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The synthesis and characterization of technetium and rhenium hydrazinopyrimidine chelate complexes †

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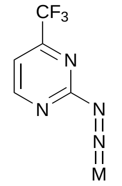
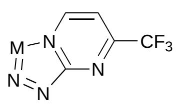
Organohydrazide chelate complexes of rhenium and technetium, which are defined as complexes containing a metal–nitrogen–nitrogen linkage, have been synthesized using 2-hydrazino-4-(trifluoromethyl)pyrimidine. The complexes all contain a chelating organohydrazide that forms a five-membered ring with the metal center. The chelate ring forms a delocalized π system and contributes to the unique electronic characteristics of these d^4, octahedral complexes, which all have ^{1}H NMR spectra characteristic of diamagnetic complexes. An X-ray structural analysis of $Tc^{III}(NNC_4H_2N_2CF_3)(PPh_3)_2Cl_2$ **1** was obtained. Complex **1**, $C_{41}H_{32}Cl_2F_3N_4P_2Tc$, crystallizes in the triclinic space group $P\bar{1}$ with $a = 11.9193(3)$, $b = 12.7026(3)$, $c = 14.1335(3)$ Å, $\alpha = 109.9320(10)$, $\beta = 94.1250(10)$, $\gamma = 105.0490(10)°$, $U = 1912.14(8)$ Å^3, $Z = 2$ and $R = 0.0737$ based on 3528 unique reflections. The complex $Re^{III}(NNC_4H_2N_2CF_3)(PPh_3)_2Cl_2$ **2** was prepared and characterized. Both **1** and **2** contain a uninegative, chelating diazenido ligand. An X-ray structural analysis of $Re^{III}(NNC_4H_2N_2CF_3)(HNNC_4H_2N_2CF_3)(PPh_3)Cl_2$ **3** was obtained. Complex **3**, $C_{28}H_{20}Cl_2F_6N_8PRe$, crystallizes in the monoclinic space group $P2_1/c$ with $a = 10.1292(2)$, $b = 14.92310(10)$, $c = 20.6924(4)$ Å, $\beta = 92.4560(10)°$, $U = 3124.97(9)$ Å^3, $Z = 4$ and $R = 0.0807$ based on 4472 unique reflections. Complex **3** contains a monodentate, uninegative diazenido ligand and a chelating, α-nitrogen protonated, neutral diazene ligand.

The synthesis and characterization of rhenium and technetium organohydrazide complexes has been of interest for some time due to the importance of this chemistry to the radiopharmaceutical industry and to the elucidation of the chemistry of transition-metal complexes with metal–nitrogen multiple bonds.[1–12] The reaction chemistry of chelating organohydrazines with rhenium and technetium metal centers has been explored recently.[13–18] The chelating organohydrazide complexes formed with rhenium and technetium are important since they are potential imaging agents that can be derivatized with proteins or other biologically relevant molecules in order to design them for uptake by specific biological systems. The reactivity of organohydrazines with the metal–oxo moiety of technetium makes them ideal for use in existing radiopharmaceutical kits containing technetium–oxo complexes.

Pyrimidine derivatives play an important role in biological systems and can be found in nucleic acids. Some metal complexes with hydrazine derivatives of pyrimidines have been synthesized with particular emphasis on the late transition metals cobalt,[19] nickel,[20,21] platinum,[22] copper,[23] zinc[24] and mercury.[21] These metal complexes have been synthesized in order to study the role of the metal ions in some biological systems and do not display redox chemistry during organohydrazide complexation with the metal. In contrast, the chemistry of hydrazinopyrimidine derivatives with the Group 7 metals is expected to display redox chemistry to form metal–organohydrazide complexes. In particular, the synthesis and characterization of complexes of rhenium and technetium with the organohydrazine 2-hydrazino-4-(trifluoromethyl)pyrimidine is described here. The complexes display the organohydrazide in three ligand forms, the terminal diazenido(1-) ligand (**A**), the chelating diazenido(1-) ligand (**B**) and the α-nitrogen protonated neutral, organodiazene ligand (**C**).



