Anion Sensors

A Dimetallic Cage with a Long Ellipsoidal Cavity for the Fluorescent Detection of Dicarboxylate Anions in Water**

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Host–guest chemistry is governed by the principle of size and shape complementarity: given a particular guest, a concave host must be designed whose cavity presents geometrical features complementary to those of the guest.[1] Moreover, the cavity must offer groups capable of establishing strong yet reversible interactions with the guest. A classical example is provided by octamine cages such as **1** and **2**, in which two tren subunits (tren = tris(2-aminoethyl)amine) are linked by either aliphatic (-CH_2CH_2-, **1**) or aromatic (1,3-xylyl, **2**) spacers. In aqueous acidic solution, the six secondary amine

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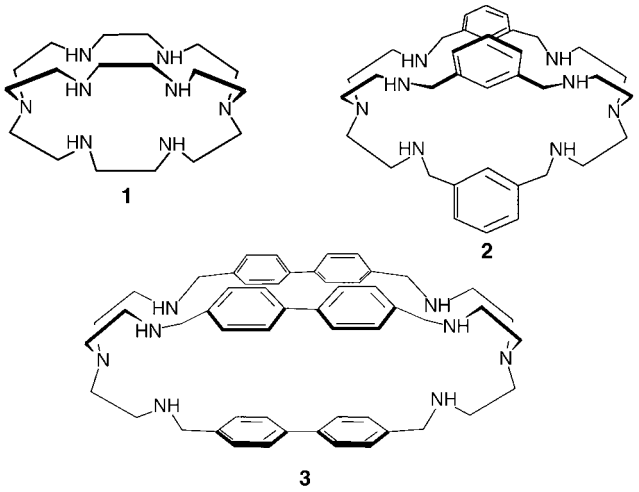


nitrogen atoms of each cage are protonated and the positively charged cavity is suitable for the inclusion of an inorganic anion.[2] The length of the spacer defines the shape and the size of the cavity and the selectivity towards the anion. The hexammonium cage **1** provides a spherical cavity and selectively includes the spherical F^- ion.[3] The hexammonium cage **2** offers an ellipsoidal cavity suitable for the inclusion of the rodlike ion N_3^-.[4] However, other positively charged species, namely transition metal ions, can be placed within a bistren cage for interaction with an included anion. In particular, the dicopper(II) complex with the all-amine cryptand **2** incorporates ambidentate anions such as N_3^-,[5] NCO^-,[5] and HCO_3^-[6] to give stable inclusion complexes: Each metal center is coordinated by a tren subunit in a trigonal bipyramidal arrangement, and an axial position is available for interaction with a further ligand. Thus, an ambidentate anion such as N_3^- can place its terminal donor atoms in the two available axial sites to bridge the two Cu^{II} centers. Equilibrium investigations in water at pH 7 have shown that the dicopper(II) cryptate of **2** selectively incorporates N_3^- to give a very stable inclusion complex[7] in which the Cu^{II}–Cu^{II} distance is 6.10 Å. Anions with either a shorter (e.g. NO_3^-) or a larger (e.g. NCS^-) "bite" ("bite" indicates the distance between two consecutive donor atoms) show a distinctly lower affinity towards inclusion.

Herein we describe the inclusion properties of the dicopper(II) cryptate complex with the polycyclic octamine ligand **3**, whose tren subunits are linked by 4,4′-ditolyl spacers to provide an unusually long ellipsoidal cavity. Such a cavity is suitable for inclusion of ambidentate anions whose donor groups are well separated, as may be the case with either aromatic or aliphatic dicarboxylates. Dicarboxylate anions are among the most attractive targets for molecular recognition and sensing since several -COO^- functional groups are present in a variety of biomolecules such as amino acids and proteins. As an example, the glutamate ion, an amino acid containing two -COO^- groups, is a major excitatory transmitter in the central nervous system and its determination both temporally and spatially is required by neurophysiologists.[8]

Cryptand **3** was obtained in good yield through a modification of a reported procedure,[9] followed by the slow evaporation of an aqueous solution containing **3** and copper(II) nitrate (1:2) to yield crystals of a complex of formula $[Cu^{II}_2(\mathbf{3})(H_2O)_2](NO_3)_4\cdot 2H_2O$ of suitable quality for X-ray diffraction studies.[10] The structure of the dimetallic complex is shown as an ORTEP plot in Figure 1. Both

