

Intermolecular Interactions in the Crystal of a New Nickel(II)-cobalt(II)-nickel(II) Trinuclear Complex Containing a Macrocyclic Complex Ligand

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A new trinuclear complex $[\text{Co}(\text{NiL})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$ was synthesized by using a macrocyclic complex ligand $[\text{NiL}]$, where L is the dianion of diethyl-5,6,7,8,16,17-hexahydro-6,7-dioxo-16*H*-dibenzo[*e,n*] [1,4,8,12]tetraazacyclopentadecine-13,19-dicarboxylate. X-ray analysis revealed that the two Ni(II) ions have the same distorted N_4 square planar coordination geometries. The Co(II) ion resides in a distorted octahedral O_6 coordination environment. In the crystal, $\pi \cdots \pi$ interaction between a phenyl ring and three non-aromatic π -systems involving Ni and N atoms was observed together with $\text{C-H} \cdots \text{O}$ and $\text{O-H} \cdots \text{O}$ hydrogen bonds. These non-covalent interactions link the dications and the perchlorate anions to form a 3D supramolecular network.

Key words: Nickel(II)-Cobalt(II)-Nickel(II) Complex, Crystal Structure, Non-Covalent Interaction, Macrocyclic Oxamido Ligand

1. Introduction

Non-covalent interactions are currently active fields of research [1 – 12]. They are important for chemistry, biology, materials science *etc.* [1, 4 – 8, 13 – 25]. $\pi \cdots \pi$ interaction is one of the important non-covalent interactions. It contributes to self-assembly or molecular recognition processes and the packing of molecules incorporating aromatic groups in crystals [1, 6, 13 – 17], plays a role in the binding and conformations of nucleic acids and proteins [1, 6, 18], can enhance the electron transfer reactivity of the copper protein pseudoazurin [19], and can influence the conductivity of some molecular conductors [21, 22], the behavior of some liquid crystalline materials [23, 24], and the electronic and optical properties of materials [24, 25]. $\pi \cdots \pi$ interaction has also been used in the preparation of devices for the detection of polycyclic aromatic hydrocarbons and in the resolution of *rac*-phenylalanine [13, 14]. Hydrogen bonds, whether weak or strong, are also important non-covalent interactions. They can play vital roles in molecular recognition processes, the reactivity and structure of biomolecular species, the stability of inclusion complexes, crystal engineering, molecular conformation and so forth [6 – 8]. The coordinating properties of *N,N'*-disubstituted oxamides with coordinating

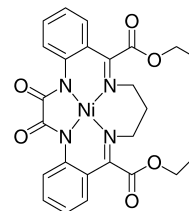
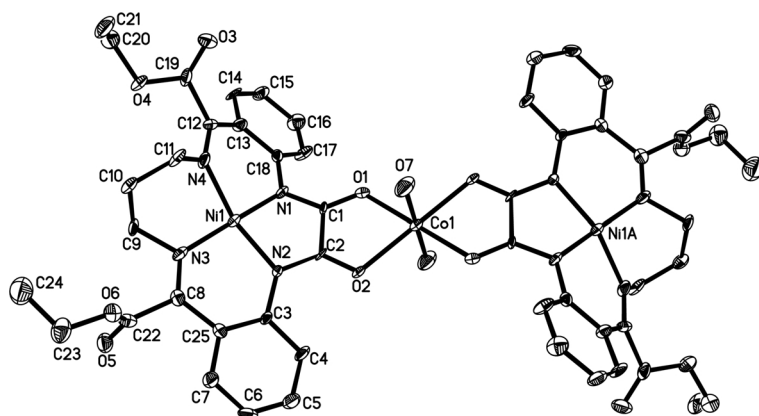


Chart 1. $[\text{NiL}]$.

groups are particularly interesting. They are suitable ligands for designing polynuclear complexes and have remarkable properties such as stabilizing high oxidation states of late first-row transition metal ions and mediating ferro- and antiferromagnetic coupling between metal centers [26 – 32]. Mono-metal complexes of macrocyclic oxamido ligands incorporating phenyl groups have combinations of sites capable of being involved in metal-ligand coordination, $\pi \cdots \pi$ interaction and $\text{O-H} \cdots \text{O}$ and $\text{C-H} \cdots \text{O}$ hydrogen bonding. Therefore, they can be used as blocks to construct organic-inorganic hybrid supramolecular architectures and polynuclear complexes of different properties and functions. As a continuation of our work in macrocyclic oxamido complexes and non-covalent interactions [27 – 31], we now present a new Ni(II)-Co(II)-Ni(II) trinuclear complex with a mononuclear complex of a macrocyclic oxamido

Fig. 1. Structure of $[\text{Co}(\text{NiL})_2(\text{H}_2\text{O})_2]^{2+}$.

