A Novel Mixed-Valence Cu^I/Cu^{II} Coordination Polymer: Solvothermal Synthesis, Crystal Structure, and Magnetic Properties of $Cu^ICu^{II}(2\text{-Pyrazinecarboxylate})_2(H_2O)(ClO_4)$

Cai-Ming Liu,*[a] De-Qing Zhang,*[a] Jian-Lin Luo,[b] Nan-Lin Wang,[b] Huai-Ming Hu,[a] and Dao-Ben Zhu*[a]

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The solvothermal reaction between $Cu(ClO_4)_2\cdot6H_2O$ and 2-pyrazinecarboxylic acid in methanol yields a novel mixed-valence Cu^I/Cu^{II} coordination polymer, $Cu^ICu^{II}(2\text{-pyrazinecarboxylate})_2(H_2O)(ClO_4)$ (**1**), in which a three-dimensional supramolecular array with square channels (9.3 × 9.3 Å) is formed through crisscross arrangement of the one-dimensional $Cu^ICu^{II}(2\text{-pyrazinecarboxylate})_2(H_2O)^+$ coordination polymer cation chains in the adjacent layers. Complex **1** exhibits weak ferromagnetic interactions.

Introduction

Crystal engineering of coordination polymers has been one of the most rapidly developing areas in the past decade, due mainly both to theoretical aspects related to the topologies of novel frameworks and to the interesting physical and chemical properties of these rationally designed functional solids.[1] Their potential applications have been demonstrated in, for example, nonlinear optical,[2] electrical,[3] and magnetism materials.[4] Furthermore, because specific pore size, type, and functions of cavity have become designable, their implications in molecular recognition and host-guest chemistry,[5] and also as zeolite mimics,[6] are particularly attractive. Generally, treatment of transition metal ions with rigid or flexible polyfunctional ligands by self-assembly processes is one basic strategy to afford varied polymers with such features as diamondoid, honeycomb grid, square grid, ladder, brick wall, and octahedral frameworks.[3−7] Hydro(solvo)thermal techniques have also been developed for the preparation of a series of coordination polymers.[2,6d,6e,8] Here we present the solvothermal synthesis, crystal structure, and magnetic properties of a novel mixed-valence Cu^I/Cu^{II} coordination polymer: $Cu^ICu^{II}(2\text{-pyrazinecarboxylate})_2(H_2O)(ClO_4)$ (**1**), in which the $Cu^ICu^{II}(2\text{-pyrazinecarboxylate})_2(H_2O)^+$ coordination polymer cation chains in adjacent layers are arranged in a cross-like fashion to generate a three-dimensional supramolecular array with square channels. In addition, the coordination polymer chain in complex **1** adopts an unusual *cis* configuration

Results and Discussion

Synthesis

Complex **1** was obtained as black blocks in 60% yield through a solvothermal reaction. A mixture of 2-pyrazinecarboxylic acid (0.4 mmol) and $Cu(ClO_4)_2\cdot6H_2O$ (0.4 mmol) in methanol (1 mL) was placed in a sealed thick Pyrex tube (ca. 20 cm long), which was kept at 80 °C under autogenous pressure for 2 d. The formation of Cu^I in **1** suggests that the methanol solvent and the 2-pyrazinecarboxylic acid may serve as effective reducing agents for Cu^{II} to Cu^I even under very mild solvothermal conditions. Similar trends have also been observed in the hydro(solvo)thermal syntheses of mixed-valence Cu^I/Cu^{II} tetranuclear complexes $[Cu_4(obpy)_4(tp)]$[9a] and $[Cu_4(ophen)_4(tp)]$[9a] (Hophen = 2-hydroxy-1,10-phenanthroline, Hobpy = 6-hydroxy-2,2′-bipyridine, tp = terephthalate) and mixed-valence Cu^I/Cu^{II} coordination polymers $[Cu_4\{1,4\text{-}C_6H_4(COO)_2\}_3(4,4'\text{-bipy})_2]_n$,[8a] $[Cu_2(ipO)(4,4'\text{-bpy})]$-(ipOH = 2-hydroxyisophthalate),[9b] $Cu^I_2Cu^{II}(hedpH_2)_2(4,4'\text{-bpy})_2\cdot2H_2O$ (hedp = 1-hydroxyethylidenediphosphonate),[9c] but higher temperatures were required.

