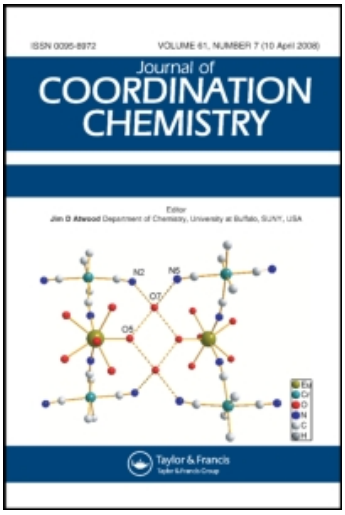

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Mercury(II) complexes of pyrrolidinedithiocarbamate, crystal structure of bis{[μ²-(pyrrolidinedithiocarbamato-*S*,*S* ')(pyrrolidinedithiocarbamato-*S*,*S* ')mercury(II)]}

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Mercury(II) complexes of pyrrolidinedithiocarbamate, crystal structure of bis{[μ^2-(pyrrolidinedithiocarbamato-*S*,*S*′)(pyrrolidinedithiocarbamato-*S*,*S*′)mercury(II)]}

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Mercury(II) complexes of pyrrolidinedithiocarbamate (PDTC) having the general formula [Hg(PDTC)X] (X = Cl^-, SCN^-, and CN^-) and [$Hg(PDTC)_2$] have been prepared and characterized by elemental analysis, IR, and NMR. The crystal structure of [$Hg(PDTC)_2$] has also been determined by X-ray crystallography, showing that the complex is a centrosymmetric dimer, [$Hg_2(PDTC)_4$] (bis[μ^2-(pyrrolidinedithiocarbamato-*S*,*S*′)(pyrrolidinedithiocarbamato-*S*,*S*′)mercury(II)]) (**1**). The solid-state structure of **1** contains two crystallographically equivalent Hg(II) centers in a distorted tetrahedron.

Keywords: Mercury(II); Pyrrolidinedithiocarbamate; Crystal structure

1. Introduction

Metal complexes of dithiocarbamates have applications in agriculture, medicines, industry, and in analytical and organic chemistry [1–10]. Dithiocarbamates such as diethyldithiocarbamate and pyrrolidinedithiocarbamate (PDTC) display cytotoxic properties and have been used to treat metal poisoning [1, 10–17]. Dithiocarbamate ligands have also been employed in the construction of new supramolecular structural motifs including polymetallic nanosized macrocycles [18–20]. Mercury(II)-dithiocarbamates have interesting properties of thin films and nanosized materials [21, 22]. Mercury is one of the most toxic, heavy metals found in solid and liquid waste from chloro-alkali, paint, paper/pulp, battery, pharmaceutical, oil refinery, and mining

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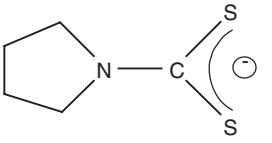

Scheme 1. Structure of PDTC.

industries [23]. Dithiocarbamates are among the most common extractants used for removal of mercury from aqueous solution [23–25]. A number of mercury(II)-dithiocarbamates have been prepared and characterized in recent years [26–34]. Crystal structures of mercury(II)-dithiocarbamates show that they exist both as mononuclear ($[Hg(S_2CNR_2)_2]$) and as binuclear complexes ($[Hg(S_2CNR_2)_2]_2$). In mononuclear complexes, both dithiocarbamate ligands are coordinated *S*,*S*′-bidentate to the mercury surrounded by four sulfur donors [22–30, 35–37], while binuclear molecules contain bidentate chelating ligands and pairs of chelating and bridging ligands [31–34, 37, 38]. In some cases, mononuclear units aggregate to form polymeric structures, for example, in bis[*N*,*N*-di(2-hydroxyethyl)dithiocarbamato-*S*,*S*′] mercury(II) [39]. The structure of mononuclear complex of mercury(II) with PDTC, bis(pyrrolidinedithiocarbamato)mercury(II), $[Hg(S_2CN(CH_2)_4)_2]$, has been determined and features chelating dithiocarbamate ligands that form asymmetric Hg–S bonds in a heavily distorted tetrahedral geometry [29]. In this study, we isolate a binuclear mercury(II)-pyrrolinedithiocarbamate complex, $[Hg_2(PDTC)_4]$ the crystal structure of which is being reported. Three other mercury(II)-PDTC complexes, [Hg(PDTC)X] ($X = Cl^-$, SCN^-, and CN^-) have also been prepared and characterized. Recently, we reported the crystal structure of a similar zinc(II) complex of PDTC, $[Zn_2(PDTC)_4]$ [40]. The structure of PDTC is shown in scheme 1.

