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Hydrogen Bonding

Closed and Open Clamlike Structures Formed by Hydrogen-Bonded Pairs of Cyclotricatechylene Anions that Contain Cationic “Meat”**

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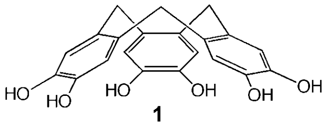
Hydrogen bonding between phenolic groups is a central structural feature of some classical clathrate systems, and leads to three-dimensional host networks with cavities in which a variety of guests can be accommodated. The β-quinol derivatives structurally characterized in the middle of last century by Palin and Powell's pioneering work,[1] and by studies on Dianin's compound[2] and related systems are archetypal examples of this feature. We report herein that the hexaphenolic compound cyclotricatechylene (ctc.H_6, **1**) has a propensity to form hydrogen-bonded pairs reminiscent of a clam because of its relatively rigid domed shape together with its sticky polyphenolic rim; the clamshells are anionic and the flesh within is provided by various cations. The tris(catechol) **1**, which has provided us with a number of interesting metal derivatives, is one of a number of polycatechol derivatives whose coordination polymers and oligomers we are presently investigating.[3] Cyclotriveratrylene, the hexamethyl ether of **1**, has been widely studied on account of the opportunities for supramolecular associations offered by its bowl-shaped cavity, which is a feature shared by **1**.[4]



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The reaction of ctc.H_6 with RbCl and guanidinium chloride in aqueous acetone in the presence of excess ammonia yields a crystalline product of formal composition $[C(NH_2)_3]_2[Rb(ctc.H_5)(ctc.H_4)]\cdot 15\,H_2O$.[5] The $[Rb(ctc.H_5)(ctc.H_4)]^{2-}$ ion possesses an unusual clamlike structure (Figure 1). The two separate shell-like components of the clam are provided by ctc-derived anions, which are bound together by six hydrogen bonds. Surprisingly, a “bare”, unsolvated Rb^+ ion is located at the center of the clam and makes contact with six aromatic rings that are face-on to it. The two ctc-derived components of the clam are oriented so that the pairs of oxygen atoms from single catechol units in one partner slot into the spaces between separate catechol groups in the other (Figure 1). The Rb center is located on a twofold axis. The six oxygen atoms of a single ctc anion are very close to coplanar, the average O_6 planes of the two partners being parallel and separated by 1.06 Å. The clam adopts a “closed” arrangement (in contrast to some “partially open” examples described below); each oxygen atom forms a hydrogen bond to an oxygen atom from the partner shell, to give a total of six hydrogen bonds (O···H−O separations of 2.46–2.69 Å). The twelve aromatic carbon atoms bound to the methylene groups make the closest contacts to the Rb center (shortest Rb···C, 3.36 Å). The centers of the six aromatic rings form an almost perfect octahedral arrangement around the metal center (the twelve *cis* angles vary from 87° to 94°). The negative charge on the clam is balanced in the crystal by

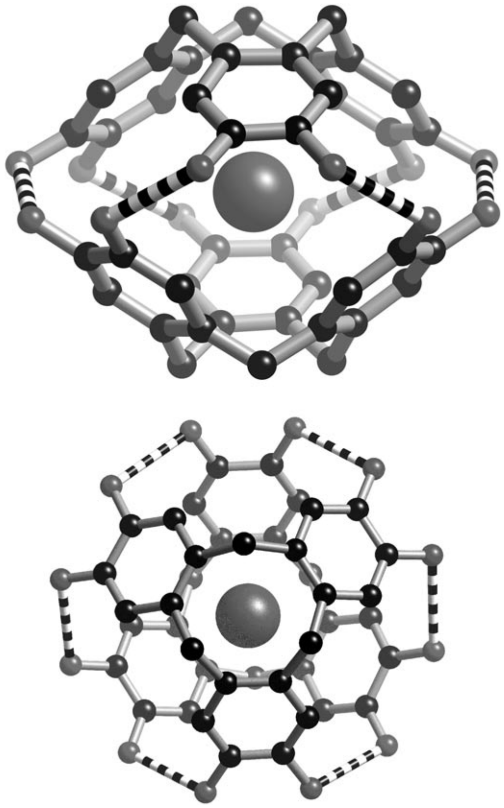

Figure 1. Two views of the clamlike $[Rb(ctc.H_5)(ctc.H_4)]^{2-}$ ion. The banded connections represent O···H−O hydrogen bonds.

