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FULL PAPER

An unusual pendant-arm macrocycle formed by condensation of a cobalt(III) tripodal complex with methanal

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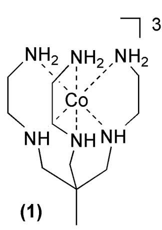
The reaction of $[Co(ten)]^{3+}$ {ten = 4,4′,4″-ethylidynetris(3-thiabutan-1-amine)} with methanal and base in acetonitrile or water led to the synthesis of an unusual pendant-arm macrocyclic complex, 8-(4′-ammonio-2′-thiabutyl)-8-methyl-1-oxa-6,10-dithia-3,13-diazacyclo-tetradecane(chloro)cobalt(III) triperchlorate trihydrate. The structure of the complex has been established by X-ray crystallographic analysis and such molecules can readily be tied to polymers and proteins. The synthesis, chemical reactions, spectroscopy and electrochemical properties of the macrocyclic complex are described.

Introduction

Tripodal cobalt(III) complexes have been instrumental in the template syntheses of many cage molecules. For example, $[Co(sen)]^{3+}$ {sen = 4,4′,4″-ethylidynetris(3-azabutan-1-amine)} (**1**) has been used to synthesize hexaaza cage molecules[1,2] while the use of $[Co(ten)]^{3+}$ {ten = 4,4′,4″-ethylidynetris(3-thiabutan-1-amine)} (**2**) has produced cage complexes bearing three amine and three thioether donor groups.[3,4] These reactions generally involve the addition of methanal to two or three of the coordinated tripodal amines, generating coordinated and reactive methanimines which then condense with a carbon acid or ammonia to complete the encapsulation process.[1–4]

The first cage synthesis using $[Co(sen)]^{3+}$ reported a tripodal by-product (**3**) arising from reactions with methanal only.[1] In later work a tripod containing three coordinated methanimines (**4**) was isolated and used to synthesize an arsenic-capped cage molecule.[5] The present study describes the synthesis, structure and properties of a novel macrocyclic complex formed by the reaction of $[Co(ten)]^{3+}$ with methanal.



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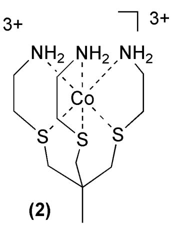

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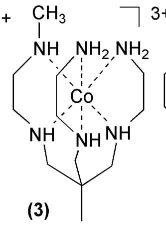

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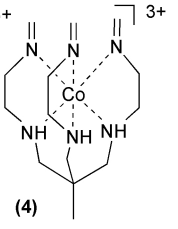

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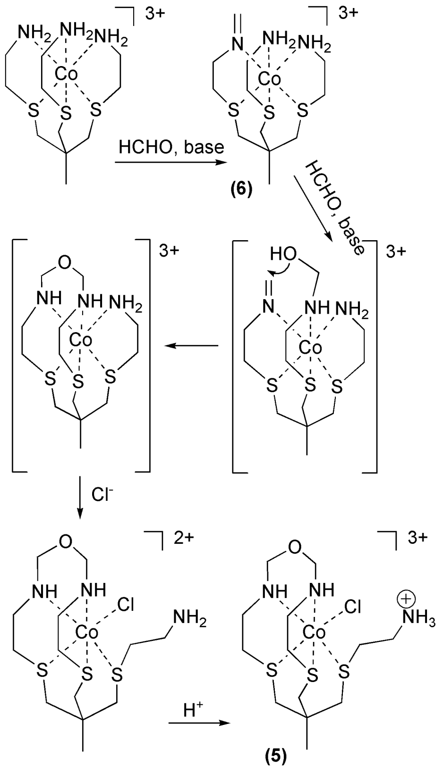


Scheme 1

Results and discussion

$[Co(ten)]Cl_3$ reacted with methanal and triethylamine in acetonitrile to produce a purple species (Scheme 1, **5**) whose structure has been elucidated by X-ray crystallography. Two arms of the tripodal ligand have been converted to a macrocycle by linking two amine groups with an ether bridge. The macrocyclic part of the complex is bonded to the metal ion through two thioether and two secondary amine links while the bridging ether is uncoordinated. The third strand of the tripod has become a pendant arm coordinated only through its thioether group, while the sixth coordination site is occupied by a chloride ion *cis* to the pendant arm. The boat conformation of the macrocycle is essentially the same as in the relevant section of the parent tripod. An ORTEP diagram of the structure is shown in Fig. 1 and a selection of bond lengths and angles is listed in Table 1. The bond lengths and angles of the macrocycle moiety are similar to those of the parent tripod[6] except for the ether bridge. The Co–S bond length in the pendant arm is significantly longer than those in the ring. The

