Synthesis and characterization of hexaosmium carbonyl clusters containing pyridine ligands: crystal and molecular structures of $[Os_6(CO)_{15}(\mu_4\text{-}\eta^2\text{-}CO)(C_5H_5N)_3]$, $[Os_6(CO)_{15}(\mu\text{-}H)(\mu\text{-}CO)(\mu_3\text{-}O)(C_5H_5N)(\mu\text{-}\eta^2\text{-}NC_5H_4)]$ and $[Os_6(CO)_{14}(\mu\text{-}H)(\mu\text{-}CO)(MeCN)(C_5H_5N)(\mu\text{-}\eta^2\text{-}NC_5H_4)]$

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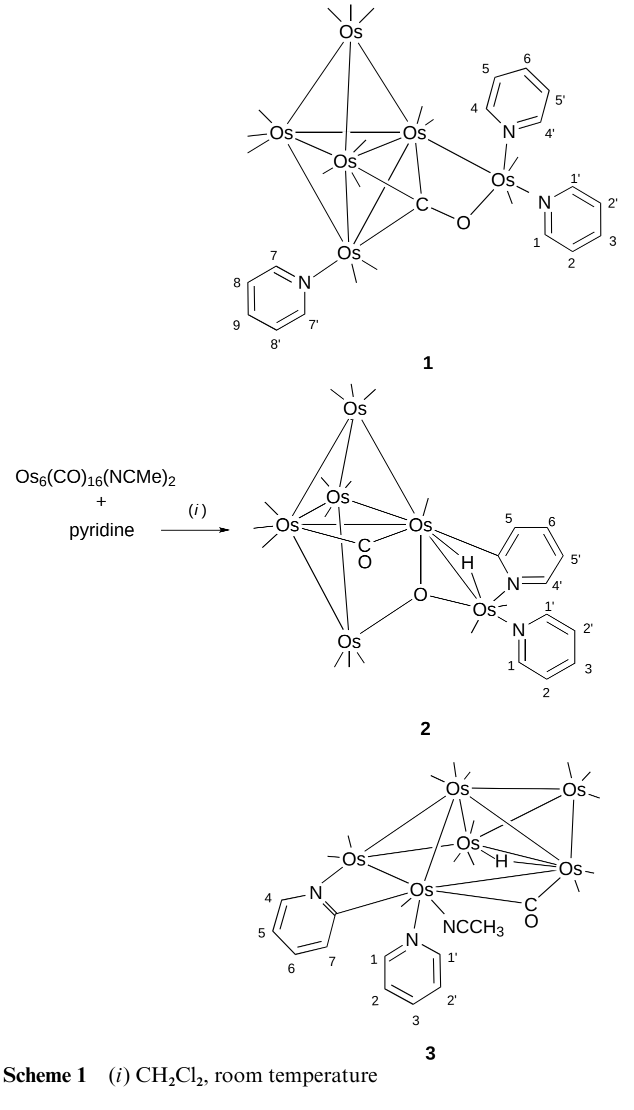
Reaction of $[Os_6(CO)_{16}(MeCN)_2]$ with 1 equivalent of pyridine in CH_2Cl_2 at room temperature afforded three new clusters: $[Os_6(CO)_{15}(\mu_4\text{-}\eta^2\text{-}CO)(C_5H_5N)_3]$ **1**, $[Os_6(CO)_{15}(\mu\text{-}H)(\mu\text{-}CO)(\mu_3\text{-}O)(C_5H_5N)(\mu\text{-}\eta^2\text{-}NC_5H_4)]$ **2** and $[Os_6(CO)_{14}(\mu\text{-}H)(\mu\text{-}CO)(MeCN)(C_5H_5N)(\mu\text{-}\eta^2\text{-}NC_5H_4)]$ **3** in 32, 10 and 25% yields respectively. Both clusters **2** and **3** contain an orthometallated pyridine ligand but with different metal core geometries. The molecular structure of cluster **2** revealed the presence of a novel μ_3-O group bridging three osmium centres.