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external guanidinium cations that participate in an extended hydrogen-bonded network.

Although examples exist in which alkali-metal cations are in an immediate environment that consists entirely of carbon,[6] these compounds were all generated, to the best of our knowledge, in the strict absence of water. It is therefore quite remarkable, in the system described above, that Rb^+ prefers to associate with the carbon π systems rather than water or phenolic groups, both of which are abundantly available (the compound was generated in media containing approximately 50% H_2O). Despite the fact that water is stripped relatively readily from the larger alkali-metal cations ($\Delta H_{\mathrm{hydr}} = 293\ \mathrm{kJ\,mol^{-1}}$ for Rb^+ and $264\ \mathrm{kJ\,mol^{-1}}$ for Cs^+)[7], compared to, for example, the smaller Li^+ ($\Delta H_{\mathrm{hydr}} = 519\ \mathrm{kJ\,mol^{-1}}$),[7] the observed preference for a carbon environment when water is abundantly available remains remarkable.

A clamlike $[Rb(ctc.H_5)(ctc.H_4)]^{2-}$ unit almost identical to that described above is found in the crystalline compound $Rb_2[Rb(ctc.H_5)(ctc.H_4)]\cdot 3.5\,H_2O$, which was obtained by the diffusion of ammonia gas into solutions of $ctc.H_6$ and RbCl in aqueous methanol.[8] A very closely related clamlike $[Cs(ctc.H_5)(ctc.H_4)]^{2-}$ unit is found in the compound $[C(NH_2)_3]_2[Cs(ctc.H_5)(ctc.H_4)]\cdot 2\,(CH_3)_2CO\cdot 5\,H_2O$, which was obtained from solutions of CsCl, guanidinium chloride, $ctc.H_6$, and excess ammonia in aqueous acetone.[9]

Electrospray mass spectrometry (ESMS) studies suggest that not only do the clamlike units survive in solution when the above solids are dissolved, but also that the clams self-assemble when the components are mixed in solution. Negative-ion spectra, in which the major peak in both cases corresponds to $[M(ctc.H_5)_2]^-$ (M = Rb or Cs) are obtained from methanolic solutions of the solid guanidinium salts of the Rb and Cs clams. The same dominant peaks are observed for solutions of $ctc.H_6$, excess ammonia, and either RbCl or CsCl.

Interestingly, attempts to form a clam-type structure with K^+ ions were unsuccessful, which suggests that this cation is too small to fit snugly into the interior of the closed clam. A crystalline compound of composition $K(ctc.H_5).C_2H_5OH$ is obtained from solutions of $ctc.H_6$, KNO_3, and excess ammonia in aqueous ethanol.[10] In this compound, a K^+ ion is located within the bowl of a single $ctc.H_5^-$ unit (closest K···C contact, 3.17 Å) and also associates with two other $ctc.H_5^-$ ions, but through their oxygen atoms (Figure 2). Again, it is interesting that a product in which an alkali metal cation associates significantly with aromatic π systems (approximately one hemisphere of the space around the cation is occupied in this manner) is generated from a reaction mixture that contains a substantial proportion of water.

A crystalline compound of composition $(NH_4)[(NMe_4)(ctc.H_5)_2]\cdot 2\,(CH_3)_2CO\cdot 3\,H_2O$ was obtained from solutions of $ctc.H_6$, NMe_4Cl, and excess ammonia in aqueous acetone.[11] Two crystallographically distinct but geometrically very similar clamlike $[(NMe_4)(ctcH_5)_2]^-$ units, clams A and B, are present in this compound. These clams are no longer in the closed-up arrangement seen in the Rb and Cs examples above. Rather, they are now partially opened to accommodate the larger NMe_4^+ ion (see the representation of clam A in Figure 3), the two average O_6 planes being inclined at a dihedral angle of 11.2° in clam A and 12.4° in clam B. For both clams A and B, the hinge of the opened clam is provided by two equivalent hydrogen bonds (O···O, 2.58 Å in clam A and 2.55 Å in clam B), which are formed between a single catechol component of the upper shell and a single catechol component of the lower shell, the upper pair of oxygen atoms being vertically above the lower—twofold axes pass through the midpoints of the groups of four oxygen centers in both clams A and B. These NMe_4^+ clams thus differ from the closed Rb^+ and Cs^+ clams, not only in the relative inclination of the two component shells, but also in their relative orientations around their individual pseudo-threefold axes.