A



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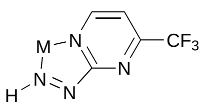

C

Results and Discussion

The organohydrazines can react with metal complexes to form metal–organohydrazide complexes. This article presents complexes that contain two general ligand forms: the uninegative diazenido and the neutral, α-nitrogen protonated diazene. The potentially chelating organohydrazine, 2-hydrazino-4-(trifluoromethyl)pyrimidine, provides an additional co-ordination mode, **B**. The chelated organohydrazide ligands form an extended π system with the metal, and the unique electronic characteristics of complexes $Tc(NNC_4H_2N_2CF_3)(PPh_3)_2Cl_2$ **1**, $Re(NNC_4H_2N_2CF_3)(PPh_3)_2Cl_2$ **2**, and $Re(NNC_4H_2N_2CF_3)(HNNC_4H_2N_2CF_3)(PPh_3)Cl_2$ **3** may be attributed to the formation of this system. Complexes **1**–**3** are d^4, octahedral complexes that do not show any contact shifting in the ^{1}H NMR spectra. All three complexes show sharp resonances in the range δ 6 to 8 of their ^{1}H NMR spectra, which is where these resonances are expected to be found in diamagnetic complexes; however, complexes **1**–**3** are assigned to the formal oxidation state of +3.

The reaction of pertechnetate or perrhenate with the hydrazinopyrimidine ligand in methanol leads to a deep red solution. The resulting product has not been isolated as a solid in either case; however, if triphenylphosphine is added to the reaction mixture, isolable products are formed. The reaction

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† This paper is dedicated to the late Sir Geoffrey Wilkinson. He profoundly influenced the direction of the senior author's life. In the first instance by accepting an unknown from South Wales into his research group, fostering him and then sending him to Harvard University as the first of a stream of his students that have had successful careers in the United States.

Table 1 Selected bond lengths (Å) and angles (°) for complex **1**

Tc–N(1)	1.810(8)	Tc–Cl(2)	2.390(2)
Tc–N(3)	2.181(7)	Tc–P(1)	2.473(3)
Tc–Cl(1)	2.385(2)	Tc–P(2)	2.472(3)
N(1)–N(2)	1.267(10)	C(4)–N(3)	1.364(11)
N(2)–C(4)	1.413(11)		
N(1)–Tc–N(3)	69.7(3)	N(3)–Tc–Cl(2)	83.7(2)
N(1)–Tc–Cl(1)	107.6	Cl(1)–Tc–Cl(2)	99.04(8)
N(3)–Tc–Cl(1)	176.5(2)	P(1)–Tc–P(2)	175.58(9)
N(1)–Tc–Cl(2)	153.3(2)	N(2)–N(1)–Tc	138.0(6)

chemistry of the hydrazinopyrimidine ligand with rhenium and technetium shows some differences. When triphenylphosphine is added to the pertechnetate reaction mixture, **1**, which contains two *trans*-triphenylphosphines, one chelated unprotonated diazenido ligand and two chloride ligands, is formed. In contrast, the addition of triphenylphosphine to the perrhenate reaction mixture leads to the formation of **3**, which consists of one triphenylphosphine, one chelated protonated diazene ligand, one unprotonated diazenido ligand and two chloride ligands. If $ReO(PPh_3)_2Cl_3$ is used as the starting material, **2**, which is analogous to the technetium product **1**, is formed in low yield. Interestingly, if this reaction is carried out in the presence of added HCl, a mixture of **2** and **3** is formed, as seen by mass spectral analysis and ^1H NMR spectroscopy. The reason for the difference in reactivity between rhenium and technetium is unknown, and this reactivity is different to that observed for reactions of rhenium and technetium with 2-hydrazinopyridine.[18] In the reactions with 2-hydrazinopyridine, a complex containing one organohydrazide ligand of the uninegative, chelated diazenido form, $M(NNC_5H_4N)(PPh_3)_2Cl_2$, can be isolated in moderate yield for both rhenium and technetium.

