Synthesis, Crystal Structure and Properties of a Cobalt(II) Coordination Polymer with Cyclohexane-1,2,3,4,5,6-hexacarboxylic Acid

Wei Xu and Yue-Qing Zheng

Center of Applied Solid State Chemistry Research, Ningbo University, Ningbo, 315211, P. R. China

Reprint requests to Prof. Dr. Yue-Qing Zheng. Fax: Int. +574/87600747.
E-mail: yqzhengmc@163.com

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Hydrothermal reaction of $CoCl_2 \cdot 6H_2O$, H_6chhc (all-*cis*-1,2,3,4,5,6-cyclohexanehexacarboxylic acid), phen (1,10-phenanthroline), and NaOH in aqueous solution afforded a new coordination polymer $Co(phen)(H_2O)(H_2chhc)_{1/2}$, which crystallizes in the space group $P\bar{1}$ with the cell constants a = 7.267(2), b = 10.749(2), c = 10.826(2) Å, α = 97.86(3), β = 103.62(3), γ = 95.00(3)°, V = 807.8(3) Å^3 and Z = 2. The $[Co(phen)(H_2O)]^{2+}$ cations in the title complex are interlinked by the di-protonated $(H_2chhc)^{4-}$ anions in a $\eta^6\mu_4$ bridging mode to form $^1_\infty[Co(phen)(H_2O)(H_2chhc)_{1/2}]$ polymer chains running along the [100] direction. Variable temperature magnetic susceptibility studies revealed the presence of weak, long-range antiferromagnetic ordering and zero-field splitting [$J = -0.32(5)$ cm^{-1} and D = 11.5(1) cm^{-1} with g = 2.306(4)]. The IR spectrum and results of thermal and elemental analyses are also presented.

Key words: Co(II) Complex, Cyclohexane-1,2,3,4,5,6-hexacarboxylic Acid, Coordination Polymer, Crystal Structure, Properties

Introduction

Current interest in coordination polymers is rapidly expanding owing to their intriguing structural topologies and their potential properties as functional materials [1 – 4]. In the past few decades, the development has allowed to rationally design and prepare supramolecular architectures [5 – 7]. Most studies have shown that the diversity of properties of the framework structures of such materials greatly depends on the selection of the metal centers and the organic spacers [8 – 10]. One particularly fruitful family of coordination polymers utilizes carboxylate ligands as organic spacers to bridge two or more metal centers thus creating 1D, 2D, and 3D networks. Although various rigid polycarboxylate ligands, such as benzenepolycarboxylates and pyridinepolycarboxylates, have been widely used to construct stable metal organic frameworks, only a few cases of carboxylic acid-type ligands with flexible backbones or an adaptable conformation, for example, cycloalkane-polycarboxylates and tetrahydrofuran-tetracarboxylates, have been reported so far [11 – 15]. As part of our ongoing systematic investigations on coordination polymers [16 – 18], our present work has been focused on the exploration of cyclohexane-1,2,3,4,5,6-hexacarboxylic acid (H_6chhc), a typical flexible cycloalkane polycarboxylic acid, which has a single-bonded ring skeleton in combination with equatorial or axial orientations of six carboxyl groups. The coordination chemisty of cyclohexane-1,2,3,4,5,6-hexacarboxylic acid has remained practically unexplored. Its great flexibility makes both the prediction and control of the final coordination networks more difficult [19 – 23]. Herein, we report the synthesis, structural characterization and magnetic properties of the complex $Co(phen)(H_2O)(H_2chhc)_{1/2}$ with partially deprotonated cyclohexane-1,2,3,4,5,6-hexacarboxylate H_2chhc^{4-} anions and 1,10-phenanthroline ligands.