High nuclearity carbonyl clusters have attracted interest owing to the rapid expansion of cluster chemistry.[1–3] Lewis and co-workers[4] have reported that a novel μ_4-η^2-CO bridging group was observed in a bis(pyridine)hexaosmium cluster $[Os_6(CO)_{17}(py)_2]$ (py = pyridine) from the reaction of $Os_6(CO)_{18}$ with pyridine. Apart from this cluster species, the dianionic pentaosmium carbonyl cluster $[Os_5(CO)_{15}]^{2-}$ was also isolated as the major product in the same reaction. This finding represents the pioneering work on N-donor ligands towards hexaosmium cluster systems.[4] However, to our knowledge, further explorations on this hexanuclear system are limited. Therefore, we have investigated whether or not other substituted derivatives of $Os_6(CO)_{18}$ can be obtained from a more reactive starting material, namely $[Os_6(CO)_{16}(MeCN)_2]$. Establishing the structural and chemical properties of these high nuclearity species is important for designing analogous systems containing functionalized pyridines. We have reported some examples of triosmium systems based on this principle recently.[5] In this article we describe the preparation and spectroscopic studies of three new pyridine-containing hexaosmium clusters. Their molecular structures have also been determined by single-crystal X-ray crystallographic techniques.

Results and Discussion

Treatment of 1 equivalent pyridine with the preformed labile bis(acetonitrile)hexaosmium carbonyl cluster $[Os_6(CO)_{16}(MeCN)_2]$ in CH_2Cl_2 at room temperature over a period of 24 h led to a dark brown reaction mixture. Separation of products by TLC on silica gave three major products: $[Os_6(CO)_{15}(\mu_4\text{-}\eta^2\text{-}CO)(C_5H_5N)_3]$ **1**, $[Os_6(CO)_{15}(\mu\text{-}H)(\mu\text{-}CO)(\mu_3\text{-}O)(C_5H_5N)(\mu\text{-}\eta^2\text{-}NC_5H_4)]$ **2** and $[Os_6(CO)_{14}(\mu\text{-}H)(\mu\text{-}CO)(MeCN)(C_5H_5N)(\mu\text{-}\eta^2\text{-}NC_5H_4)]$ **3** in 32, 10 and 25% yields respectively, see Scheme 1. In addition several uncharacterized products in very low yields were also obtained. However, it is interesting to note that no significant amount of the $[Os_5(CO)_{15}]^{2-}$ dianion and $[Os_6(CO)_{17}(py)_2]$ were detected, although they are the major products from the reaction of $Os_6(CO)_{18}$ and pyridine.[4] Using excess pyridine in the reaction led to a higher yield of cluster **1** (38%) at the expense of **2** (5%). However, treatment of cluster **2** with pyridine did not lead to the formation of **1**. Therefore, **2** is unlikely to be an intermediate for the formation of **1**. The yield of **3** is not significantly affected by excess pyridine.



Scheme 1 (*i*) CH_2Cl_2, room temperature

All three new hexaosmium pyridine clusters were characterized by spectroscopic techniques and X-ray crystallography. A perspective drawing of cluster **1** with the atomic numbering scheme is shown in Fig. 1. Selected bond parameters are presented in Table 1. The metal core geometry of **1** can be described as a trigonal bipyramid with a 'spike' metal atom [Os(6)] appended to the equatorial plane of the bipyramid which is essentially the same as that in the previously reported $[Os_6(CO)_{17}(py)_2]$.[4] A salient structural feature of **1** is a CO lig-

Table 1 Selected bond distances (Å) and angles (°) for cluster **1**

Os(1)–Os(2)	2.887(4)	Os(4)–Os(6)	2.858(4)
Os(1)–Os(3)	2.745(4)	Os(5)–N(1)	2.06(6)
Os(1)–Os(4)	2.793(4)	Os(6)–N(2)	2.14(4)
Os(2)–Os(3)	2.873(4)	Os(6)–N(3)	2.14(5)
Os(2)–Os(4)	2.812(5)	Os(2)–C(14)	2.24(6)
Os(3)–Os(4)	2.763(4)	Os(4)–C(14)	1.95(6)
Os(2)–Os(5)	2.793(4)	Os(5)–C(14)	2.18(6)
Os(3)–Os(5)	2.788(4)	Os(6)–O(14)	2.07(4)
Os(4)–Os(5)	2.817(4)	C(14)–O(14)	1.41(6)
Os(2)–Os(4)–Os(6)	109.4(1)	Os(6)–O(14)–C(14)	92(3)
Os(4)–Os(6)–O(14)	74(1)	Os(4)–C(14)–O(14)	129(4)

