl^2$	85.73(3)	$O^1–C^{32}$	1.201(4)	$O^2S^1C^{34}$	107.30(16)
$S^1–C^{35}$	1.769(3)	$S^1Ir^1Cl^3$	90.29(3)				
			II				
$Ir^1–Cl^1$	2.3600(12)	$Cl^{1a}Ir^1Cl^1$	180.0	$S^1–O^1$	1.468(4)	$Cl^4Ir^2Cl^{4b}$	180.0
$Ir^1–Cl^{1a}$	2.3600(12)	$Cl^{2a}Ir^1Cl^1$	90.81(5)	$S^1–C^{34}$	1.781(5)	$S^2Ir^2Cl^{3b}$	88.71(4)
$Ir^1–Cl^2$	2.3596(12)	$Cl^2Ir^1Cl^1$	89.19(5)	$S^1–C^{33}$	1.763(5)	$S^2Ir^2Cl^3$	91.29(4)
$Ir^1–Cl^{2a}$	2.3596(12)	$Cl^2Ir^1Cl^{2a}$	180.0	$S^2–O^2$	1.468(4)	$S^2Ir^2Cl^4$	90.48(4)
$Ir^1–S^1$	2.3171(12)	$S^{1a}Ir^1Cl^1$	88.51(4)	$S^2–C^{35}$	1.762(5)	$S^{2b}Ir^2S^2$	180.0
$Ir^1–S^{1a}$	2.3170(12)	$S^1Ir^1Cl^1$	91.49(4)	$S^2–C^{36}$	1.772(6)	$O^1S^1Ir^1$	117.95(16)
$Ir^2–Cl^{3b}$	2.3560(11)	$S^1Ir^1Cl^{2a}$	93.50(5)	$P^1–C^1$	1.789(5)	$C^1P^1C^{31}$	108.29(13)
$Ir^2–Cl^3$	2.3559(11)	$S^1Ir^1Cl^2$	86.50(5)	$P^1–C^{21}$	1.790(5)	$C^1P^1C^{31}$	109.56(12)
$Ir^2–Cl^4$	2.3659(11)	$S^{1a}Ir^1S^1$	180.00(6)	$P^1–C^{11}$	1.791(5)	$C^{21}P^1C^1$	113.50(13)
$Ir^2–Cl^{4b}$	2.3659(11)	$Cl^3Ir^2Cl^{3b}$	180.0	$P^1–C^{31}$	1.804(4)	$C^{21}P^1C^{11}$	104.80(13)
$Ir^2–S^2$	2.3054(12)	$Cl^{3b}Ir^2Cl^4$	89.93(4)	$N^1–C^{32}$	1.127(6)	$C^{11}P^1C^{31}$	110.5(2)
$Ir^2–S^{2b}$	2.3054(12)	$Cl^3Ir^2Cl^4$	90.07(4)				
Symmetry codes: [a] $–x, –1–y, –z$; [b] $–x, –y, –z$							
			III				
$Ir^1–Cl^{1a}$	2.3511(12)	$Cl^{1a}Ir^1Cl^1$	180.00(8)	$Ir^2–S^{2b}$	2.3073(10)	$Cl^3Ir^2Cl^{4b}$	91.01(5)
$Ir^1–Cl^1$	2.3511(13)	$Cl^{1a}Ir^1Cl^2$	90.30(5)	$S^1–C^{35}$	1.769(6)	$Cl^3Ir^2Cl^4$	88.99(5)
$Ir^1–Cl^2$	2.3517(14)	$Cl^1Ir^1Cl^2$	89.70(5)	$S^1–O^1$	1.459(5)	$Cl^4Ir^2Cl^{4b}$	180.0
$Ir^1–Cl^{2a}$	2.3517(14)	$Cl^2Ir^1Cl^{2a}$	179.999(1)	$S^1–C^{36}$	1.773(9)	$S^2Ir^2Cl^{3b}$	88.23(4)
$Ir^1–S^1$	2.3110(15)	$S^1Ir^1Cl^1$	91.28(5)	$S^2–O^2$	1.462(3)	$S^2Ir^2Cl^3$	91.77(4)
$Ir^1–S^{1a}$	2.3110(15)	$S^{1a}Ir^1Cl^1$	88.72(5)	$S^2–C^{38}$	1.770(6)	$S^{2b}Ir^2Cl^4$	92.53(4)
$Ir^2–Cl^3$	2.3542(11)	$S^1Ir^1Cl^{2a}$	92.45(6)	$S^2–C^{37}$	1.775(5)	$S^2Ir^2Cl^4$	87.46(4)
$Ir^2–Cl^{3b}$	2.3541(11)	$S^1Ir^1Cl^2$	87.55(6)	$P^1–C^1$	1.790(4)	$S^2Ir^2S^{2b}$	180.0
$Ir^2–Cl^4$	2.3586(12)	$S^1Ir^1S^{1a}$	180.0	$P^1–C^{31}$	1.821(5)	$C^1P^1C^{31}$	112.5(2)
$Ir^2–Cl^{4b}$	2.3586(12)	$Cl^{3b}Ir^2Cl^3$	180.00(5)	$P^1–C^{11}$	1.797(5)	$C^1P^1C^{21}$	109.5(2)
$Ir^2–S^2$	2.3073(10)	$Cl^{3b}Ir^2Cl^{4b}$	89.00(5)	$P^1–C^{21}$	1.794(5)	$C^{11}P^1C^{31}$	107.0(2)
Symmetry codes: [a] $–x, –1 – y, 2–z$							

