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ARTICLE

Manganese-Calcium Clusters Supported by Calixarenes

Cite this: DOI: 10.1039/x0xx00000x

Rebecca O. Fuller^a, George A. Koutsantonis^{a*}, Ivan Lozic^a, Mark I. Ogden^b, and Brian W. Skelton^c

Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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The structure of the oxygen-evolving complex of photosystem II, which contains a cubane-like metal-oxo cluster incorporating four manganese(III,IV) cations, along with a calcium cation, has focussed attention on synthetic analogues of this cluster. Despite this activity, there are relatively few structurally characterised coordination clusters with this combination of metal cations. The calixarenes are synthetically versatile and well established cluster-supporting ligands, which to date have not been reported to support a calcium/manganese cluster. Here we report that *p*-*t*-butylthiacalix[4]arene supports CaMn₂ and Ca₂Mn₂ clusters, whereas reactions of *p*-*t*-butylcalix[4]arene, *p*-*t*-butylsulfinylcalix[4]arene, and *p*-*t*-butylsulfonylcalix[4]arene, under the same conditions, produced only homometallic manganese complexes.

Introduction

The structure of the oxygen-evolving complex of photosystem II contains a cubane-like metal-oxo cluster incorporating four manganese(III,IV) cations, along with a calcium ion that is known to be essential for activity (Figure 1),¹⁻⁵ although its function is duplicated by strontium.⁶

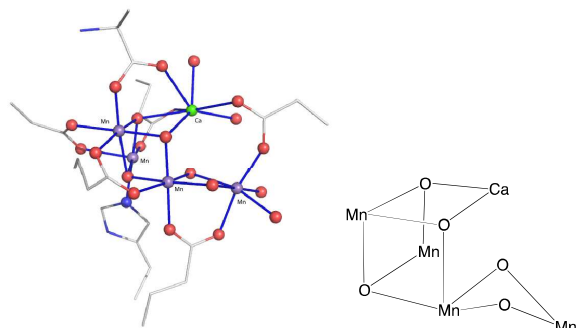


Figure 1. The core of the OEC derived from PDB file 3ARC and a schematic representation of the core.

This has driven increased interest in heterometallic complexes incorporating these metals.⁷⁻¹⁰ While the role of the redox-inactive metal ion is still being actively investigated, the influence of this cation on electron transfer processes in synthetic systems has been elegantly demonstrated recently.^{8, 11, 12} Despite this activity, relatively few calcium/manganese clusters have been structurally characterised.^{7, 13-16}

We, and others, have reported homometallic manganese clusters supported by calix[4]arene and thiacalix[4]arene ligands. While most of these have been structurally

characterised as Mn(II) complexes¹⁷⁻²⁵, a series of Mn(III)/Mn(II) tetranuclear^{26, 27} and pentanuclear²⁸ complexes and a dinuclear Mn(III)/Mn(IV) complex²⁹ illustrate that higher oxidation states can be supported. Both Mn(II),³⁰ and Mn(III)^{31, 32} heterometallic manganese complexes with these ligands have been reported, but only with lanthanoid cations. These include a fascinating series of [Mn(III)₄Ln(III)₄]^{31, 32} complexes, where the magnetic properties range from single molecule magnet to enhanced magnetocaloric effect, depending on the lanthanoid cation that is incorporated.

Given the potential importance of Mn/Ca heterometallic complexes, we have investigated the potential of calix[4]arene and thiacalix[4]arene ligands to support clusters with this composition. The interchange of calcium and lanthanoids is well established in biological systems,^{33, 34} and has been investigated in calixarene complexes.³⁵ Hence it seemed likely that such Mn/Ca complexes should be accessible, and indeed this proved to be the case in some systems. We report here the first examples of Mn/Ca clusters supported by a calixarene ligand, in particular *p*-*t*-butylthiacalix[4]arene, L^S.

Experimental

Syntheses

All reactions were conducted using standard laboratory equipment, open to air. All samples were dried in a drying pistol at 1-2 mm Hg and 50-60 °C for at least 4 hours.