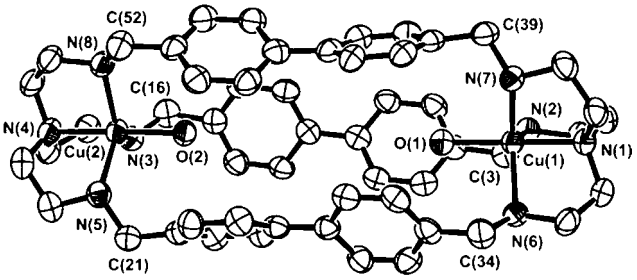
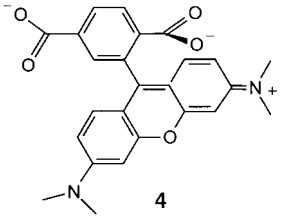


Figure 1. An ORTEP view of the $[Cu^{II}_2(\mathbf{3})(H_2O)_2](NO_3)_4\cdot 2H_2O$ complex. Thermal ellipsoids are drawn at the 30% probability level. Hydrogen atoms, four nitrate counterions, and two isolated water molecules have been omitted for clarity. Element symbols are reported only for atoms bonded to metal centers and for carbon atoms that define the three ditolyl spacers. Selected bond lengths [Å] and angles [°] around the two Cu^{II} metal centers: Cu(1)-N(1) 2.001(3); Cu(2)-N(4) 2.000(3); Cu(1)-N(2) 2.140(4); Cu(2)-N(3) 2.152(4); Cu(1)-N(6) 2.131(3); Cu(2)-N(5) 2.160(4); Cu(1)-N(7) 2.134(3); Cu(2)-N(8) 2.124(4); Cu(1)-O(1) 1.982(3); Cu(2)-O(2) 1.971(3); N(1)-Cu(1)-N(2) 85.91(13); N(4)-Cu(2)-N(3) 86.25(16); N(1)-Cu(1)-N(6) 85.19(14); N(4)-Cu(2)-N(5) 84.80(15); N(1)-Cu(1)-N(7) 85.43(14); N(4)-Cu(2)-N(8) 85.27(14); N(1)-Cu(1)-O(1) 179.86(14); N(4)-Cu(2)-O(2) 178.42(15); N(2)-Cu(1)-N(6) 119.80(14); N(3)-Cu(2)-N(5) 118.82(14); N(2)-Cu(1)-N(7) 115.82(14); N(3)-Cu(2)-N(8) 120.72(15); N(2)-Cu(1)-O(1) 94.06(13); N(3)-Cu(2)-O(2) 92.54(15); N(6)-Cu(1)-N(7) 122.55(14); N(5)-Cu(2)-N(8) 118.58(15); N(6)-Cu(1)-O(1) 94.95(12); N(5)-Cu(2)-O(2) 94.90(13); N(7)-Cu(1)-O(1) 94.45(12); N(8)-Cu(2)-O(2) 96.24(14).

copper(II) ions are included within the cage and are coordinatively bound to the tren subunits. In particular, each Cu^{II} ion shows a trigonal bipyramidal coordination and, as usually observed with Cu^{II} complexes of tren derivatives, the equatorial Cu–N bond lengths (mean values of 2.135(4) Å for Cu(1), and 2.145(4) Å for Cu(2)) are longer than the axial Cu–N bond lengths of 2.001(3) and 2.000(3) Å, respectively. The other axial site is occupied by a water molecule. In particular, the Cu–O bond lengths (1.982(3) and 1.971(3) Å) are similar to that observed in the mononuclear precursor complex $[Cu^{II}(tren)(H_2O)]^{2+}$ (1.975(6) Å).[15] The three ditolyl spacers show dihedral angles between the phenyl planes of 32.8(2), 34.3(2), and 36.8(2)°. Similar values have been observed in the crystalline 4,4′-ditolyl compound (36 and 40° for the two molecules present in the asymmetric unit).[16] This suggests the absence of any steric constraints in the carbon backbone of the cage. The presence of especially long spacers results in a Cu–Cu separation of 11.305(6) Å, which is the longest distance ever observed for dimetallic bistren cryptate complexes.

