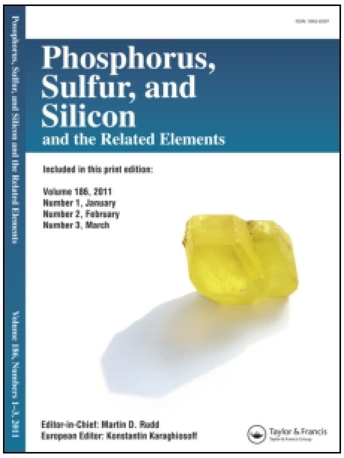

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Synthesis, Structures, and Properties of Plumboles

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SYNTHESIS, STRUCTURES, AND PROPERTIES OF PLUMBOLES

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Reactions of 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene with dichlorodiphenylplumbane gave hexaphenylplumbole 1 and spirobiplumbole 2. These structures were determined by X-ray diffraction analysis. Electronic structures of 1 and 2 were discussed by the aid of NMR analysis and theoretical calculations. The compounds 1 and 2 were found to be the first fluorescent organolead compounds.

Keywords Fluorescence; hexaphenylplumbole; spirobiplumbole; theoretical calculation; X-ray diffraction analysis

INTRODUCTION

For a decade, group 14 metalloles have received considerable attention in terms of their application to π-conjugated polymers[1] as well as the aromaticity of their anionic species.[2] One of the most simple metalloles is a hexaphenyl derivative, which can be prepared from the corresponding commercially available dichlorodiphenylmetallane and 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene.[3] From siloles to stannoles, structural and spectroscopic properties of hexaphenylmetalloles have already been reported.[4–6] Although a few derivatives of a plumbole, which is the heaviest of group 14 metalloles, have been synthesized,[7] their structural details in the solid state have never appeared. We report in this article the first X-ray diffraction analysis of hexaphenylplumbole **1** and spirobiplumbole **2**; the latter was unexpectedly formed by the reaction of 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene with dichlorodiphenylplumbane.[8] Spectroscopic details of **1** and **2** are also discussed with their theoretical calculations.

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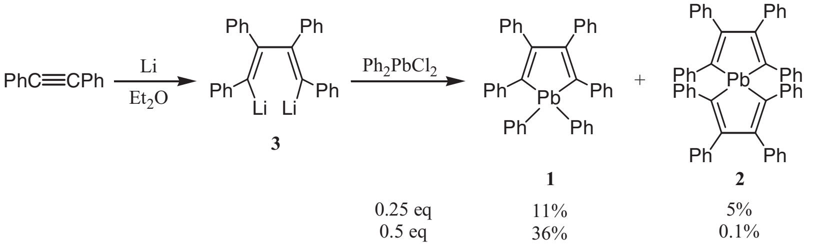
RESULTS AND DISCUSSION

Reaction of 1,4-Dilithio-1,2,3,4-tetraphenyl-1,3-butadiene (3) with Dichlorodiphenylplumbane

To synthesize hexaphenylplumbole **1**, 1,4-dilithio-1,2,3,4-tetraphenyl-1,3-butadiene (**3**), prepared from diphenylacetylene and lithium, was treated with dichlorodiphenylplumbane, which was about 0.25 equivalents to diphenylacetylene. The reaction conditions were almost the same as those reported by Zavistoski and Zuckerman, who first succeeded in the synthesis of **1**.[7a] After purifying the crude product by column chromatography, an unexpected product, spirobiplumbole **2** (5%), was obtained together with the expected hexaphenylplumbole **1** (11%) (Scheme 1). When the 1,4-dilithio-1,3-butadiene **3** was treated with 0.5 equivalents of diphenylacetylene in a manner similar to the literature,[7b,7c] careful separation of the crude product afforded the expected **1** (36%) together with spirobiplumbole **2** (0.1%). Thus, spirobiplumbole **2** was missed in the previous reports.[7] Reaction of hexaphenylplumbole **1** with 1,4-dilithio-1,3-butadiene **3** did not proceed, and the starting **1** was recovered. Hence, spirobiplumbole **2** was not formed directly from hexaphenylplumbole **1**, although details of the mechanism are still unclear.