I, [Mn₂(Ca-2dmf)₂(L^S)₂]

H₄L^S·CHCl₃ (200 mg, 0.24 mmol) was dissolved in dmf (1 mL) by adding Et₃N dropwise in excess. A solution of MnCl₂·4H₂O (49 mg, 0.25 mmol) and CaCl₂·2H₂O (35 mg,

0.25 mmol) in dmf (1 mL) was then added. Needle-like crystals of Et_3NHCl formed within minutes. The supernatant solution was filtered and transferred into a sample vial. Light yellow cube-like crystals deposited after 2 days, and were subject to a single crystal X-ray structure determination, which gave results consistent with a formulation $1\cdot3\text{dmf}\cdot0.4\text{H}_2\text{O}$. The crystals were isolated and dried under ambient conditions (5.1 mg, 0.002 mmol, 1.1 %). Analysis: $(\text{C}_{40}\text{H}_{44}\text{O}_4\text{S}_4)_2\text{Mn}_2(\text{Ca}\cdot2\text{dmf})_2\cdot2(\text{H}_2\text{O})$ calc. C: 56.59, H: 6.20, N: 2.87, found C: 56.72, H: 6.13, N: 2.31%. The procedure was repeated, resulting in crystals of a different solvate, $1\cdot2\text{dmf}$, as determined by a structural analysis.

2, $[(\text{HL}^S)_2\text{Mn}(\text{Ca}\cdot2\text{dmf})_2]$

To a stirred suspension of $\text{H}_4\text{L}^S\cdot\text{CHCl}_3$ (101 mg, 0.11 mmol) in dmf (5 mL) was added $\text{Mn}(\text{OAc})_3\cdot2\text{H}_2\text{O}$ (32 mg, 0.12 mmol) and $\text{Ca}(\text{OAc})_2\cdot\text{H}_2\text{O}$ (21 mg, 0.12 mmol). The reaction mixture was left stirring for 22 hours, after which the solution was filtered and left to stand. Yellow plate-like crystals deposited after 3 days, and were subject to a single crystal X-ray structure determination, which gave results consistent with a formulation of $2\cdot4\text{dmf}$. The crystals were isolated and dried under ambient conditions (24 mg, 0.01 mmol, 11.2%). Analysis: $(\text{C}_{40}\text{H}_{45}\text{O}_4\text{S}_4)_2\text{Mn}(\text{Ca}\cdot2\text{dmf})_2\cdot4\text{H}_2\text{O}$ calc. C: 57.09, H: 6.56, N: 2.89, found C: 57.21, H: 6.25, N: 2.32%. The procedure was repeated, resulting in crystals of a different solvate, $2\cdot3.55\text{dmf}$, as determined by a structural analysis.

Crystallography

The crystal data for $1\cdot3\text{dmf}\cdot0.39\text{H}_2\text{O}$, $1\cdot2\text{dmf}$, $2\cdot4\text{dmf}$, and $2\cdot3.55\text{dmf}$ are summarized in Table 1. Diffraction data were collected at 100(2) K (150(2) K for $1\cdot2\text{dmf}$) on an Oxford Diffraction Gemini or Xcalibur diffractometer fitted with graphite-monochromated $\text{Mo K}\alpha$ radiation (for $1\cdot3\text{dmf}\cdot0.39\text{H}_2\text{O}$ and $2\cdot4\text{dmf}$) or $\text{Cu K}\alpha$ radiation (for $1\cdot2\text{dmf}$ and $2\cdot3.55\text{dmf}$). Following analytical absorption corrections and solution by direct methods, the structures were refined against F^2 with full-matrix least-squares using the program SHELXL-97.³⁶ Unless stated below, non-hydrogen atoms were refined with anisotropic displacement parameters with hydrogen atoms were added at calculated positions and refined by use of a riding model with isotropic displacement parameters based on those of the parent atoms.

