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Thiolate Complexes of Osmium(III) and Osmium(IV). Crystal Structures of $[Os(SC_6F_5)_2(O_2CPh)(PMe_2Ph)_2]$ and $[OsCl-(SC_6F_5)_3(PMe_2Ph)]^{\dagger}$

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Treatment of $[Os(SR)_3(PMe_2Ph)_2]$ (R = C₆F₅ or C₆HF₄) with PhCO₂H or with HCl in acetone gives, respectively, the red paramagnetic osmium(III) derivatives $[Os(SR)_2(O_2CPh)(PMe_2Ph)_2]$ 1 and the green, five-co-ordinate, diamagnetic osmium(IV) complexes $[OsCl(SR)_3(PMe_2Ph)]$ 2. X-Ray crystallography has shown that 1 (R = C₆F₅) has an octahedral structure with *trans*-thiolates, *cis*-phosphines and a chelating benzoate ligand and that 2 (R = C₆F₅) has a trigonal-bipyramidal structure with thiolates in the equatorial plane.

Thiolate ligands are of high current interest because of their relevance to catalytic processes involving metals with sulphur ligand environments (*e.g.* nitrogen fixation and hydrodesulphurisation) and their ability to stabilise unusual geometries and oxidation states by variation of their steric and electronic properties.¹

We have been investigating the chemistry of ruthenium and osmium with thiolate ligands, particularly with co-ligands such as dinitrogen² and carbon monoxide,³ where the metals are in relatively low oxidation states (II or III). Here we describe an extension of this work to the preparation of new thiolate complexes of osmium in oxidation states III and IV.

Results and Discussion

Preparation and Structures of $[Os(SC_6F_5)_2(O_2CPh)(PMe_2-Ph)_2]$ and $[OsCl(SC_6F_5)_3(PMe_2Ph)]$.—We are interested in the reaction of various acidic reagents with osmium thiolate complexes, undertaken in order to obtain thiolate complexes in higher oxidation states. In this particular example the reagents were PhCO_2H and HCl, which have afforded benzoate and chloride derivatives of the unsaturated osmium thiolate precursor $[Os(SR)_3(PMe_2Ph)_2]$ (R = C₆F₅ or C₆HF₄) according to the reactions shown in Scheme 1.



Scheme 1

The Os^{III} complexes 1 ($R = C_6F_5$ or C_6HF_4) were isolated as paramagnetic red crystals and have been structurally characterised for $R = C_6F_5$, which is an octahedral benzoate complex as shown in Fig.1. Atomic coordinates are listed in Table 1 and molecular dimensions in Table 2.



Fig. 1 View of a molecule of $[Os(SC_6F_5)_2(O_2CPh)(PMe_2Ph)_2]$

The structure of $1 (R = C_6 F_5)$ consists of discrete essentially octahedral molecules, with one angle (O-Os-O) rather small (59.7°) because of the constrained bite of the chelating benzoate ligand. The trans Os-S distances are somewhat shorter than those found ³ in the Os^{II} compound $[Os(SC_6F_5)_2(CO)_2]$ (PEt₂Ph)₂], *i.e.* 2.329(1) and 2.335(1) versus 2.477(1) Å (mean). The cis-Os-P distances [2.293(1) and 2.300(1)] are shorter than those in the above dicarbonyl [2.407(1) (trans)] and in [OsCl(SC₆F₅)(N₂)(PMe₂Ph)₃]² [2.375(1) and 2.381(1) (trans); 2.326 Å (unique)]. This shortening might be expected on passing to the higher oxidation state in 1 ($R = C_6F_5$). Other dimensions are unexceptional, but it is noteworthy that the arrangement of the aryl groups of the SC₆F₅ and benzoate ligands is layered, with the C_6F_5 rings close to eclipsed (Fig. 2). This type of packing has been observed in other SC₆F₅ complexes.

Compounds 2 are green, diamagnetic and have the trigonalbipyramidal structure shown in Fig. 3. Atomic coordinates for 2 ($R = C_6F_5$) are listed in Table 3 and molecular dimensions in Table 4. The loss of PMe₂Ph giving five-co-ordination is presumably a consequence of steric pressure from the bulky SC₆F₅ groups. Compounds 2 are rare examples of osmium(IV) thiolate complexes; the analogue [Os(SC₆H₂Prⁱ₃-2,4,6)₄(CH₃CN)] has been reported and probably has a

^{† (}Benzoato-O,O')bis(dimethylphenylphosphine)bis(pentafluorobenzenethiolato-S)osmium(III) and chloro(dimethylphenylphosphine)tris(pentafluorobenzenethiolato-S)osmium(IV).