Table 1 Bond distances (Å) and angles (°) for the macrocyclic complex (**5**)

Co–Cl	2.239 (1)	N(3)–C(4)	1.503 (6)
Co–N(3)	2.016 (4)	N(13)–C(12)	1.491 (6)
Co–N(13)	2.016 (4)	N(13)–C(14)	1.494 (6)
Co–S(6)	2.224 (1)	N(Am)–C(4′)	1.494 (7)
Co–S(10)	2.214 (1)	O(1)–C(2)	1.408 (7)
Co–S(2′)	2.251 (1)	O(1)–C(14)	1.393 (6)
S(6)–C(5)	1.814 (5)	C(4)–C(5)	1.503 (6)
S(6)–C(7)	1.823 (4)	C(7)–C(8)	1.533 (6)
S(10)–C(9)	1.818 (5)	C(8)–C(Me)	1.534 (6)
S(10)–C(11)	1.821 (5)	C(9)–C(8)	1.540 (7)
S(2′)–C(1′)	1.828 (5)	C(12)–C(11)	1.519 (7)
S(2′)–C(3′)	1.817 (4)	C(1′)–C(8)	1.526 (6)
N(3)–C(2)	1.481 (6)	C(3′)–C(4′)	1.499 (7)
Cl–Co–N(3)	91.7 (1)	Co–S(10)–C(9)	111.2 (2)
Cl–Co–N(13)	89.7 (1)	Co–S(10)–C(11)	97.5 (2)
Cl–Co–S(6)	178.89 (8)	C(11)–S(10)–C(9)	102.5 (2)
Cl–Co–S(10)	86.62 (5)	Co–S(2′)–C(1′)	109.6 (2)
Cl–Co–S(2′)	93.85 (5)	Co–S(2′)–C(3′)	112.8 (2)
N(3)–Co–N(13)	91.2 (2)	C(1′)–S(2′)–C(3′)	100.7 (2)
S(6)–Co–N(3)	88.0 (1)	C(2)–O(1)–C(14)	114.7 (4)
S(6)–Co–N(13)	89.2 (1)	N(3)–C(2)–O(1)	111.0 (4)
S(6)–Co–S(10)	93.66 (4)	N(3)–C(4)–C(5)	111.3 (3)
S(6)–Co–S(2′)	87.22 (4)	S(6)–C(5)–C(4)	106.4 (3)
S(10)–Co–N(3)	178.3 (1)	S(6)–C(7)–C(8)	116.3 (3)
S(10)–Co–N(13)	88.5 (1)	C(7)–C(8)–C(9)	111.9 (4)
S(2′)–Co–N(3)	88.7 (1)	C(7)–C(8)–C(Me)	106.5 (3)
S(2′)–Co–N(13)	176.4 (1)	C(7)–C(8)–C(1′)	113.0 (4)
S(2′)–Co–S(10)	91.72 (5)	C(9)–C(8)–C(Me)	106.1 (4)
Co–N(3)–C(2)	115.0 (3)	C(9)–C(8)–C(1′)	111.6 (4)
Co–N(3)–C(4)	113.0 (3)	C(1′)–C(8)–C(Me)	107.3 (4)
C(2)–N(3)–C(4)	108.2 (3)	S(10)–C(9)–C(8)	115.8 (3)
Co–N(13)–C(12)	111.2 (3)	S(10)–C(11)–C(12)	106.2 (3)
Co–N(13)–C(14)	117.7 (3)	N(13)–C(12)–C(11)	108.8 (4)
C(14)–N(13)–C(12)	107.9 (4)	N(13)–C(14)–O(1)	111.2 (4)
Co–S(6)–C(5)	96.8 (1)	S(2′)–C(1′)–C(8)	116.0 (3)
Co–S(6)–C(7)	112.2 (1)	S(2′)–C(3′)–C(4′)	112.0 (3)
C(5)–S(6)–C(7)	103.8 (2)	N(Am)–C(4′)–C(3′)	112.0 (4)

Am = ammonio.