For $1\cdot3\text{dmf}\cdot0.39\text{H}_2\text{O}$, tertiary butyl groups 14n, 54n, 74n and the solvent dmf were all modelled as being disordered over two sets of sites with occupancies refined to 0.589(3) and its complement after trial refinement found the values not to be significantly different. A relatively large peak was modelled as being a water molecule associated with one of the disordered dmf molecules. No water molecule associated with the other component of the disordered dmf could be located. The carbon atoms of the tert-butyl group 54n were refined with isotropic displacement parameters. Water molecule hydrogen atoms were not located.

For $1\cdot2\text{dmf}$, tertiary butyl groups 14n and 74n and the solvent dmf 30n were all modelled as being disordered over two sets of sites with occupancies constrained to 0.5 for the

tert-butyl groups and refined to 0.666(12) and its complement for the two components of the dmf molecule. The geometries of the disordered groups were refined with restrained geometries. Since attempts to model the solvent were not successful, the program Platon/Squeeze³⁷ was used to effectively eliminate this electron density.

For $2\cdot4\text{dmf}$, tertiary butyl groups 24n, 74n, 84n and the solvent dmf molecules 10n and 30n were all modelled as being disordered over two sets of sites. The two components of dmf 10n were assigned equal occupancies after trial refinement. The occupancies of the remaining disordered atoms were refined to 0.703(2) and its complement after trial refinement found the values for each disordered group not to be significantly different. The carbon atoms of the disordered tert-butyl groups 24n and 74n were refined with isotropic displacement parameters. Geometries of the disordered tert-butyl groups were restrained to ideal values. The hydrogen atoms involved in hydrogen bonding between adjacent phenoxy groups were refined with O-H distances restrained to ideal values.

For $2\cdot3.55\text{dmf}$, tertiary butyl groups 14n and 64n and the coordinated dmf molecule 50n were all modelled as being disordered over two sets of sites. The occupancies of the two components of each of the disordered tert-butyl atoms were constrained to 0.5 after trial refinement with those of the disordered dmf refined to 0.63(2) and its complement. Two solvent dmf molecules were refined with identical site occupancies after trial refinement found these to be similar. Geometries of the disordered tert-butyl groups were restrained to ideal values. The hydrogen atoms involved in hydrogen bonding between adjacent phenoxy groups were refined with O-H distances restrained to ideal values.

Results and Discussion

The attempted syntheses of Ca/Mn complexes of calixarene ligands, H_4L , H_4L^S , $\text{H}_4\text{L}^{\text{SO}}$, and $\text{H}_4\text{L}^{\text{SO}_2}$ (Figure 2) were carried out by simply adding a mixture of both metal cations (as chlorides or acetates) to a solution of the ligand under basic conditions. Where chlorides were used, triethylamine was added as the base, whereas no additional base was added when acetate salts were used. In some cases, manganese(III) acetate was used in an effort to form complexes at the higher oxidation state.

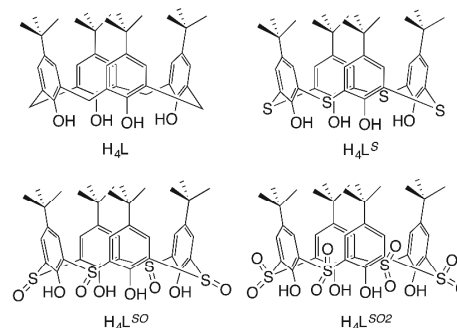


Figure 2. The calixarene ligands used in this study.

Following the synthesis of $[\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2(\text{OH})_2(\text{L})_2(\text{solvent})_6]$ reported by Karotsis *et al.*,^{26, 38} H_4L was made to react with mixtures of manganese and calcium chloride salts. In all cases, the crystalline products did not include calcium, and instead homometallic $\text{Mn}^{\text{III}}_2\text{Mn}^{\text{II}}_2$ complexes identical to those reported previously were isolated, varying only in the coordinated and lattice solvent molecules (see Figure S.1, Table S.1).

