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Two dimensional heteropolynuclear Zn(II) and Cd(II)-tetracyanopalladate(II) complexes with the 1-ethylimidazole ligand exhibiting C-H···Pd interactions

Fulya Çetinkaya^a, Güneş Süheyla Kürkçüoğlu^{b,*}, Okan Zafer Yeşilel^c, Orhan Büyükgüngör^d

^a Eskişehir Osmangazi University, The Institute of Science, Department of Physics, 26480 Eskişehir, Turkey

^b Eskişehir Osmangazi University, Faculty of Arts and Sciences, Department of Physics, 26480 Eskişehir, Turkey

^c Eskişehir Osmangazi University, Faculty of Arts and Sciences, Department of Chemistry, 26480 Eskişehir, Turkey

^d Ondokuz Mayıs University, Faculty of Arts and Sciences, Department of Physics, TR-55139 Samsun, Turkey

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ABSTRACT

The cyano-bridged heteronuclear complexes $[Zn(etim)_2Pd(\mu-CN)_4]_n$ (1) and $[Cd(etim)_2Pd(\mu-CN)_4]_n$ (2) (etim = 1-ethylimidazole), have been synthesized and characterized by FT-IR, Raman spectroscopy, thermal and elemental analyses. The crystal structures of the complexes have been determined by X-ray single crystal diffraction. In the complexes, the Pd(II) ion is coordinated by four cyano ligands, forming a square-planar geometry, and the Zn(II) or Cd(II) ions are coordinated by six N atoms from four bridging cyano ligands and two etim ligands in a distorted octahedral geometry. The most important features of the complexes are the presence of C-H···Pd hydrogen-bonding interactions between the Pd(II) ion and the hydrogen atoms of the etim ligand.

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1. Introduction

The synthesis and rational design of coordination polymers are being given considerable attention owing to their interesting structural properties and potential applications [1–3]. Recently, cyano bridged coordination polymers, together with their diverse bonding and structural chemistry, have had widespread applications in the field of chemistry, pharmacy and industry, therefore they have been attracting increasing attention from scientists and chemists [4–6].

For many years there has been considerable interest in the activation of C–H bonds by transition metal complexes. In this connection, many examples of transition metal complexes showing agostic or anagostic C–H···M interactions have been recognized [7–13]. In simpler terms, agostic and anagostic interactions describe two electron three-center bonding interactions, and hydrogen bonding describes a four electron three-center interaction, respectively [14]. Recently a few examples of three-center four-electron anagostic interactions have been reported [7,11,15–18]. This hydrogen bonding interaction plays a crucial role in constructing supramolecular networks [19]. In the literature, four electron three-center interactions with Ni(II) in square planar [Ni(CN)₄]^{2–} complexes have been studied [11,17,20], but knowledge of these interactions with Pd(II) are scarce.

In previous studies, cyano complexes were obtained using imidazol and imidazole derived ligands [12,21-26]. As a part of our continuing research on the syntheses and characterizations of cyano complexes containing imidazole and imidazole derivative ligands, the 1-ethylimidazol ligand having CH groups, was used. Furthermore, the main purpose for the preparation of these complexes, using Pd(II) metal with a d⁸ system and forming a square planar geometry, was to analyze the effect of C-H···M interactions in the crystal packing. We define in this study, the syntheses, spectral (FT-IR and Raman), thermal and elemental analyses of the complexes $[Zn(etim)_2Pd(\mu-CN)_4]_n$ (1) and $[Cd(etim)_2 Pd(\mu-CN)_4]_n$ (2). The molecular and crystal structures of the cyano-bridged heteronuclear polymeric complexes 1 and 2 have been designated by X-ray single crystal diffraction. The thermal decomposition behaviors of the complexes were followed up in the temperature range 30-700 °C in a static air atmosphere.