Results and Discussion

Syntheses

Tong and coworkers have reported that, under hydrothermal conditions, reaction of $CoCl_2 \cdot 6H_2O$, cyclohexane-1,2,3,4,5,6-hexacarboxyic acid (all-*cis*), 2,2′-bipyridyl and NaOH, in an aqueous solution with the molar ratio of 1.5 : 0.5 : 1.0 : 1.5 at 175 °C, produced a 3D metal-organic framework [Co_3-

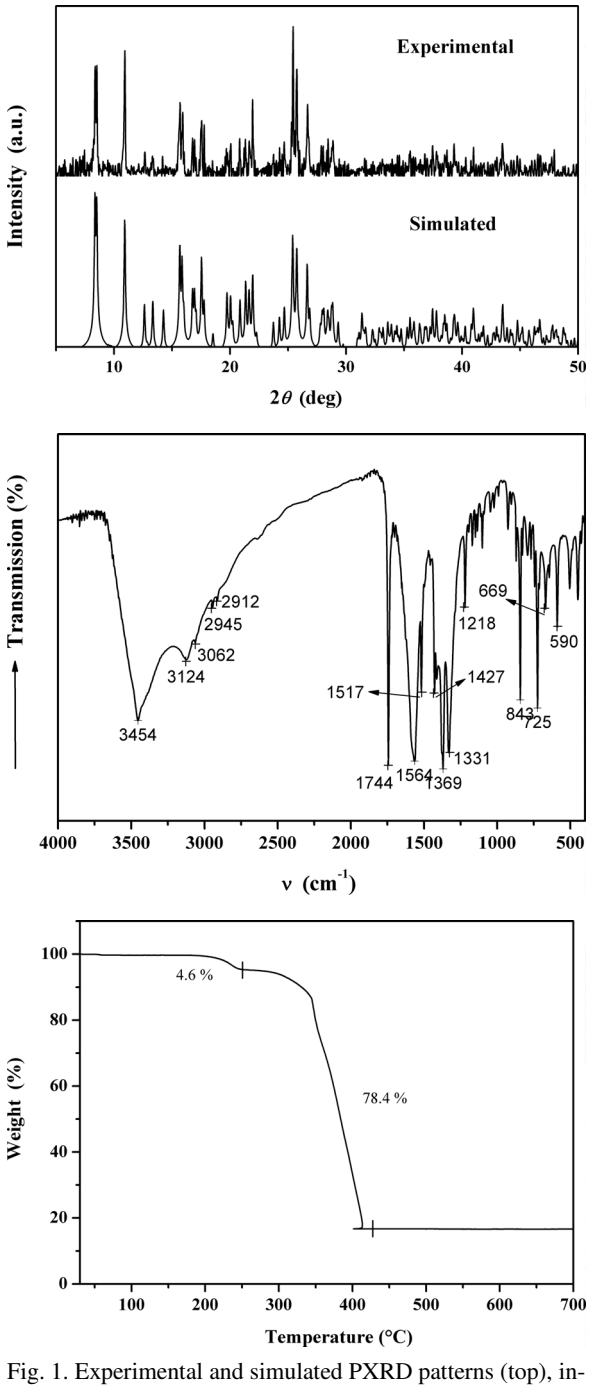

Fig. 1. Experimental and simulated PXRD patterns (top), infrared spectrum (middle), and TG curve for the title compound (bottom).

$(H_2O)_6(chhc)]_n$ [23]. We found that in the presence of 1,10-phenanthroline hydrothermal reactions of $CoCl_2 \cdot 6H_2O$, H_6chhc and NaOH in an aqueous solution in the molar ratio of 1.0 : 1.0 : 0.5 : 2 at 170 °C also yielded $[Co_3(H_2O)_6(chhc)]_n$ as a metal-organic framework. However, the molar ratio of $CoCl_2 \cdot 6H_2O$, H_6chhc, phen, and NaOH of 1.0 : 1.0 : 0.5 : 1.0 led to the formation of the 1D coordination polymer Co(phen)-$(H_2O)(H_2chhc)_{1/2}$. If the amount of NaOH is equivalent to 1.5 under the same conditions, we obtain a mixture of $[Co_3(H_2O)_6(chhc)]_n$ and Co(phen)(H_2O)-$(H_2chhc)_{1/2}$. The phase purity of the crystalline product was confirmed by comparing an experimental powder X-ray diffraction (PXRD) pattern with the one simulated on the basis of the single crystal data (Fig. 1), as well as by an elemental analysis. The title compound was found to be stable in air and insoluble in common solvents such as water, ethanol, acetone *etc*.