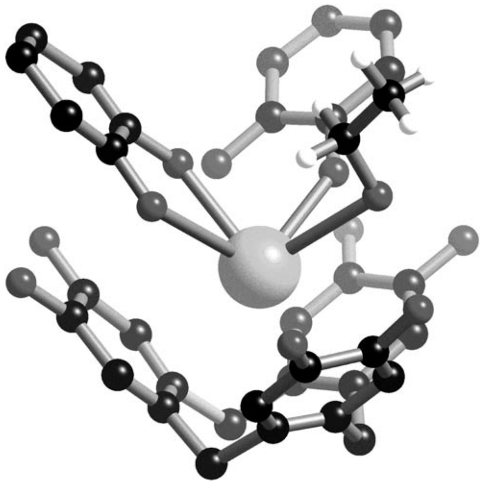

Figure 2. The environment of the K^+ cation in $K(ctc.H_5)\cdot C_2H_5OH$.

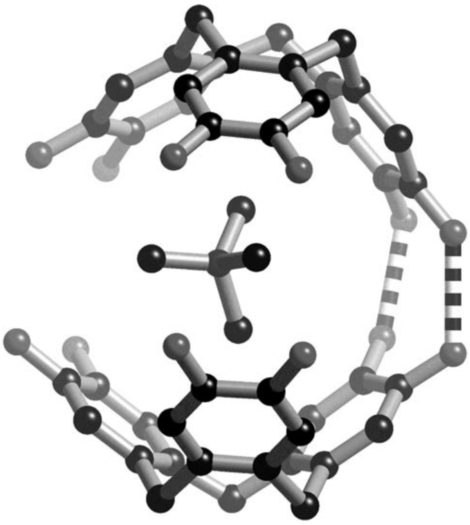

Figure 3. View of clam A in $(NH_4)[(NMe_4)(ctc.H_5)_2]\cdot 3\,H_2O\cdot 2\,(CH_3)_2CO$. Hydrogen bonds are represented by banded connections. Only one orientation of the tetramethylammoniumion ion is shown.

Crystals of composition $(NEt_4)[(NEt_4)(ctc.H_5)_2]\cdot 4\,H_2O$ suitable for X-ray diffraction studies were obtained from solutions containing $ctc.H_6$, NEt_4Br, and excess ammonia in aqueous acetone.[12] As in the NMe_4 system above, there are two crystallographically distinct clam units (clams C and D). A view of clam D is shown in Figure 4. In order to accommodate the larger NEt_4^+ ion, clams C and D are opened up much wider than clams A and B, the dihedral angles between the two O_6 planes being 25.4° for clam C and 26.3° for clam D. The hinge in clam C consists of a single hydrogen bond (2.64 Å) and the hinge in clam D of two hydrogen bonds (2.23 Å and 2.82 Å; Figure 4).

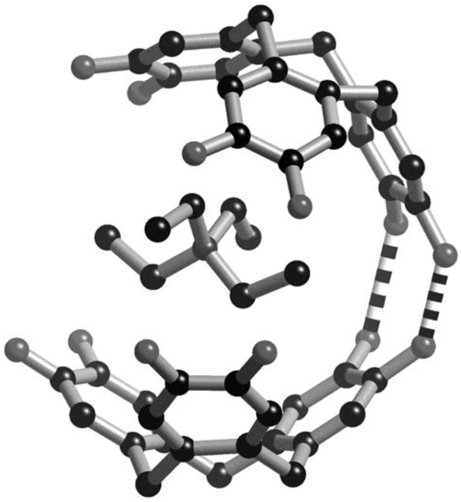

Figure 4. View of clam D in $(NEt_4)[(NEt_4)(ctc.H_5)_2]\cdot 4H_2O$. Hydrogen bonds are represented by banded connections. Only one orientation of the tetraethylammonium ion is shown.