Similarly, reaction of $\text{H}_4\text{L}^{\text{SO}_2}$ with mixtures of calcium and manganese salts resulted in the precipitation of only homometallic manganese complexes. A tetranuclear anionic complex, $[\text{Mn}_4(\text{OH})(\text{L}^{\text{SO}_2})_2]^-$, was isolated as a triethylammonium salt, rather than the potassium salt previously reported by Lamouchi *et al* (Figure S.2).²⁰ A 2:1 $\text{Mn}:\text{L}^{\text{SO}_2}$ complex was also isolated, where the calixarene assumes a 1,2-alternate conformation (Figure S.3). A similar motif has been observed previously with copper,³⁹ molybdenum,⁴⁰ tungsten,⁴⁰ and terbium.⁴¹ Structural and synthetic details for these homometallic complexes are provided in the Supporting Information. Reactions of L^{SO} with Mn/Ca mixtures did not result in any materials appropriate for single crystal X-ray structure determination.

The thiacalix[4]arene, $\text{H}_4\text{L}^{\text{S}}$, proved to be a more successful system for this combination of metal ions, under the conditions explored. Reacting $\text{H}_4\text{L}^{\text{S}}$ with a 1:1 mixture of manganese(II) chloride and calcium chloride, in the presence of triethylamine, resulted in the formation of pale yellow crystals suitable for single crystal X-ray structure determination. The results of the structure determination were consistent with a complex formulated as $[\text{Mn}_2(\text{Ca}\cdot 2\text{dmf})_2(\text{L}^{\text{S}})_2] \cdot 1.3\text{dmf}\cdot 0.4\text{H}_2\text{O}$, Figure 3. The metal ions in the tetranuclear structure are planar, and assume an approximately square arrangement, with like metals on adjacent corners. The cluster is ligated by two fully deprotonated L^{S} anionic ligands in the cone conformation, with all the phenolate O atoms bridging two metal centres, and all S atoms bound to a single metal atom. The result is a trigonal prismatic O_4S_2 coordination sphere about the Mn atoms. The Ca atoms are each also bound in a unidentate fashion to two dmf solvent molecules, resulting in an O_6S_2 coordination sphere, best described as a distorted square antiprism. As expected, the $\text{Ca}\dots\text{S}$ distances (2.9171(8) – 2.9719(8) Å) are substantially longer than the $\text{Ca}\dots\text{O}$ distances (2.379(2) – 2.478(2) Å), and are similar to those found in O_6S_2 calcium complexes of L^{S} ^{25, 42} and oxa-thia crown ethers.⁴³