The crystal structure of complex **I** is formed by weak cation–anion hydrogen bonding (C–H···Cl 2.52–2.76 Å and C–H···O 2.38–2.62 Å). The strongest of them are $H^{19B}···Cl^4$ (2.52 Å) and $H^{19A}···O^1$ (2.38 Å).

In the crystal of complex **II**, there are intermolecular contacts, along with cation–anion contacts. In the crystal of complex **III**, solvate DMSO molecules are linked to cations and anions by

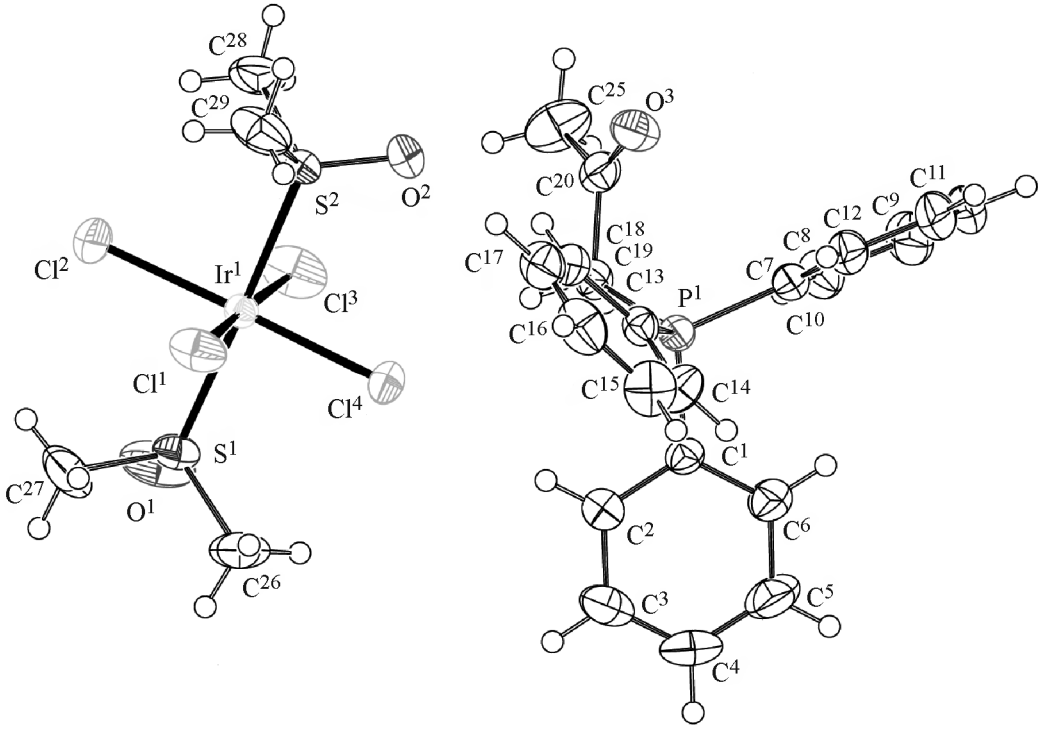

Fig. 1. General view of complex **I.**

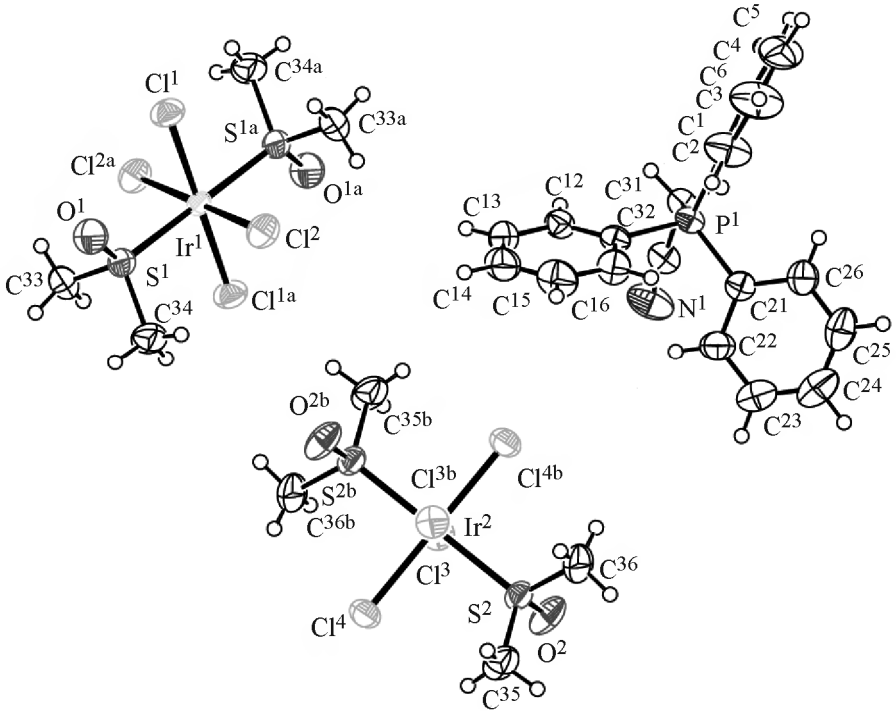

Fig. 2. General view of complex **II.**

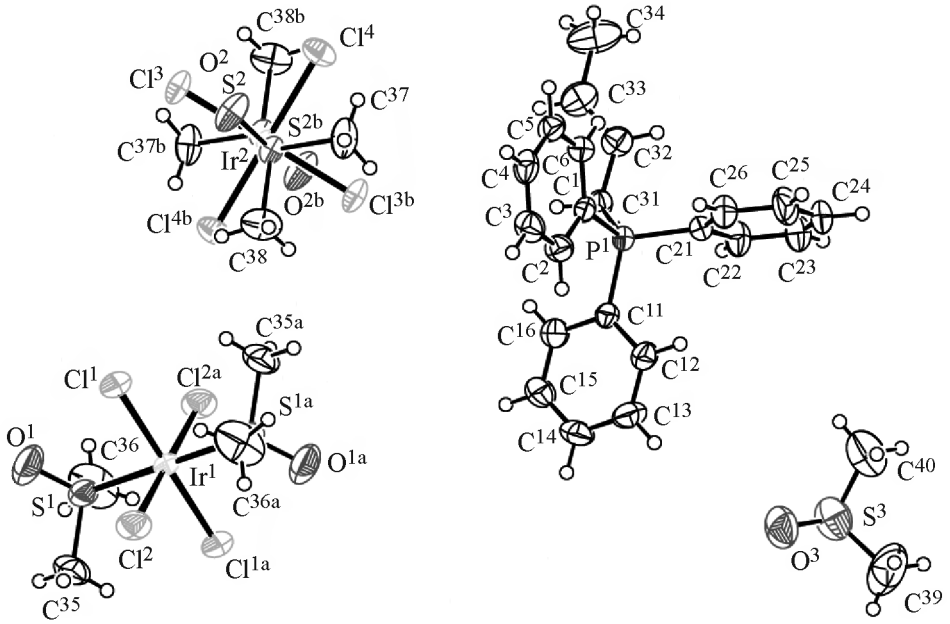

Fig. 3. General view of complex **III.**

$H^{39B}\cdots Cl^{1}$ (2.89 Å), $O^{3}\cdots o\text{-}H^{22}$ (2.45 Å), and $O^{3}\cdots H^{31A}$ (2.33 Å) hydrogen bonds.

