Linear recognition of dicarboxylates by ditopic macrocyclic complexes†‡

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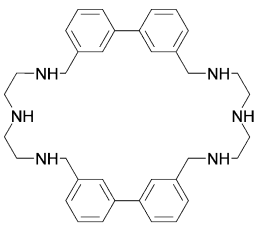
A new macrocyclic ligand, whose dicopper complex acts as a receptor for dianions in water at physiological pH, was prepared, and comparison with a structurally isomeric but larger complex demonstrates that the selectivity pattern for dicarboxylate binding obeys the principles of preorganization and linear recognition.

Dicarboxylate anions are among the most important targets for molecular recognition and sensing since several $-COO^-$ functional groups are present in a variety of molecules of biological relevance. Glutamate, for example, an amino acid containing two $-COO^-$ groups, is a major excitatory transmitter in the central nervous system and its sensitive determination is of great interest in a variety of areas of bioanalytical and biomedical research.[1] Moreover, considerable effort has been devoted to the development of ditopic anion receptors capable of signaling recognition events to be used as sensing probes for dicarboxylates.[2]

The use of receptors containing coordinatively unsaturated transition metal ions continues to attract much attention because of their ability to recognize anions even in very competitive media.[3] The final target of receptors for anions of biological interest is their use in physiological conditions, and metal–ligand interactions offer peculiar features to obtain this goal. They can be highly energetic as a result of the strong ligand–field stabilization energy effects induced by coordination. The energy of the metal–ligand interaction is, in most cases, much higher than the energy associated with electrostatic interactions, providing an obvious advantage for recognition purposes. Thus, d block metal complexes possessing one (or more) vacant binding site(s) can act as receptors for anions displaying coordinating properties. Polytopic ligands can be used to preorganize two or more metal centers in space so that a definite binding geometry can be achieved. These features can be exploited to gain high affinities and good selectivity.[4]

Herein, we describe the synthesis of the new ligand **1**, the preparation of its dicopper complex and the X-ray crystallographic characterization of the latter. Our aim was to compare the inclusion properties of the two dicopper(II) macrocyclic complexes obtained from ligands **1** and **2**,[5] whose dien subunits are linked by 3,3′-ditolyl and 4,4′-ditolyl spacers, respectively, which provide two cavities of different size between the two Cu(II) ions. Such cavities are suitable for inclusion of ambidentate anions whose donor groups are well separated, as in the case of linear aliphatic and aromatic dicarboxylates. By investigating the different binding tendencies of these receptors towards dicarboxylate anions, we demonstrate that selectivity between dianions of varying dimensions can be obtained with a simple ligand design based on co-linear fitting.



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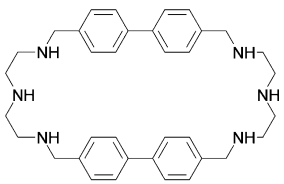

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X-Ray diffraction analysis of crystals grown from the $[Cu_2(\mathbf{1})](NO_3)_4$ complex revealed a structure in which molecules of Et_2O and H_2O are included. Macrocycle **1** acts as a ditopic ligand towards two metal centers and the two Cu(II) atoms appear in a square pyramidal coordination, with 3 secondary amines and a water molecule in equatorial positions, and an apical oxygen belonging to a nitrate anion (Fig. 1). Selected geometrical features are reported in the supplementary information.‡ The two metal centers show similar short equatorial bond distances and a long apical bond distance with the nitrate oxygen. Both metal centers are clearly displaced from the equatorial best plane towards the apical oxygen; these displacements are 0.21(1) Å for Cu(1) and 0.22(1) Å for Cu(2) and confirm the square pyramidal coordination for the two Cu(II) atoms.

In particular, even if the O(11) and O(7) nitrate oxygens are placed in positions that could produce an octahedral environment for the two metal centers, the distances from the Cu(II) atoms (Cu(1)–O(11): 2.77(1) and Cu(2)–O(7): 2.88(1) Å) are too large for any significant bond interaction.

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† The HTML version of this article has been enhanced with colour images.

‡ Electronic supplementary information (ESI) available: ^{1}H-NMR and ^{13}C-NMR spectra of **1**, selected bond distances in the crystal, a simplified sketch of the infinite molecular chains that form along the *a* axis in the crystal and a representative competitive spectrofluorimetric titration of $[Cu_2(\mathbf{1})]^{4+}$]. See DOI: 10.1039/b616492g.