It is interesting to note that complexes containing organohydrazide ligands can be synthesized from metal synthons ranging from the formal oxidation state of +7 to +3. The reaction of the organohydrazine with the acetonitrile complex $Tc(MeCN)(PPh_3)_2Cl_3$ leads to a complex in the formal oxidation state +3. The co-ordinated acetonitrile may be reduced in the process of oxidizing the organohydrazine to the organohydrazide ligand.[18]

The chelated, unprotonated diazenido ligands found in complexes **1** and **2** and the monodentate, unprotonated diazenido ligand found in **3** are all uninegative ligands which form a σ bond and a π bond with the metal center. This multiple bonding of the uninegative diazenido ligands is indicated by the X-ray structural determination of **1** (Fig. 1, Table 1) in which the technetium–α-nitrogen bond length is 1.810(8) Å and by the X-ray structural determination of **3** (Fig. 2, Table 2) in which the rhenium–α-nitrogen bond length is 1.756(9) Å. The chelating diazene found in **3** is protonated on the α-nitrogen, making the overall charge on this ligand form neutral. The metal–nitrogen bond length of 1.937(9) Å is longer than that found for the uninegative diazenido ligand forms, as expected. The ^1H NMR spectrum of **3** displays a broad resonance at δ 18.1 that is assigned to the α-nitrogen proton of the chelated diazene ligand. In addition to the longer metal–nitrogen bond length of the diazene ligand, the diazene metal–nitrogen–nitrogen bond angle of 129.0(7)° is indicative of sp^2 hybridization of the α-nitrogen in contrast to the nearly linear diazenido metal–nitrogen–nitrogen bond angle of 173.2(8)°, which is indicative of sp hybridization of the α-nitrogen. The extended π system formed with the metal by the chelating organohydrazide may explain the non-contact shifted ^1H NMR spectra observed for the formally +3 complexes **1**–**3**. The lone pair of electrons is donated by the pyrimidine nitrogen into the t_{2g} set of the metal. This donation allows the M^{III} product to behave as a diamagnetic pseudo-M^I complex.

Table 2 Selected bond lengths (Å) and angles (°) for complex **3**

Re–N(1)	1.937(9)	N(1)–N(2)	1.322(13)
Re–N(3)	2.140(9)	N(5)–N(6)	1.267(12)
Re–N(5)	1.756(9)	N(2)–C(1)	1.372(14)
Re–Cl(1)	2.420(3)	C(1)–N(3)	1.363(13)
Re–Cl(2)	2.379(3)	N(6)–C(6)	1.414(13)
Re–P(1)	2.455(3)		
N(1)–Re–N(3)	71.8(3)	N(1)–Re–Cl(1)	98.7(3)
N(5)–Re–N(1)	90.6(4)	N(3)–Re–Cl(1)	84.0(2)
N(5)–Re–N(3)	161.7(3)	Cl(2)–Re–Cl(1)	85.58(10)
N(5)–Re–Cl(2)	107.0(3)	Cl(1)–Re–P(1)	165.09(9)
N(1)–Re–Cl(2)	161.6(3)	Re–N(1)–N(2)	129.0(7)
N(3)–Re–Cl(2)	91.0(2)	Re–N(5)–N(6)	173.2(8)
N(5)–Re–Cl(1)	94.0(3)		