Crystal Structure

As shown in Figure 1 (top), the crystal structure of **1** consists of one-dimensional $Cu^ICu^{II}(2\text{-pyrazinecarboxylate})_2(H_2O)$ cations and discrete perchlorate anions. Each Cu^{II}

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[a] Center for Molecular Science, Institute of Chemistry, Organic Solids Laboratory, Chinese Academy of Sciences,
Beijing 100080, P. R. China
E-mail: cmliu@iccas.ac.cn
[b] Institute of Physics, Chinese Academy of Sciences,
Beijing 100080, P. R. China

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atom is situated in a distorted square-pyramidal environment, with the two oxygen atoms and the two nitrogen atoms from two chelating 2-pyrazinecarboxylate ligands at the equatorial positions, and a coordinated water molecule at the apical position. The coordination environment of Cu^{II} in complex **1** is similar to that in [Cu(2-methylpyrazine-5-carboxylate)$_2$(H$_2$O)]·3H$_2$O,[10] but quite different from that in Cu(2-pyrazinecarboxylate)$_2$(H$_2$O)$_2$,[11] which has a disordered octahedral coordination sphere. The Cu^{II} centers in linear Cu(2-pyrazinecarboxylate)$_2$[11] and three-dimensional [Cu(pyzca)$_2$]$_2$Cd$_4$I$_8$]$_n$[12] (pyzca = 2-pyrazinecarboxylate) also have octahedral configurations. The Cu−Ow bond length of 2.228(9) Å (see Table 1) is similar to that in [Cu(2-methylpyrazine-5-carboxylate)$_2$(H$_2$O)]·3H$_2$O [2.257(2) Å],[9] but shorter than that in Cu(2-pyrazinecarboxylate)$_2$(H$_2$O)$_2$ (2.39 Å).[11]

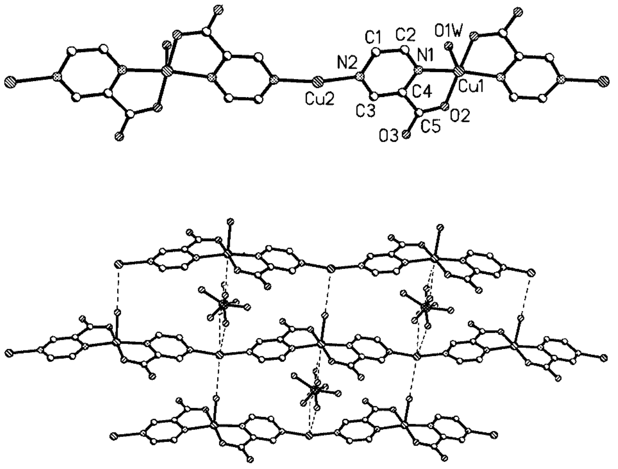

Figure 1. ORTEP figure of the cation chain in complex **1** at the 50% probability level showing the numbering scheme; all hydrogen atoms are omitted for clarity (top); illustration of the two-dimensional network layer formed by the mixed-valence Cu^{I}/Cu^{II} coordination polymer chains with Cu···O$_{perchlorate}$ short contacts (bottom)

Table 1. Selected distances [Å] and angles [°] for complex **1**; symmetry code: $^{\#1}$ $y - 1, x + 1, -z$; $^{\#2}$ $y, x, -z$

Cu(1)−N(1)	1.971(5)	Cu(1)−O(2)	1.941(3)
Cu(1)−O(2)$^{\#1}$	1.941(3)	Cu(1)−N(1)$^{\#1}$	1.971(5)
Cu(1)−O(1 W)	2.228(9)	Cu(2)−N(2)	1.949(5)
Cu(2)−N(2)$^{\#2}$	1.949(5)		
O(2)$^{\#1}$−Cu(1)−O(2)	176.0(3)	O(2)$^{\#1}$−Cu(1)−N(1)	96.39(16)
O(2)−Cu(1)−N(1)	83.18(16)	O(2)−Cu(1)−N(1)$^{\#1}$	96.39(16)
N(1)−Cu(1)−N(1)$^{\#1}$	167.7(4)	O(2)−Cu(1)−O(1 W)	92.02(13)
N(1)−Cu(1)−O(1 W)	96.2(2)	N(1)$^{\#1}$−Cu(1)−O(1 W)	96.2(2)
N(2)−Cu(2)−N(2)$^{\#2}$	161.2(3)		