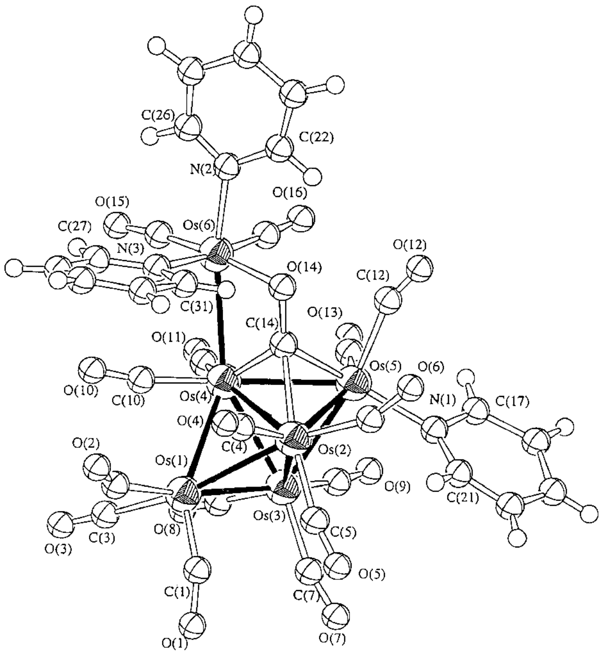


Fig. 1 Molecular structure of cluster **1** showing the atomic labelling scheme for non-hydrogen atoms

and co-ordinated to the metal core in a dihapto fashion. This co-ordination mode leads to considerable weakening of the CO bond strength as evident from the solid state (KBr disc) IR spectroscopic measurement (μ_4-η^2-CO, 1340.7 cm^{-1}). A significantly longer CO distance [1.41(6) Å] is also found for this unusual co-ordination mode. This CO vector is essentially perpendicular to the least-squares plane defined by Os(2), Os(4) and Os(5). It is interesting to note that in the ruthenium cluster [$Ru_8(\mu$-$H)_2(\mu_6$-η^2-$CO)(CO)_{19}(\eta^6$-$C_{16}H_{16})$] with a μ_6-η^2-CO ligand recently reported by Johnson and co-workers,[6] this kind of CO perpendicular to the metal basal plane arrangement is also present. As far as the electron counting is concerned, cluster **1** contains 88 cluster valence electrons (CVE) and is consistent with ten metal–metal bonds observed in the structure according to the effective atomic number (EAN) rule.

The molecular structure of cluster **2** is depicted in Fig. 2 and some important bond parameters are given in Table 2. The metal core can be described as an edge-bridging tetrahedron with an additional 'spike' atom. A similar core geometry has been observed in [$Os_6(CO)_{18}(CNC_6H_4Me)_2$].[7] A novel structural feature of cluster **2** is that a μ_3-oxo atom is embraced in the semi-open environment described by Os(4), Os(5) and Os(6). This bridging oxo group adopts a distorted 'T' shaped co-ordination geometry with the angles Os(4)–O(17)–Os(6), Os(4)–O(17)–Os(5) and Os(5)–O(17)–Os(6) of 87.3(6), 108.9(7) and 152.6(8)° respectively, which sum to a value of *ca.* 350.0°. The atom O(17) is slightly deviated (0.33 Å) from the plane defined by Os(4)–Os(5)–Os(6). The capping modes of μ_3-oxo[8a] or μ_4-oxo[8b] in osmium cluster systems have been reported, and numerous examples are also known in ruthenium systems.[9–15] However, to our knowledge, there are no structurally characterized examples of the μ_3-oxo group in a 'T' shaped environment in an osmium system. Another interesting feature of cluster **2** is the formation of an orthometallated pyridine ring that arises from C–H fission to form a bridging hydride as evident from ^{1}H NMR spectroscopic studies. This triply-bridged Os(4)–Os(6) distance [2.823(1) Å] is shorter than the corresponding distance [2.858(4) Å] in cluster **1**. Assuming that the μ-CO and μ_3-O groups act as two- and four-electron donors respectively, then cluster **2** is a 90-electron species which is consistent with the nine metal–metal bonds observed in the structure according to the EAN rule.