Peaks that correspond to the anions $[(NR_4)(ctc.H_5)_2]^-$ ($R = Me$ or Et) are seen in the ES mass spectra of solutions of the two tetraalkylammonium products in methanol (see the Supporting Information) but other species are also present.

In summary, the results reported herein provide unusual examples in which alkali metal cations (specifically Rb^+ and Cs^+) prefer to surround themselves entirely by aromatic π systems, rather than the oxygen centers of either water or catechol subunits. This effect is remarkable given that the compounds are generated in media that contain approximately 50% H_2O, and is, to the best of our knowledge, without precedent. It appears that complementary hydrogen-bonded interactions favor the formation of closed anionic clams when the clam interior can be nicely occupied by a cation of the appropriate size (such as Rb^+ or Cs^+). Use of the K^+ cation fails to give a clam, presumably because it is too small, whereas larger NMe_4^+ and NEt_4^+ cations give "opened up" clams in which the clam hinge consists of only a pair of hydrogen bonds (or in the case of NEt_4-clam C, only a single hydrogen bond). The fact that clam formation persists even when most of the hydrogen bonding is disrupted by the incorporation of larger ions such as NMe_4^+ and NEt_4^+ emphasizes the importance of the electrostatic attraction between host and guest.

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[5] Crystals of $[C(NH_2)_3]_2[Rb(ctc.H_5)(ctc.H_4)]\cdot 15H_2O$ suitable for X-ray diffraction studies were obtained by liquid–liquid diffusion. A solution of $ctc.H_6$ (as prepared by J. A. Hyatt, *J. Org. Chem.* **1978**, *43*, 1808; 24 mg, 0.065 mmol) and excess NH_3 methanol (3 mL) was layered over an aqueous solution (3 mL) of RbCl (31 mg, 0.26 mmol) and $C(NH_2)_3Cl$ (2 5 mg, 0.26 mmol). Deep-red crystals began to form in the mixing zone after 24 h. The crystals were filtered off after 48 h, washed with water and dried in air. Yield: 8 mg (24%); elemental analysis calcd (%) for $C_{44}H_{53}N_6O_{16}Rb$ (i.e., $[C(NH_2)_3]_2[Rb(ctc.H_5)(ctc.H_4)]\cdot 4H_2O$): C 52.5, H 5.3, N 8.3; found: C 52.3, H 5.5, N 8.2. Crystal data for $[C(NH_2)_3]_2[Rb(ctc.H_5)(ctc.H_4)]\cdot 15H_2O$: $M_r = 1205.57$, tetragonal, $I\text{-}42d$, a, $b = 21.0505(11)$ Å, $c = 27.9810(13)$ Å, $V = 12399.0(11)$ Å^3, $Z = 8$, $\theta_{max} = 73.77°$, $Cu_{K\alpha}$ radiation, $\lambda = 1.54184$ Å, $T = 130$ K, $\mu(Cu_{K\alpha}) = 1.810$ mm^{-1}, 11552 reflections measured, 5509 unique which were used in all calculations, 380 parameters, The structure was solved by direct methods (SHELX97)^{13}, $wR2 = 0.2388$ (all data) and $R1 = 0.0887$ ($I > 2\sigma(I)$). CCDC 710723 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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[8] Crystals of $Rb_2[Rb(ctc.H_5)(ctc.H_4)]\cdot 3.5H_2O$ suitable for X-ray diffraction studies were obtained by diffusion of ammonia vapor into a solution of $ctc.H_6$ (24 mg, 0.065 mmol) and RbCl (31 mg, 0.26 mmol) in a 1:1 methanol/water mixture (6 mL). Deep-red crystals began to form in the mixing zone within hours. The crystals were filtered off after 24 h, washed with water, and dried in air. Yield: 23 mg (67%); elemental analysis calcd (%) for $C_{42}H_{39}O_{15}Rb_3$ (ie., $Rb_2[Rb(ctc.H_5)_2]\cdot 3H_2O$): C 48.5, H 3.8; found: C 48.4, H 3.6. Crystal data for $Rb_2[Rb(ctc.H_5)_2]\cdot 3.5H_2O$:

$M_r = 1049.15$, trigonal, $R\text{-}3c$, $a = b = 20.3022(7)$, $c = 50.5721(15)$ Å, $V = 118052.1(10)$ Å^3, $Z = 18$, $\theta_{max} = 73.39°$, $Cu_{K\alpha}$ radiation, $\lambda = 1.54184$ Å, $T = 130$ K, $\mu(Cu_{K\alpha}) = 5.276$ mm^{-1}, 24301 reflections measured, 3950 unique which were used in all calculations, 290 parameters. The structure was solved by direct methods (SHELX97)^{12}, $wR2 = 0.3953$ (all data) and $R1 = 0.1212$ ($I > 2\sigma(I)$). CCDC 710726 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.

[9] Crystals of $[C(NH_2)_3]_2[Cs(ctc.H_5)(ctc.H_4)]\cdot 2(CH_3)_2CO.5H_2O$ suitable for X-ray diffraction studies were obtained by liquid–liquid diffusion. A solution of ctc.H_6 (24 mg, 0.065 mmol) and excess NH_3 in acetone (3 mL) was layered over an aqueous solution (3 mL) of CsCl (44 mg, 0.26 mmol) and $(C(NH_2)_3)Cl$ (25 mg, 0.26 mmol). Pale-yellow crystals began to form in the mixing zone after 24 h. The crystals were filtered off after 48 h, washed with water and dried in air. Yield: 22 mg (64%); elemental analysis calcd (%) for $C_{44}H_{51}N_6O_{15}Cs$ (namely, $[C(NH_2)_3]_2[Cs(ctc.H_5)(ctc.H_4)]\cdot 3H_2O$): C 51.0, H 5.0, N 8.1; found: C 50.8, H 5.1, N 8.1. Crystal data for $[C(NH_2)_3]_2[Cs(ctc.H_5)(ctc.H_4)]\cdot 5H_2O$: $M_r = 1189.01$, monoclinic, $P2_1/c$, $a = 13.84310(10)$, $b = 17.9893(2)$, $c = 20.8354(2)$ Å, $\beta = 98.8590(10)°$. $V = 5126.69(8)$ Å^3, $Z = 4$, $\theta_{max} = 73.37°$. $Cu_{K\alpha}$ radiation, $\lambda = 1.54184$ Å, $T = 130$ K, $\mu(Cu_{K\alpha}) = 6.347$ mm^{-1}, 29961 reflections measured, 10128 unique which were used in all calculations, 631 parameters, The structure was solved by direct methods (SHELX97)^{13}, $wR2 = 0.0986$ (all data) and $R1 = 0.0331$ ($I > 2\sigma(I)$). CCDC 710724 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.

[10] Crystals of $K(ctc.H_5).C_2H_5OH$ suitable for X-ray diffraction studies were obtained by liquid–liquid diffusion. A solution of ctc.H_6 (24 mg, 0.065 mmol) and excess NH_3 in ethanol (4 mL) was layered over an aqueous solution (4 mL) of KNO_3 (26 mg, 0.26 mmol). Orange-red crystals began to form in the mixing zone between the two layers after 24 h. The crystals were filtered off after 48 h, washed with water and dried in air. Yield: 9 mg (31%), Elemental analysis calcd (%) for $C_{21}H_{21}O_8K$ (i.e., $K(ctc.H_5)\cdot 2H_2O$): C 57.3, H 4.8; found: C 57.3, H 4.7. Crystal data for $K(ctc.H_5)\cdot EtOH$: $M_r = 450.51$, monoclinic, $P2_1/c$, $a = 9.15170(10)$, $b = 11.1653(2)$, $c = 19.4241(3)$ Å, $\beta = 97.0830(10)°$, $V = 1969.64(5)$ Å^3, $Z = 4$, $\theta_{max} = 73.16°$, $Cu_{K\alpha}$ radiation, $\lambda = 1.54184$ Å, $T = 130$ K, $\mu(Cu_{K\alpha}) = 2.764$ mm^{-1}, 9521 reflections measured, 3867 unique which were used in all calculations, 324 parameters, The structure was solved by direct methods (SHELX97)^{13}, $wR2 = 0.1828$ (all data) and $R1 = 0.0687$ ($I > 2\sigma(I)$). CCDC 710722 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.