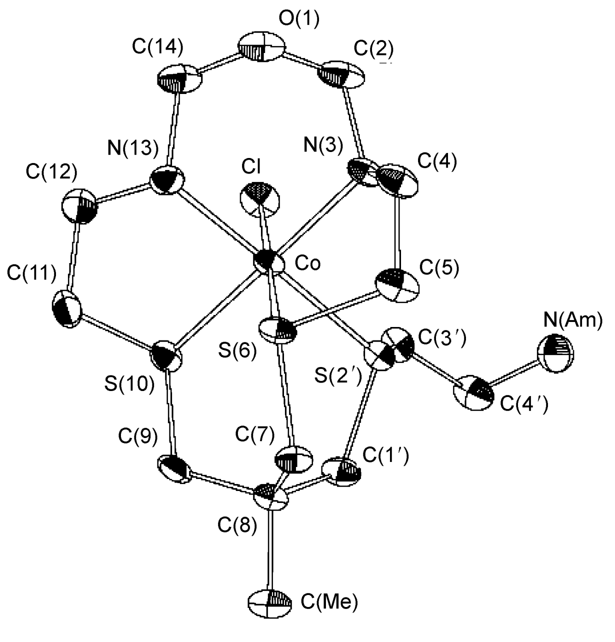


Fig. 1

^1H and ^{13}C NMR spectra are consistent with the X-ray analysis, indicating retention of the structure in solution. The only unusual features are the low-field signals of the methylene groups in the ether bridge (^1H $\delta = 4.44$, 4.95 ppm; ^{13}C $\delta = 80.0$, 81.2 ppm). The complex was stable indefinitely in aqueous acid solution but decomposed rapidly in a range of basic solvents in the absence of added methanal, reverting largely to $[Co(ten)]^{3+}$ and some $[Co(H_2O)_6]^{2+}$. In aqueous acidic solution the complex underwent irreversible reduction at 0.2 V {*vs.* SCE, $I = 0.10$ M $(NaClO_4)$}. This irreversibility is not surprising since the chloride ion is very likely to be lost rapidly and readily from the Co(II) ion.

Complex **5** was also formed when the above reaction was carried out in water or aqueous acetonitrile but under those conditions it was accompanied by a bright red complex (Scheme 1, **6**) in roughly equal amounts. Traces of other cobalt(III) species were observed during chromatography for all these reactions but the amounts were too small for isolation or identification. Some $[Co(H_2O)_6]^{2+}$ and ten·3HCl were also obtained, reflecting the greater ease of reduction of N_3S_3 cobalt(III) complexes compared with their N_6 analogues.[7] Complex **6** decomposed rapidly to $[Co(ten)]^{3+}$ in basic or neutral solution in the absence of added methanal. It was stable only for a limited period in acid solution (decomposing to $[Co(ten)]^{3+}$ and also $[Co(H_2O)_6]^{2+}$) and could not be crystallised analytically pure. However NMR spectra were obtained which were consistent with a tripodal complex bearing a single methanimine. A similar species (bearing a single *exo*-imine) has been isolated from the reaction of the tris(ethanediamine)-cobalt(III) ion with methanal.[8]

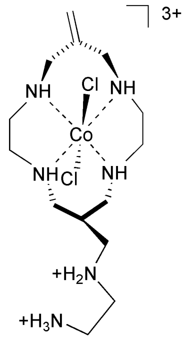
A number of experiments were conducted for the methanal/$[Co(ten)]^{3+}$ reactions in water or acetonitrile, varying the reagent concentrations and the reaction time. Fluctuating yields of complexes **5** and **6** were the only result, no new species was detected in isolable amounts. It was clear that the *exo*-imine species **6** forms rapidly, but in water or water/acetonitrile the addition of the second methanal is comparatively slow so that under those conditions both species may be isolated from the reaction mixture. When the solvent was varied, using DMF, DMSO and aqueous ethanol, no reaction at all was detected.

The simplest mechanism for the reactions of $[Co(ten)]^{3+}$ with methanal, consistent with all available data, is summarized in Scheme 1. The first step consists of condensation of methanal with a coordinated amine and elimination of water to form complex **6**, followed by the addition of a second methanal forming an *N*-hydroxymethyl substituent. The next step is likely to be addition of the hydroxymethyl group to the *exo*-imine group, followed by substitution of the third amine by a chloride ion, resulting in the unprotonated form of the pendant-arm macrocycle **5**. The order of the last two steps is open to debate. However, inspection of models revealed that formation of the ether bridge led to steric hindrance at the remaining primary amine which could facilitate its substitution by chloride ion. Indeed, when the bridge was broken in basic solution in the absence of methanal, the original $[Co(ten)]^{3+}$ tripod reformed rapidly.