A perspective drawing of cluster **3** with the atomic number-

Table 2 Selected bond distances (Å) and angles (°) for cluster **2**

Os(1)–Os(2)	2.829(2)	Os(4)–Os(6)	2.823(1)
Os(1)–Os(3)	2.684(2)	Os(4)–O(17)	2.07(2)
Os(1)–Os(4)	2.905(1)	Os(5)–O(17)	2.09(2)
Os(2)–Os(3)	2.783(2)	Os(6)–O(17)	2.02(2)
Os(2)–Os(4)	2.835(1)	Os(6)–N(1)	2.09(2)
Os(3)–Os(4)	2.788(1)	Os(4)–C(17)	2.08(3)
Os(2)–Os(5)	2.911(2)	Os(6)–N(2)	2.13(2)
Os(3)–Os(5)	2.793(2)		
Os(4)–O(17)–Os(6)	87.3(6)	Os(5)–O(17)–Os(6)	152.6(8)
Os(4)–O(17)–Os(5)	108.9(7)		

Table 3 Selected bond distances (Å) and angles (°) for cluster **3**

Os(1)–Os(2)	2.916(4)	Os(4)–Os(6)	2.764(4)
Os(1)–Os(3)	2.805(4)	Os(5)–Os(6)	2.834(4)
Os(1)–Os(4)	2.770(4)	Os(6)–C(18)	2.14(6)
Os(2)–Os(3)	2.823(4)	Os(5)–N(1)	2.13(6)
Os(2)–Os(4)	2.790(4)	Os(6)–N(2)	2.24(5)
Os(2)–Os(5)	2.817(4)	Os(6)–N(3)	2.16(5)
Os(2)–Os(6)	2.968(4)	Os(6)–C(12)	2.25(6)
Os(3)–Os(4)	2.940(4)	Os(4)–C(12)	1.94(7)
Os(3)–Os(5)	2.864(4)		
Os(3)–Os(5)–N(1)	152(1)	Os(1)–Os(3)–Os(5)	121.7(1)
Os(4)–Os(6)–C(18)	151(1)	Os(1)–Os(4)–Os(6)	127.6(1)

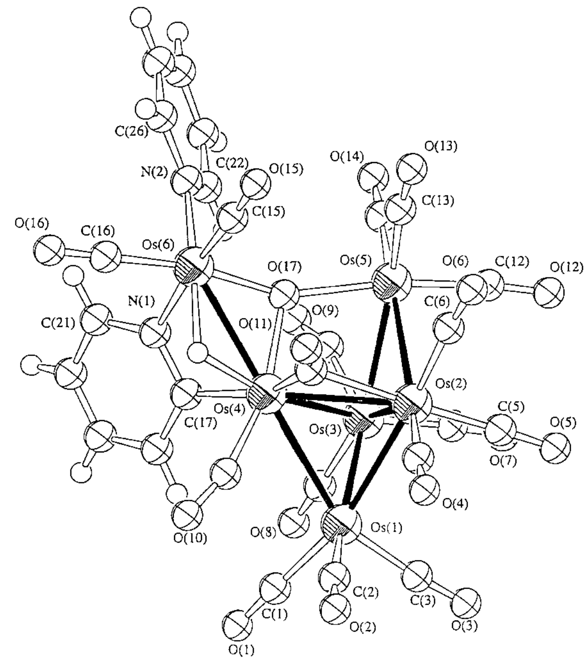


Fig. 2 Molecular structure of cluster **2**. Details as in Fig. 1

Table 4 Spectroscopic data for clusters **1**–**3**

Cluster	IR,[a] ν(CO)/cm^{-1}	^{1}H NMR,[b] δ	Mass spectrum,[c] *m/z*
1	2064ms, 2028s, 2014s, 2004s, 1983ms, 1962w, 1945ms	8.75 (2 H$^{7,7'}$, dd, *J* = 6.8, 1.6), 8.74 (2 H$^{1,1'}$, dd, *J* = 6.7, 1.6), 8.63 (2 H$^{4,4'}$, dd, *J* = 6.4, 1.8), 7.90 (1 H^9, tt, *J* = 7.6, 1.6), 7.77 (1 H^3, tt, *J* = 7.6, 1.7), 7.68 (1 H^6, tt, *J* = 7.7, 1.7), 7.45 (2 H$^{8,8'}$, m), 7.31 (2 H$^{2,2'}$, m), 7.29 (2 H$^{5,5'}$, m)	1826 (1827)
2	2091w, 2062s, 2032s, 2016ms, 1981w, 1956w	8.58 (2 H$^{1,1'}$, dd, *J* = 6.8, 1.3), 8.48 (1 H$^{4'}$, m), 7.62 (1 H^5, dd, *J* = 6.4, 1.5), 7.48 (1 H^3, tt, *J* = 7.6, 1.3), 7.27 (2 H, m), 6.96–7.09 (1 H$^{5'}$, m), 6.82–6.92 (1 H^6, m), −16.20 (1 H, s, OsH)	*d*
3	2072ms, 2029s, 2018s, 1999ms, 1978w, 1952w	8.61 (1 H^7, m), 8.58 (2 H$^{1,1'}$, dd, *J* = 6.6, 1.5), 8.04 (1 H^3, tt, *J* = 7.2, 1.6), 7.58 (2 H$^{2,2'}$, m), 7.43 (1 H^4, dd, *J* = 6.2, 1.5), 6.72 (1 H^5, m), 6.58 (1 H^6, m), −15.30 (1 H, s, OsH)	1760 (1719)[e]

[a] In CH_2Cl_2. [b] In CD_2Cl_2; *J* values in Hz. [c] Simulated values given in parentheses. [d] No satisfactory mass spectrum. [e] $[M - CH_3CN]^+$.