Scheme 1 Synthesis of hexaphenylplumbole **1** and spirobiplumbole **2**.

Structures of Hexaphenylplumbole 1 and Spirobiplumbole 2

We succeeded in the first X-ray diffraction analysis of **1** and **2** (Figures 1 and 2). The five-membered rings of both plumboles are almost planar, as was observed in other group 14 metalloles.[4–6] The Pb—C bond lengths of the five-membered rings of **1** and **2** range from 2.203 Å to 2.211 Å, nearly the same as those of tetraphenylplumbole (2.188–2.227 Å).[9] The Pb—C(Ph) bond lengths in **1** are 2.197(4) and 2.217(4) Å, almost the same as those in the five-membered rings. The C—Pb—C bond angle in the five-membered ring of **1** is 82.41(14)°, almost the same as that found in **2** [82.2(2) and 81.6(3)°], but is much smaller than the C(Ph)—Pb—C(Ph) bond angle [113.98(14)°]. The two five-membered rings in **2** are situated in a perpendicular fashion but slightly deviate from symmetric arrangement to the vector between the lead atom and the center of the C(2)—C(3) bond. The C—C bond lengths of the plumbole rings of **1** and **2** alter, as do those of the cyclopentadiene.

Theoretical Studies of Hexaphenylplumbole 1 and Spirobiplumbole 2

To understand the electronic states of hexaphenylplumbole **1** and spirobiplumbole **2**, the structures of **1** and **2** were optimized with the hybrid density functional theory at the B3LYP[10] level using the LANL2DZ basis set augmented by a *d* polarization function ($\xi = 0.179$) for Pb[11] and 6-31G(d) for C and H[12] using the Gaussian03 program.[13] As

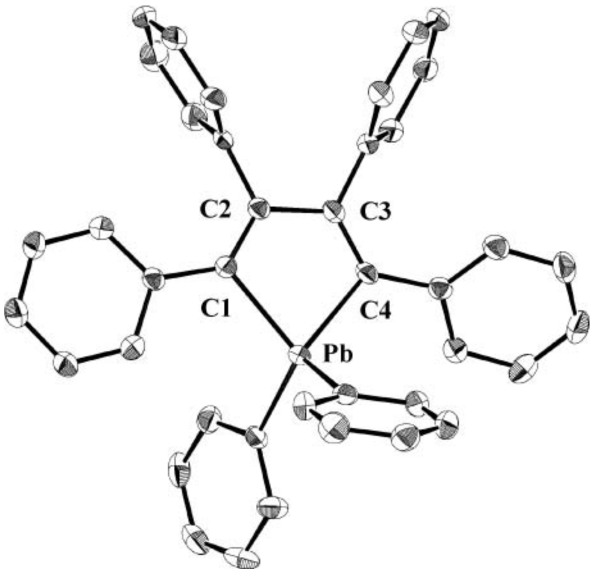


Figure 1 ORTEP drawing of **1** with thermal ellipsoids plots (40% probability for nonhydrogen atoms). All hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Pb1−C1 2.211(4); Pb1−C5, 2.217(4); C1−C2, 1.354(5); C2−C3, 1.522(5); C3−C4, 1.345(6); C1−Pb1−C4, 82.41(14).

Tables I and II show, the optimized geometries of **1** and **2** were consistent with the crystal structures found by X-ray diffraction analysis. The calculated Pb−C bond lengths in the five-membered rings of **1** and **2** are 2.197 and 2.191 Å, respectively, in good agreement with the X-ray measured values. Natural population analysis was also carried out using the optimized structures. The lead atoms are highly positively charged (1.78 and 1.77 for **1** and **2**, respectively), whereas the α-carbons are negatively charged (−0.40 and −0.39 for **1** and **2**, respectively). The β-carbons are almost neutral (−0.04 and −0.03 for **1** and **2**, respectively).