Description of the crystal structure

The asymmetric unit of the title compound contains one Co^{2+} cation, one phen ligand, one-half di-protonated cyclohexane-1,2,3,4,5,6-hexacarboxylate anion H_2chhc^{4-}, and one aqua ligand. As illustrated in Fig. 2, the H_2chhc^{4-} anions assume an *e*,*e*,*e*,*e*,*e*,*e*-conformation with the central ring adopting a chair-shaped conformation, the carboxylate and carboxyl groups being located at the equatorical sites, suggesting that the conformation of the ligand was changed from all-*cis* in the starting reagent into all-*trans* under the hydrothermal condition [23]. This configuration of the di-protonated cyclohexane-

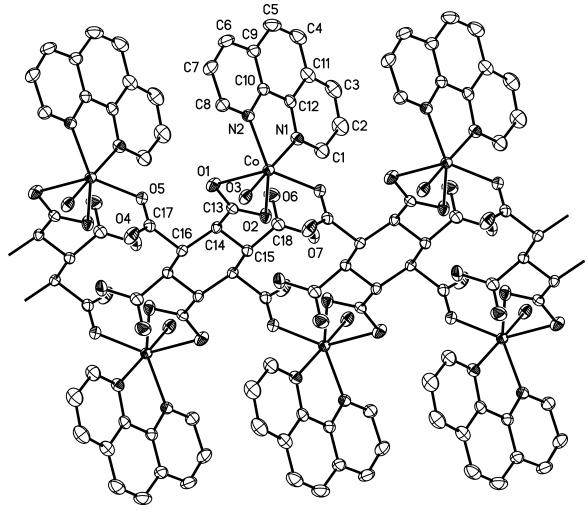

Fig. 2. ORTEP view of the polymer chain [Co(phen)(H_2O)-$(H_2chhc)_{1/2}]_n$ of the title compound. The displacement ellipsoids are drawn at 45 % probability level, hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths (Å), angles (deg) and hydrogen bond contacts for the title compound with estimated standard deviations in parentheses[a].

Distances			
Co–O1	2.356(2)	Co–O5$^{\#1}$	2.045(2)
Co–O2	2.163(2)	Co–N1	2.132(2)
Co–O3	2.071(2)	Co–N2	2.112(2)
Angles			
O1–Co–O2	57.59(7)	O2–Co–N2	141.77(8)
O1–Co–O3	87.59(8)	O3–Co–O5$^{\#1}$	88.84(8)
O1–Co–O5$^{\#1}$	143.29(7)	O3–Co–N1	171.92(9)
O1–Co–N1	99.90(9)	O3–Co–N2	99.28(8)
O1–Co–N2	89.87(8)	O5$^{\#1}$–Co–N1	86.93(9)
O2–Co–O3	98.76(8)	O5$^{\#1}$–Co–N2	126.73(8)
O2–Co–O5$^{\#1}$	86.99(8)	N1–Co–N2	77.87(9)
O2–Co–N1	87.90(8)		

Hydrogen bond contacts

D–H	d(D–H)	d(H···A)	d(D–H···A)	∠(D–H···A)	A
O3–H3B	0.83	2.05	2.827(3)	156	O1$^{\#2}$
O3–H3C	0.82	1.84	2.624(3)	160	O4$^{\#1}$
O7–H7B	0.85	1.85	2.695(3)	171	O2$^{\#3}$

[a] Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $x+1, y, z$; $^{\#2}$ $-x+1, -y+1, -z+2$; $^{\#2}$ $-x+1, -y+1, -z+1$.

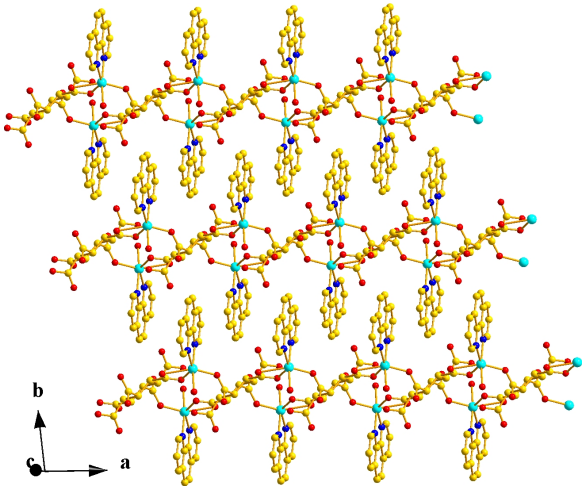

Fig. 3 (color online). A layer in the crystals of Co(phen)-(H_2O)(H_2chhc)$_{1/2}$ parallel to the (001) plane.