2. Experimental

2.1. Materials and instrumentation

Zinc(II) chloride (ZnCl₂, 98%), cadmium(II) chloride hemipentahydrate (CdCl₂·2.5H₂O, 98%), palladium(II) chloride (PdCl₂, 99%), 1ethylimidazole (C₅H₈N₂, 95%) and potassium cyanide (KCN, 96%) were purchased from commercial sources and used without further purification. The FT-IR spectra of the complexes were recorded as KBr pellets in the range 4000–400 cm⁻¹ (2 cm⁻¹ resolution) on a



^{*} Corresponding author. Tel.: +90 222 2393750; fax: +90 222 2393578. *E-mail address:* gkurkcuo@ogu.edu.tr (G.S. Kürkçüoğlu).

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Fig. 1. (a) The FT-IR spectra of etim and the complexes and (b) Raman spectra of the complexes.

Table 1

The vibration (FT-IR and Raman) wavenumbers of etim in the complexes (cm⁻¹).

Assignments [31]	etim (liquid)	1		2	
		FT-IR	Raman	FT-IR	Raman
$v_{s}(CH)$ of CH=CH	3134 sh	3144 sh	3166 m	3147 w	3162 m
$v_{as}(CH)$ of CH=CH	3107 m	3119 m	3129 s	3122 m	3130 m
$v_{as}(CH_3)$, $v_{as}(CH_2)$	2981 s	2986 m	3002 m	2985 m	3004 m
$v_s(CH_3)$, $v_s(CH_2)$	2940 m	2942 m	2976 m	2942 m	2975 m
$v_{s}(CH_{2})$	2889 w	2894 w	2892 m	2891 w	2893 m
v(C=C) v(C=N)	1676 w	1670 w	1667 vw	1665 w	1671 vw
v(R), combination	1596 w	1597 m	-	1597 m	1596 vw
v(R), combination	1510 vs	1518 s	1545 w	1515 s	1529 w
$\delta_{as}(CH_2)_{scis}$	1465 m	1470 m	1469 w	1468 m	1472 w
$\delta_{as}(CH_3)_{scis}$	1448 m	1458 m	1450 vw	1456 w	-
v(R), combination	1394 m	1397 m	1391 vw	1397 m	-
$\delta(CH), v(R)$	1385 m	1378 m	-	1380 m	1388 w
$\delta(CH), v(R)$	1355 m	1347 w	1359 m	1355 m	1359 m
$v(R)$, $\delta(CH_2)_{twist}$	1287 m	1288 w	-	1289 w	-
Combination	1250 w	1259 w	1270 vw	1255 sh	1272 w
Combination	1228 vs	1243 s	-	1241 s	-
$\rho(CH_3), \rho(CH_2), \nu(R)$ combination	1194 sh	-	1205 vw	1191 vw	1204 vw
$\rho(CH_3), \rho(CH_2), \nu(R)$ combination	1110 s	1122 s	1136 w	1121 s	1136 w
$\rho(CH_3), \rho(CH_2), \nu(R)$ combination	1078 vs	1090 s	1100 m	1090 s	1103 m
$\delta(\mathbf{R})$	1034 m	1037 m	1054 w	1036 m	1054 w
γ(CH)	958 m	968 m	-	962 m	966 vw
γ(CH)	908 s	945 s	936 vw	940 s	930 vw
γ(CH), ν(C–C)	875 sh	878 vw	863 vw	880 vw	865 w
γ (CH), ν (C–C)	819 s	836 s	-	833 s	822 vw
γ(CH), ν(C–C)	742 s	747 s	754 vw	747 s	758 w
$v(CH_2-N)$, $v(C-CH_2)$	667 vs	659 s	663 w	658 s	666 m
δ(C-H)	624 m	617 m	622 vw	618 m	620 w
δ(CH ₂), ν(C-C)	515 vw	511 vw	527 vw	514 vw	-

Abbreviations used: ν, stretching; δ, deformation; t, twisting; ρ, rocking; γ, out-of-plane bending; s, strong; m, medium; w, weak; sh, shoulder; v, very.

Table 2

The wavenumbers of the $[Pd(CN)_4]^{2-}$ vibrations in the complexes (cm^{-1}) .