Supplementary data available: see Instructions for Authors, J. Chem. Soc., Dalton Trans., 1991, Issue 1, pp. xviii-xxii.

Atom	x	у	Z	Atom	x	у	Z
Os	3053.7(1)	2298.5(1)	2187.6(1)	C(31)	5717(5)	3187(4)	2631(6)
S(1)	1947(1)	3723.6(7)	1863(1)	C(32)	6886(10)	3039(10)	3149(18)
C(11)	782(4)	3857(3)	221(4)	C(33)	7507(14)	3260(12)	2443(24)
C(12)	-366(4)	3566(3)	-153(5)	C(34)	6949(17)	3569(9)	1244(19)
F(12)	-625(3)	3177(2)	735(3)	C(35)	5812(14)	3775(13)	778(11)
C(13)	-1300(5)	3677(4)	-1434(6)	C(36)	5178(9)	3572(11)	1456(8)
F(13)	-2396(3)	3391(3)	-1743(5)	C(37)	4754(5)	4059(4)	4100(6)
C(14)	-1079(5)	4071(4)	-2345(5)	C(38)	5962(5)	2232(5)	4928(6)
F(14)	-1957(4)	4194(3)	-3593(3)	P(4)	2771(1)	1854.9(8)	3929(1)
C(15)	46(6)	4380(3)	-2029(5)	C(41)	3002(5)	2635(3)	5182(4)
F(15)	253(4)	4792(3)	-2953(3)	C(42)	3962(7)	2451(6)	6443(5)
C(16)	958(4)	4274(3)	- 748(5)	C(43)	4097(9)	3079(7)	7369(7)
F(16)	2036(3)	4580(2)	-475(3)	C(44)	3341(10)	3855(7)	7043(8)
S(2)	4269(1)	940.1(8)	2439(1)	C(45)	2390(9)	4045(5)	5862(8)
C(21)	3582(4)	427(3)	948(4)	C(46)	2226(7)	3424(4)	4901(6)
C(22)	2770(5)	-250(3)	728(5)	C(47)	1170(5)	1619(4)	3272(5)
F(22)	2509(4)	-514(3)	1667(4)	C(48)	3532(6)	746(4)	4819(5)
C(23)	2217(6)	-657(4)	-416(7)	O(51)	1451(2)	1737(2)	685(3)
F(23)	1430(5)	-1281(3)	- 560(5)	O(52)	2637(3)	2479(2)	141(3)
C(24)	2457(7)	-404(5)	-1384(6)	C(50)	1689(3)	2036(3)	-200(3)
F(24)	1895(5)	- 770(4)	-2528(4)	C(51)	910(4)	1858(3)	-1570(4)
C(25)	3252(7)	254(5)	-1221(6)	C(52)	-77(4)	1331(3)	-1888(5)
F(25)	3486(5)	515(4)	-2191(4)	C(53)	-802(6)	1152(5)	-3192(5)
C(26)	3823(5)	663(3)	-69(4)	C(54)	-529(7)	1486(5)	-4124(6)
F(26)	4612(3)	1308(2)	82(4)	C(55)	419(6)	2026(5)	-3805(5)
P(3)	4851(1)	2939.9(9)	3463(1)	C(56)	1157(5)	2220(4)	-2527(5)

Table 1 Final atomic coordinates (fractional $\times 10^4$) for 1 (R = C₆F₅) with estimated standard deviations (e.s.d.s) in parentheses

Table 2 Selected bond dimensions for 1 ($R = C_6F_5$) (distances in Å, angles in °) with e.s.d.s in parentheses. (*) Indicates angles with e.s.d.s less than 0.05°