Schiff base [NiL] (Chart 1) as a new “complex ligand”. L is the dianion of diethyl-5,6,7,8,16,17-hexahydro-6,7-dioxo-16*H*-dibenzo[*e,n*][1,4,8,12]tetraazacyclopentadecine-13,19-dicarboxylate. In the crystal of the trinuclear complex, $\pi \cdots \pi$ interaction between a phenyl ring and the array of a Ni(II) ion and three separate unclosed π -systems was observed. Descriptions of $\pi \cdots \pi$ interactions involving non-aromatic groups are rare [1,9,33], though those between aromatic groups are numerous. The $\pi \cdots \pi$ interaction organizes the $[\text{Cu}(\text{NiL})_2(\text{H}_2\text{O})_2]^{2+}$ dications to form 1D supramolecular chains. C–H \cdots O and O–H \cdots O hydrogen bonds further link the 1D chains and the perchlorate anions to form a 3D supramolecular network.

2. Results and Discussion

2.1. Molecular structure of $[\text{Co}(\text{NiL})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$

The complex is composed of a centrosymmetric trinuclear complex dication $[\text{Co}(\text{NiL})_2(\text{H}_2\text{O})_2]^{2+}$ (Fig. 1) and two perchlorate ions. In the complex dication, the oxamido groups of the two macrocyclic ligands [NiL] chelate the Co(II) centre. Each Ni atom resides in the cavity of its macrocyclic ligand. The Ni–N bond lengths are in the range of 1.835 ~ 1.906 Å. The two Ni atoms have a significantly distorted square-planar N_4 environment. The deviations of the four donor atoms from their mean plane are in the range of $-0.246 \sim 0.259$ Å. The distance between Ni(1) and the coordination plane is 0.075 Å. Co(1) resides in a distorted octahedral surrounding with the four O atoms of the two oxamido groups from the two [NiL] ligands and the two O atoms of the two H_2O ligands as donors. The Co–O bond lengths are in the range of

Table 1. Selected bond lengths (Å) and bond angles (°) for the complex.

Bond lengths		Bond angles	
Co(1)–O(1)	2.052(5)	O(1)–Co(1)–O(7)	93.2(2)
Co(1)–O(7)	2.089(6)	O(1)#1–Co(1)–O(7)	86.8(2)
Co(1)–O(2)	2.137(5)	O(1)#1–Co(1)–O(7)#1	93.2(2)
Ni(1)–N(1)	1.835(7)	O(1)–Co(1)–O(2)#1	101.4(2)
Ni(1)–N(3)	1.850(7)	O(1)#1–Co(1)–O(2)#1	78.6(2)
Ni(1)–N(2)	1.886(6)	O(7)–Co(1)–O(2)#1	89.5(2)
Ni(1)–N(4)	1.906(7)	O(7)#1–Co(1)–O(2)#1	90.5(2)
O(1)–C(1)	1.237(9)	O(1)–Co(1)–O(2)	78.6(2)
O(2)–C(2)	1.229(8)	O(1)#1–Co(1)–O(2)	101.4(2)
O(3)–C(19)	1.194(10)	O(7)–Co(1)–O(2)	90.5(2)
O(4)–C(19)	1.320(10)	O(7)#1–Co(1)–O(2)	89.5(2)
O(4)–C(20)	1.459(10)	N(1)–Ni(1)–N(3)	169.6(3)
O(5)–C(22)	1.211(10)	N(1)–Ni(1)–N(2)	85.3(3)
O(6)–C(22)	1.320(10)	N(3)–Ni(1)–N(2)	95.9(3)
O(6)–C(23)	1.441(11)	N(1)–Ni(1)–N(4)	89.7(3)
C(1)–C(2)	1.518(11)	N(3)–Ni(1)–N(4)	92.5(3)
N(1)–C(1)	1.315(9)	N(2)–Ni(1)–N(4)	159.5(3)
N(1)–C(18)	1.414(10)	C(1)–N(1)–C(18)	120.9(7)
N(2)–C(2)	1.316(10)	C(1)–N(1)–Ni(1)	112.4(6)
N(2)–C(3)	1.420(9)	C(18)–N(1)–Ni(1)	126.4(5)
N(3)–C(8)	1.291(10)	C(2)–N(2)–C(3)	123.2(7)
N(3)–C(9)	1.491(9)	C(2)–N(2)–Ni(1)	109.2(5)
N(4)–C(12)	1.289(10)	C(3)–N(2)–Ni(1)	125.7(5)
N(4)–C(11)	1.472(10)	C(8)–N(3)–C(9)	117.4(7)
C(8)–C(22)	1.511(12)	C(8)–N(3)–Ni(1)	127.6(6)
C(8)–C(25)	1.478(11)	C(9)–N(3)–Ni(1)	114.9(5)
		C(12)–N(4)–C(11)	123.7(7)
		C(12)–N(4)–Ni(1)	126.4(6)
		C(11)–N(4)–Ni(1)	109.1(5)