Assignments [21]	$K_2[Pd(CN)_4] \cdot H_2O$	1	2
A _{1g} , ν ₁	(2169) vs	(2201) vs	(2197) vs
B_{1g} , v_4	(2159) s	(2188) sh	(2184) m
v_8 , $v(CN)$, E_u	2135 vs	2169 vs	2163 vs
ν ₈ , ν(C ¹³ N), E _u	2112 sh	2129 w	2123 w
ν ₉ , ν(PdC), E _u	486 w	489 w	486 w
A_{1g} , v_2	(436) m	(452) m	(452) m
v_{10} , δ (PdCN), E_u	393 m	407 m	404 m
E _g , ν ₁₆	(295)	(299) sh	-

Abbreviations used: s, strong; m, medium; w, weak; sh, shoulder; br, broad; v, very. The symbols v, δ , and π refer to valence, in-plane and out-of-plane vibrations, respectively.

The bands observed in the Raman spectra are given in the parentheses.

Perkin Elmer 100 FT-IR spectrometer which was calibrated using polystyrene and CO_2 bands. The Raman spectra of the complexes were recorded in the range 4000–250 cm⁻¹ on a Bruker Senterra Dispersive Raman instrument using laser excitation of 785 nm. A Perkin Elmer Diamond TG/DTA thermal analyzer was used to record simultaneous TG, DTG and DTA curves in a static air atmosphere at a heating rate of 10 K min⁻¹ in the temperature range 30–700 °C using platinum crucibles. Elemental analyses were carried out on a LECO, CHNS-932 analyzer for C, H and N at the Middle East Technical University Central Laboratory.

2.2. Crystallographic analyses

Diffraction experiments were carried out at 296 K on a Stoe IPDS diffractometer. The structures were solved by direct methods and refined using the programs SHELXS97 and SHELXL97 [27]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods [27]. The hydrogen atoms were placed in geometrically idealized positions and refined as riding atoms. The following procedures were implemented in our analysis: data

Table	3
<u> </u>	1

Crystal data and structure refinement parameters for the complexes.

Complexes	1	2
Empirical formula	C14H16N8PdZn	C14H16N8PdCd
Formula weight (g mol ⁻¹)	468.12	515.15
Temperature (K)	296	
Wavelength (Å)	0.71073 Mo Ka	
Crystal system	monoclinic	monoclinic
Space group	C2/m	C2/m
Unit cell dimension		
a (Å)	16.2957(14)	16.6188(16)
b (Å)	7.4062(6)	7.5863(8)
c (Å)	7.6595(8)	7.8533(8)
β (°)	105.591(7)	108.472(8)
V (Å ³)	890.40(14)	939.09(17)
Ζ	2	2
Absorption coefficient (mm ⁻¹)	2.37	2.10
D_{calc} (Mg m ⁻³)	1.746	1.822
Theta range for data collection (°)	2.6-27.9	3.1-28.3
Measured reflections	4651	2881
Independent reflections	1005	1044
Reflections with $[I > 2\sigma(I)]$	942	819
Absorption correction	x-red32, Stoe & Cie,	2002 [28]
Refinement method	Full-matrix least-so	uares on F ² [27]
R _{int}	0.100	0.024
Final R indices $[I > 2\sigma(I)]$	0.033	0.018
Final wR indices (all data)	0.092	0.042
Goodness-of-fit (GOF) on F^2	1.14	1.07
$\Delta ho_{ m max}$ (e Å ⁻³)	0.64	0.48
$\Delta ho_{ m min}$ (e Å $^{-3}$)	-0.89	-0.39

collection: x-AREA, cell refinement: x-AREA, data reduction: x-RED [28]; program(s) used for molecular graphics were as follows: MERCURY [29]; software used to prepare material for publication: WINGX [30].

2.3. Syntheses of the complexes

The starting material $K_2[Pd(CN)_4]$ ·H₂O was prepared by the reaction between KCN and PdCl₂ in a mole ratio of 4:1 in aqueous

Table 4 Selected geometric parameters (Å, $^\circ)$ for 1 and 2.