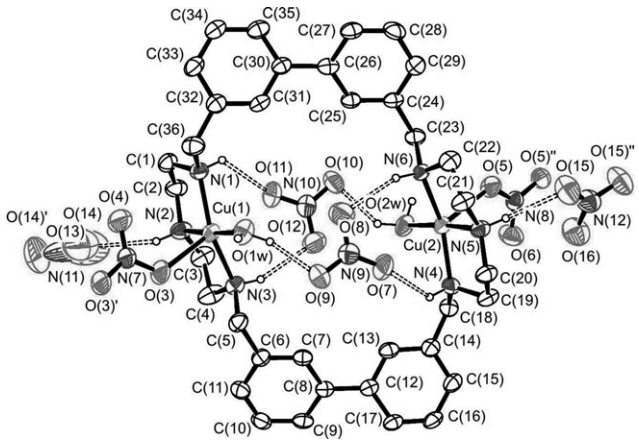


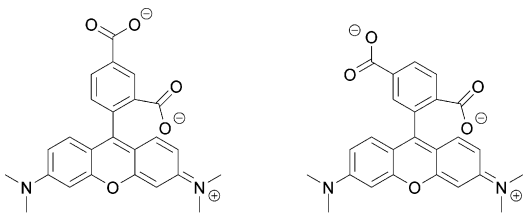
Fig. 1 An ORTEP plot of the $[Cu_2(\mathbf{1})(NO_3)_4(H_2O)_2]\cdot Et_2O\cdot 1.5(H_2O)$ crystal (thermal ellipsoids are drawn at the 30% probability level, only H bonded to secondary amines and to water molecules are shown, Et_2O solvent molecule and water molecules not bonded to metal centers have been omitted for clarity, symmetry code: $' = 1 - x, y, z$; $'' = 2 - x, y, z$). N(7), O(4), N(8), O(6), N(11), O(13), N(12) and O(16) atoms lie on two crystallographic mirror planes and this leads to the correct stoichiometry (1 : 4) between the $[Cu_2(\mathbf{L})(H_2O)_2]^{4+}$ cationic complex and the $(NO_3)^-$ anion groups. Dashed lines show the hydrogen-bond interactions.

The positions of these two nitrate groups, as well as those of the other nitrates not bonded to metal centers, are maintained by hydrogen-bond interactions: two with NH groups of the ligand and one with an OH group belonging to the coordinated water molecule (Fig. 1).

In the solid state, the apical nitrate groups bind two Cu(II) atoms from two symmetrically equivalent ditopic ligands to produce an infinite molecular chain parallel to the *a* axis of the crystal (see supplementary information‡). 1D chain structures have been previously observed in the crystal structure of $[Cu_2(\mathbf{2})](SO_4)_2$ molecular complex.[5b] In the $[Cu_2(\mathbf{2})](SO_4)_2$ crystal, the presence of the three nitrogen atoms from the diethylenetriamine moiety and the two oxygen atoms from two SO_4^{2-} anions assures a square pyramidal coordination for each Cu(II) atom, which is similar to that observed in the $[Cu_2(\mathbf{1})(NO_3)_4(H_2O)_2]$ crystal. However, the different spacers make the molecular chains quite different. In particular, the 3,3′-ditolyl spacers keep the two metal centers very close in the same macrocycle; the intramolecular Cu(1)–Cu(2) distance of 7.53(1) Å in the $[Cu_2(\mathbf{1})(NO_3)_4(H_2O)_2]$ complex has to be compared with the intramolecular Cu–Cu distance of 11.34 Å in the $[Cu_2(\mathbf{2})(SO_4)_2]$ crystal. Furthermore, macrocycle **1** in the $[Cu_2(\mathbf{1})(NO_3)_4(H_2O)_2]$ salt exhibits a chair-like conformation because the two diethylenetriamine moieties chelated to the metal center are placed above and below the bis(3,3′-ditolyl) best plane, whereas macrocycle **2** in the $[Cu_2(\mathbf{2})(SO_4)_2]$ crystal is in a boat-like conformation.