The inclusion tendencies of the $[Cu^{II}_2(\mathbf{3})(H_2O)_2]^{4+}$ complex towards dicarboxylates were investigated in neutral aqueous solution following the "fluorescent indicator dis-

placement" approach.[17] According to this approach, a receptor **R** (e.g. the cryptate complex $[Cu_2^{II}(\mathbf{3})(H_2O)_2]^{4+}$) first binds and quenches a fluorescent indicator **I**. Then, the envisaged substrate **S** (e.g. a dicarboxylate ion) displaces **I** from the receptor cavity and allows **I** to fluoresce again, thus signalling the binding of **S**. We chose carboxy-rhodamine (**4**) as the fluorescent indicator; **4** contains two carboxylate groups and emits at 571 nm (orange fluorescence) upon excitation at 496 nm (isosbestic point).



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First, we investigated the interaction of rhodamine with the receptor $[Cu_2^{II}(\mathbf{3})(H_2O)_2]^{4+}$. An aqueous HEPES-buffered solution (pH 7) of the fluorescent indicator (2.5×10^{-7} M), was titrated with a standard solution of the cryptate complex. Addition of the dicopper complex induced a gradual decrease of the fluorescence intensity I_F of **4** until complete quenching occurred as shown in Figure 2. Least-squares nonlinear fitting of the titration profile (Figure 2, inset)[18] indicates the formation of a 1:1 adduct between the cryptate and **4** with an association constant $\log K_I = 7.0 \pm 0.2$. This suggests that the benzene-1,4-dicarboxylate moiety of **4** is included within the cryptate and the two -COO^- groups coordinate the two Cu^{II} centers. In this situation, the transition metal centers could effectively quench the fluorophore through either an electron transfer or an electronic energy transfer process.

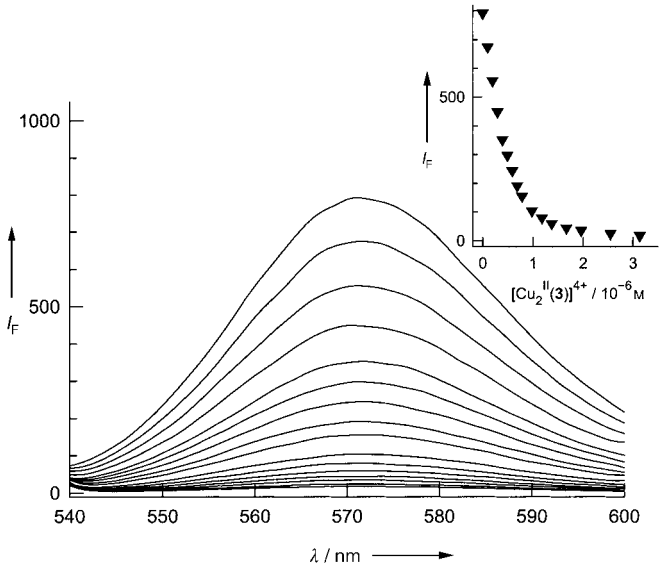

Figure 2. Emission spectra of an aqueous solution of the rhodamine indicator **4** (2.5×10^{-7} M) when titrated with the complex $[Cu_2^{II}(\mathbf{3})]^{4+}$. Inset: titration profile (I_F versus the concentration of $[Cu_2^{II}(\mathbf{3})]^{4+}$).

We then prepared an aqueous solution containing the cryptate complex $[Cu_2^{II}(\mathbf{3})]^{4+}$ (2.5×10^{-6} M) and the indicator **4** (2.5×10^{-7} M) whose fluorescence was thereby completely quenched through its incorporation into the complex. Then, the solution was adjusted to pH 7 and was titrated with a selection of dicarboxylate substrates.

Initially, we considered the family of positional phthalate isomers. We observed that titration with benzene-1,2-dicarboxylate (phthalate) and benzene-1,3-dicarboxylate (isophthalate) derivatives led to no (1,2-) or only minor (1,3-) rhodamine fluorescence emission (see Figure 3). However,

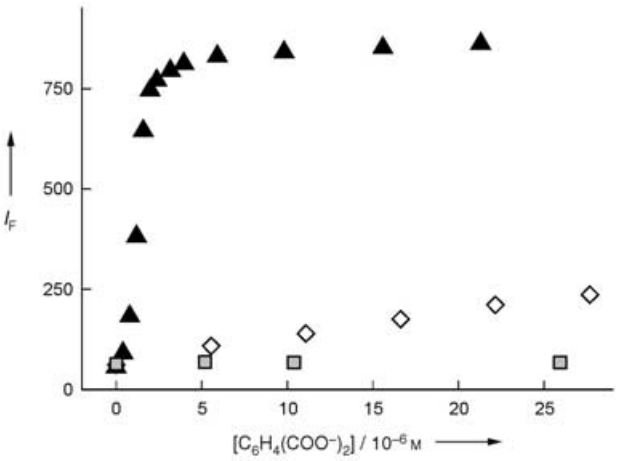

Figure 3. Titration of a solution of $[Cu_2^{II}(\mathbf{3})]^{4+}$ (2.5×10^{-6} M) and **4** (2.5×10^{-7} M) with *m*,*n*-benzenedicarboxylates in an aqueous solution buffered at pH 7. ▲ 1,4-, ◇ 1,3-, □ **1,2-benzenedicarboxylate.**