#1 = $-x + 1, -y + 1, -z + 1$.

2.052 ~ 2.137 Å. The distances between the Co atom and each Ni atom are both 5.155 Å and that between the two Ni atoms is 10.310 Å. Interestingly, O(1), O(2), C(1), C(2), N(1), N(2), Co(1), O(1)#1, O(2)#1, C(1)#1, C(2)#1, N(1)#1 and N(2)#1 are almost coplanar and the largest deviation from their mean plane is 0.194 Å.

Table 2. Contact distances (Å) between overlapping [NiL] in the crystal.

O(5)···C(1) ^a	3.093(9)	O(5)···C(2) ^a	3.059(10)
Ni(1)···C(5) ^a	3.774(8)	Ni(1)···C(6) ^a	3.789(9)
Ni(1)···C(7) ^a	3.775(8)		
N(1)···C(6) ^a	3.620(9)	N(1)···C(7) ^a	3.446(10)
N(2)···C(8) ^a	3.674(10)	N(2)···C(25)	3.693(10)
N(3)···C(3) ^a	3.669(9)	N(3)···C(4) ^a	3.474(10)

^a2a = -x, 1 - y, -z.

The N(1)-C(1) and N(2)-C(2) bond lengths in the oxamido groups are 1.315 and 1.316 Å, respectively, and thus closer to the double bonds N(3)-C(8) (1.291 Å) and N(4)-C(12) (1.289 Å) rather than to the single bonds N(3)-C(9) (1.491 Å) and N(4)-C(11) (1.472 Å). The sums of the three bond angles around N(1) and N(2) are very close to 360° (359.7 and 358.1°, respectively). The above values imply that N(1) and N(2) are sp²-hybridized and that the π -electrons in the oxamido groups are delocalized to form conjugated systems. The length of C(1)-C(2) (1.518 Å) reveals that the C-C bond in the oxamido group is a single bond. The above analyses imply that the oxamido group is divided into two separate π -systems. The Schiff base group C(12)=N(4) is conjugated with the C(13)~C(18) phenyl group since the bond length of C(12)-C(13) (1.405 Å) is in the range of those of the C-C bonds in the phenyls. The other Schiff base group C(8)=N(3) is not involved in any conjugated system, as suggested by the normal lengths of C-C and C-N single bonds around C(8)=N(3).