(a) Co-ordination sphere of the osmium atom

Os-S(1)	2.329(1)	Os-S(2)	2.335(1)
Os-P(3)	2.293(1)	Os-P(4)	2.300(1)
Os-O(51)	2.167(2)	Os-O(52)	2.201(3)
S(1)-Os-S(2)	174.7(1)	P(3)-Os- $P(4)$	93.2(*)
S(1)-Os-P(3)	90.8(*)	S(2)-Os-P(3)	86.3(*)
S(1)-Os-P(4)	91.1(*)	S(2) - Os - P(4)	93.4(*)
S(1) - Os - O(51)	90.8(1)	S(2) - Os - O(51)	91.3(1)
P(3) - Os - O(51)	168.8(1)	P(4)-Os-O(51)	97.8(1)
S(1) - Os - O(52)	88.0(1)	S(2)-Os-O(52)	88.8(1)
P(3) - Os - O(52)	109.3(1)	P(4) - Os - O(52)	157.5(1)
O(51)-Os-O(52)	59.7(1)		

(b) Pentafluorothiop	henolate ligands		
S(1)-C(11) Os-S(1)-C(11)	1.769(4) 107.6(1)	S(2)-C(21) Os-S(2)-C(21)	1.761(4) 107.0(1)
(c) Dimethylphenylp	hosphine ligands		
P(3)–C(31) P(3)–C(37) P(3)–C(38)	1.803(8) 1.834(6) 1.827(5)	P(4)-C(41) P(4)-C(47) P(4)-C(48)	1.818(5) 1.822(6) 1.815(5)
Os-P(3)-C(31) Os-P(3)-C(37) C(31)-P(3)-C(37) Os-P(3)-C(38) C(31)-P(3)-C(38) C(37)-P(3)-C(38)	113.2(2) 117.6(2) 102.3(3) 116.4(2) 103.0(3) 102.3(3)	Os-P(4)-C(41) Os-P(4)-C(47) C(41)-P(4)-C(47) Os-P(4)-C(48) C(41)-P(4)-C(48) C(47)-P(4)-C(48)	121.6(2) 106.9(2) 103.4(3) 116.8(3) 104.5(2) 101.0(3)
(d) Benzoate ligand			
O(51)–C(50) C(50)–C(51)	1.271(6) 1.473(5)	O(52)-C(50)	1.270(5)
Os-O(51)-C(50) O(51)-C(50)-O(52) O(52)-C(50)-C(51)	92.1(2) 117.7(3) 121.0(4)	Os-O(52)-C(50) O(51)-C(50)-C(51)	90.5(3) 121.3(4)

trigonal-bipyramidal structure like its structurally characterised ruthenium analogue.⁵ In the structures of 2 ($R = C_6F_5$) and $[Ru(SC_6H_2Pr^i_3-2,4,6)_4(CH_3CN)]$,⁵ the thiolate ligands occupy



Fig. 2 A molecule of $[Os(SC_6F_5)_2(O_2CPh)(PMe_2Ph)_2]$ viewed down the S(2)-S(1) vector, showing the alignment of the stacked SC_6F_5 and benzoate ligands



Fig. 3 View of a molecule of $[OsCl(SC_6F_5)_3(PMe_2Ph)]$

Table 3 Final atomic coordinates (fractional $\times 10^4$) for 2 (R = C₆F₅) with e.s.d.s in parentheses