2. Experimental

2.1. *Chemicals*

Ammonium PDTC is a product of Sigma Chemical Company. $HgCl_2$ was obtained from Merck Chemical Co., Germany.

2.2. *Synthesis of complexes*

[Hg(PDTC)Cl] and $[Hg(PDTC)_2]$ were prepared by mixing 0.271 g (1 mmol) $HgCl_2$ in 15 mL methanol and PDTC ligand in 20 mL methanol in the mole ratios of 1 : 1 and 1 : 2, respectively. The addition of PDTC in the colorless metal ion solution resulted in formation of off white or yellow precipitates immediately. After stirring for 30 min, the precipitates were filtered off and dried. Yellow crystals of **1** were prepared by dissolving 0.03 g of $[Hg(PDTC)_2]$ in 3 mL DMSO on heating and then cooling the resulting solution.

[Hg(PDTC)(SCN)] was prepared by mixing a solution of 0.271 g (1 mmol) of $HgCl_2$ in 15 mL methanol with a 2 mmol (0.195 g) solution of KSCN in 20 mL methanol. After stirring the mixture for 15 min one equivalent (0.164 g) of PDTC in 20 mL methanol was added. The mixture was stirred for further 30 min. For the preparation of [Hg(PDTC)(CN)], $Hg(CN)_2$ was prepared first by reaction of 1 mmol $HgCl_2$ in methanol with 2 mmol KCN in water. Then, 0.253 g (1 mmol) $Hg(CN)_2$ in 15 mL methanol was mixed with a solution of 1 mmol PDTC in 20 mL methanol, resulting in formation of off white precipitates immediately. The mixture was stirred for further 30 min. In both cases after stirring, the precipitates were filtered off, washed with methanol, and dried in air.

2.3. *IR and NMR measurements*

IR data were obtained with the Perkin-Elmer FTIR 180 spectrophotometer from 4500 to 400 cm^{-1} using KBr pellets. ^1H NMR spectra of the complexes in DMSO-d_6 were obtained on a Jeol JNM-LA 500 NMR spectrometer operating at 500.00 MHz at 297 K using 0.10 mol solution. ^{13}C NMR spectra were obtained at 125.65 MHz with ^1H broadband decoupling at 298 K. The spectral conditions were 32 K data points, 0.967 s acquisition time, 1.00 s pulse delay and 45° pulse angle. The ^{13}C chemical shifts were measured relative to TMS.

2.4. *X-ray structure determination*

Single crystal data collection for **1** was performed at 173 K (−100°C) on a one-circle Stoe Image Plate Diffraction System [41] using Mo-Kα graphite monochromated radiation: image plate distance 70 mm, ϕ oscillation scans 0–200°, step $\Delta\phi = 1.0°$, exposure time 2 min, 2θ range 3.27–52.1°, d_{min}–d_{max} = 12.45–0.81 Å. The structure was solved by direct methods using SHELXS-97 [42]. The refinement and all further calculations were carried out using SHELXL-97 [42]. Hydrogens were included in calculated positions and treated as riding C–H = 0.99 Å and $U_{iso}(H) = 1.2U_{eq}$(parent N- or C-atom). The non-H atoms were refined anisotropically using weighted full-matrix least-squares on F^2. An empirical absorption correction was applied using the MULscanABS routine in PLATON [43]; transmission factors: T_{min}/T_{max} = 0.154/0.287. Crystal data and details of the structure determination are summarized in table 1.