NMR Studies of Hexaphenylplumbole 1 and Spirobiplumbole 2

In the ^{13}C NMR spectrum of **1**, the *ipso*-carbon of the phenyl ring on the lead atom resonated at 153.79 ppm with the largest Pb−C coupling constant of 406 Hz, similar to the corresponding carbon of 1,1,2,3,4,5-hexaphenylstannole.[4] The α-carbons in the five-membered ring resonated at 153.50 ppm with a very large Pb−C coupling constant of 346 Hz, while the β-carbons in the five-membered ring resonated at 153.05 ppm with a reasonable Pb−C coupling constant (163 Hz). The β-carbons in the five-membered ring of

Table I Geometry of **1**

	Calculated/Å or deg	Measured/Å or deg
Pb-C(α)	2.197	2.2 11 (4), 2.217(4)
C(α)-C(β)	1.362	1.354(5), 1.345(6)
C(β)-C(β)	1.520	1.522(5)
C(α)-Pb-C(β)	82.8	82.41(14)

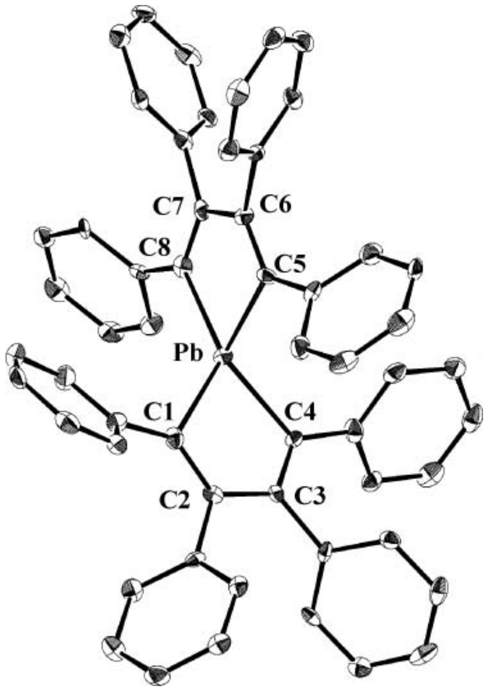


Figure 2 ORTEP drawing of **2** with thermal ellipsoids plots (40% probability for nonhydrogen atoms). All hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Pb1−C1, 2.211(7); Pb1−C4, 2.203(6); Pb1−C5, 2.207(7); Pb1−C8, 2.203(7); C1−C2, 1.346(9); C2−C3, 1.494(10); C3−C4, 1.353(9); C1−Pb1−C4, 82.2(2); C5−Pb1−C8, 81.6(3).

group 14 metalloles except for the plumboles are reported to resonate at the lowest field, whereas the α-carbons and the *ipso*-carbons are reported to resonate at the field higher than the formers (for example, the signals of the β-, α-, and *ipso*-carbons 1,1,2,3,4,5-hexaphenylstannole were observed at 155.14, 144.76, and 138.04 ppm, respectively).[4] Since the α-carbons of **1** are calculated to be negatively charged, its low-field resonance is attributable to paramagnetic contribution of the Pb−C bond. In the ^{13}C NMR spectrum of **2**, similar trends were observed: the α- and β-carbons in the five-membered ring resonated at 153.50 and 152.17 with Pb−C coupling constants of 269 and 162 Hz, respectively. As the central atom becomes heavier from silicon to lead, the resonances of each of the α-, β-, and *ipso*-carbons shift to the downfield.

Table II Geometry of **2**

	Calculated/Å or deg	Measured/Å or deg
Pb-C(α)	2.191	2.211(7), 2.203(6), 2.207(7), 2.203(7)
C(α)-C(β)	1.360	1.346(9), 1.353(9), 1.320(9), 1.356(9)
C(β)-O(β)	1.518	1.494(10), 1.524(9)
C(α)-Pb-C(β)	82.9	82.2(2), 81.6(3).