Reactions linking coordinated amines with two methanal units to form ether bridges are not particularly common. The first example of this type of reaction in an octahedral complex was the reaction of methanal with glycinatobis(ethanediamine)-cobalt(III) to form an N_4O_2 macrocyclic complex.[9] More commonly, coordinated primary amines are linked with a single methanal to form NH–CH_2–NH bridges,[10] in this instance however that would lead to a very strained structure.

The partial or complete separation of one arm of a tripodal ligand from the metal ion is not a common event in these types of reactions. Tripodal addition products formed from reactions of $[Co(sen)]^{3+}$ and methanal have already been described (see above). N_6 macrocyclic reaction products, with and without pendant arms, have been synthesized from decomposition reactions of a chloro-substituted N_6 Co(III) cage complex, rather than directly from reactions of methanal with coordinated amines.[11] One species with a completely uncoordinated pendant arm, [6-(4′-ammonio-2′-azoniabutyl)-13-methylene-1,4,8,11-tetraazacyclotetradecane(dichloro)cobalt(III) (**7**), has been structurally characterized[11] and, as noted for complex **5**, the bridge between the coordinated amines is bent and would contribute to the substitution of the pendant arm amines by chloride ions. The coordinated chloride ions are *trans* to each other and the macrocyclic moiety is in the chair conformation with the donor amine sites being approximately coplanar.

Another complex similar to **5**, 13-(4′-amino-2′-thiabutyl)-13-methyl-6-nitro-1,11,-dithia-4,8-diazacyclotetradec-4-enato(6)-cobalt(III), has been synthesized from the decomposition reaction in aqueous base of a nitro-capped N_3S_3 Co(III) cage.[12] In this complex, **8**, the pendant arm remained coordinated by *both* its thioether and primary amine groups. The amines of the macrocycle were linked by a nitronate-like bridge which was nearly planar and did not sterically hinder the coordinated primary amine.



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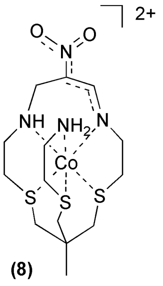

(8)

The pendant-arm macrocycle **5** and its precursor, complex **6**, are common by-products in syntheses of N_3S_3 cobalt(III) cages.[13] Formation of complex **6**, a tripod with an *exo*-imine, is unremarkable as it is the anticipated initial product of the reaction of $[Co(ten)]^{3+}$ with methanal. That the pendant-arm macrocycle **5** was formed in reasonable yield under the same conditions contrasts with the outcomes seen with structurally similar hexaamine systems. In those cases, the addition of more than one methanal molecule produced a tripodal complex with multiple coordinated *exo*-imines as the major product, *e.g.* **4**.[5] Clearly in N_3S_3 systems the addition of the hydroxymethyl substituent to the first exo-imine is competitive with dehydration to form a second *exo*-imine. The explanation almost certainly lies in the effects of the thioether groups on the geometry of $[Co(ten)]^{3+}$ and related complexes.[3,6,14,15] These cause the cobalt–amine bonds to be longer than usual so that the reduction potential is more positive and the amine reactions do not exactly mirror those of their N_6 analogues and the cobalt(II) state is more accessible.

These examples create new opportunities for making pendant-arm macrocycles with varying properties. In this case, the ligating group of the pendant arm is a thioether, less common in cobalt(III) systems, but the pendant amine could be tied readily to other ligands both biological and chemical by standard strategies.[16–18] Such molecules can be used as markers for proteins or peptides either labelled with radioactive isotopes or a paramagnetic oxidation state.

Experimental

Syntheses

Caution! Perchlorate salts are potentially explosive and should be handled with care and in small quantities.

Caution! Methanal is a carcinogen and reactions involving it should be carried out in a well ventilated fumehood and also quenched with acetic acid (instead of hydrochloric acid) to avoid formation of carcinogenic halogenoethers.