2.5. *Antimicrobial studies of the complexes*

Antimicrobial activities of two of the mercury(II)-dithiocarbamate compounds prepared here were estimated by minimum inhibitory concentration (MIC); $\mu g\,mL^{-1}$ [44]. Standard culture media of bacteria, *Escherichia coli* (ATCC 13706) and *Pseudomonas aeruginosa* (MTCC 424), and molds, *Aspergillus niger* (MTCC 1349) and *Penicillium citrinum* (MTCC 5215), were obtained from Qingdao Yijia Huuyi Co., China. Bacteria were inoculated into 5 mL of liquid SCD medium (soybean, casein, and digest) and cultured for 24 h at 35.5°C. The cultured fluids were diluted, adjusted to a concentration of 10^5–10^6 microorganisms per mL^{-1} and used for inoculation in the

Table 1. Crystallographic data and processing parameters for crystal, intensity collection, and refinement data.

Empirical formula	$C_{20}H_{32}Hg_2N_4S_8$
Formula weight	986.16
Temperature (K)	173 (2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	*P–1*
Unit cell dimensions (Å, °)	
a	7.4809(10)
b	7.952(10)
c	12.4906(13)
α	101.060(12)
β	100.416(12)
γ	91.536(8)
Volume (Å^3), *Z*	715.77(16), 1
Calculated density (g cm^{-3})	2.288
Absorption coefficient (mm^{-1}) (Mo-Kα) (mm^{-1})	11.314
F(000)	468
Crystal size (mm^3)	$0.38 \times 0.11 \times 0.11$
θ range for data collection (°)	2.8–25.9
Limiting indices	$-9 \le h \le 8$; $-9 \le k \le 9$; $-15 \le l \le 15$
Reflections collected	5692
Independent reflection	2609 [R(int) = 0.04]
Data parameters	2354/154
Absorption: T_{min}/T_{max}	0.770/1.437
Nref/	2609/
R indices	$R_1 = 0.0325$, $wR_2 = 0.0807$, $S = 1.00$
Maximum and average shift/error	0.001/0.00
Minimum and maximum residual density [e Å^{-3}]	−2.44, and 1.63

$w = [\sigma^2(F_o^2) + (0.05862P)^2]^{-1} = 0.0777$, where $P = (F_o^2 + 2F_c^2)/3$.

MIC test. In the case of mold culture, the agar slant (potato and dextrose) medium with 1-week cultivation at 27°C was gently washed with saline containing 0.05% Tween 80. The spore suspension obtained was adjusted to 10^5 microorganisms per mL^{-1} and used for inoculation in the MIC test. The mercury(II)-dithiocarbamate complexes were suspended in water, and solutions were then diluted with SCD medium for bacteria and with GP medium (Glucose and Polypeptone) for mold. Using twofold diluted solutions from 1000 to 10 mg mL^{-1}, 1 mL of culture medium containing various concentrations of test materials was inoculated with 0.1 mL of the microorganism suspension. Bacteria were cultured for 24 h at 35.5°C and mold for 7 days at 25°C. Growth of the microorganisms was monitored during this period. When no growth of microorganism was observed in the medium containing the lowest concentration of test materials, the MIC of the test material was defined at this point of dilution.

3. Results and discussion

Reaction of $HgCl_2$ with PDTC in the molar ratios of 1 : 1 or 1 : 2 in methanol yielded two different products, [Hg(PDTC)Cl] and [Hg(PDTC)$_2$], unlike $ZnCl_2$ where we obtained only one product with both molar ratios [40]. This suggests that the kinetic preference of PDTC for mercury(II) is not as strong as for zinc(II) where only

Table 2. IR spectral data (cm^{-1}).

Compound	ν(N–CSS)	ν(–SCS)	ν(C≡N)
PDTC	1410	995	–
[Hg(PDTC)Cl]	1501	1090	–
[Hg(PDTC)$_2$]	1477	1010	–
[Hg(PDTC)(SCN)]	1478	995	2116
[Hg(PDTC)(CN)]	1480	993	2103

Table 3. ^{1}H and ^{13}C NMR chemical shifts of PDTC and two complexes in DMSO-d$_6$.