1		2	
Bond lengths Zn1–N1	2 092(3)	Cd1-N1	2 272(3)
Zn1-N3 Pd1-C6	2.201(3) 1.997(4)	Cd1-N3 Pd1-C6	2.368(2) 1.986(2)
Bond angles N1-Zn1-N3 N1 ⁱ -Zn1-N3 N3 ⁱ -Zn1-N3 ⁱⁱ N3 ⁱ -Zn1-N3 ⁱⁱⁱ C6-Pd1-C6 ^{iv} C6-Pd1-C6 ^v	91.32(10) 88.68(10) 91.56(17) 88.44(17) 90.30(2) 180.00(0)	N1-Cd1-N3 N1-Cd1-N3 ^{iv} N3-Cd1-N3 ^v N3-Cd1-N3 ^{vi} C6-Pd1-C6 ⁱ C6-Pd1-C6 ⁱⁱ	91.89(8) 88.11(8) 86.85(11) 93.15(11) 89.03(13) 90.97(13)
C6-Pd1-C6 ^{vi}	89.70(2)	C6-Pd1-C6 ⁱⁱⁱ	180.00(0)

Symmetry codes: (i) -x + 1, -y + 1, -z + 1; (ii) x, -y + 1, z; (iii) -x + 1, y, -z + 1; (iv) -x + 1, y, -z + 2; (v) -x + 1, -y, -z + 2; (vi) x, -y, z (for 1); (i) x, -y, z; (ii) -x + 1, y, -z + 2; (iii) -x + 1, -y + 1, -z + 1; (v) x, -y + 1, z; (vi) -x + 1, y, -z + 1 (for 2).

solution. The complexes were prepared by dissolving 1 mmol (0.307 g) of K₂[Pd(CN)₄]·H₂O in water solution (10 mL). To this solution, 4 mmol (0.385 g) of etim dissolved in ethanol (10 mL) and 1 mmol of the metal chloride (ZnCl₂ = 0.136 g or CdCl₂·2.5H₂·O = 0.228 g) dissolved in water were added with stirring. The mixtures were stirred for approximately 3 h at 60 °C in a temperature-controlled bath. The obtained solutions were filtered off and cooled to room temperature. Within a few days bright colored crystals formed that were separated by filtration and dried in air. The freshly prepared complexes were analyzed for C, H and N. The obtained results are as follows: *Anal.* Calc. for complex C₁₄H₁₆-N₈PdZn (1) (M_w = 468.12 g mol⁻¹): C, 35.92; H, 3.44; N, 23.94. Found: C, 36.08; H, 3.82; N, 24.28%, for complex C₁₄H₁₆N₈PdCd (2) (M_w = 515.15 g mol⁻¹): C, 32.64; H, 3.13; N, 21.75. Found: C, 32.64; H, 3.23; N, 21.87%.



Fig. 2. (a) The molecular structure of complex **1** (b) an infinite 2D layer of complex **1**. *Symmetry codes*: (i) 1 – *x*, *y*, 1 – *z*, (ii) 1 – *x*, 1 – *y*, 1 – *z*, (iii) *x*, 1 – *y*, *z*, (iv) *x*, *y*, 1 + *z*, (v) *x*, *y*, 1 – *z*, (vi) *x*, *y* – 1, *z*, (vii) *x*, *y* – 1, *z*, (viii) *x*,

3. Results and discussion

3.1. Vibrational spectra

The FT-IR spectra of etim and the complexes, and Raman spectra of the complexes are illustrated in Fig. 1(a) and (b), respectively. The spectra of the complexes are found to be very similar. As can be seen from Fig. 1, the presence of bands belonging to the ligand in the FT-IR and Raman spectra of the complexes shows the existence of etim in the complexes. The wavenumbers of etim observed in the FT-IR and Raman spectra of the complexes are given in Table 1, together with the vibrational data of free etim [31]. The spectra of the complexes were analyzed in a previous study, which observed a similar set of wavenumber shifts [23]. A glance at Table 1 shows considerable shifts to higher or lower wavenumber occur for

numerous absorption bands in the spectra of the complexes, due to v(CH), v(CH₃), v(R), δ (CH₂), v(C=C), δ (CH), combination, ρ CH₃) and γ (CH) vibration modes. For all the complexes, the observed bands in the range 3166–3129 cm⁻¹ in the vibrational spectra can be assigned to v(CH) stretching vibrations. The stretching vibrations of all the complexes have upward shifts in wavenumber when compared to the free molecule, while the stretching vibrations of the imidazole ring at 1676 cm⁻¹ is shifted to the low wavenumber region. The bands at 1596–1394 cm⁻¹ in the free etim ligand are significantly shifted to higher wavenumbers in the complexes. When the aromatic ring nitrogen is involved in complex formation, certain ring modes, particularly at 1287–908 cm⁻¹, increase in value both due to the coupling with M–N (ligand) bond vibrations and due to alterations of the ring force field. These shifts can be explained as the coupling of the internal modes of the etim