Thus, a series of complexes with phosphonium cations and $[IrCl_4(DMSO)_2]^-$ anions, where the S-coordinated DMSO molecules occupy *trans* positions, have been synthesized and structurally characterized for the first time. Intermolecular interactions in the $[Ph_3RP]^+[trans\text{-}IrCl_4(DMSO)_2]^-$ crystals are due to weak hydrogen bonding.

EXPERIMENTAL

The IR spectra of complexes **I–III** were measured on a Bruker Tensor 27 spectrometer from KBr pellets in the range 4000–400 cm^{-1}.

The X-ray diffraction analysis of crystals of complexes **I–III** was performed on a D8 Quest Bruker diffractometer (MoK_α radiation, λ 0.71073 Å, graphite monochromator) at 296 K. Data collection and processing, refinement of unit cell parameters, as well as inclusion of absorption were performed using SMART and SAINT-Plus programs [2]. Structure solution and refinement were performed using SHELXL/PC program [3]. The structures were solved by a direct method and refined by least-squares in the anisotropic approximation for non-hydrogen atoms.

Full lists of atomic coordinates and bond lengths and angles are deposited in the Cambridge Crystallographic Data Center (CCDC 997261–997263).

Acetonyltriphenylphosphoium *trans*-tetrachlorobis(dimethyl sulfoxide)iridate (I). A solution of 0.022 g (0.06 mmol) of acetonyltriphenylphosphoium chloride in 5 mL of water was added to a stirred solution of 0.030 g (0.06 mmol) of sodium hexachloroiridate(III) in 5 mL of water. The solid residue after evaporation of water was dissolved in 2 mL of DMSO. Compound **I** formed as yellow crystals on slow evaporation of the solvent. Yield 0.038 g (74%), mp 188°C. IR spectrum, ν, cm^{-1}: 3015, 2905, 2829, 2770, 1710, 1588, 1486, 1439, 1402, 1377, 1366, 1311, 1295, 1154, 1116, 1015, 994, 972, 937, 908, 857, 830, 804, 783, 752, 719, 691, 507, 490, 450, 420. Found, %: C 36.78; H 4.06. $C_{25}H_{32}Cl_4IrO_3PS_2$. Calculated, %: C 37.08; H 3.96.

Complexes **II** and **III** were synthesized by the same procedure.

(Cyanomethyl)triphenylphosphonium *trans*-tetrachlorobis(dimethyl sulfoxide)iridate (II). Yield 61%, yellow crystals, decomp. point 192°C. IR spectrum, ν, cm^{-1}: 3111, 3073, 3018, 2919, 1590, 1484, 1438, 1401, 1379, 1311, 1295, 1185, 1121, 1097, 1071, 1041, 1015, 995, 925, 868, 754, 722, 697, 539, 505, 457,

436, 423. Found, %: C 36.24; H 3.77. $C_{24}H_{29}Cl_4Ir \cdot NO_2PS_2$. Calculated, %: C 36.36; H 3.66.

(2-Butenyl)triphenylphosphonium *trans*-tetrachlorobis(dimethyl sulfoxide)iridate (III). Yield 86%, yellow crystals, decomp. point 136°C. IR spectrum, ν, cm^{-1}: 3055, 3010, 2921, 1586, 1484, 1438, 1403, 1308, 1291, 1137, 1113, 1019, 996, 971, 918, 835, 756, 724, 691, 542, 514, 486, 420. Found, %: C 38.57; H 4.32. $C_{26}H_{34}Cl_4IrO_2PS_2$. Calculated, %: C 38.66; H 4.21.

REFERENCES

1. Alberti, F.M., Fiol, J.J., Garcia-Raso, A., Torres, M., Terron, A., Barcelo-Oliver, M., Prieto, M.J., Moreno, V., and Molins, E., *Polyhedron,* 2010, vol. 29, p. 34. DOI: 10.1016/j.poly.2009.05.082.
2. *SMART and SAINT-Plus*, Versions 5.0, Data Collection and Processing Software for the SMART System, Madison, WI: Bruker, 1998.
3. *SHELXTL/PC*, Versions 5.10, An Integrated System for Solving, Refining and Displaying Crystal Structures From Diffraction Data, Madison, WI: Bruker, 1998.