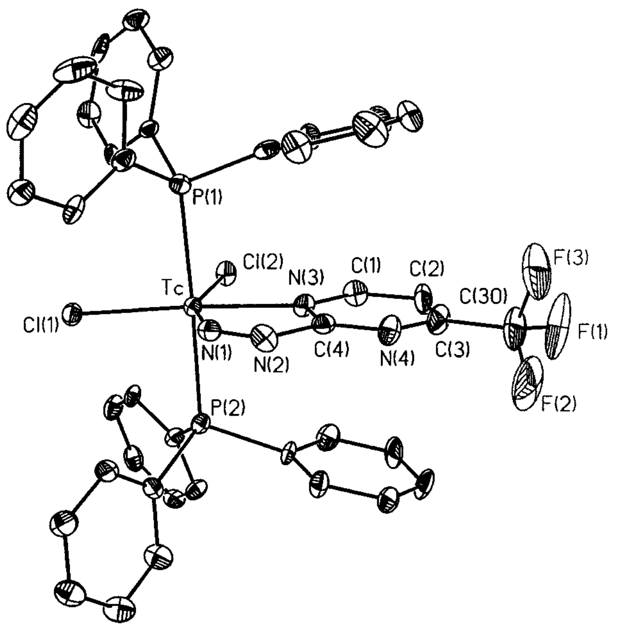


Fig. 1 An ORTEP[25] plot of complex **1** with 35% ellipsoids

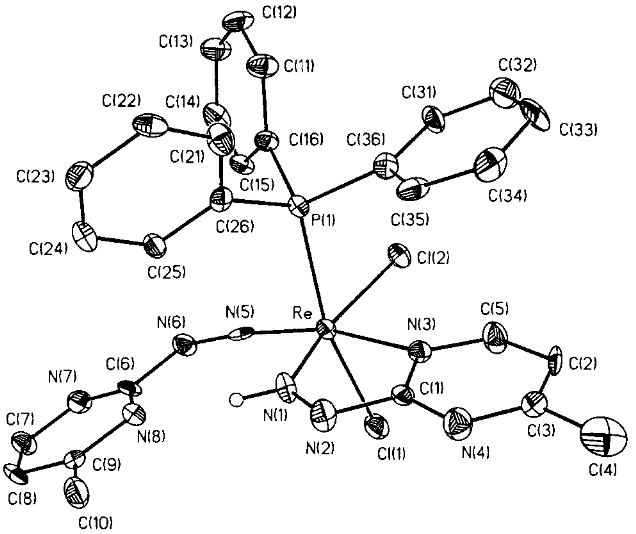
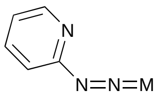
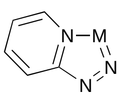


Fig. 2 An ORTEP plot of complex **3** with 35% ellipsoids including the α-N hydrogen atom. The fluorine atoms have been omitted for clarity

Three of the four organohydrazide ligand forms (**I**–**IV**) encountered in the complexes synthesized from hydrazinopyridine reactions[16–18] are found in the complexes synthesized from hydrazinopyrimidine. The neutral zwitterionic form seen for hydrazinopyridine has not been seen in the complexes formed from hydrazinopyrimidine.[16] A possible explanation for the absence of this ligand form is the presence of the trifluoro-



I



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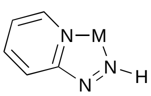
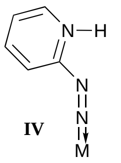


III



IV

methyl substituent on the hydrazinopyrimidine used in these reactions. The trifluoromethyl substituent causes the nitrogens of the pyrimidine ring to be less basic than the nitrogens of an unsubstituted pyrimidine ring, and as a result, protonation at these sites does not occur.

Conclusion

The organohydrazine 2-hydrazino-4-(trifluoromethyl)-pyrimidine reacts with technetium(VII), rhenium(VII), rhenium(V) and technetium(III) synthons to form metal–organohydrazide complexes. The organohydrazine acts to reduce the metal center, with the exception of the metal–acetonitrile synthon, and in the process, the organohydrazine is oxidized to an organohydrazide ligand form. In the case of the metal–acetonitrile synthon, the acetonitrile may be reduced to form the organohydrazide complex. The complexes derived from the higher oxidation state synthons are formally assigned as +3 in oxidation state. The d^4, octahedral M^{III}–organohydrazide complexes have ^1H NMR spectra that are characteristic of diamagnetic complexes. This characteristic may be attributed to the π system formed by the chelating organohydrazide with the metal center.

Experimental

CAUTION! Technetium-99 is a weak β-emitter ($E = 0.292$ MeV,‡ $t_{\frac{1}{2}} = 2.12 \times 10^5$ years). All work has been done in laboratories approved for the use of low levels of radioactive materials. Precautions have been detailed elsewhere.[26]

Ammonium pertechnetate was supplied as a gift from DuPont Biomedical Products. Reagents and solvents were used as received unless otherwise specified. Proton NMR spectra were recorded on Varian XL-300 or Varian Unity-300 FTNMR spectrometers. The chemical shifts are referenced to the residual proton impurity in the deuteriated solvent. Fast atom bombardment (FAB) mass spectra of samples dissolved in a *p*-nitrobenzyl alcohol matrix were recorded with a Finnigan MAT 8200 mass spectrometer equipped with an Ion TechFAB gun operating at an accelerated voltage of 8 kV. The FAB gun produced a beam of 6–8 keV xenon neutrals. Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

Syntheses

The complexes $ReO(PPh_3)_2Cl_3$[27] and $Tc(MeCN)(PPh_3)_2Cl_3$[28] were prepared by the literature methods.