2.2. Non-covalent interactions

In the crystal, each complex ligand [NiL] of a trinuclear complex dication overlaps with one of the two [NiL] ligands of a neighbouring trinuclear complex dication (Fig. 2 and Fig. 3). In an arrangement of such two overlapping segments, each carbon atom on one phenyl ring (C(3)~C(7) and C(25)) of each [NiL] segment contacts N(1), N(2), N(3) and/or Ni(1) of the other [NiL] segment with atom-to-atom distances (Table 2) in the range of those of $\pi \cdots \pi$ interaction [1, 11]. N(1), N(2) and N(3) in a [NiL] segment belong to three separate unclosed π -systems according to the analyses in the above paragraph. Therefore, the $\pi \cdots \pi$ interaction occurs between the phenyl ring and the Ni atom and the three unclosed π -systems. It is conceivable that such an arrangement of the three relating π -systems and the Ni(II) ion and the charge distribution of this

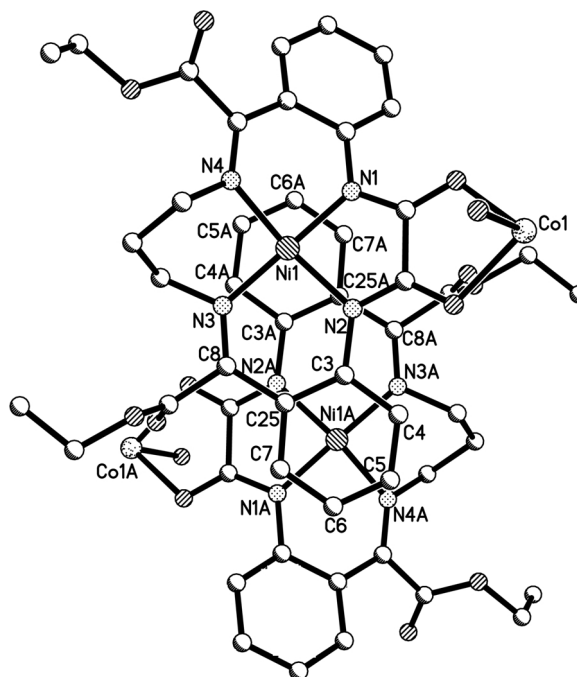


Fig. 2. Plot showing the $\pi \cdots \pi$ interaction between two overlapping [NiL] fragments in two neighbouring trinuclear dications. The [NiL] fragment related by symmetry in each trinuclear dication is neglected.

arrangement match those of the phenyl ring to result in the $\pi \cdots \pi$ interaction [1, 15]. The $\pi \cdots \pi$ interaction organizes the trinuclear dications to form supramolecular 1D chains (Fig. 3) in the crystal.

It can also be seen from Table 3 that O(5) (the oxygen atom of a carbonyl group) of each of the two overlapping [NiL] fragments is close to C(1) and C(2) (the two carbon atoms of the oxamido group) from the other of the two overlapping [NiL] fragments with distances as short as 3.093 and 3.059 Å, both of which are significantly shorter than the sum of the van der Waals radii of the oxygen and carbon atoms [34]. This kind of short intermolecular oxamido-carbonyl O···C contacts, which failed to catch our eye when preparing the related manuscripts, also occur in the crystals of another macrocyclic oxamido Ni(II) complex similar to [NiL] (with O···C contacts of 2.989 and 3.105 Å) [35] and its trinuclear complex (with O···C contacts of 3.078 and 3.226 Å) [31]. These short O···C contacts may imply that a kind of intermolecular interaction (to be named an oxamido-carbonyl interaction) different from and stronger than van der Waals forces is present. The short contacts may also be caused by the $\pi \cdots \pi$ interaction described in the above paragraph and may be