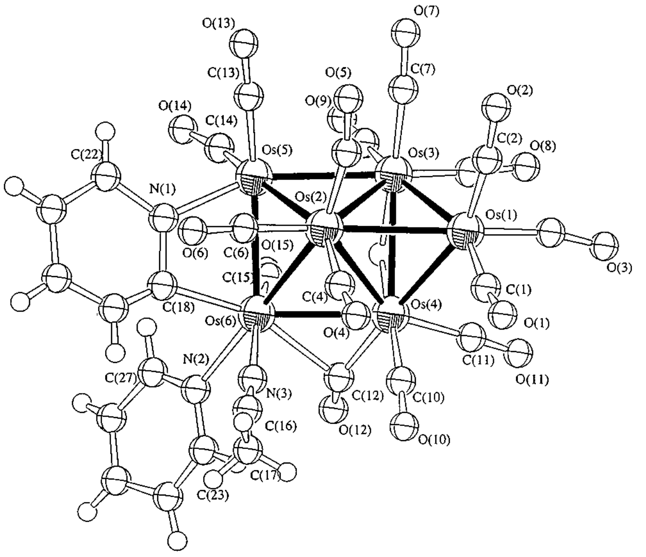


Fig. 3 Molecular structure of cluster **3**. Details as in Fig. 1

ing scheme is shown in Fig. 3. Some important bond parameters are tabulated in Table 3. The metal core arrangement of **3** can be described as a monocapped square pyramid with two pyridine ligands in the co-ordination sphere. One of the pyridine moieties acts as a bridging ligand in an orthometallated fashion while the other behaves as a simple two-electron donor ligand. The hydride, although not located by X-ray analysis, was estimated to bridge across the Os(3)–Os(4) edge by potential energy calculations. An acetonitrile ligand is found to co-ordinate to the Os(6) atom which is labile. The mass spectra of **3** revealed an intense ion envelope centred at *m/z* 1719 in addition to the very weak signal of the parent ion at *m/z* 1760. We believe this is an interesting compound that may lead to cluster species with 86 CVE which could adopt a bicapped tetrahedron structure as in the parent cluster $Os_6(CO)_{18}$.

Experimental

All reactions were carried out under an atmosphere of dry dinitrogen using standard Schlenk techniques. Dichloromethane was dried over CaH_2 prior to use.[16] Pyridine was purchased from Aldrich and used as received. Vacuum pyrolysis of $Os_3(CO)_{12}$ gave the hexaosmium cluster $Os_6(CO)_{18}$[17] and the compound $[Os_6(CO)_{16}(MeCN)_2]$ was prepared by the literature method.[18] Infrared spectra were recorded on a Bio-Rad FTS-7 spectrometer using a 0.5 mm solution cell, ^{1}H NMR spectra on a Bruker DPX 300 NMR spectrometer using CD_2Cl_2 with reference to $SiMe_4$ (δ 0) and mass spectra on a Finnigan MAT 95 instrument with the fast atom bombardment (FAB) technique. Elemental analyses were conducted by Butterworth Laboratories, UK. Routine separation of products in air was performed by thin-layer chromatography (TLC) on plates coated with Merck Kieselgel 60 GF_{254}.