The coordination sphere of the Cu^{I} site in complex **1** is defined by two crystallographically equivalent nitrogen donors from two Cu^{II}(2-pyrazinecarboxylate)$_2$(H$_2$O) molecules, with a Cu2−N2 distance of 1.949(5) Å. This coordination mode is quite similar to those of the Ag^{I} centers in Ag[Cu(2-methylpyrazine-5-carboxylate)$_2$(H$_2$O)$_2$]·(BF$_4$)[10] and Ag[Cu(2-methylpyrazine-5-carboxylate)$_2$(H$_2$O)$_2$]·(NO$_3$).[10] The N2−Cu2−N2^{i} (^{i} y, x, $-z$) bond angle of 161.2(3)° is a little smaller than the N2−Ag−N2 angle [165.7(2)°] in Ag[Cu(2-methylpyrazine-5-carboxylate)$_2$(H$_2$O)$_2$]·(BF$_4$),[10] but much larger than the N2−Ag−N2 angle [153.31(18)°] in Ag[Cu(2-methylpyrazine-5-carboxylate)$_2$(H$_2$O)$_2$]·(NO$_3$).[10]

The one-dimensional mixed-valence Cu^{I}/Cu^{II} cation chain is made up of alternating Cu^{I} centers and Cu^{II}(2-pyrazinecarboxylate)$_2$(H$_2$O) fragments. The intrachain Cu^{I}···Cu^{I}, Cu^{I}···Cu^{II}, and Cu^{II}···Cu^{II} distances are 13.203, 6.663, and 13.203 Å, respectively. Interestingly, all coordination water molecules in the same cation chain are arranged in a *cis* orientation. It is noteworthy that **1** is the first coordination polymer derived from 2-pyrazinecarboxylate known to adopt a *cis* configuration. Only a few examples of *cis* configurations in complexes of other carboxylate-substituted pyrazine derivatives are known, among them the two-dimensional {Cu$_2$(pzdc)$_2$(pyz)}$_n$ (pzdc = 2,3-pyrazinedicarboxylate, pyz = pyrazine),[13a] the one-dimensional {Co[pyz(COO)COOH]$_2$(H$_2$O)$_2$},[13b] and the mononuclear [NiL$_2$(H$_2$O)$_2$] (L = 1,4-dihydropyrazine-2,3-dione-5,6-dicarboxylate).[13c]

The disordered ClO$_4^-$ anions are located between a Cu^{I} center and a Cu^{II} center of adjacent mixed-valence Cu^{I}/Cu^{II} cation chains (the related interchain Cu^{II}···Cu^{I} distance is 7.508 Å), with the shortest Cu^{I}···O$_{perchlorate}$ contact 2.684 Å and the shortest Cu^{II}···O$_{perchlorate}$ contact 2.865 Å (Figure 1, bottom). The chlorine atom of the ClO$_4^-$ anion is a little closer to the Cu^{II} center than to the Cu^{I} center (the Cu···Cl contacts are 3.669 and 3.838 Å for Cu^{II} and Cu^{I}, respectively). The mixed-valence Cu^{I}/Cu^{II} coordination polymer chains are therefore bound to each other through ClO$_4^-$ anions to generate a two-dimensional network layer parallel to the *ab* plane with the shortest interchain Cu^{II}···Cu^{I} distance 5.695 Å.