	δ (^{1}H)		δ (^{13}C)		
Species	N–CH$_2$	C–CH$_2$	N–CH$_2$	C–CH$_2$	CS$_2$
PDTC	3.65	1.84	52.89	25.72	208.20
[Hg(PDTC)(SCN)]	3.72	2.03	55.81	26.48	196.69
[Hg(PDTC)(CN)]	3.63	2.00	56.70	26.49	195.39

[Zn(PDTC)$_2$]$_2$ is formed with both molar ratios. Elemental analyses (Supplementary material) of Hg(SCN)$_2$ and Hg(CN)$_2$ products correspond to [Hg(PDTC)(SCN)] and [Hg(PDTC)(CN)], respectively. TGA curve of [Hg(PDTC)Cl] shows a mass loss of 72% at 315°C associated with the release of both PDTC and Cl^- (calculated value for combined mass loss = 73.5%). For [Hg(PDTC)$_2$] mass loss corresponding to the release of PDTC is 81.7%, suggesting the formula is [Hg(PDTC)(Cl)]. Decomposition of residual mercury starts after 315°C and is completed at 650°C after complete evaporation of mercury.

3.1. *IR and NMR studies*

For dithiocarbamate compounds, three main regions are of interest: the 1580–1450 cm^{-1} region which is primarily associated with stretching of C–N of N–CSS^-; the 1060–940 cm^{-1} region, associated with ν(–CSS); and the 420–250 cm^{-1} region which is associated with ν(M–S) [45]. Table 2 shows that ν(N–CSS) of PDTC is shifted to higher frequency upon coordination, consistent with an increase of carbon–nitrogen double bond character. The ν(N–CSS) of these complexes is in the range observed for the other PDTC complexes of Pd^{2+} ([Pd(PDTC)$_2$] = 1500 cm^{-1}) [46] and Cu^{2+} ([Cu(PDTC)$_2$] = 1500 cm^{-1}) [47]. A band near 1000 cm^{-1} belongs to ν(–CSS) and is indicative of bidentate dithiocarbamate [48]. Methylene C–H bands are observed at 2925 cm^{-1}. The cyanido and thiocyanato complexes showed the C≡N stretching bands around 2100 cm^{-1}.

NMR spectra were recorded for only two complexes because the other two were partially soluble. The ^{1}H and ^{13}C NMR chemical shifts of PDTC and the complexes are given in table 3. The ^{1}H NMR spectra exhibited two triplets for N(CH$_2$)$_2$ and the ring (CH$_2$)$_2$ protons around 3.6 and 2.0 ppm, respectively. In ^{13}C{^{1}H} NMR, the CS$_2$ resonance shifted upfield while the signal for N–CH$_2$ carbons appeared downfield compared to free ligand positions. The carbon resonances for CN^- and SCN^- were not

observed. A significant upfield shift of ~12 ppm in the CS_2 resonance is attributed to lowering of the C=S bond order upon coordination and a shift of N–C electron density producing partial double bond character in C–N, due to which deshielding is observed in the N–CH_2 carbons. The ^1H and ^{13}C NMR chemical shift values are in accord with reported references [40, 46, 49].

3.2. *X-ray structure description*

The molecular structure of **1**, together with atomic labeling, is shown in figure 1. Selected bond lengths and angles are presented in table 4. The complex is binuclear with each mercury coordinated to one terminal and two bridging PDTC ligands. The dimeric structure is centrosymmetric and features an eight-membered $[–S–C–S–Hg–]_2$ ring with

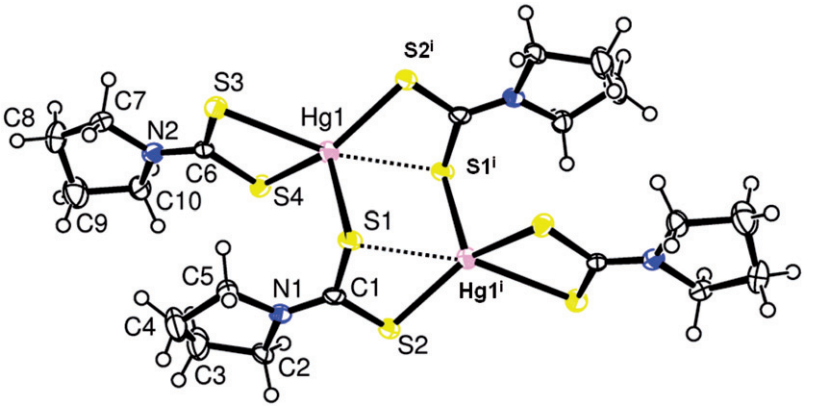

Figure 1. A view of the molecular structure of the centrosymmetric dimer of **1**, with displacement ellipsoids drawn at the 50% probability level; symmetry code: i: $1-x$, $1-y$, $1-z$.