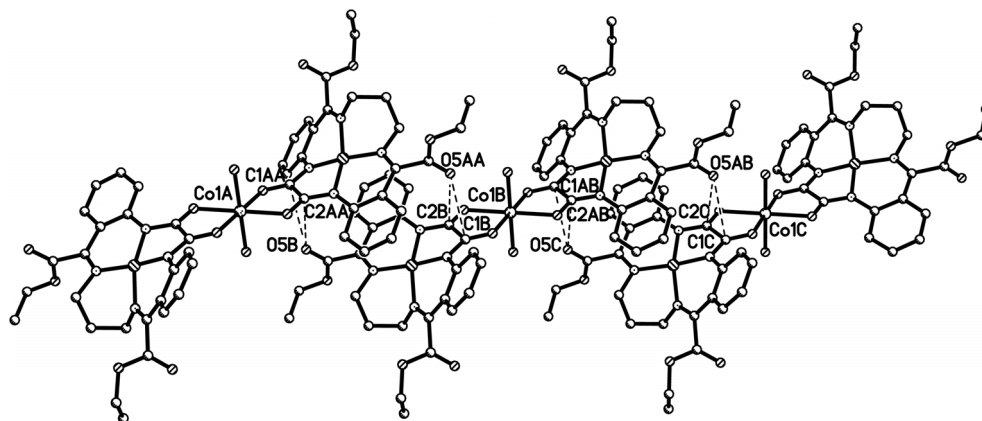


Fig. 3. Supramolecular 1D chain of the trinuclear dications. The dashed lines show the intermolecular contacts between the oxygen atom of a carbonyl group of one [NiL] fragment and the two carbon atoms of the oxamido group of a neighbouring [NiL] fragment in another trinuclear dication.

D...A	d _{D...A} (Å)	d _{H...A} (Å)	∠D-H...A(°)	Symmetry code for A
O(5)...O(7)	2.865(10)			$x, -1+y, z$
O(7)...O(11)	2.909(10)			$1/2-x, 1/2+y, 1/2-z$
C(9)...O(3)	3.226(11)	2.586	123.7	$1/2-x, -1/2+y, 1/2-z$
C(14)...O(11)	3.368(11)	2.500	155.3	
C(17)...O(9)	3.258(11)	2.557	132.5	$-1/2-x, 1/2+y, 1/2-z$
C(20)...O(1)	3.062(10)	2.361	128.6	$1/2-x, -1/2+y, 1/2-z$
C(23)...O(9)	3.401(11)	2.592	141.0	$1/2+x, 1/2-y, 1/2+z$
C(24)...O(11)	3.348(11)	2.576	138.2	$1/2-x, -1/2+y, 1/2-z$

Table 3. Parameters of O-H...O and C-H...O hydrogen bonds in the crystal.

destabilizing in nature, since a small number of shorter destabilizing local interactions can be enforced by a much larger number of stabilizing distances, with net energy advantage [11]. Evidence from the IR spectra of the title complex supports the idea of an oxamido-carbonyl interaction (see 2.3). Arene-carbonyl interactions reported by Kim *et al.* were attributed to attractive $n(sp^2)-\pi^*$ charge-transfer complexations and dipole-quadrupole interactions [3]. Rather like arene-carbonyl interactions, the oxamido-carbonyl interaction, if it really exists, can also be rationalized to be dominated by attractive $n(sp^2)-\pi^*$ charge-transfer interactions (from the oxygen atom of the ester carbonyl to the two carbon atoms of the oxamido group) and dipole-dipole attractions between the ester carbonyl and the oxamido group (attraction between the negatively charged oxygen atom of the ester carbonyl and the two positively charged carbon atoms of the oxamido group).

Every H₂O ligand forms two O-H...O hydrogen bonds, one with O(5) (the O atom of an ester carbonyl) from a [NiL] fragment in a neighbouring trinuclear cation, and the other with O(11) (an O atom of a perchlorate ion). Several H atoms bound to C

atoms on each [NiL] fragment have contacts with O atoms from neighbouring trinuclear cations or perchlorate ions. The parameters of these contacts (see Table 3) are in the range of those of C-H...O hydrogen bonds [6]. The C-H...O and the O-H...O hydrogen bonds link the 1D supramolecular chains of the trinuclear dications and the perchlorate ions to form a 3D supramolecular network.

2.3. IR spectra

The band at 1735 cm⁻¹ in the IR spectrum of the free [NiL] [36] can be assigned to the absorption of C=O (ester) [27, 28, 31]. There are two corresponding C=O (ester) bands (1735 and 1715 cm⁻¹) in the IR spectrum of the title complex. The existence of these two bands in this range means that the two C=O (ester) groups in the [NiL] ligand in a trinuclear dication are in different environments. The reason which causes the splitting may be that only the atom O(5) is involved in the oxamido-carbonyl interaction as described above. The strong band at *ca.* 1610 cm⁻¹ is attributed to $\nu(C=O)$ (oxamido) [27, 28, 31]. The broad $\nu(O-H)$ (H₂O) band at *ca.* 3400 cm⁻¹ indicates hy-

drogen bonding. The broad band at *ca.* 1100 cm⁻¹ is assigned to the absorption of ClO₄⁻.