Atom	x	y	Z	Atom	x	у	z
Os	2017.0(1)	-1236.9(1)	2561.0(1)	C(41)	665(3)	-2492(2)	3650(2)
Cl(1)	- 347.2(7)	-1369.1(4)	2375.2(4)	C(42)	160(4)	-2483(2)	4460(2)
P(2)	4314.5(7)	-1110.8(4)	2733.5(5)	F(42)	758(3)	-2105(1)	5102(1)
C(21)	5146(3)	-531(2)	2022(2)	C(43)	-976(4)	-2865(2)	4634(2)
C(22)	4464(3)	-26(2)	1599(2)	F(43)	-1429(3)	-2852(1)	5439(1)
C(23)	5113(4)	424(2)	1087(3)	C(44)	-1610(4)	-3244(2)	3994(3)
C(24)	6463(4)	364(2)	982(3)	F(44)	-2722(3)	- 3594(1)	4163(2)
C(25)	7148(4)	-131(2)	1389(3)	C(45)	-1143(4)	-3255(2)	3184(3)
C(26)	6507(3)	-574(2)	1907(2)	F(45)	-1778(3)	-3625(1)	2553(2)
C(27)	4836(3)	-800(2)	3810(2)	C(46)	-1(3)	-2891(2)	3018(2)
C(28)	5145(4)	-1919(2)	2604(3)	F(46)	444(2)	-2941(1)	2227(1)
S(3)	1885.2(7)	-182.8(4)	3088.2(5)	S(5)	2384.7(7)	-1461.1(4)	1193.0(5)
C(31)	246(3)	88(2)	3253(2)	C(51)	922(3)	-1680(2)	579(2)
C(32)	-256(3)	625(2)	2799(2)	C(52)	653(3)	-2356(2)	321(2)
F(32)	415(2)	881(1)	2156(2)	F(52)	1435(2)	-2855(1)	587(1)
C(33)	-1458(4)	903(2)	2987(3)	C(53)	-423(4)	-2533(2)	-205(2)
F(33)	-1905(3)	1417(1)	2531(2)	F(53)	- 698(3)	-3190(1)	-432(1)
C(34)	-2168(3)	645(2)	3645(3)	C(54)	-1230(3)	-2030(2)	-492(2)
F(34)	3334(2)	913(1)	3835(2)	F(54)	-2279(2)	-2198(2)	-1015(1)
C(35)	-1701(3)	113(2)	4092(2)	C(55)	-992(3)	-1365(2)	-247(2)
F(35)	-2397(2)	-133(1)	4738(1)	F(55)	-1799(2)	-874(1)	-514(2)
C(36)	- 507(3)	-163(2)	3900(2)	C(56)	88(3)	-1194(2)	286(2)
F(36)	-76(2)	-672(1)	4370(1)	F(56)	315(2)	-534(1)	528(1)
S(4)	2187.7(8)	-2067.2(4)	3470.0(6)				

Table 4	Selected bond	dimensions	in 2 (R	$= C_6 F_5$) (distances	in	Å,
angles in	°) with e.s.d.s in	1 parentheses					

(a) Co-ordination sphere of the osmium atom *

(,	- F		
Os-Cl(1)	2.408(1)	Os-S(3)	2.196(1)
Os-P(2)	2.339(1)	Os-S(4)	2.195(1)
Os-S(5)	2.201(1)		
Cl(1)-Os-P(2)	179.7	P(2)–Os–S(4)	85.9
Cl(1)-Os- $S(3)$	92.6	P(2)-Os-S(5)	85.7
Cl(1)-Os- $S(4)$	94.2	S(3)-Os-S(4)	118.1
Cl(1)-Os-S(5)	94.0	S(3)-Os-S(5)	122.0
P(2)-Os- $S(3)$	87.6	S(4)-Os- $S(5)$	118.7
(b) Dimethylphen	ylphosphine ligar	nd	
P(2)-C(21)	1.822(3)	P(2)-C(28)	1.814(4)
P(2)-C(27)	1.818(4)		
Os-P(2)-C(21)	117.1(1)	C(21)-P(2)-C(27)	104.3(2)
Os-P(2)-C(27)	112.7(1)	C(21)-P(2)-C(28)	105.3(2)
Os-P(2)-C(28)	112.5(1)	C(27)-P(2)-C(28)	103.7(2)
(c) Pentafluoroth	iophenolate ligan	ds	
S(3)-C(31)	1.776(3)	S(5)-C(51)	1.772(3)
S(4)-C(41)	1.768(3)		
Os-S(3)-C(31)	114.4(1)	Os-S(5)-C(51)	112.9(1)
Os-S(4)-C(41)	113.4(1)		
* Angles about th	e Os atom have e	$a.s.d.s < 0.05^{\circ}$.	

the equatorial positions of the trigonal bipyramid. In 2 (R = C_6F_5), the thiolate aryl substituents are all 'down' towards and around the smaller chloride ligand, whereas the above ruthenium complex analogue has the more usual¹ 'two up-one down' arrangement. The Os-S distances [2.201(1), 2.196(1) and 2.195(1) Å] are shorter than those of 1 ($\mathbf{R} = C_6 F_5$), as might be expected from a further increase of the oxidation state to Os^{IV} and from the reduction in co-ordination number. The axial Os-P distance is, however, longer at 2.339(1) Å than the Os-P distances in 1 ($R = C_6 F_5$) and longer than, or close to, the Os-P distances in the osmium(II) complexes discussed above. In view of the different environment of the phosphine ligands in the series of compounds under discussion, for instance PMe₂Ph can be trans to O, Cl, S or P in five- and six-co-ordinate complexes, it would be unwise to draw too many inferences from these data, but clearly the oxidation state of the central metal is not