Preparation of $Tc(NNC_4H_2N_2CF_3)(PPh_3)_2Cl_2$ 1. *Method 1.* To $Tc(MeCN)(PPh_3)_2Cl_3$ (0.04652 g) in a 100 cm^3 round bottom flask equipped with a stir bar were added methanol (10 cm^3) and 2-hydrazino-4-(trifluoromethyl)pyrimidine (0.02519 g). An additional 15 cm^3 of methanol was added, and the reaction was heated for 1.5 h. At the end of this time, the solution was deep red, and a peach-tan colored solid had precipitated from the reaction solution. The solid was filtered off on a fritted glass funnel, washed with methanol and dried *in vacuo*. The product was recrystallized from CH_2Cl_2–MeOH–Et_2O. Yield (0.0262 g, 50%) (Found: C, 56.0; H, 3.8; N, 6.4. $C_{41}H_{32}Cl_2F_3N_4P_2Tc$ requires C, 56.6; H, 3.7; N, 6.4%). FAB (+) mass spectrum: *m/z* 870 (*M*, 24%). $\delta_H(CD_2Cl_2)$: 7.95 (d, 1 H), 7.6–7.4 (m, 12 H), 7.4–7.2 (m, 18 H), 6.4 (d).

Method 2. In a 50 cm^3 round bottom flask with a stir bar, NH_4TcO_4 (aq) (0.5 cm^3, 0.4187 M) was evaporated to dryness. The pertechnetate was dissolved in methanol (5 cm^3) and 2-hydrazino-4-(trifluoromethyl)pyrimidine (0.10533 g) was added along with an additional 10 cm^3 of methanol. To the reaction mixture a 0.48 M HCl methanolic solution (0.5 cm^3) was added. There was an immediate color change to deep red. The reaction was stirred at room temperature for 3 h, and then it was evaporated to approximately 1 cm^3. To the deep red solution PPh_3 (0.13661 g) was added, and the mixture was stirred for 1 h at room temperature. The mixture was heated for 2 h at reflux. A tan-peach solid precipitated out of solution. The reaction mixture was allowed to cool to room temperature, then it was filtered on a fritted glass funnel, washed with methanol and dried *in vacuo*. The product obtained from this method is spectroscopically identical to that obtained by method 1. X-Ray quality crystals were obtained by recrystallization from CH_2Cl_2–methanol–diethyl ether. Yield (0.0289 g, 16%).

Preparation of $Re(NNC_4H_2N_2CF_3)(PPh_3)_2Cl_2$ 2. To a 100 cm^3 round bottom flask with a stir bar containing $ReO(PPh_3)_2Cl_3$ (0.0973 g) and methanol (15 cm^3) was added 2-hydrazino-4-(trifluoromethyl)pyrimidine (0.0461 g). The reaction mixture was heated overnight. The solution was deep red with a pink precipitate. The reaction mixture was filtered on a fritted glass funnel, and the solid washed with methanol and dried *in vacuo*. The product is formed in very low yield (< 5%). The amount isolated is enough to obtain a ^1H NMR spectrum and a mass spectrum. FAB (+) mass spectrum: *m/z* 956 (*M*, 12%). $\delta_H(CD_2Cl_2)$: 7.52–7.42 (m, 12 H), 7.4–7.2 (m, 19 H), 6.26 (d, 1 H). Note: the integration of the multiplet at δ 7.4–7.2 indicates an additional proton, which can be attributed to a proton resonance from the pyrimidine ring.