1,2,3,4,5,6-hexacarboxylate anions is identical to that observed in Ni_2(phen)$_2$(H_2chhc) [24]. The carboxylate groups display two coordination modes: the O4–C17–O5 group is monoatomically bonded to one metal ion, and the O1–C13–O2 group is chelating one metal ion. As a result, the anions exhibit an overall $\eta^6\mu_4$ coordination mode. The other carboxyl groups are not engaged in coordination to the metal ions and form strong hydrogen bonds to the neighboring carboxylate groups.

The Co atoms are octahedrally coordinated by two N atoms of a phen ligand and four O atoms of one H_2O molecule and two carboxylate groups from different H_2chhc^{4-} anions. The Co–O bond lengths fall in the range 2.045(2) – 2.356(2) Å, and the two Co–N distances are 2.112(2) and 2.132(1) Å (Table 1), thus falling in the expected region [25, 26]. In the title complex, the H_2chhc^{4-} anions are each coordinated to four $[Co(phen)(H_2O)]^{2+}$ units, leading to polymeric chains $^1_\infty$[Co(phen)(H_2O)(H_2chhc)$_{1/2}$] running along the [100] direction with the phen ligands *exo*-orientated, as shown in Fig. 2. In the chain, there are two intrachain hydrogen bonds, O3–H3C···O4$^{\#1}$ and O7–H7B···O2$^{\#3}$ (Table 1). The phen ligands of two adjacent supramolecular chains are stacked with the quinoline fragments at alternating distances of 3.47 and 3.56 Å. Obviously, these π-π stacking interactions are responsible for the supramolecular assembly of the chains into layers parallel to (001) (Fig. 3). The aqua ligands donate hydrogen atoms to the carboxylate oxygen atoms to form interlayer hydrogen bonds (d(O3···O1$^{\#2}$) = 2.827(3) Å, ∠O3–H3B···O1$^{\#2}$ = 156°, #2: $-x+1, -y+1, -z+2$), such that the layers are assembled into a three-dimensional supramolecular architecture.

Infrared spectra

The infrared spectrum (Fig. 1) in the range 4000 – 400 cm^{-1} shows a strong broad band centered at 3454 cm^{-1} due to the absorption from OH stretching vibrations of water molecules, in agreement with the X-ray crystallographic analysis described above. The absorption peak near 1744 cm^{-1} characteristic of a -COOH group is also observed. The strong absorption band centered at 1564 cm^{-1} is ascribed to the asymmetric stretching vibration of the -COO groups, while the symmetric stretching vibrations of the -COO group result in absorptions at 1427 and 1369 cm^{-1}.

The resulting $\Delta\nu_{\text{as-s}} = (\nu(CO_2)_{\text{asym}} - \nu(CO_2)_{\text{sym}})$ values of 137 and 195 cm^{-1} are consistent with the bidentate and monodentate fashion of the carboxylate groups, according to the established correlation of $\Delta\nu_{\text{as-s}}$ with the coordination modes of carboxylate groups [27]. As far as the 1,10-phenanthroline and 1,2,3,4,5,6-hexacarboxylate rings are concerned, the out-of-plane C–H bending vibrations cause weak absorptions at 3062, 2945 and 2912 cm^{-1}, respectively. The absorptions in the range 660 – 1218 cm^{-1} can be attributed to the skeletal vibrations of the phen ligand.

Thermal analysis

The thermogravimetric curve (Fig. 1) shows that the title complex decomposes in two steps. The compound is stable below 200 °C. The first weight loss of 4.6 % over the 200 – 250 °C range corresponds well to the calculated value of 4.2 % for one water molecule. The dehydrated intermediate thus may be stoichiometrically formulated as "Co(phen)(H_2chhc)$_{1/2}$". The weight loss of 78.4 % in the second step between 280 and 420 °C is in good agreement with the value of 78.4 % calculated for the decomposition of the organic ligands. The weight of the residue remaining after heating above 420 °C is 17.0 %, close to the calculated value of 17.4 % for one mol CoO.