Within a layer, all mixed-valence Cu^{I}/Cu^{II} coordination polymer chains show the same orientation (along one of two diagonal lines of the *ab* plane). However, chains from each pair of adjacent layers are always crisscrossed through the Cu^{I}···O$_{carboxylate}$ short contacts of 2.464 Å and the Ow···O$_{carboxylate}$ hydrogen bond of 2.720 Å (Figure 2), resulting in a three-dimensional supramolecular array with square channels (9.3 × 9.3 Å) running along the *c* axis (Figure 3). This structure is quite different from those of the Ag[Cu(2-methylpyrazine-5-carboxylate)$_2$(H$_2$O)$_2$]·(BF$_4$)[10] and Ag[Cu(2-methylpyrazine-5-carboxylate)$_2$(H$_2$O)$_2$]·(NO$_3$),[10] in which all the Cu^{II}/Ag^{I} mixed-metal coordination polymer chains run in one direction, so square cavities cannot be generated. To the best of our knowledge, the only reported example of chains in adjacent layers being arranged in a cross-like fashion to generate a three-dimensional supramolecular array with channels is [Cu(4,4′-bipy)(H$_2$O)$_3$(SO$_4$)]·2H$_2$O,[14] in which the adjacent chains of Cu(4,4′-bipy)(H$_2$O)$_3$(SO$_4$) are arranged in a cross-like fashion at the midpoints of the 4,4′-bipy ligands, and so rhombic channels (11.12 × 11.12 Å) are formed.

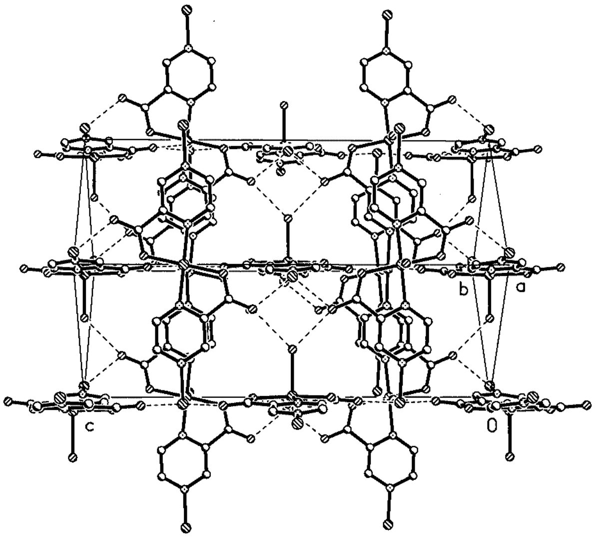

Figure 2. Perspective view showing some hydrogen bonds and short contacts between mixed-valence Cu^I/Cu^{II} coordination polymer chains from the same network layer and/or from neighboring network layers; all disordered perchlorate ions and hydrogen atoms are omitted for clarity

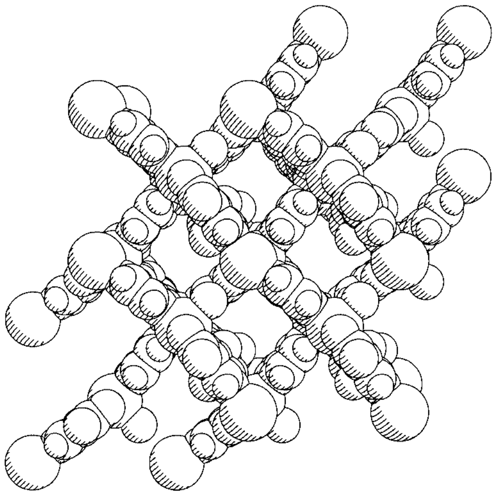

Figure 3. Space-filling model of complex **1**, viewed down the *c* axis

Magnetic Properties

The variation in the molar magnetic susceptibilities χ was investigated for complex **1** in the 5−300 K temperature range in a 10 kG applied field. The inset of Figure 4 shows that the χT value continuously increases with cooling while going from 250 to 9 K, and then drops down to 5 K, indicating the presence of a ferromagnetic exchange interaction. The room-temperature χT value of 0.375 emu·K·mol^{-1} is in good agreement with that of **1**, uncoupled $S = 1/2$ spins of Cu^{2+} atom ($\approx$ 0.375 emu·K·mol^{-1}; supposed $g = 2.0$ for Cu^{2+}), confirming that only half of the Cu atoms in complex **1** are Cu^{II} atoms. It was surprising to find that there is ferromagnetic exchange interaction between two Cu^{II} atoms 13.203 Å apart. Perhaps the uncoupled electron of the Cu^{II} atom is delocalized to some degree over the Cu^{II} and Cu^I centers. A quite recently reported mixed-oxidation-state Cu^I/Cu^{II} cluster complex $[(PAH)_4Cu^{II}_4Cu^I_2Br_{10}]$ (PAH = picolinamide hydrazone) also exhibited weak ferromagnetic exchange.[15] The temperature dependence of χ is interpreted in terms of a one-dimensional ferromagnetic chain,[16] by use of Equation (1) with $K = J/(2K_BT)$. The theoretical best fitting to the experimental data is obtained with $J/K_B = 1.80$ K and $C = 0.375$ emu·K·mol^{-1}. The deviation factor defined by $R = [(\chi_{obsd.} - \chi_{calcd.})^2/\chi_{obsd.}{}^2]^{1/2}$ is equal to 0.04437.