Syntheses

The cluster $[Os_6(CO)_{16}(MeCN)_2]$ (50 mg, 0.03 mmol) was dissolved in CH_2Cl_2 (25 cm^3) and stirred with dropwise addition of 1 equivalent of pyridine (2.42 cm^3 diluted in 10 cm^3 CH_2Cl_2) under ambient conditions. After the reaction had proceeded for 24 h, the volume was reduced to 5 cm^3 *in vacuo*. Subsequent purification by TLC using hexane–CH_2Cl_2 (3:4, v/v) as eluent afforded three brown bands with R_f values of 0.55, 0.70 and 0.30 respectively. The clusters **1**–**3** were isolated as deep brown solids in 32, 10 and 25% yields respectively (Found for cluster **1**: C, 20.2; H, 0.8; N, 2.0. Calc. for $C_{31}H_{15}N_3O_{16}Os_6$: C, 20.4; H, 0.8; N, 2.3. Cluster **2**: C, 17.9; H, 0.6; N, 1.6. Calc. for $C_{26}H_{10}N_2O_{17}Os_6$: C, 17.7; H, 0.6; N, 1.6. Cluster **3**: C, 18.6; H, 0.6; N, 2.6. Calc. for $C_{27}H_{13}N_3O_{15}Os_6$: C, 18.4; H, 0.7; N, 2.4%). Table 4 summarizes the experimental data of IR, ^{1}H NMR and FAB mass spectroscopies.

Crystallography

Single crystals of clusters **1**–**3** suitable for X-ray crystallographic studies were mounted in Lindermann glass capillaries or glass fibres using epoxy resin. Brown crystals of cluster **1** were obtained as a solvate of stoichiometry **1**·$CHCl_3$·EtOH by slow evaporation of a toluene–$CHCl_3$–ethanol solution at −10 °C for 2 d. Slow evaporation from a solution of cluster **2** in toluene–$CHCl_3$ at room temperature for 4 d afforded some rod-shaped crystals while crystals of cluster **3** were obtained as a solvate of stoichiometry **3**·$CHCl_3$ from a solution of toluene–$CHCl_3$ at room temperature after 2 d. Diffraction data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer (for cluster **1**) using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) and the ω–2θ scan technique. For clusters **2** and **3**, data were collected on a MAR research image plate scanner. A summary of the crystallographic data and structure refinement is listed in Table 5. All intensity data were corrected for Lorentz and polarization effects. An absorption correction by the ψ scan method was applied for structure **1**. However, no absorption corrections were made for **2** and **3**. Space groups of all of the crystals were determined from a Laue symmetry check and their systematic absences were confirmed by successful refinement of the structures. The structures were solved by a combination of direct methods and Fourier-difference techniques (SIR 92[19] for **1** and SHELXS 86[20] for **2** and **3**). Structure refinements were made on *F* by full-matrix least-squares analysis. The hydrogen atoms of the organic moieties were generated in their idealized positions whereas all metal hydrides were estimated by potential energy calculations.[21] All calculations were performed on a Silicon-Graphics computer using the program package TEXSAN.[22]

CCDC reference number 186/707.

Table 5 Summary of crystal data and data collection parameters for clusters **1**–**3**

	1	**2**	**3**
Empirical formula	$C_{34}H_{22}Cl_3N_3O_{17}Os_6$	$C_{26}H_{10}N_2O_{17}Os_6$	$C_{28}H_{14}Cl_3N_3O_{15}Os_6$
M	1992.12	1763.57	1879.99
Crystal colour, habit	Brown, block	Brown, block	Brown, block
Crystal size/mm	0.12 × 0.18 × 0.21	0.18 × 0.20 × 0.24	0.11 × 0.13 × 0.19
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	*C*2/*c* (no. 15)	$P2_12_12_1$ (no. 19)	*C*2/*c* (no. 15)
a/Å	13.712(2)	11.533(1)	37.667(2)
b/Å	16.836(2)	16.732(1)	10.840(1)
c/Å	39.704(3)	17.229(2)	19.711(1)
β/°	96.58(2)	—	106.94(2)
U/Å^3	9105(1)	3324.7(2)	7698(1)
Z	8	4	8
D_c/g cm^{-3}	2.906	3.523	3.244
F(000)	7120	3088	6640
μ(Mo-Kα)/cm^{-1}	169.15	229.05	199.91
ω Scan width/°	(0.55 + 0.35 tan θ)	—	—
2θ Range/°	4–45	2–52	2–52
Scan speed/° min^{-1}	16	—	—
Transmission coefficients	0.3155–1.0000	—	—
No. reflections collected	6507	29 148	24 887
No. unique reflections	6255	3533	4813
No. observed reflections [$I > 3\sigma(I)$]	2509	2992	1825
R	0.086	0.035	0.064
R′	0.077	0.049	0.083
g In weighting scheme	0.002	0.004	0.004
Goodness of fit	2.21	2.23	1.92
Maximum Δ/σ	0.01	0.02	0.02
No. parameters	282	235	247
Maximum, minimum density in Δ*F* map/e Å^{-3}, close to Os	0.85, −0.91	1.33, −2.58	2.09, −3.12

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