Absorption and Fluorescence Spectra of Hexaphenylplumbole 1 and Spirobiplumbole 2

Optical properties of newly obtained hexaphenylplumbole **1** and spirobiplumbole **2** were also investigated. The electronic absorption and fluorescence spectra of **1** and **2** are shown in Figures 3 and 4, respectively. The absorption maxima of **1** and **2** are observed at 351 nm, in a region similar to those of other hexaphenylmetalloles of group 14 atoms.[4] As the absorptions can be assigned to $\pi-\pi^*$ transitions of the butadiene skeletons, the wavelengths of the absorption maxima are independent of the central group 14 atoms. In sharp contrast to the nonfluorescent nature of general organolead compounds, **1** and **2** are fluorescent at room temperature. The fluorescence maxima of **1** and **2**, excited at 328 and 335 nm, appear at 404 and 394 nm, respectively, remarkably blue-shifted compared to those of other hexaphenylmetalloles of group 14 atoms (for Si: 496, Ge: 486, Sn: 494 nm).[4] To the

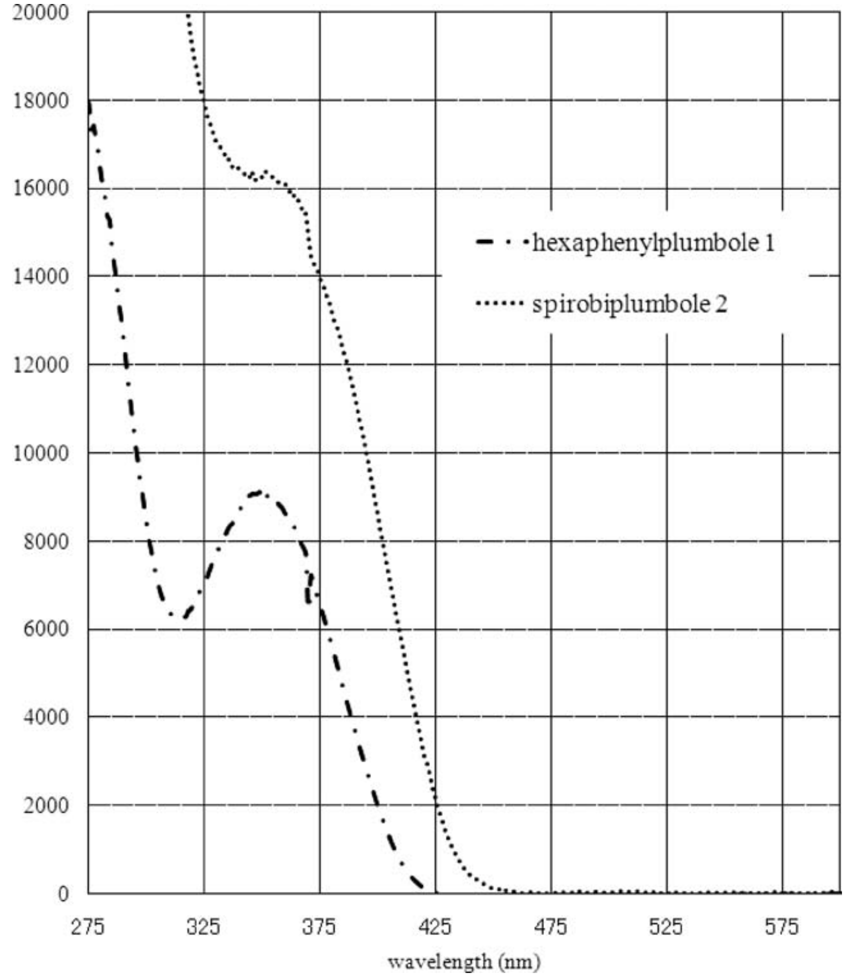


Figure 3 Absorption spectra of **1** (in acetonitrile) and **2** (in dichloromethane).