addition of the 1,4-derivative (terephthalate) fully restored rhodamine fluorescence. Thus, receptor $[Cu^{II}{}_2(\mathbf{3})]^{4+}$ clearly discriminates terephthalate from the other isomeric dicarboxylates. Through nonlinear fitting of the titration profiles in Figure 3, the binding constants K_S for the 1:1 adducts of the dicopper(II) cryptate and the three dicarboxylates were calculated,[19] and their values are reported in Figure 4. Importantly, to determine K_S values for 1,2- and 1,3-derivatives, anion concentrations up to 10^{-3} M had to be employed.

In Figure 4, the association constant K_I for the cryptate with the indicator is reported as a horizontal line. The diagram shows that only the 1,4-derivative has a higher affinity towards the cryptate than the rhodamine indicator, resulting in the displacement of the latter. On the other hand, 1,2- and 1,3-derivatives exhibit distinctly lower K_S values and cannot displace the indicator (in the concentration range considered in Figure 3). This highly selective behavior can be explained on the basis of geometrical considerations.

The molecular structure in Figure 1 shows that the distance between the oxygen atoms of the two coordinated water molecules is 7.355(4) Å, whereas the distance between two opposite oxygen atoms in the terephthalate ion is 7.39 Å, as observed from the X-ray crystal structure of its ammonium salt.[20] It follows that the terephthalate ion has an almost

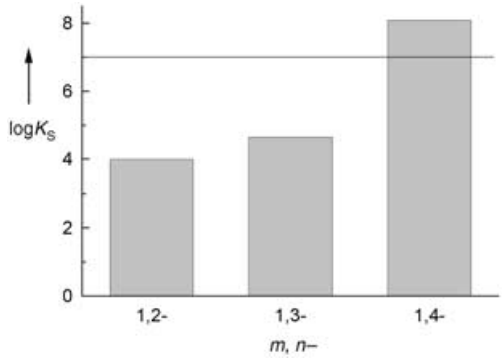

Figure 4. Equilibrium constants for the interaction of the receptor $[Cu_2^{II}(\mathbf{3})]^{4+}$ with *m*,*n*-benzenedicarboxylates (bars) and the fluorescent indicator **4** (horizontal line). The position of the horizontal line with respect to the bars determines the selectivity of the chemosensor ensemble $\{\mathbf{4}+[Cu_2^{II}(\mathbf{3})]^{4+}\}$ towards the chosen dicarboxylate.

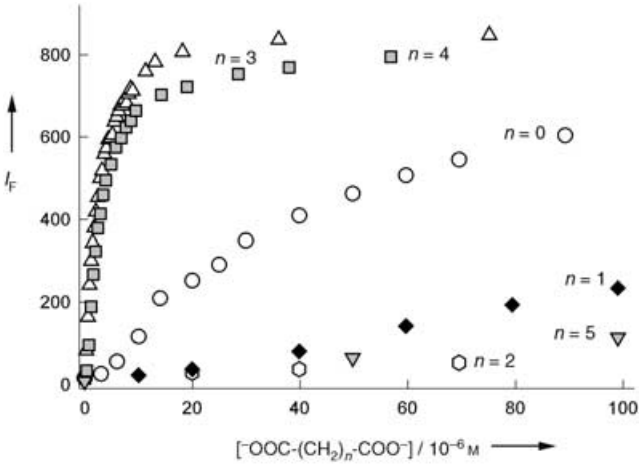

Figure 5. Titration of a solution of $[Cu_2^{II}(\mathbf{3})]^{4+}$ (2.5×10^{-6} M) and **4** (2.5×10^{-7} M) with aliphatic dicarboxylates of formula $^{-}OOC\text{-}(CH_2)_n\text{-}COO^{-}$ in an aqueous solution buffered at pH 7.