[11] Crystals of $(NH_4)[(NMe_4)(ctc.H_5)_2]\cdot 2(CH_3)_2CO\cdot 3H_2O$ suitable for X-ray diffraction studies were obtained by liquid–liquid diffusion. A solution of ctc.H_6 (24 mg, 0.065 mmol) and excess NH_3 in acetone (3 mL) was layered over an aqueous solution (3 mL) of NMe_4Cl (28 mg, 0.26 mmol). Colorless crystals began to form in the mixing zone within hours. The crystals were filtered off after 24 h, washed with water and dried in air. Yield: 17 mg (58%); elemental analysis calcd (%) for $C_{46}H_{67}N_2O_{15.5}$ (i.e., $(NH_4)[(NMe_4)(ctc.H_5)_2]\cdot 3.5H_2O$): C 62.4, H 6.5, N 3.2; found: C 62.5, H 6.7, N 3.1. Crystal data for $(NH_4)[(NMe_4)(ctc.H_5)_2]\cdot 2(CH_3)_2CO\cdot 3H_2O$: $M_r = 1003.16$, monoclinic, $P2/c$, $a = 20.5092(9)$, $b = 9.3264(3)$, $c = 26.1228(10)$ Å, $\beta = 95.696(4)°$, $V = 4972.0(3)$ Å^3, $Z = 4$, $\theta_{max} = 57.50°$, $Cu_{K\alpha}$ radiation, $\lambda = 1.54184$ Å, $T = 130$ K, $\mu(CuK_\alpha) = 0.824$ mm^{-1}, 27223 reflections measured, 23636 unique which were used in all calculations, 637 parameters, The structure was solved by direct methods (SHELX97)^{13}, $wR2 = 0.2932$ (all data) and $R1 = 0.1028$ ($I > 2\sigma(I)$). CCDC 710725 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.

[12] Crystals of $(NEt_4)[(NEt_4)(ctc.H_5)_2]\cdot 4H_2O$ suitable for X-ray diffraction studies were obtained by liquid–liquid diffusion. A solution of ctc.H_6 (24 mg, 0.065 mmol) and excess NH_3 in acetone (3 mL)was layered over an aqueous solution (3 mL) of NEt_4Br (55 mg, 0.26 mmol). Colorless crystals began to form in the mixing zone within hours. The crystals were filtered off after 24 h, washed with water and dried in air. Yield: 19 mg (53%); elemental analysis calcd (%) for $C_{58}H_{82}N_2O_{16}$ (i.e., $(NEt_4)[(NEt_4)(ctc.H_5)_2]\cdot 5.5H_2O$) C 63.9, H 7.9, N 2.6; found: C 64.0, H 7.6, N 2.5. Crystal data for $(NEt_4)[(NEt_4)(ctc.H_5)_2]\cdot 4H_2O$: $M_r = 1063.26$, monoclinic, $P2_1/m$, $a = 14.637(5)$, $b = 24.856(5)$, $c = 15.980(5)$ Å, $\beta = 96.187(5)°$, $V = 5780(3)$ Å^3, $Z = 4$, $\theta_{max} = 67.50°$. $Cu_{K\alpha}$ radiation, $\lambda = 1.54184$ Å, $T = 130$ K, $\mu(Cu_{K\alpha}) = 0.725$ mm^{-1}, 21537 reflections measured, 10287 unique which were used in all calculations, 528 parameters, The structure was solved by direct methods (SHELX97)^{13}, $wR2 = 0.3535$ (all data) and $R1 = 0.1120$ ($I > 2\sigma(I)$). CCDC 710727 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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