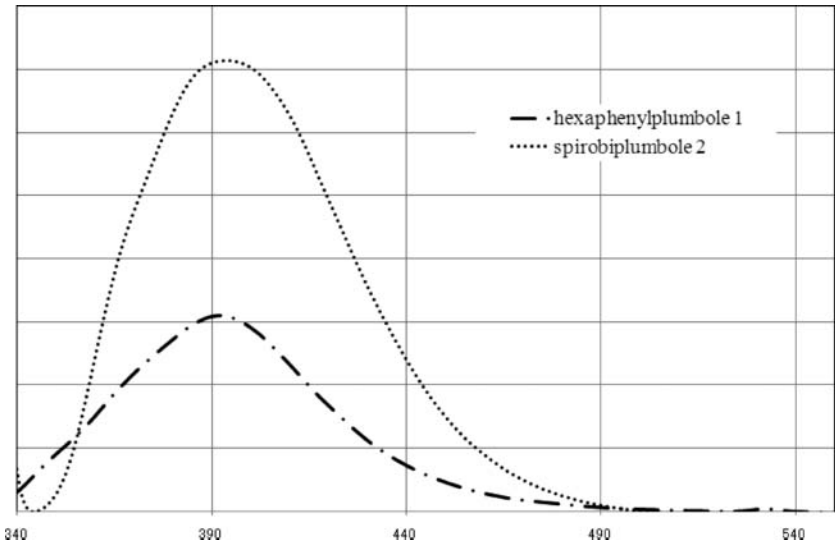


Figure 4 Fluorescence spectra of **1** (excited at 325 nm in acetonitrile) and **2** (excited at 335 nm in dichloromethane).

best of our knowledge, **1** and **2** are the first examples of fluorescent organolead compounds, although the reason for the remarkable blue shift is unclear.

EXPERIMENTAL

All reactions were carried out under argon atmosphere. Dichlorodiphenylplumbane was synthesized from tetraphenylplumbane[14] according to the literature.[8] Diethyl ether used in the synthesis was distilled from sodium benzophenone ketyl under an argon atmosphere. ^{1}H (400 MHz), ^{13}C (101 MHz), and ^{207}Pb (84 MHz) NMR spectra were recorded on a Bruker DPX-400 or a DRX-400 spectrometer. For ^{207}Pb NMR spectroscopy, tetrakis(*p*-methoxyphenyl)plumbane was used as an external standard (−153 ppm).[15] Preparative gel permeation chromatography (GPC) was carried out on an LC-918 (Japan Analytical Ind. Co., Ltd.) with JAIGEL-1H and -2H columns using chloroform as an eluent. Column chromatography was carried out with Merck aluminum oxide 90.

Reaction of 1,4-Dilithio-1,3-butadiene with Dichlorodiphenylplumbane (0.25 eq)

An ether (25 mL) suspension of the 1,4-dilithio-1,3-butadiene prepared from diphenylacetylene (7.861 g, 43.2 mol) and lithium (0.300 g, 43.2 mol) was added to dichlorodiphenylplumbane (4.382 g, 10.1 mmol) at room temperature. The resulting mixture was heated under reflux for 3 h. After removal of materials insoluble in ether and then in dichloromethane by filtrations, the residue was chromatographed on alumina (hexane:ethyl acetate = 10:1) and GPC to afford 1,1,2,3,4,5-hexaphenylplumbole (**1**) (770 mg, 11%) and 2,2,2′,2′,3,3,3′,3′-octaphenylbiplumbole (**2**) (430 mg, 5%). **1**: mp 152–155 °C(dichloromethane+ethanol). ^{1}H NMR(CDCl$_3$) δ 6.84–6.88(m, 4H), 6.90–7.06(m, 16H), 7.32–7.50(m, 6H), 7.52–7.76(m, 4H); ^{13}C NMR(CDCl$_3$) δ 125.31(d, J(Pb-C) = 10 Hz), 125.78(d), 127.37(d), 127.86(d), 128.73(d, J(Pb-C) = 20 Hz), 129.33(d, J(Pb-C) = 33 Hz), 129.96(d, J(Pb-C) = 81 Hz), 130.51(d), 136.99(d, J(Pb-C) = 108 Hz), 141.86(s, J(Pb-C) = 110 Hz), 144.09(s, J(Pb-C) = 74 Hz), 153.05(s, J(Pb-C) = 163 Hz, C_β), 153.50(s, J(Pb-C) = 346 Hz, C_α), 153.79(s, J(Pb-C) = 406 Hz, C_{ipso}); ^{207}Pb NMR(CDCl$_3$) δ −24.5. Anal. Calcd for $C_{40}H_{30}Pb$: C, 66.92; H, 4.21. Found: C, 66.88; H, 4.15. **2**: mp 232°C(decomp)(dichloromethane+ethanol). ^{1}H NMR(CDCl$_3$) δ 6.80–6.82(m, 8H), 6.87–6.92(m, 8H), 6.95–7.01(m, 16H), 7.06–7.10(m, 8H); ^{13}C NMR(CDCl$_3$) δ 125.67(d, J(Pb-C) = 10 Hz), 125.97(d), 127.43(d), 127.85(d),129.86(d, J(Pb-C) = 35 Hz), 130.34(d), 141.74(s, J(Pb-C) = 108 Hz), 143.16(s, J(Pb-C) = 80 Hz), 152.17(s, J(Pb-C) = 162 Hz, C_β), 154.79(s, J(Pb-C) = 269 Hz, C_α); ^{207}Pb NMR(CDCl$_3$) δ 188.8. Anal. Calcd for $C_{56}H_{40}Pb$: C, 73.10; H, 4.38. Found: C, 72.37; H, 4.26.