To measure affinities between receptors and anions, a spectrofluorimetric investigation was carried out following the chemosensing ensemble (CE) paradigm: a receptor **R** first interacts and quenches the emission of a fluorescent indicator **I**; then, the envisaged substrate **S** displaces **I** from the receptor cavity, **I** recovers its original fluorescence; thus signaling the recognition of **S**.[3a, 6] Using this approach, $[Cu_2(\mathbf{2})]^{4+}$ had already been investigated as an anion receptor, focusing on its affinity towards phosphates and adenine nucleotides.[5a]

The choice of the fluorescent indicator to be used in the chemosensing ensemble approach is crucial; a preliminary screening of several indicators to be used with $[Cu_2(\mathbf{1})]^{4+}$ was performed using various dyes containing one or two carboxylic functionalities. A buffered solution (HEPES 0.05 M, pH 7) of each indicator (5×10^{-7} M) was divided into four vials, and an increasing amount of receptor was added (respectively 0 (control), 1, 10 and 100 equivalents). Observation with UV light allowed estimation of the order of magnitude of receptor concentration needed to fully quench the dye emission, without performing a complete titration, and thus to choose the dyes with higher affinities for the receptors. The dyes used were fluorescein, 5-carboxyfluorescein, 6-carboxyfluorescein, 5-TAMRA (**3**) and 6-TAMRA (**4**). The test results indicated that the best affinities for receptor $[Cu_2(\mathbf{1})]^{4+}$ were obtained using 5-TAMRA and 5-CF (5-carboxyfluorescein), while the preference of $[Cu_2(\mathbf{2})]^{4+}$ for 6-CF and 6-TAMRA and the corresponding affinity constants had been established in previous work.[5a] 5- and 6-TAMRA were selected as the fluorescent indicators of choice for complexes $[Cu_2(\mathbf{1})]^{4+}$ and $[Cu_2(\mathbf{2})]^{4+}$, respectively, since they also demonstrated a higher photostability with respect to CF when used in the assays.



3 **4**

The high affinities of **3** and **4** for receptors $[Cu_2(\mathbf{1})]^{4+}$ and $[Cu_2(\mathbf{2})]^{4+}$, respectively, suggested that the 1,3- (or 1,4-) benzenedicarboxylate moieties are included within the macrocyclic complex and the two COO^- coordinate the two Cu(II) centers, in a bridging mode. In this situation, the two cations should be able to quench the fluorophore emission through either a mechanism of energy or electron transfer.[7] Moreover, the selectivities shown by the two macrocycles towards indicators **3** or **4** suggested an expected preference in the complexation of 1,3- or 1,4-aromatic dicarboxylates (see below). A spectrofluorimetric titration was performed and a complete quenching of indicator was obtained when adding an excess of $[Cu_2(\mathbf{1})]^{4+}$ (up to 50 equivalents) to indicator **3**. From the titration data (emission intensity *vs.* receptor concentration) the 1 : 1 association constant for receptor $[Cu_2(\mathbf{1})]^{4+}$ and indicator **3** was calculated, giving a log *K* value of 6.4 ± 0.2 M^{-1}.

The complexation ability of receptors $[Cu_2(\mathbf{1})]^{4+}$ and $[Cu_2(\mathbf{2})]^{4+}$ towards aromatic and aliphatic dicarboxylates was tested by means of competition assays. The solutions (buffered at pH 7 with 0.05 M HEPES) were composed of a mixture of indicator and receptor at a concentration that ensures quantitative complexation and thus almost complete quenching of the indicator, as calculated from the **I** + **R** quenching titrations. At the complex concentration used, only

Table 1 Association constants (log units) between receptors and anions

	$[Cu_2(\mathbf{1})]^{4+}$	$[Cu_2(\mathbf{2})]^{4+}$	$[Cu_2(\mathbf{5})]^{4+}$
Phthalate	5.0(3)	5.6(3)	4.0(2)
Isophthalate	5.6(3)	7.1(3)	4.8(2)
Terephthalate	4.1(3)	7.4(3)	8.0(2)
Malonate[a] (n = 1)	4.9(2)	4.1(2)	—
Succinate[a] (n = 2)	5.5(2)	5.6(2)	4.1(2)
Glutarate[a] (n = 3)	5.2(3)	6.2(2)	6.9(2)
Adipate[a] (n = 4)	4.2(3)	6.3(2)	7.0(2)
Pimelate[a] (n = 5)	4.0(3)	5.7(2)	4.8(2)