perfect O–O bite and displaces the two water molecules to bridge the two Cu^{II} centers without inducing any endoergonic rearrangement of the cage. On the other hand, an unfavorable rearrangement is expected to occur with the inclusion of isophthalate and phthalate ions, whose O–O distances are distinctly smaller (4.98 Å,[21] and 3.16 Å,[22] respectively). This therefore suggests that the terephthalate fragment has the correct length to place an oxygen atom from each -COO^{-} group in the available coordination site (the axial position of a trigonal bipyramid) of each of the two Cu^{II} ions, thus maintaining the cage framework in its more relaxed arrangement. Rhodamine **4** itself also contains the benzene-1,4-dicarboxylate fragment, which ensures the most favorable fit. Its association constant is one order of magnitude lower than that of the terephthalate anion probably owing to repulsive effects exerted by the appended fluorogenic fragment (steric) and by the positive charge on the fluorophore (electrostatic). A colorimetric method based on an anion-induced reaction has recently been reported to discriminate the 1,2-derivative with respect to the 1,3- and 1,4-isomers in solution in dioxane–water (70:30 v/v).[23]

We next considered the family of aliphatic dicarboxylates $^{-}OOC\text{-}(CH_2)_n\text{-}COO^{-}$ with $n=0$–5. Figure 5 displays the profiles obtained upon titration of the dicopper(II) cryptate–rhodamine solution with the envisaged dicarboxylate in a solution buffered at pH 7. High selectivity was also observed in this case. In particular, glutarate ($n=3$) and adipate ($n=4$) both displaced the indicator from the receptor as observed from the rhodamine fluorescence emission. However, upon contraction (succinate, $n=2$) and expansion (pimelate, $n=5$) of the aliphatic chain joining the -COO^{-} groups, no displacement of the indicator occured and the fluorescence remained almost quenched.

The association constants for the varying dicarboxylates ($n=2$–5), shown in the bar diagram in Figure 6 and calculated through nonlinear fitting of titration profiles account for the described behaviour. Even though glutarate and adipate exhibit association constants similar to that of rhodamine (Figure 6, horizontal line), they compete successfully for the

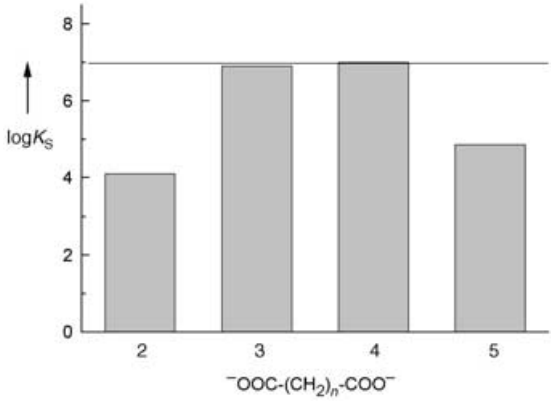

Figure 6. Equilibrium constants for the interaction of the receptor $[Cu_2^{II}(\mathbf{3})]^{4+}$ with $^{-}OOC\text{-}(CH_2)_n\text{-}COO^{-}$ dicarboxylates (bars) and the fluorescent indicator **4** (horizontal line). In the abscissa, $n=$ number of methylene groups in the spacer.

receptor when they are present in a much higher concentration than the indicator. Succinate and pimelate exhibit association constants well below that of the indicator and therefore cannot displace rhodamine from the receptor. The highest inclusion affinity is exhibited by glutarate and adipate whose crystallographically determined O–O distances (7.20[24] and 7.83 Å,[25] respectively) are the closest to that observed between the oxygen atoms of the coordinated water molecules in the $[Cu_2^{II}(\mathbf{3})(H_2O)_2]^{4+}$ complex. Dicarboxylates exhibiting smaller (succinate, 6.04 Å)[26] or larger (pimelate, 9.67 Å)[27] O–O distances give much less stable inclusion complexes.

The oxalate anion ($n=0$, see Figure 5) also exhibits competitive behavior. However, least-squares treatment of titration data shows that the dicopper(II) cryptate undergoes stepwise inclusion of *two* oxalate ions, with $\log K_{S1}=6.1\pm0.3$ and $\log K_{S2}=3.2\pm0.3$. The inclusion of two distinct molecules

was also observed in the case of malonate ($\log K_{S1} = 4.8 \pm 0.3$; $\log K_{S2} = 3.2 \pm 0.3$). This behavior is explained by the relatively small size of the two anions which is insufficient to encompass the distance between the two metal centers so that they prefer individual coordination to each Cu^{II} ion. Despite this observation, the dicopper(II) cryptate $[Cu^{II}_2(\mathbf{3})]^{4+}$ still clearly discriminates glutarate and adipate anions from oxalate anions.