$$\chi = (C/T)[(1 + 5.7979916\,K + 16.902653\,K^2 + 29.376885\,K^3 + 29.832959\,K^4 + 14.036981\,K^5)/(1 + 1.27979916\,K + 7.0086780\,K^2 + 8.6538644\,K^3 + 4.5743114\,K^4)]^{2/3} \qquad (1)$$

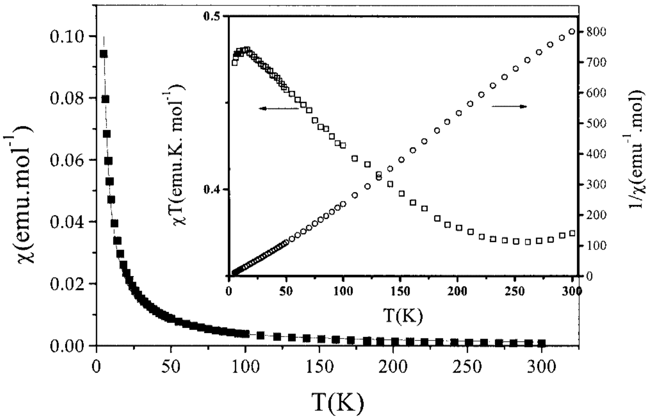

Figure 4. Temperature dependence of magnetic susceptibility of **1**: χ vs. T plots; inset, χT and/or χ^{-1} vs. T plots

IR and XPD Spectra

The strong and broad peak around 3454 cm^{-1} in the IR spectrum of complex **1** is mainly attributable to the presence of coordinated water molecules. The strong band at 1649 cm^{-1} is assignable to the antisymmetric C=O stretching vibration of the coordinated carboxylate group, while the strong band at 1120 cm^{-1} is typical of the uncoordinated perchlorate.

The powder XRD pattern of the complex and the pattern simulated on the basis of the single-crystal structure are presented in Figure 5. The diffraction peaks in both patterns correspond well in position, indicating the phase purity of the sample as synthesized.

In summary, this study illustrates that a three-dimensional supramolecular array with channels as exemplified by **1** can be achieved through crisscross arrangement of one-dimensional chains from parallel layers, and that solvothermal (or hydrothermal) synthesis is an effective method by which to obtain mixed-valence Cu^I/Cu^{II} coordination polymers.