Magnetic properties

The magnetic properities of the title complex are illustrated in Fig. 4 in the form of $\chi_m T$ and χ_m *versus* T plots (χ_m being the magnetic susceptibility per one Co(II) ion). At 300 K, the $\chi_m T$ value is 2.43 $cm^3\,mol^{-1}\,K$, which is slightly larger than the spin-only value of 1.88 $cm^3\,mol^{-1}\,K$ for one isolated Co(II) ion (S = 3/2 and g = 2.0). On lowering the temperature, the $\chi_m T$ value decreases gradually to *ca.* 2.33 $cm^3\,mol^{-1}\,K$ at 50 K, followed by an abrupt decrease to a maximum value of 1.43 $cm^3\,mol^{-1}\,K$ at 2 K, which suggests an overall long-range antiferromagnetic ordering. The best fit of the χ_m *versus* T plot to the Curie-Weiss equation $\chi_m = C/(T - \Theta)$ gave the Curie constant C = 2.50(4) $cm^3\,mol^{-1}\,K$ and the Weiss constant $\Theta = -1.76(6)$ K. The cyclohexane ring has a single-bonded ring skeleton offering no effective pathway to magnetic exchange. The above structure description shows that the effective transmitting pathway of the magnetic coupling between the magnetic centers may be through the intermolecular hydrogen bond interactions between the aqua ligand and the carboxylate groups. However, the zero field splitting and/or spin-orbit coupling may also play an important role regarding the magnetic properties, as commonly seen for species containing divalent cobalt. A fit of the data to the phenomenological Rueff expression (Eq. 1) [28 – 30], which has largely been used for modeling S = 3/2 was performed.

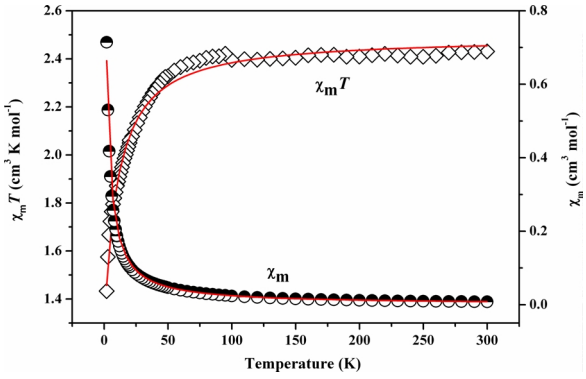

Fig. 4 (color online). Temperature dependence of the magnetic susceptibility of the title compound (χ_m being the magnetic susceptibility per one Co(II) ion). Solid lines represent the best fits.

$$\chi_m T = A^{-D/kT} + B^{J/kT} \qquad (1)$$

where $A + B = C = (5Ng^2\beta^2/4k)$.

The best fit values to Eq. 1 were A = 0.66(4) $cm^3\,mol^{-1}\,K$ and B = 1.83(5) $cm^3\,mol^{-1}\,K$, g = 2.306(4), J = −0.32(5) cm^{-1} and D = 11.5(1) cm^{-1}, with $R = 7.8 \times 10^{-4}$ ($R = \Sigma[(\chi_m)_{\text{obs}} - (\chi_m)_{\text{calc}}]^2/[(\chi_m)_{\text{obs}}]^2$). The fitting results indicate that the surrounding of Co(II) is to be descried as a strong-field state in a slightly distorted octahedral arrangement, which is consistent with the crystal structure. The small negative J and positive D values show the presence of weak, long-range antiferromagnetic ordering in this compound *via* a cooperation of single-ion effects.

Experimental Section

Materials

All chemicals of reagent grade were commercially available and used without further purification.

Physical methods

Powder X-ray diffraction measurements were carried out with a Bruker D8 Focus X-ray diffractometer to check the phase purity (CuK_α radiation; λ = 1.54056 Å). Single-crystal X-ray diffraction data were collected on a Rigaku

Table 2. Crystal structure data for **1**.