Ion exchange chromatography was performed with Dowex 50W × 2 (200–400 mesh) resin. The ten ligand complexes, $[Co(ten)]Cl_3$ and $[Co(ten)]Cl_2ClO_4$, were prepared by published syntheses.[3,4]

Experiments have shown that the rate of reaction of $[Co(ten)]^{3+}$ with paraformaldehyde in acetonitrile is sensitive to the counterion used. $[Co(ten)]Cl_2ClO_4$ was soluble in acetonitrile but reaction with paraformaldehyde was slow; after 30 min, three-quarters of the starting material was still present. $[Co(ten)]Cl_3$, even in the presence of excess sodium perchlorate, was only slightly soluble in acetonitrile but after 30 min reaction it was consumed completely. Accordingly $[Co(ten)]Cl_3$ with sodium perchlorate was used for reactions with paraformaldehyde in acetonitrile.

8-(4′-Ammonio-2′-thiabutyl)-8-methyl-1-oxa-6,10-dithia-3,13-diazacyclotetradecane(chloro)cobalt(III) triperchlorate trihydrate (5)

$[Co(ten)]Cl_3$ (1.0 g), $NaClO_4$ (3.0 g) and paraformaldehyde (0.5 g) were stirred in acetonitrile (15 mL) for 10 min and triethylamine (2 mL) was added. The suspension was stirred in a stoppered flask for 30 min and then neutralized with acetic acid, diluted with water and chromatographed on Dowex. Elution with 1 M HCl removed some $[Co(H_2O)_6]^{2+}$ and the title complex was eluted with 2 M HCl and the eluate reduced to dryness by rotary evaporation. (Ten·3HCl and some highly charged Co(III) material remained on the column.) The purple residue was taken up in water and crystallized with aqueous $NaClO_4$, washed with ethanol and ether, and air-dried (0.40 g, 24%). Crystals were obtained by slow evaporation at ~20 °C of a solution of complex **5** in aqueous sodium perchlorate and ethanol. ^1H NMR δ (D_2O) 1.38 (3H), $\mathbf{CH_3}$; 2.7–3.5, complex methylene envelope; 4.18 (2H) mult., CH_2–$\mathbf{CH_2}$–NH_3; 4.44 (2H) d, 4.95 (2H) d, O–$\mathbf{CH_2}$–N. ^{13}C NMR δ (D_2O) 29.0, $\mathbf{CH_3}$; 36.8 (2C), 38.5, 39.1, 41.3, 41.8, $\mathbf{CH_2}$–S; 41.2, $\mathbf{C_q}$; 42.3, 48.2, 49.8, CH_2–CH_2–N; 80.0, 81.2, O–CH_2–N. Electronic spectrum (in 1 M HCl) [λ_{max}/nm (ε_{max}/dm^3 cm^{-1} mol^{-1})]: 529 (402), 407 (468), 365 (560 sh). Analysis for $Co_1C_{13}H_{36}N_3S_3Cl_4O_{16}$ calc. (found): %C 19.83 (20.04); %H 4.61 (4.56); %N 5.34 (5.29).

11-Amino-7-(4-amino-2-thiabutyl)-7-methyl-2-aza-5,9-dithiaundec-1-enecobalt(III) trichloride (6)

$[Co(ten)]Cl_2ClO_4$ (1.0 g) was dissolved in aqueous methanal (20 mL) diluted with an equal volume of water then Na_2CO_3 (1.0 g) was added. The solution was stirred for 5 min and then neutralized with acetic acid in a large beaker. The solution was diluted with water and chromatographed on Dowex. Elution of the column with 1 M HCl removed a small amount of $[Co(H_2O)_6]^{2+}$ and the bright red title complex was then eluted with 2 M HCl. A minor amount of complex **5** and some ten·3HCl remained on the column. The eluate was reduced to dryness by rotary evaporation, leaving a bright red, deliquescent chloride salt (0.47 g). Attempts to crystallize this complex analytically pure were unsuccessful. ^1H NMR δ (D_2O) 1.39 (3H), $\mathbf{CH_3}$; 2.8–3.4, complex methylene envelope; 5.25 (2H) br., 5.50 (2H) br., $\mathbf{NH_2}$; 8.05 (1H) d, 8.25 (1H) d, N=$\mathbf{CH_2}$. ^{13}C NMR δ (D_2O) 29.5, –$\mathbf{CH_3}$; 35.0, 36.7, 39.1, 39.5 (2C), 40.5, S–$\mathbf{CH_2}$; 39.3, $\mathbf{C_q}$; 42.2, 45.8, 64.5, N–$\mathbf{CH_2}$–; 176.5, N=$\mathbf{CH_2}$. Within 15 min from dissolution of this complex, there was no evidence of other species being present.