Table 4. Selected geometric parameters (Å, °) for $[Hg_2(PDTC)_4]$ (**1**).

Hg1–S1	2.6344(15)	Hg1 . . . Hg1^i	3.9654(16)
Hg1–S1^i	3.1042(15)	S1–C1	1.732(6)
Hg1–S2^i	2.4466(16)	S2–C1	1.728(5)
Hg1–S3	2.4860(15)	S3–C6	1.708(6)
Hg1–S4	2.4858(15)	S4–C6	1.742(5)
N1–C1	1.296(7)	N2–C6	1.309(7)
N1–C2	1.483(8)	N2–C7	1.468(7)
N1–C5	1.476(8)	N2–C10	1.470(9)
S1–Hg1–S3	108.94(5)	Hg1–S1–C1	95.79(19)
S1–Hg1–S4	109.83(5)	Hg1–S1–Hg1^i	87.01(4)
S1–Hg1–S1^i	92.99(4)	Hg1^i–S1–C1	75.85(18)
S1–Hg1–S2^i	103.71(5)	Hg1^i–S2–C1	97.1(2)
S3–Hg1–S4	69.34(5)	Hg1–S3–C6	81.07(17)
S1^i–Hg1–S3	157.51(5)	Hg1–S4–C6	89.1(2)
S2^i–Hg1–S3	112.98(5)	S1–C1–S2	121.2(3)
S1^i–Hg1–S4	99.09(4)	S3–C6–S4	120.4(3)
S2^i–Hg1–S4	143.46(5)		
S1^i–Hg1–S2^i	64.51(4)		

Symmetry code: i: $1-x$, $1-y$, $1-z$.

$Hg\cdots Hg^{i}$ separation of 3.9654(16) Å (symmetry code $^{i}1-x, 1-y, 1-z$). This central ring has a chair conformation. To a first approximation, the coordination polyhedron of mercury is distorted tetrahedron, built from four relatively strongly bound sulfurs [Hg–S = 2.4466(16) to −2.7617(15) Å]. However, mercury is weakly bound to the fifth bridging sulfur with a Hg–$S1^{i}$ distance of 3.1042(15) Å. This value is lower than the sum of the van der Waals radii of Hg and S (3.3 Å) [50]. Thus, the geometry of the mercury coordination polyhedron is close to trigonal bipyramidal (TBP). Two of the four S–Hg–S bond angles show very significant distortions from tetrahedral geometry (table 4). The average bond lengths for the Hg–S and C–S bonds are similar to those observed in other Hg-dithiocarbamate complexes [12, 29, 30]. All the ligands are coordinated in an anisobidentate way with one Hg–S bond appreciably shorter than the other. The two Hg–S_2–C four-membered rings are almost planar [torsion angle Hg1–S3–C6–N2 is 178.5(3)°]. The N–CS_2 of the terminal and bridging dithiocarbamates show planar geometry with sp^2-hybridized carbon. The smaller N–C(S_2) bond lengths [1.296(7) and 1.309(7) Å] compared to the other N–C bond distances [1.468(7)–1.483(8) Å] are in agreement with a marked double bond character in the N–C(S_2) bond. In the crystal the dimeric [Hg_2(PDTC)$_4$] molecules are linked to each other through a C–H$\cdots$S interaction (table 5). These non-covalent intermolecular interactions result in formation of a ribbon-like polymeric architecture, as shown in figure 2. The structure of [Hg_2(PDTC)$_4$] is isostructural to several other Hg-dithiocarbamate complexes reported earlier [22, 31, 32]. The structure of the mononuclear Hg-PDTC complex, bis(pyrrolidinedithiocarbamato)-mercury(II), [Hg(PDTC)$_2$], in which the central mercury is asymmetrically chelated by two dithiocarbamate ligands leads to a heavily distorted tetrahedral geometry [29].