3. Conclusion

In summary, this article describes the synthesis and intermolecular interactions in the crystal structure of a new Ni(II)-Co(II)-Ni(II) trinuclear complex. In the crystal, $\pi \cdots \pi$ interaction occurs between a phenyl ring and three separate non-aromatic π -systems involving nickel and nitrogen atoms. This $\pi \cdots \pi$ interaction provides an example that not only aromatic rings but also other types of π -systems can participate in $\pi \cdots \pi$ interaction. Intermolecular oxamido-carbonyl C \cdots O contacts significantly shorter than the sum of the van der Waals radii of the oxygen and carbon atoms were also observed, but their confirmation needs further study. A network of hydrogen bonds, both weak and strong, exists in the crystal and leads to a three-dimensional supramolecular architecture.

4. Experimental Section

4.1. General

All starting materials were of reagent grade and were used as purchased. The mononuclear complex [NiL] was prepared by a literature method [36]. IR spectra were recorded as KBr discs on a Shimadzu IR-408 infrared spectrophotometer in the 4000–600 cm⁻¹ region. Elemental analyses of C, H and N were carried out on a Perkin-Elmer 240 analyzer.

Caution! Although we have not encountered any problems, it should be kept in mind that perchlorate salts of metal complexes are potentially explosive, and should be handled with care.

4.2. Preparation of [Co(NiL)₂(H₂O)₂](ClO₄)₂

A mixture of [NiL] (0.11 g, 0.2 mmol), Co(ClO₄)₂ · 6H₂O (0.074 g, 0.2 mmol) and C₂H₅OH (70 ml) was stirred and heated to 70 °C for 25 min. The mixture was then cooled to room temperature and filtered. The filtrate was evaporated slowly at room temperature over 30 d and red crystals suitable for X-ray single-crystal investigation were obtained (yield 29.9%, 0.041 g). C₅₀H₅₂Cl₂CoN₈Ni₂O₂₂ (1364.25): calcd. C 43.98, H 3.84, N 8.21; found C 44.30, H 4.07, N 8.53.

4.3. X-ray structure analysis

Crystal data were collected by ω -scans technique with a Bruker Smart 1000-CCD area detector. Semi-empirical

Table 4. Data collection and processing parameters.

Empirical formula	C ₅₀ H ₅₂ Cl ₂ CoN ₈ Ni ₂ O ₂₂
Formula weight	1364.25
Temperature	293(2) K
Wavelength	0.71073 Å
Monochromator	Graphite
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>
Unit cell dimensions	<i>a</i> = 9.654(5) Å <i>b</i> = 12.089(6) Å <i>c</i> = 23.259(11) Å β = 94.021(9)°
Volume, <i>Z</i>	2708(2) Å ³ , 2
Calculated density	1.673 g/cm ³
Absorption coefficient	1.181 mm ⁻¹
<i>F</i> (000)	1402
Crystal size	0.25 × 0.20 × 0.10 mm
θ Range for data collection	2.35° to 25.03°
Limiting indices	−11 ≤ <i>h</i> ≤ 10, −8 ≤ <i>k</i> ≤ 14, −27 ≤ <i>l</i> ≤ 27
Reflections collected / unique	10178/4735 [<i>R</i> _{int} = 0.1604]
Completeness to θ = 25.03	98.9%
Max. and min. transmission	0.8911 and 0.7568
Data / parameters	4735 / 381
Goodness-of-fit on <i>F</i> ²	0.880
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0649, <i>wR</i> 2 = 0.1221
<i>R</i> indices (all data)	<i>R</i> 1 = 0.2194, <i>wR</i> 2 = 0.1670
Largest diff. peak and hole	0.507 and −0.873 e·Å ⁻³

absorption corrections were performed using the SADABS program. The structure was solved using Direct Methods and successive Fourier difference syntheses (SHELXS-97), and refined using the full-matrix least-squares method on *F*² with anisotropic displacement parameters for all non-hydrogen atoms (SHELXL-97) [37]. Hydrogen atoms were added theoretically and refined with riding model positional parameters and fixed isotropic displacement parameters. Further details of the structure analysis are given in Table 4.

5. Supplementary Material

CCDC-226801 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK].

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