Mechanistic studies

In these experiments, the reaction products were isolated by chromatography on Dowex unless otherwise indicated; the columns were washed with water then eluted successively with 1, 2 and 3 M HCl. The complexes were isolated as their chloride salts by rotary evaporation of the eluates and were identified by ^1H and ^{13}C NMR spectroscopies.

$[Co(ten)]Cl_3$ (0.5 g) was slurried in acetonitrile (15 mL) and paraformaldehyde (0.6 g) and triethylamine (2 mL) were added successively. The suspension was stirred for 20 min then quenched with acetic acid, diluted with water and the products were isolated and identified. The experiment was repeated with reaction times of 5 and 50 min. The experiment was repeated with some water (0.5 mL) added to the acetonitrile solvent and finally using aqueous methanal with dissolved sodium carbonate as the solvent with no added paraformaldehyde for reaction times of 10 and 30 min.

Complex **5** was dissolved in aqueous sodium carbonate solution, and in dimethylsulfoxide and dimethylformamide, both with added triethylamine. After 5 min the solutions were acidified with acetic acid, then diluted with water and chromatographed to isolate and identify the reaction products. Complex **6** was reacted in the same way.

Spectra

NMR spectra were recorded with a Varian Gemini 300 MHz spectrometer; the solvent was D_2O and the internal reference was dioxane $\{\delta = 3.70$ ppm (^{1}H) and $\delta = 67.4$ ppm (^{13}C)$\}$. UV-visible spectra were recorded with a Cary 5G spectrophotometer.

Electrochemistry

Cyclic voltammetry was carried out under nitrogen with a glassy carbon working electrode using a BAS 100 electrochemical analyser in 0.10 M $NaClO_4$ solution with a platinum wire auxiliary electrode and a saturated calomel reference electrode at 25 °C. The scan speed was 100 mV s^{-1}.

X-Ray crystallography

Crystal data – **5** = $C_{13}H_{30}ClCoN_3S_3.3(ClO_4).3(H_2O)$, M_c 787.46. Monoclinic, space group $P2_1/n$, a 8.0402(3), b 32.169(1), c 11.8590(4) Å, β 109.662(1)°, V 2888.4(2) Å^3, Z 4, T 120 (2) K, λ (Mo-Kα) 0.71073 Å, $\rho_{calc.}$ 1.811 Mg m^{-3}, μ(Mo-Kα) 1.260 mm^{-1}, crystal size 0.48 × 0.18 × 0.08 mm, min./max. transmission 0.634/0.906, index ranges $-10 \le h \le 11$, $-12 \le k \le 44$, $-12 \le l \le 15$, θ_{max} 30.04°, reflections collected 23467, independent reflections 7461, reflections for refinement 5891 ($I > 4\sigma(I)$), parameters 363, goodness of fit 1.29, $R(F_o)$, $R_w(F_o)$ 0.064, 0.064.

Structure solution and refinement – A crystal was mounted on a Siemens (now Bruker) SMART CCD area detector diffractometer. Data were collected with the crystal cooled to 120(2) K in a cold nitrogen gas stream (CRYOSTREAM cooler).[19] The data collection covered a hemisphere of reciprocal space by combining three sets of exposures with $\phi = 0$, 88 and 180°. Data collection programs were SMART, SAINT and XPREP.[20] The structure was solved by direct methods program SIR97;[21] Programs used to refine and display the structure were modified ORFLS[22] in KRYSTAL;[23] molecular graphics: ORTEPIII[24] in KRYSTAL. The structure appears to have three potential water sites, OW1, OW2 and OW3. However, as pointed out by a referee, there are short contacts between OW1 and OW3 (1.07 Å) and also between OW2 and OW3 (1.74 Å). Furthermore, the displacement parameters of OW2 (0.176 Å^2) and OW3 (0.088 Å^2) have high values compared with that of OW1 (0.055 Å^2). This implies that the water sites, and in particular OW2 and OW3, are only partially occupied, possibly indicating that at the temperature at which the structure was determined (120 K) there were only two waters of solvation in the lattice instead of the three detected by microanalysis at 25 °C.

Atomic coordinates, molecular bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

CCDC reference number 185897.

See http://www.rsc.org/suppdata/dt/b2/b205832d/ for crystallographic data in CIF or other electronic format.

Acknowledgements

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