3.3. *Antimicrobial activities*

Antimicrobial activities of two of the mercury(II)-dithiocarbamate complexes (average of three measurements) estimated by MIC ($\mu g\,mL^{-1}$) are listed in table 6; [Hg(PDTC)(CN)] is particularly effective against bacteria. Both complexes did not show activity against yeasts.

4. Conclusion

This study shows that PDTC reacts with HgX_2 to form complexes [Hg(PDTC)(X)] and [Hg(PDTC)$_2$]. The antimicrobial activities of the complexes indicate powerful antibacterial activity. The crystal structure presented in this study is among the few complexes in which one bridging sulfur binds with both mercury producing a four-membered ring rather than an eight-membered ring observed in many

Table 5. Non-bonded interaction (Å, °) in the complex [Hg_2(PDTC)$_4$].

Donor–H$\cdots$Acceptor	D–H	H$\cdots$A	D$\cdots$A	∠D–H$\cdots$A
C2–H2B$\ldots$$S2^{ii}$	0.99	2.87	3.789(7)	154

Symmetry code: ii: $2-x, 1-y, 1-z$.

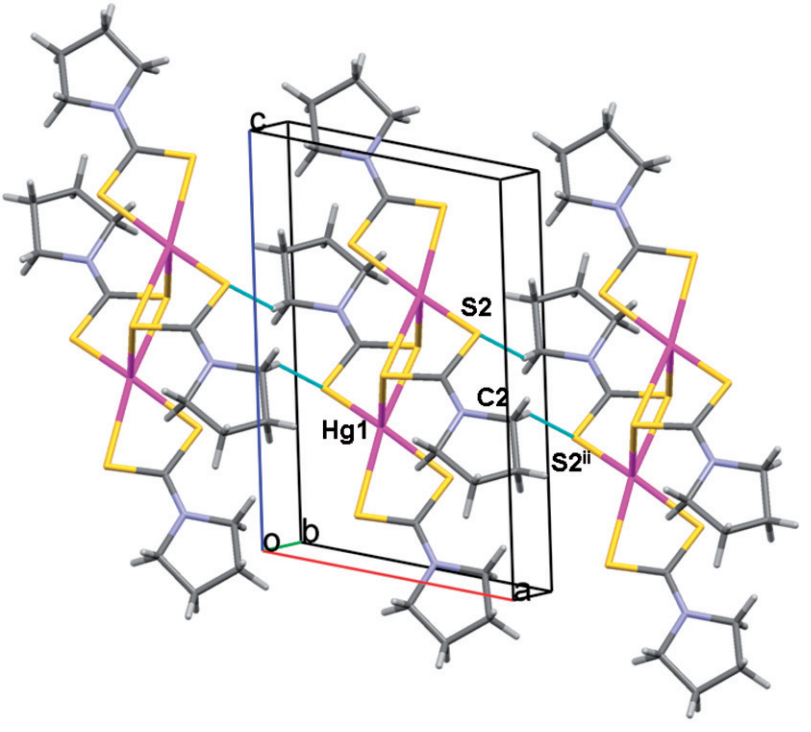

Figure 2. A view along the *b*-axis of the crystal packing and the C2–H2b...S2^{ii} interaction in $[Hg_2(PDTC)_4]$; symmetry code: ii: $2-x$, $1-y$, $1-z$.

Table 6. Antimicrobial activities of mercury(II)-PDTC complexes evaluated by the MIC.

	Microbial activity (in terms of MIC: $\mu g\,mL^{-1}$)					
Complexes	*Escherichia coli*	*Pseudomonas aeruginosa*	*Aspergillus niger*	*Penicillium citrinum*	*Candida albicans*	*Saccharomyces cerevisiae*
$[Hg(PDTC)_2]$	410 ± 6	390 ± 8	740 ± 10	710 ± 6	>1000	>1000
[Hg(PDTC)(CN)]	70 ± 2	50 ± 3	820 ± 9	160 ± 3	>1000	>1000

dithiocarbamate complexes. The structure is stabilized by non-covalent intermolecular C–H···S interactions.

Supplementary material

Supplementary crystallographic data of **1** (CCDC No. 745857) can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223-336033.

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