paramount in determining osmium-phosphorus bond distances. As would be expected from their formally d⁴ electronic arrangement and their geometry, compounds 2 are diamagnetic as is $[Os(SC_6H_2Pr_{3}^{i}-2,4,6)_4(MeCN)]$.⁵ Their ¹H, ¹⁹F and ³¹P NMR spectra (Experimental section) are as expected if their solid-state structure is maintained in solution.

Conclusion

Use of the bulky SC_6F_5 ligand allows stabilisation of new sixco-ordinate complexes of Os^{III} and five-co-ordinate complexes of Os^{IV}. The latter compounds are of potential use in further syntheses because of their unsaturation and are a likely source of reactive metal centres by reduction. Work in these areas will be reported at a later date.

Experimental

NMR spectra were obtained using a JEOL FX 270 instrument, with chemical shifts quoted relative to SiMe₄ (¹H), CFCl₃ (¹⁹F) or $P(OMe)_3$ (³¹P-{¹H}). IR spectra were obtained using a Perkin-Elmer SP3-200 instrument and magnetic data using a recording Faraday magnetic balance. Elemental analyses were by Mr. C. Macdonald of the Nitrogen Fixation Laboratory.

Although a dinitrogen atmosphere was used in preparations, rigorous exclusion of air was not attempted and this may have aided these oxidation reactions.

Preparations.— $[Os(SR)_2(O_2CPh)(PMe_2Ph)_2] \mathbf{1} (R = C_6F_5)$ or C_6HF_4). The complex $[Os(SR)_3(PMe_2Ph)_2]$ (R = C_6F_5 or C_6HF_4) (0.1 mmol) was dissolved in acetone (15 cm³) and PhCO₂H (0.012 g, 0.1 mmol) in acetone (15 cm³) was added and the mixture was shaken at room temperature for ca. 12 h. The resulting red solution was evaporated to dryness under vacuum to give a solid which was washed with cold ethanol and recrystallised from ethanol as red rhombs.

1 (R = C₆F₅). Yield 87%; m.p. 198 °C (decomp.); μ_{eff} 2.05 (Found: C, 41.9; H, 2.6. C₃₅H₂₇F₁₀O₂OsP₂S₂ requires C, 42.6; H, 2.7%).

1 ($R = C_6 HF_4$). Yield 84%; m.p. 170 °C (decomp.) (Found:

C, 44.7; H, 3.4. $C_{35}H_{29}F_8O_2OsP_2S_2$ requires C, 44.3; H, 3.1%). [OsCl(SR)₃(PMe₂Ph)] **2** (R = C₆F₅ or C₆HF₄). The compound [Os(SR)₃(PMe₂Ph)₂] (R = C₆F₅ or C₆HF₄) (0.1

mmol) was dissolved in acetone (15 cm^3) , HCl (0.1 mol dm⁻³, 2 cm³) was added and the mixture was shaken at room temperature for *ca*. 24 h. The resulting yellow-green solution was evaporated to dryness under vacuum. The solid product was washed with cold ethanol and recrystallised from ethanol as very dark green *needles*.

2 (R = C_6F_5). Yield 82%; m.p. 179 °C (decomp.) (Found: C, 32.0; H, 1.1. $C_{26}H_{11}ClF_{15}OsPS_3$ requires C, 32.5; H, 1.2%). NMR (CDCl₃): ¹H, δ 2.5, 2.55, [d, ²J(PH) 10.08 Hz, PCH₃], 7.58-8.01 (m, C_6H_5); ¹⁹F, δ -131.4 (2-F), -150.91, -150.99, -151.08 (4-F), -162.75 (3-F) (m, SC₆F₅); ³¹P-{¹H}, δ -170.33 (s, PMe₂Ph).