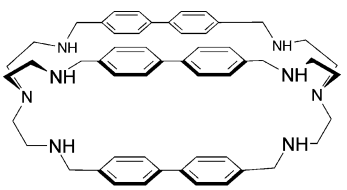
[a] Dicarboxylates $^{-}OOC–(CH_2)_n–COO^{-}$, with n ranging from 1 to 5. Values for complex $[Cu_2(\mathbf{5})]^{4+}$ are taken from ref. 7.

the 1 : 1 indicator to receptor complex was calculated to be present. For each receptor–indicator couple, standard solutions of anions were added, and the emission spectra were recorded. Spectrofluorimetric titration data were processed, and the receptor association constants were calculated. Data are summarized in Table 1.

Fig. 2 graphically illustrates the trends of the calculated affinity constants for the aromatic dicarboxylates investigated. As can be clearly seen from comparison between Fig. 2a and b, different selectivity patterns are observed on the basis of intercationic distance. In the case of receptor $[Cu_2(\mathbf{2})]^{4+}$, a preference is observed for terephthalate, having the two carboxylate functionalities further apart, while in the case of $[Cu_2(\mathbf{1})]^{4+}$ preference is observed for the 1,3-isomer, isophthalate. In other words, in the "smaller" receptor the isophthalate fragment is preferred, as already expected from its preference for 5-TAMRA and 5 CF.

Fig. 3 shows the calculated stability constants as a function of the aliphatic chain length connecting the two anionic functions for the series of linear aliphatic dicarboxylates $^{-}OOC–(CH_2)_n–COO^{-}$, with n ranging from 1 to 5. Once again, a certain degree of selectivity was observed with both receptors. In particular, Fig. 3b represents the situation for $[Cu_2(\mathbf{2})]^{4+}$. In this case, glutarate (n = 3) and adipate (n = 4) show the highest inclusion constants, while upon shortening and elongation of the aliphatic chain joining the $–COO^{-}$ groups a lower affinity was calculated. This situation is reminiscent of what was observed with the dicopper complex of bistren cage **5**, where in the same conditions a strong peak selectivity for linear aliphatic dicarboxylates[7] with n = 3–4 was observed, although in that case log K's were one log unit higher.

Moving to $[Cu_2(\mathbf{1})]^{4+}$, the situation changes. As observed in Fig. 3a, the selectivity peak shifts to n = 2–3; the highest affinity is found for succinate, while all other anions are too long to fit the quite short Cu–Cu distance. Furthermore, the stability constants for the best matching anions of selectivity peaks are distinctly lower for the two macrocyclic complexes $[Cu_2(\mathbf{1})]^{4+}$ and $[Cu_2(\mathbf{2})]^{4+}$ than for the cryptate complex $[Cu_2(\mathbf{5})]^{4+}$. One would predict that preorganization of the cage structure of $[Cu_2(\mathbf{5})]^{4+}$ should result in generally higher affinities, as stated by the preorganization principle:[8] "the more highly hosts and guests are organized for binding and for low solvation prior to their complexation, the more stable will be their complexes." However, the rigidity of $[Cu_2(\mathbf{5})]^{4+}$, as compared to the relative flexibility of $[Cu_2(\mathbf{1})]^{4+}$ and $[Cu_2(\mathbf{2})]^{4+}$, accounts for the lower stability constants of $[Cu_2(\mathbf{5})]^{4+}$ with non-fitting anions; the overall effect is the very high selectivity of $[Cu_2(\mathbf{5})]^{4+}$, which is reduced for the two macrocyclic complexes here described. Even the comparison of the log K values obtained for $[Cu_2(\mathbf{1})]^{4+}$ and $[Cu_2(\mathbf{2})]^{4+}$ give some important advice. Complex $[Cu_2(\mathbf{1})]^{4+}$ shows generally lower affinities for the best matching anions, *i.e.* for the selectivity peaks. This behaviour has to be ascribed to the greater flexibility of one of the receptors. $[Cu_2(\mathbf{1})]^{4+}$ possesses two 3,3′-ditolyl spacers, and the free rotation around the aryl–aryl bond allows for the presence of a family of conformations in which the distance between the polyamino fragments of the macrocycle can be substantially varied as the substituents in the 3- and 3′-positions are in a *syn* or *anti* configuration with respect to each other.[13]