Reaction of 1,4-Dilithio-1,3-butadiene with Dichlorodiphenylplumbane (0.5 eq)

An ether (25 mL) suspension of the 1,4-dilithio-1,3-butadiene prepared from diphenylacetylene (14.300 g, 78.6 mol) and lithium (0.600 g, 86.4 mol) was added to dichlorodiphenylplumbane (16.957 g, 39.2 mmol) at room temperature. The resulting mixture was heated under reflux overnight. After removal of materials insoluble in ether and then in dichloromethane by filtrations, the residue was chromatographed on alumina (hexane:ethyl acetate = 20:1) and GPC to afford 1,1,2,3,4,5-hexaphenylplumbole (**1**) (6.325 g, 22%) and 2,2,2′,2′,3,3,3′,3′-octaphenylbiplumbole (**2**) (36 mg, 0.1%).

X-Ray Crystallographic Analysis of 1

Crystals suitable for X-ray diffraction were obtained by recrystallization in dichloromethane and ethanol solution of **1**. The intensity data were collected at −175°C on a Bruker SMART APEX equipped with a CCD area detector with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and graphite monochromater. Formula $C_{40}H_{30}Pb$, FW = 717.84, crystal dimension 0.50 × 0.45 × 0.30 mm, triclinic, space group P-1, $Z = 2$, a = 9.3600(8) Å, b = 10.2428(8) Å, c = 16.7280(14) Å, α = 78.558(2)°, β = 80.022(2)°, γ = 74.594(2)°,V = 1503.0(2) Å^3, D_{calcd} = 1.586 g cm^{-3}, $R_1 = 0.027$ ($I > 2\sigma(I)$, 4923 reflections), $_wR_2 = 0.067$ (for all reflections) for 5274 reflections and 370 parameters, GOF = 1.071. CCDC-710794 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk).

X-Ray Crystallographic Analysis of 2

Crystals suitable for X-ray diffraction were obtained by recrystallization in dichloromethane and ethanol solution of **2**. The intensity data were collected at −170°C on a Bruker SMART APEX equipped with a CCD area detector with graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and graphite monochromater. Formula $C_{56}H_{40}Pb$, FW = 920.07, crystal dimension 0.12 × 0.12 × 0.04 mm, orthorhombic, space group

$P2_12_12_1$, $Z = 4$, $a = 10.0189(6)$ Å, $b = 10.1222(6)$ Å, $c = 40.186(2)$ Å, $V = 4075.4(4)$ Å^3, $D_{\mathrm{calcd}} = 1.500$ g cm^{-3}, $R_1 = 0.039$ ($I > 2\sigma(I)$, 6836 reflections), $_wR_2 = 0.080$ (for all reflections) for 7574 reflections and 514 parameters, GOF = 1.021. CCDC-710795 contains the supplementary crystallographic data for this compound. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; Email: deposit@ccdc.cam.ac.uk).

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