Recognition of aromatic and aliphatic dicarboxylates by a hexammonium cage in which the two tren subunits are linked by long carbon spacers (i.e. -CH_2-C_6H_4-CH_2-C_6H_4-CH_2-; -C_6H_4- = 1,4-phenyl) has been investigated through ^{1}H NMR titrations conducted in solution in D_2O adjusted to pH 6. The highest inclusion affinity was observed for terephthalate ($\log K = 4.4$) whereas no particular selectivity was noted in the case of $^-$OOC-$(CH_2)_n$-COO$^-$ anions, for which log$K$ values ranged from 3.1 to 3.4 upon moving from $n = 2$ to $n = 7$.[28] This lack of selectivity may be attributed to the higher flexibility of the spacers (an sp^3 carbon atom joins the two phenyl rings) and to the nondirectional character of the electrostatic interactions.

In conclusion, this work has demonstrated that the dicopper(II) complex of a rigid bistren cryptand such as **3** is an ideal receptor for difunctional anions which are neatly discriminated on the basis of the distance between their functional groups. In particular, the investigated cryptate performs chain-length recognition of aliphatic dicarboxylates. The strong metal–ligand interactions established between the receptor and the anion easily compensate for unfavorable dehydration effects and allow recognition in pure water at pH 7— a rare occurrence when anion recognition is based on electrostatic interactions such as hydrogen bonding.[29] Most of the studies on carboxylate recognition to date have been carried out in non-aqueous solvents.[30]

Moreover, the use of a fluorescent indicator in an "indicator displacement" approach provides sharp signalling of the recognition event. The transition metals present in the receptor cavity quench the included fluorophore until it is displaced by the substrate to provide a valuable OFF–ON switching of the signal.[31] Finally, changing the length of the spacer allows the selective recognition of $^-$OOC-$(CH_2)_n$-COO$^-$ dicarboxylates of different n values: in such a case an appropriate bidentate indicator that fits the Cu^{II}–Cu^{II} distance within the receptor is required.

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[10] Crystal data for $[Cu^{II}_2(\mathbf{3})(H_2O)_2](NO_3)_4 \cdot 2H_2O$ ($C_{54}H_{74}Cu_2N_{12}O_{16}$): $M_r = 1274.35$, $T = 293$ K, crystal dimensions $0.55 \times 0.30 \times 0.15$ mm^3, orthorhombic, $Pna2_1$ (No. 33), $a = 34.0372(20)$, $b = 11.2959(6)$, $c = 15.6098(10)$ Å, $V = 6001.6(6)$ Å, $Z = 4$, $\rho_{calcd} = 1.410$, $F(000) = 2672$, $\mu = 0.785$ mm^{-1}, $Mo_{K\alpha}$ radiation ($\lambda = 0.7107$ Å), $2\theta_{max} = 52°$, 44805 measured , 11535 independent ($R_{int} = 0.0334$), 9813 strong reflections [$I_o > 2\sigma(I_o)$], 773 refined parameters, $R1 = 0.0526$ (strong data) and 0.0620 (all data), $wR2 = 0.1400$ (strong data) and 0.1476 (all data), GOF = 1.053, 0.98/−0.35 max./min. residual electron density. Diffraction data were collected on a Bruker-Axs Smart-Apex CCD based diffractometer. Omega rotation frames (scan width 0.3°, scan time 20 s, sample-to-detector distance 8 cm) were processed with the SAINT software (Bruker-Axs Inc.) and corrected for Lorentz and polarization effects. Absorption effects were analytically evaluated by the SADABS software[11] and correction was applied to the data (0.75 and 0.89 min. and max. transmission factor). The structure was solved by direct methods (SIR-97)[12] and refined by full-matrix least-square procedures on F^2 using all reflections (SHELXL-97).[13] Calculations were performed with the WinGx package.[14] All non-hydrogen atoms were refined with anisotropic temperature factors, except for those of the N(12) nitro group, that showed the three O atoms disordered over two alternative positions with the same statistical probability. Hydrogen atoms were placed using the appropriate AFIX instructions. CCDC 233940 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).
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