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In summary, a new macrocyclic ligand was prepared, and the X-ray structure of the dicopper complex was solved, showing a peculiar molecular infinite chain of macrocycles connected by bridging anions. This work has demonstrated

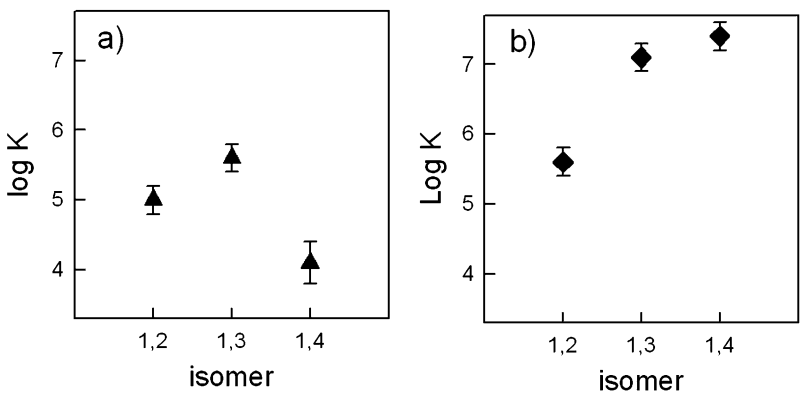

Fig. 2 Equilibrium constants for the interaction of receptors $[Cu_2(\mathbf{1})]^{4+}$ (a) and $[Cu_2(\mathbf{2})]^{4+}$ (b) with 1,n-benzenedicarboxylates.

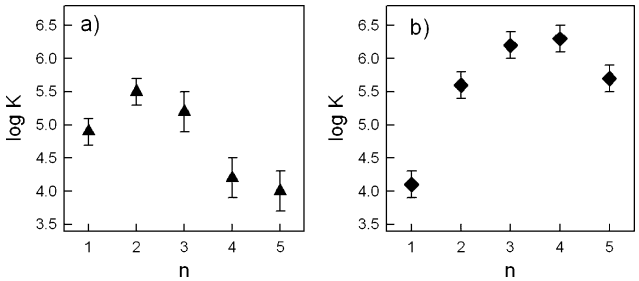

Fig. 3 Equilibrium constants for the interaction of receptors $[Cu_2(\mathbf{1})]^{4+}$ (a) and $[Cu_2(\mathbf{2})]^{4+}$ (b) with $^{-}OOC–(CH_2)_n–COO^{-}$ dicarboxylates. In abscissa, n = number of methylene groups in the spacer.

that the dicopper(II) complex of **1** and **2** are suitable receptors for dicarboxylates, which can be discriminated on the basis of the distance between their functional groups. The investigated macrocyclic complexes show selectivity patterns which obey the principle of linear molecular recognition,[9] based on ditopic binding between two copper ions. Noticeably, changing the length of the spacer allows the selective recognition of $^{-}OOC–(CH_2)_n–COO^{-}$ dicarboxylates with different n values. As expected, the highest affinities and best discrimination factors are obtained with more rigid receptors, as one can see from comparison of the stability constants obtained with $[Cu_2(\mathbf{5})]^{4+}$, $[Cu_2(\mathbf{2})]^{4+}$ and $[Cu_2(\mathbf{1})]^{4+}$.

Recognition in pure water at pH 7—a rare occurrence when anion recognition is based on electrostatic interactions or hydrogen bonding[3,4]—has been obtained using strong metal–ligand interactions. Moreover, it has been demonstrated once again that the use of a fluorescent indicator in an indicator displacement approach provides sharp signaling of the recognition event and an easy evaluation of the affinities of the receptors towards the investigated species.