2 (R = C_6HF_4). Yield 79%; m.p. 231 °C (decomp.) (Found: C, 34.4; H, 1.6. $C_{26}H_{14}ClF_{12}OsPS_3$ requires C, 34.4; H, 1.5%). NMR (CDCl₃): ¹H, δ 2.40, 2.50 [d, ²J(PH) 10.08 Hz, PCH₃], 7.04 (m, C_6HF_4), 7.75–8.05 (m, C_6H_5); ¹⁹F, δ –151.4, –159.6 (m, C_6HF_4); ³¹P-{¹H}, δ –170.55 (s, PMe₂Ph).

Crystal Structure Analysis of 1 ($\mathbf{R} = C_6F_5$).—Crystal data. $C_{35}H_{27}F_{10}O_2OSP_2S_2$, M = 985.8, triclinic, space group $P\overline{1}$ (no. 2), a = 12.468(2), b = 14.430(3), c = 11.736(2) Å, $\alpha = 87.20(1)$, $\beta = 118.47(1)$, $\gamma = 87.21(1)^\circ$, U = 1847.7 Å³, Z = 2, $D_c = 1.772$ g cm⁻³, F(000) = 962, μ (Mo-K α) = 37.3 cm⁻¹, λ (Mo-K α) = 0.710 69 Å.

Crystals are large, deep red parallelepipeds. A typical sample, ca. $0.4 \times 0.5 \times 1.3$ mm, was mounted on a glass fibre and coated with silicone grease. After photographic examination, the crystal was transferred to an Enraf-Nonius CAD4 diffractometer (with monochromated radiation) for determination of accurate cell parameters, from the settings of 25 reflections (θ ca. 14.5°) each centred in four orientations, and for measurement of diffraction intensities (to $\theta_{max} = 25^{\circ}$). During processing, the intensities were corrected for Lorentzpolarisation effects, for absorption (by semi-empirical ψ -scan methods) and to eliminate negative intensities (by Bayesian statistical methods). There was no significant deterioration of the crystal.

Of the 6482 unique reflections entered into the SHELX system,⁶ there were very few 'unobserved' reflections and, indeed, all the data were used in the structure analysis. The structure was determined by the heavy-atom method. In the refinement, by large-block-matrix least-squares methods, all the non-hydrogen atoms were allowed anisotropic thermal parameters. Hydrogen atoms were included in idealised positions (in staggered orientations in the methyl groups), but their isotropic thermal parameters were refined freely. At convergence, R = 0.036 and $R' = 0.034^6$ for the 6482 reflections weighted $w = \sigma^{-2}$.

In a final difference map, the six strongest peaks $(1-2 \text{ e } \text{ Å}^{-3})$ were close to the Os atom; the next strongest, *ca*. 0.6 e Å⁻³, were close to the phosphine ligand atoms.

Scattering factor curves for neutral atoms were taken from ref. 7. Computer programs used in this analysis have been listed above and in Table 4 of ref. 8, and were run on the MicroVAX II machine in this laboratory.

Crystal Structure Analysis of **2** ($\mathbf{R} = C_6F_5$).—Crystal data. $C_{26}H_{11}ClF_{15}OsPS_3$, M = 961.2, triclinic, space group $C\overline{1}$ (equivalent to no. 2), a = 10.123(1), b = 19.523(1), c = 15.550(1) Å, $\alpha = 92.079(5)$, $\beta = 91.796(6)$, $\gamma = 91.369(5)^\circ$, U = 3068.7 Å³, Z = 4, $D_c = 2.080$ g cm⁻³, F(000) = 1832, μ (Mo-K α) = 46.0 cm⁻¹.

This complex crystallises as opaque, very dark green needles. One needle, $ca.0.15 \times 0.20 \times 0.40$ mm, was mounted on a glass fibre for photographic and diffractometric measurements. Following a procedure very similar to that described above for 1 ($\mathbf{R} = C_6 F_5$), cell parameters were calculated from the settings of 25 reflections having θ ca. 10.5°, and intensity data were recorded to $\theta_{max} = 25^\circ$. After processing as above, 5365 unique reflections were entered into the SHELX system.⁶ The structure determination and refinement followed a similar course to that for 1 ($\mathbf{R} = C_6 F_5$) except that the methyl groups were refined as rigid units; the U_{iso} values of the hydrogen atoms were refined freely. Refinement was complete with R and $R' = 0.021^6$ for all 5365 reflections weighted $w = \sigma^{-2}$. In the final difference map, there were no features >0.25 e Å⁻³.

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