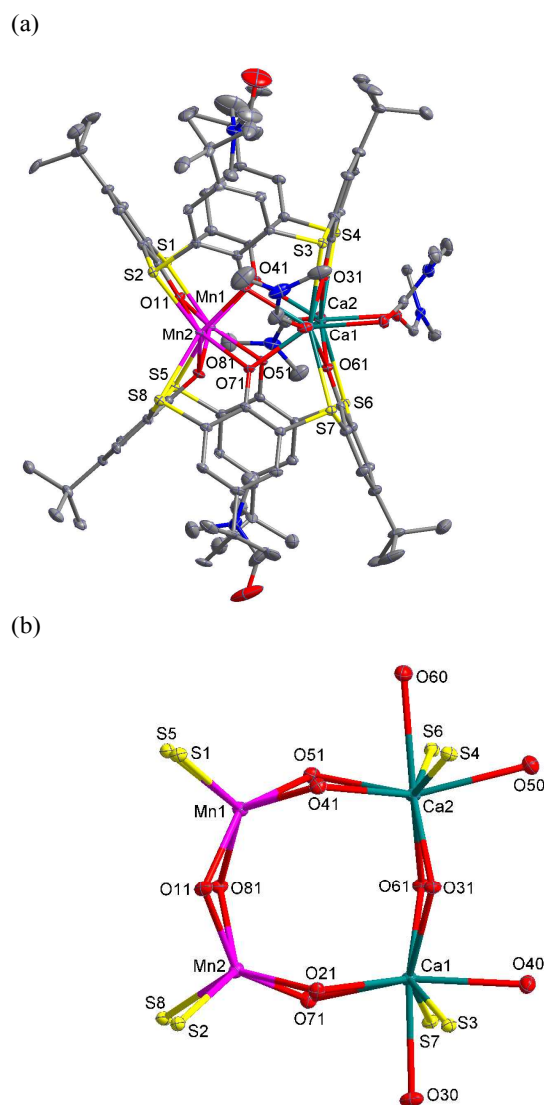


Figure 3. (a) A representation of the structure of the complex $[\text{Mn}_2(\text{Ca}\cdot 2\text{dmf})_2(\text{L}^{\text{S}})_2] \cdot 1.3\text{dmf}$. The dmf molecules included in the calixarene cavity are shown. Hydrogen atoms have been omitted. The ellipsoids are drawn at the 30% probability level with only one component of each of the disordered atoms included. (b) The core of the complex.

The two calixarene ligands are not co-planar, presumably due to the differing radii of the metal centres, with angle between the two S4 planes being $14.29(2)^\circ$. The resulting structure is similar to the previously reported Mn/Gd complex $[(\text{Mn}_2(\text{Gd}(\text{CH}_3\text{OH})_2)(\mu_4\text{-OH})(\text{L}^{\text{S}})_2)]$.³⁰ Aside from the variation in solvent molecules (dmf or methanol), the key difference is the absence of the $\mu_4\text{-OH}$ atom in the complex reported here. The angle between the two calixarene S4 planes is identical in the Mn/Ca and Mn/Gd complexes, as might be expected given the use of lanthanides as substitutes for the spectroscopically silent calcium cation in metalloenzymes.³³ Repeating the experiment resulted in the crystallisation of a different solvate, 1·2dmf, where the metal complex was essentially unchanged, but with different crystal packing. The complexes in 1·3dmf·0.4 H_2O are packed in two-dimensional sheets in the orthorhombic lattice, with the pseudo 4-fold axis of the

calixarene dimers oriented parallel to the *c*-axis. The packing in 1·2dmf is columnar, with the pseudo 4-fold axis approximately parallel to the 1T0 direction, in a triclinic unit cell (Figure S.4).

Similar reactions were carried out substituting the chloride salts with manganese and calcium acetates. In this case, no base was added aside from the acetate counterions. Despite the use of manganese(III) acetate in the reaction, pale yellow crystals were deposited, suggesting that any manganese present had been reduced to manganese(II).

In order to probe the oxidation state of the Mn ions in complexes **1** and **2** the UV-Vis spectra of the complexes were measured showing very similar features. In the case of **2**, absorbances were found at 321, 306 and 232 nm with ϵ_{max} 27, 29, and 176 L mol⁻¹ cm⁻¹, respectively. No *d-d* metal transition absorption bands were visible which is consistent with that expected for Mn(II) where these bands are very weak.⁴⁴

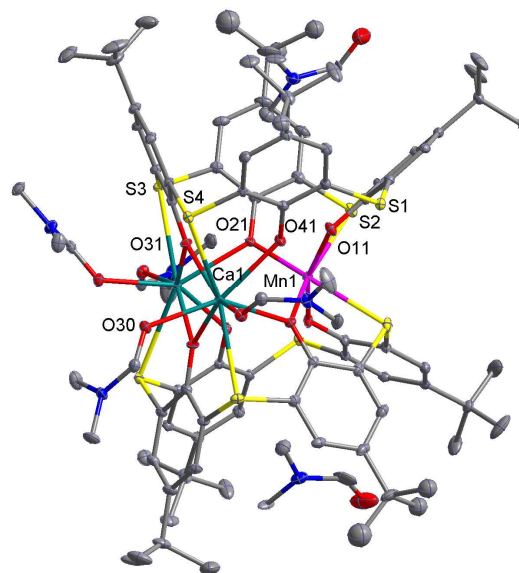
Similarly, a comparison of the bond lengths and angles of the MnO₄S₂ cores in **1** and **2** show a close correlation with that of analogous ligands sets around Mn(II) in complexes [Mn₄(L^S)₂].¹⁷ These latter complexes were further characterised with magnetic measurements that were consistent with the presence of Mn(II) ions.