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Experimental

Synthesis

3,3′-Diformylbiphenyl was prepared according to a reported method.[10]

Macrocycle **1** was prepared according to the procedure described by Chen and Martell.[11] ESI-MS: m/z (%) = 563 $[M + H]^+$ (100). ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C) δ = 7.57 (s, 4H; H-2,2′ditolyl), 7.45 (d, 4H; H-6,6′ditolyl), 7.33 (t, 4H; H-5,5′ditolyl), 7.25 (d, 4H; H-4,4′ditolyl), 3.83 (s, 8H; benzylic), 2.75 (m, 16 H; $–NHCH_2CH_2NH–$). ^{13}C-NMR (75 MHz, $CDCl_3$, 25 °C) δ = 141.2, 140.9, 128.6, 127.0, 126.8, 125.6, 53.9, 49.1, 48.7.

Synthesis of **2** has been reported elsewhere.[5a]

The dicopper complex $[Cu_2(\mathbf{1})(NO_3)_4]$ was prepared by mixing two equivalents of copper nitrate with **1** dissolved in hot methanol. After warming the sample and removing half of the solvent, a blue product was separated by filtration, $[Cu_2(\mathbf{1})(NO_3)_4]$. Elemental analysis calcd for $C_{36}H_{46}N_{10}O_{12}Cu_2$: C 46.01, H 4.94, N 14.93; found: C 45.78, H 5.01, N 14.71%. Part of the product was redissolved in methanol and, after slow diffusion of diethyl ether, blue crystals of $[Cu_2(\mathbf{1})(NO_3)_4(H_2O)_2]\cdot Et_2O\cdot 1.5(H_2O)$ suitable for X-ray analysis were obtained.

The same strategy was used for complex $[Cu_2(\mathbf{2})(NO_3)_4]$. A blue product was obtained. Elemental analysis calcd for $C_{36}H_{46}N_{10}O_{12}Cu_2$: C 46.01, H 4.94, N 14.93; found: C 45.87, H 5.05, N 14.81%.

Association constant determination

Determination of apparent association constants between the receptors and the indicators was carried out in a deaerated water solution buffered at pH = 7 with HEPES 0.05 M; concentration of the indicator was 2.5×10^{-7} M. Aliquots of a fresh standard solution of receptor complexes were added, and emission spectra of the indicators were recorded (λ_{exc} = 496 nm, isosbestic point). The chemosensing ensemble solution for competition assays was prepared by adding $[Cu_2(\mathbf{1})(NO_3)_4]$ (5×10^{-6} M) or $[Cu_2(\mathbf{2})(NO_3)_4]$ (2.5×10^{-6} M) to an aqueous solution, buffered at pH = 7 with HEPES 0.05 M, containing the indicators **3** (10^{-6} M). or **4** (2.5×10^{-7} M). The chemosensing ensemble solutions were titrated with standard solutions of anions. All spectrofluorimetric titration curves were fitted with the HYPERQUAD program[12] to evaluate the apparent association constant between receptors and indicators, and between receptors and anions.

X-Ray crystallography

Diffraction data frames collected on a Bruker-Axs SMART-APEX CCD based diffractometer were processed with the Bruker-Axs SAINT[14] software; absorption was empirically determined using SADABS[15] (0.776–0.949 min–max transmission factors). The structure was solved using SIR97[16] and refined by full matrix least squares on all F^2 with SHELXL-97.[17] Protons of water groups bonded to metal centers were located in the final ΔF maps, other H atoms were placed at the calculated positions.

Crystal data of $[Cu_2(\mathbf{1})(NO_3)_4(H_2O)_2]\cdot Et_2O\cdot 1.5(H_2O)$. $C_{40}H_{63}Cu_2N_{10}O_{16.5}$, M = 1075.08, orthorhombic, space group $Pmc2_1$ (No. 26), a = 25.430(4), b = 11.865(2), c = 16.688(2) Å, β = 90°, V = 5035.2(12) Å^3, Z = 4, Dc = 1.418 g cm^{-3}, F_{000} = 2252, MoKα radiation, λ = 0.71073 Å, μ = 0.921 mm^{-1}, T = 293(2) K, $2\theta_{max}$ = 50.2, 33 235 reflections collected, 9186 unique (R_{int} = 0.0673), 6083 with $I > 2\sigma(I)$, GoF = 1.013, $R1$ = 0.0976, w$R2$ = 0.1708 (all reflections). CCDC 633936. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b616492g

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