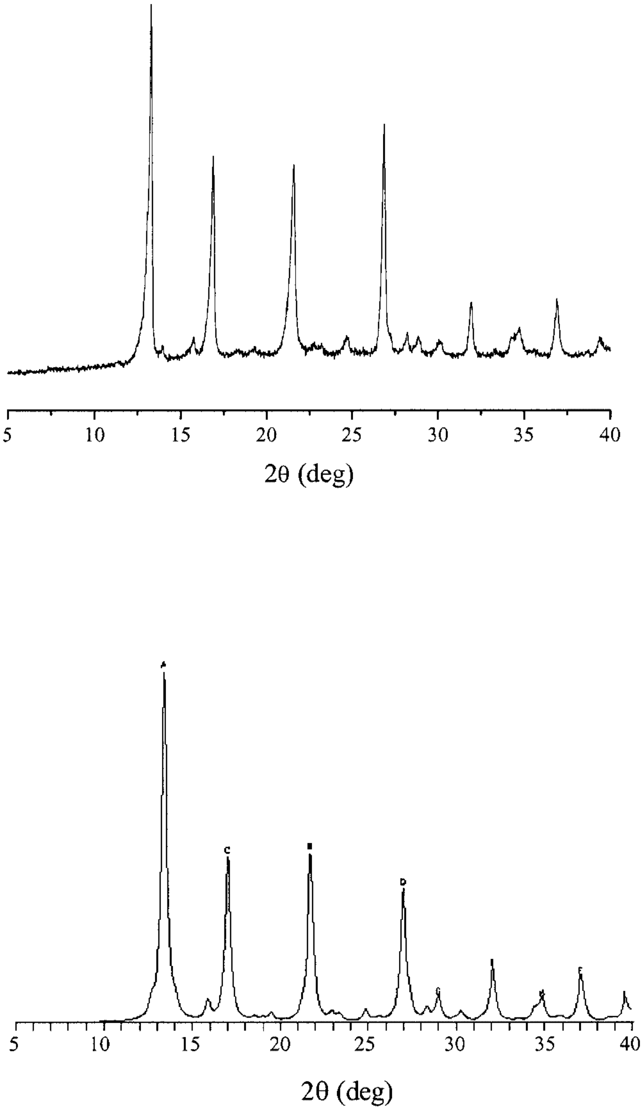

Figure 5. Experimental powder X-ray diffraction pattern of complex **1** (top) and the pattern calculated from the single-crystal data for complex **1** (bottom)

Experimental Section

General: All chemicals purchased were of reagent grade and were used without further purification. Elemental analyses (C, H and N) were performed with a Heraeus CHN-Rapid elemental analyzer. IR spectra were recorded with a Perkin−Elmer 2000 spectrophotometer on pressed KBr pellets. UV/Vis spectra were run with a U-3010 spectrophotometer. Powder X-ray diffraction (XRD) data were obtained with a Rigaku D/max-2500 X-ray diffractometer with Cu-K_α radiation ($\lambda = 1.5406$ Å). Variable-temperature magnetic susceptibility data were collected with a crystalline sample (11.75 mg) from 5 to 300 K in a magnetic field of 10 kG after zero-field cooling with a SQUID magnetometer. Diamagnetic corrections were estimated from Pascal's constants.

Synthesis of 1: A mixture of 2-pyrazinecarboxylic acid (0.4 mmol) and $Cu(ClO_4)_2{\cdot}6H_2O$ (0.4 mmol) in methanol (1 mL) was placed in a thick Pyrex tube (ca. 20 cm long), and the tube was frozen with liquid N_2, evacuated under vacuum, and sealed with a torch. The tube was then heated at 80 °C under autogenous pressure for 2 d to give dark crystals of **1** in 60% yield. An unidentified blue polycrystalline material was formed as a by-product. $C_{10}H_6ClCu_2N_4O_9$ (488.72): calcd. C 24.58, H 1.24, N 11.46; found C 24.49, H 1.32, N 11.40. UV (1×10^{-4} M, DMF): $\lambda_{max} = 273$ nm ($\varepsilon = 4.46 \times 10^4$ M^{-1}cm^{-1}), 691 nm (very broad peak, $\varepsilon = 729$ M^{-1}cm^{-1}).

***Caution:** $Cu(ClO_4)_2{\cdot}6H_2O$ is potentially explosive and should be handled with care!*

X-Ray Crystallography Analysis: The data were collected with a Rigaku RAXIS RAPID IP imaging plate system by use of Mo-K_α radiation ($\lambda = 0.71073$ Å). The structure was solved by the Patterson method and refined by a full-matrix, least-squares technique based on F^2 by use of the SHELXL 97 program. All non-hydrogen atoms except for the oxygen atoms of the perchlorate anion were refined anisotropically, and all hydrogen atoms other than those in coordinated hydrate molecule were allowed for as riding atoms. Crystal data for **1**: $C_{10}H_6ClCu_2N_4O_9$, tetragonal, space group $P4_12_12$, $M = 488.72$, $a = b = 9.3358(13)$, $c = 20.835(4)$ Å, $V = 1815.9(5)$ Å^3, $Z = 4$, $D_{calcd.} = 1.788$ gcm^{-3}, $T = 293(2)$K, $\mu = 2.539$ mm^{-1}, $R_1 = 0.0494$, $wR_2 = 0.0863$ for 1031 observed reflections[$I > 2\sigma(I)$] from 2071 independent reflections, GOF = 0.907. CCDC-187295 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, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

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