Fig. 3. (a) The molecular structure of complex **2** (b) An infinite 2D layer of complex **2**. Symmetry codes: (i) 1 – x, y, 1 – z, (ii) 1 – x, 1 – y, 1 – z, (iii) x, 1 – y, z, (iv) x, –1 + y, z, (v) x, –1 + y, 1 + z, (vi) 1 – x, y, 2 – z.

molecule with $M-N_{etim}$ vibrations. Analogous shifts on coordination have been observed in the vibrational spectra of the other metal-coordinated imidazole complexes [11,12,21,22] and are expounded as the coupling of the internal modes of the aromatic molecule with the M-N vibrations [32].

The v(CN) vibrations are the most characteristic bands in cyano groups because they give a sharp and strong band and are determined easily in the 2200–2000 cm⁻¹ range. The vibrational wavenumbers of the $[Pd(CN)_4]^{2-}$ group for $K_2[Pd(CN)_4] \cdot H_2O$ and the complexes are presented in Table 2, together with vibrational assignments of $[Pd(CN)_4]^{2-}$ [33]. The v(C=N) vibrations of the complexes are observed in the 2201–2132 cm⁻¹ region in the FT-IR and Raman spectra. The two Raman fundamentals are assigned to the bands at 2188 and 2201 cm^{-1} (for **1**), and 2184 and 2197 cm⁻¹ (for **2**). From the FT-IR spectra of the complexes, it is determined that the stretching vibration of the cyano group has shifted to approximately 17–30 cm⁻¹ higher wavenumber (see Table 2). In the region 486–393 cm⁻¹ of the FT-IR and Raman spectra, Pd-C stretches and Pd-CN bending bands were observed for complexes **1** and **2**. The bands observed at 489 and 407 cm^{-1} in the FT-IR spectrum of complex 1 might be attributed to the stretching vibrations of Pd-C and bending vibrations of Pd-CN, respectively. The same vibrational bands were observed at 486 and 404 cm^{-1} for complex **2**. The band observed at 452 cm⁻¹ in the Raman spectra of the complexes might be attributed to the stretching vibrations of Pd-C.

3.2. Structural analyses

Single-crystal X-ray analyses indicate that complexes 1 and 2 are isostructural. The details of the crystal data collection and refinement of complexes 1 and 2 are summarized in Table 3. Selected bond distances and angles for both complexes are collected in Table 4. Xray diffraction analyses reveal that complexes **1** and **2** are both two dimensional networks and crystallize in the monoclinic C2/m space group. As shown in Figs. 2(a) and 3(a), the Zn(II) and Cd(II) ions are six coordinated by four nitrogen atoms from four cyano ligands and two nitrogen atoms from two etim ligands, exhibiting a distorted octahedral geometry. The Pd(II) ions have a square planar geometry, completed by four carbon atoms from four cyano ligands. Complexes 1 and 2 have a similar network to the previously reported [Cd(mim)₂ $Ni(\mu-CN)_4]_n$ (mim = 2-methylimidazole) [11], trans-[M(N-Meim)_2] $Ni(\mu-CN)_4]_n$ (M = Cu(II), Zn(II) and Cd(II); N-Meim = N-methylimidazole) [22] and $[Cd(N-Meim)_2Pd(\mu-CN)_4]_n$ [12] complexes. The M-N bond distances (Zn1–N1 = 2.092(3) and Zn1–N3 = 2.201(3) Å for 1, Cd1–N1 = 2.272(3) and Cd1–N3 = 2.368(2) Å for **2**) are comparable to those reported for other M(II)-tetracyanopalladate(II) complexes [8,15,23]. The intralayer $Zn1\cdots Zn1^{i}$, $Zn1\cdots Zn1^{ii}$, $Cd1\cdots Cd1^{i}$ and Cd1...Cd1ⁱⁱ distances are 7.406(1), 7.606(1), 7.586(1) and 7.853(1) Å, respectively, whereas the interlayer $Zn1\cdots Zn1^{iii}$ and $Cd1\cdots Cd1^{iii}$ distances are 8.950 and 9.134 Å, respectively ((i) x, -1 + y, z, (ii) x,*y*, 1 + *z* and (iii) $\frac{1}{2} + x$, $-\frac{1}{2} + y$, *z* for **1**, (i) *x*, -1 + y, *z*, (ii) *x*, *y*, -1 + zand (iii) $-\frac{1}{2} + x$, $\frac{1}{2} + y$, *z* for **2**).