The results of the structure determination were consistent with a complex formulated as [Mn(Ca·2dmf)₂(HL^S)₂], **2**. Once again, two different solvates were isolated from different experiments, 2·4dmf, and 2·3.55dmf (Table 1), with an essentially identical complex in each. The complex is again “sandwich-like”, with the two calixarene ligands disposed on either side of the plane defined by the three metal centres (Figure 4). The environments of the two calcium atoms are quite similar to that found in the tetranuclear complex. The Mn atom is once again 6-coordinate with the O₄S₂ coordination sphere best described as a distorted octahedron. A phenol O atom from each calixarene bridges between Ca and Mn, with terminal phenol O and S atoms from each calixarene completing the metal environment. Close approaches of O11...O41 (2.44 Å), and O51...O81 (2.43 Å) are consistent with the presence of a proton in each case, as is required for charge balance. Consideration of bond lengths suggests that the protons reside on calcium-coordinated O41 and O81. The S atom that bridges the H-bond linked phenol moieties on each calixarene is not involved in metal coordination. Similar trinuclear complexes with this calixarene have been reported previously, including both homo- and hetero-metallic examples.^{25, 45, 46} The most pertinent example is a PdCa₂ complex of L^S, where the calcium cations are bound in a similar manner to that found here, with the Pd atom quite differently bound as would be expected with the typical square planar geometry of the Pd coordination sphere.²⁵

The results obtained here illustrate that the calixarene framework can support Ca/Mn clusters, but to date only with the thiacalixarene L^S. It is not obvious why the more oxygen rich L^{SO} or L^{SO2} ligands would reject calcium and produce homometallic Mn complexes, but it is interesting to note that no calcium complexes of H_nL, H_nL^{SO} or H_nL^{SO2} have been structurally characterised with the unmodified ligands (although this is not true of a larger calixarene³⁵). In contrast,

homometallic Ca complexes have been reported for H_nL^S.⁴² It may be necessary to add additional ligating groups to the phenol rim of these ligands to successfully bind calcium cations.

(a)



(b)

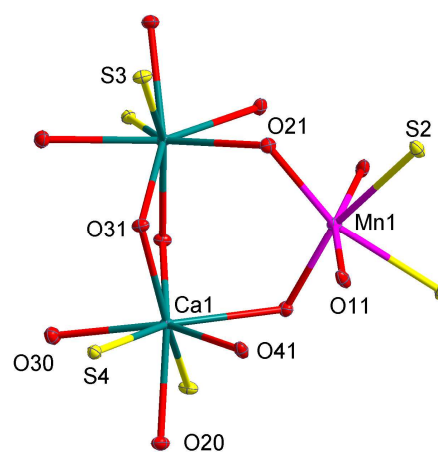


Figure 4. (a) A representation of the structure of the complex [Mn(Ca·2dmf)₂(HL^S)₂], **2**. dmf molecules included in the calixarene cavity are shown. (b) The core of the complex. Ellipsoids have been drawn at the 30% probability level.

Conclusions

It has been shown that the thiacalix[4]arene, L^S, can support heterometallic clusters composed of manganese and calcium cations, the first such clusters supported by a calixarene ligand. The other calix[4]arenes tested resulted in homometallic manganese complexes, despite the presence of calcium in the

reaction mixture. Given the low yields of the isolated metal complexes, the presence of mixed metal complexes in solution can not be ruled out. Work is now underway to clarify the solution speciation in these systems, and to study the impact that the redox-inactive metal has on the electrochemical properties of the isolated Mn/Ca complexes.

Notes and references

^a Chemistry M310, School of Chemistry and Biochemistry, University of Western Australia, Crawley, Western Australia 6009.

^b Department of Chemistry, Curtin University, GPO Box U 1987, Perth, Western Australia 6845.

^c Centre for Microscopy, Characterisation and Analysis, University of Western Australia, Crawley, Western Australia 6009.