Formula	$C_{18}H_{14}CoN_2O_7$
M_r	429.24
Crystal size, mm^3	$0.28 \times 0.21 \times 0.17$
Crystal system	triclinic
Space group	$P\bar{1}$
a, Å	7.267(2)
b, Å	10.749(2)
c, Å	10.826(2)
α, deg	97.86(3)
β, deg	103.62(3)
γ, deg	95.00(3)
V, Å^3	807.8(3)
Z	2
D_{calcd}, g cm^{-3}	1.77
$\mu(MoK_\alpha)$, cm^{-1}	1.1
$F(000)$, e	438
hkl range	$-1 \le h \le 9$; $-13 \le k \le 13$; $-14 \le l \le 13$
$((\sin\theta)/\lambda)_{max}$, Å^{-1}	0.65
Refl. measured / unique / R_{int}	3704 / 2814 / 0.0324
Param. refined	253
$R1(F)$ / $wR2(F^2)$[a] (all refl.)	0.0649 / 0.0891
GoF (F^2)[b]	1.012
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	0.33 / −0.44

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o^2) + (0.0266P)^2 + 0.5362P]^{-1}$, where $P = (\mathrm{Max}(F_o^2,0) + 2F_c^2)/3$; [b] GoF $= [\Sigma w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$.

R-Axis Rapid IP X-ray diffractometer. The C, H and N microanalyses were performed with a PE 2400II CHNS elemental analyzer. The FT-IR spectrum was recorded in the range 4000 – 400 cm^{-1} on a Shimadzu FTIR-8900 spectrometer. A thermogravimetric measurement was carried out from r. t. to 700 °C on a pre-weighed sample using a Seiko Exstar 6000 TG/DTA 6300 apparatus with a heating rate of 10 °C min^{-1}. The temperature-dependent magnetic susceptibility was determined with a Quantum Design SQUID magnetomer (Model MPMS-7) in the temperature range 2 – 300 K with an applied field of 5 kOe, and the susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants [31].

Synthesis of Co(phen)(H_2O)(H_2chhc)$_{1/2}$

$CoCl_2 \cdot 6H_2O$ (0.2382 g, 1.0 mmol), all-*cis*-H_6chhc (0.1725 g, 0.50 mmol), phen (0.1996 g, 1.0 mmol), and NaOH 1.0 ml (1 mol L^{-1}) were stirred in 10 mL H_2O. The resulting mixture was placed in a 23 mL Teflon-lined autoclave and heated at 170 °C for 4 d. The reaction system was cooled to r. t. at a rate of 20 °C h^{-1}, and red crystals of the title complex were obtained (yield: 56 % based on initial $CoCl_2 \cdot 6H_2O$ input). – IR (film): ν = 3454s, 3142w, 3062w, 2945w, 2912w, 1744vs, 1564s, 1517m, 1427w, 1369s, 1331s, 1218m, 843s, 725s, 669w, 590m cm^{-1}. – $C_{18}H_{14}CoN_2O_7$ (429.24): calcd. C 50.37, H 3.29, N 22.84; found C 50.26, H 3.37, N 22.79.

X-Ray structure determination

A suitable single crystal was selected under a polarization microscope and fixed with epoxy cement on a fine glass fiber which was then mounted on a Rigaku R-Axis Rapid IP X-ray diffractometer, operating with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) for cell determination and subsequent data collection. The reflection intensities in the θ range 1.93 – 27.50° were collected at 295 K using the ω scan technique. The employed single crystal exhibited no detectable decay during the data collection. The data were corrected for Lp and empirical absorption effects. The SHELXS-97 and SHELXL-97 programs were used for structure solution and refinement [32]. The structure was solved by using Direct Methods. Subsequent difference Fourier syntheses enabled all non-hydrogen atoms to be located. After several refinement cycles, the hydrogen atoms associated with carbon atoms were geometrically generated, and the remainder of the hydrogen atoms were located from successive difference Fourier syntheses. Finally, all non-hydrogen atoms were refined with anisotropic displacement parameters by a full-matrix least-squares technique, and hydrogen atoms with isotropic displacement parameters were set to 1.2 times the values for the associated heavier atoms. Detailed information about the crystal data and structure determination is summarized in Table 2. Selected interatomic distances and bond angles are listed in Table 1.

CCDC 805724 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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