Fig. 4. C-H...Pd interactions in **1**. Symmetry codes: (i) x, 1 + y, z, (ii) 1/2 + x, 1/2 + y, z, (iii) 3/2 - x, -1/2 + y, 1 - z.





Fig. 7. TG, DTG and DTA curves of 2.

The most striking feature of complexes **1** and **2** is the presence of C–H···M hydrogen-bonding interactions between the Pd(II) ion and the hydrogen atoms of the etim ligand (Figs. 4 and 5). The Pd1···H3 and Pd1···H5A distances (2.999 and 3.150 Å for **1**, 2.913 and 3.368 Å for **2**), and C3–H3···Pd1 and C5–H5A···Pd1 bond angles (176.05° and 169.96° for **1** and 176.95° and 166.65° for **2**) are similar those reported for the related Pd(II) complexes [15,16,18,34]. The bond length and angle indicate that these interactions are four electron three-center interactions [35,36]. To the best of our knowledge, anagostic interactions with Pd(II) are not common. These weak hydrogen bonds play an important role in the construction of the supramolecular structures [37–39]. The adjacent 2D layers of complexes **1** and **2** are further extended into three-dimensional supramolecular frameworks by weak C–H···Pd hydrogen bonding interactions.

3.3. Thermal analyses

The thermal decompositions of the complexes proceed in three stages (Figs. 6 and 7). The complexes are thermally stable up to 104 (DTA_{max.} = 145 °C) and 118 °C (DTA_{max.} = 162 °C), respectively, and then begin to decompose. The first stage between 104 and 177 °C for 1 and between 118 and 196 °C for 2 corresponds to the endothermic elimination of half-etim and one etim ligand, respectively. In the next step, in complex 1, the remaining etim ligand decomposes between 177 and 292 $^\circ C$ (DTA_{max.} = 229 and 260 $^\circ C$). In complex 2. the other etim ligand and two CN groups decompose between 196 and 312 °C (DTA_{max} = 298 °C). The final stage is related to the exothermic removal of the four CN groups in the temperature range 292-428 °C (DTA_{max} = 401 °C) for 1, and two CN groups in the temperature range 312-399 °C (DTA_{max} = 372 °C) for 2. According to the thermal analyses results, complex 2 is thermally more stable than complex 1. Such decompositions were observed for other cyano complexes [40–43]. The final decomposition products are identified as MO + Pd (M = Zn or Cd) [found (calcd.)% = 41.03 (40.11) for **1** and found (calcd.)% = 45.35 (45.58) for 2]. Analogous decomposition products were observed for cyano bridged complexes [44].

4. Conclusion

Two new cyano-bridged heteronuclear polymeric complexes, $[Zn(etim)_2Pd(\mu-CN)_4]_n$ (1) and $[Cd(etim)_2Pd(\mu-CN)_4]_n$ (2), were synthesized and characterized. The structures of the complexes were determined by using X-ray single crystal diffraction, vibrational (FT-IR and Raman) spectroscopy, thermal and elemental analysis techniques. From the crystallographic data, it was determined that the crystals packing of complexes 1 and 2 is composed of intermolecular C–H…Pd interactions. Moreover, vibrational bands belonging to the functional groups of the ligands were examined using the vibration spectra of the complexes. Important results about the ligand coordination to the metal, through which donor atoms and the coordination form, were inferred.

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Appendix A. Supplementary data

CCDC 900924 and 900925 contain the supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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