Electronic Supplementary Information (ESI) available: Syntheses and crystallographic details for Mn complexes of H₄L^{SO2} and H₄L; unit cell diagrams of **1** and **2**. See DOI: 10.1039/b000000x/

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Table 1: Crystal data and refinement details for Mn-Ca thiacalixarene (L^S) complexes, **1**, [Mn₂(Ca·2dmf)₂(L^S)₂], and **2**, [Mn(Ca·2dmf)₂(HL^S)₂].

Complex	1·3dmf·0.39H ₂ O	1·2dmf	2·4dmf	2·3.55dmf
Empirical Formula	C ₁₀₁ H _{137.78} Ca ₂ Mn ₂ N ₇ O _{15.39} S ₈	C ₉₈ H ₁₃₀ Ca ₂ Mn ₂ N ₆ O ₁₄ S ₈	C ₁₀₄ H ₁₄₆ Ca ₂ Mn ₂ N ₈ O ₁₆ S ₈	C _{102.65} H _{142.85} Ca ₂ Mn ₂ N _{7.55} O _{15.55} S ₈
Formula Weight (g/mol)	2142.72	2062.60	2155.87	2122.97
Temperature (K)	100(2)	150(2)	100(2)	100(2)
Wavelength (Å)	0.71073	1.54178	0.71073	1.54178
Radiation	Mo Kα	Cu Kα	Mo Kα	Cu Kα
Crystal System	Orthorhombic	Triclinic	Monoclinic	Orthorhombic
Space Group	<i>Pna</i> 2 ₁	<i>P</i> $\bar{1}$	<i>C</i> 2	<i>P</i> 2 ₁ 2 ₁ 2 ₁
<i>a</i> (Å)	25.2966(3)	16.5399(16)	34.7547(4)	16.8316(5)
<i>b</i> (Å)	12.60940(10)	17.1006(16)	17.0086(2)	19.3323(4)
<i>c</i> (Å)	34.4646(4)	22.1927(19)	19.4792(3)	34.4393(9)
α (°)	90	72.088(8)	90	90
β (°)	90	82.292(8)	99.0440(10)	90
γ (°)	90	85.576(8)	90	90
Volume (Å ³)	10993.3(2)	5914.5(9)	11371.6(3)	11206.3(5)
<i>Z</i>	4	2	4	4
ρ_{calc} (Mg m ⁻³)	1.295	1.158	1.259	1.258
μ (mm ⁻¹)	0.537	4.252	0.416	3.652
Crystal size (mm ³)	0.68 × 0.38 × 0.21	0.22 × 0.16 × 0.12	0.53 × 0.39 × 0.10	0.36 × 0.14 × 0.10
θ range (°) Reflections collected	2.91 to 32.89 155571	2.89 to 67.58 60835	3.57 to 34.92 135950	2.92 to 67.34 117067
Independent reflections (<i>R</i> _{int})	38737 (0.0356)	20874 (0.0896)	46615 (0.0483)	19960 (0.0848)
Absorption correction	Analytical	Analytical	Analytical	Analytical
Transmission (min, max)	0.801, 0.934	0.532, 0.669	0.853, 0.963	0.426, 0.723
Data/restraints/parameters	38737/67/1359	20874/142/1249	46615/57/1401	19960/228/1391
Goodness of fit on <i>F</i> ²	1.038	0.921	0.927	0.992
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> 1=0.0522, <i>wR</i> 2=0.1372	<i>R</i> 1=0.0976, <i>wR</i> 2=0.2536	<i>R</i> 1=0.0449, <i>wR</i> 2=0.0921	<i>R</i> 1=0.0745, <i>wR</i> 2=0.1841
<i>R</i> indices (all data)	<i>R</i> 1=0.0637, <i>wR</i> 2=0.1409	<i>R</i> 1=0.1427, <i>wR</i> 2=0.2758	<i>R</i> 1=0.0668, <i>wR</i> 2=0.0962	<i>R</i> 1=0.0969, <i>wR</i> 2=0.2044
Largest diff. peak and hole	1.353 and -0.532 e.Å ⁻³	1.799 and -0.623 e.Å ⁻³	1.186 and -0.562 e.Å ⁻³	1.241 and -0.421 e.Å ⁻³
CCDC No.	983281	983283	983284	983286