Preparation of $Re(NNC_4H_2N_2CF_3)(HNNC_4H_2N_2CF_3)(PPh_3)Cl_2$ 3. To a 100 cm^3 round bottom flask with a stir bar containing $NaReO_4$ (0.0640 g) and methanol (5 cm^3) was added 2-hydrazino-4-(trifluoromethyl)pyrimidine (0.1264 g). An additional 10 cm^3 of methanol and 1 cm^3 of a 0.48 M HCl–methanol solution were added. As the acid was added to the reaction mixture the solution darkened. The reaction mixture was heated at reflux for 1 h. After cooling to room temperature, the solvent was removed *in vacuo*, and the resulting dark red solid was redissolved in methanol (15 cm^3). To the flask PPh_3 (0.1632 g) and methanol (15 cm^3) were added. The reaction mixture was heated overnight. A red precipitate formed, which was filtered off on a fritted glass funnel, washed with methanol and dried *in vacuo*. X-Ray quality crystals were obtained by recrystallization from CH_2Cl_2–methanol–diethyl ether. Yield (0.096 g, 47%) (Found: C, 39.7; H, 2.5; N, 12.3. $C_{28}H_{20}Cl_2F_6N_8PRe\cdot 0.5\ Et_2O$ requires C, 39.0; H, 2.5; N, 12.55%). FAB (+) mass spectrum: *m/z* 871 (*M*, 23%), 835 ($M - Cl$, 100). $\delta_H(CD_2Cl_2)$: 18.1 (br, 1 H), 9.3 (d, 1 H), 8.95 (d, 1 H), 7.5–7.2 (m, 16 H), 6.95 (d, 1 H). Note: the integration of the multiplet indicates the presence of an additional proton, which can be attributed to a proton resonance from the pyrimidine ring.

Preparation of a mixture of complexes 2 and 3. To a 100 cm^3 round bottom flask equipped with a stir bar, $ReO(PPh_3)_2Cl_3$ (0.5641 g) and methanol (10 cm^3) were added. To the mixture 2-hydrazino-4-(trifluoromethyl)pyrimidine (0.3837 g) and methanol (10 cm^3) were added. A 0.48 M methanolic HCl solution (1.0 cm^3) was added. The reaction mixture was heated for 1.5 h at which time a precipitate was observed. The reaction mixture was allowed to cool to room temperature and it was filtered. The dark rose colored solid was washed with methanol and dried *in vacuo* to yield 0.1697 g of solid. The solid was identified to be a mixture of **2** and **3** by mass spectrometry and by ^1H NMR spectroscopy. FAB (+) mass spectrum: *m/z* 956 [*M* (**2**), 9%], 871 [*M* (**3**), 27].

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‡ *Non-SI unit employed*: eV ≈ 1.602×10^{-19} J.

X-Ray crystallographic data collection parameters

The data for complexes **1** and **3** were collected using a Siemens platform goniometer with a CCD detector using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The data for **1**, $C_{41}H_{32}Cl_2F_3N_4P_2Tc$, $M = 868.55$, were collected using a red-brown, prismatic crystal having dimensions $0.10 \times 0.08 \times 0.08$ mm. The crystal system was triclinic, space group $P\bar{1}$, $a = 11.9193(3)$, $b = 12.7026(3)$, $c = 14.1335(3)$ Å, $\alpha = 109.9320(10)$, $\beta = 94.1250(10)$, $\gamma = 105.0490(10)°$, $U = 1912.14(8)$ Å^3, $Z = 2$, $\mu = 0.651$ mm^{-1}, the extinction coefficient = 0.0015(3), $D_c = 1.509$ g cm^{-3}, $F(000) = 880$. The data were obtained at 183(2) K in the θ range 1.56–20.00° with limiting indices $-9 \leqslant h \leqslant 13$, $-13 \leqslant k \leqslant 14$, $-15 \leqslant l \leqslant 15$. Of the 5714 reflections collected, 3528 were independent ($R_{int} = 0.0455$). The structure was solved by direct methods.[29] Full-matrix least-squares refinement based upon F^2 with 3425 data, zero restraints, and 479 parameters converged with final residuals: $R1 = 0.0568$, $wR2 = 0.1189$ and $S = 1.135$ based upon $I > 2\sigma(I)$. All non-hydrogen atoms were refined anisotropically.

The data for **3**, $C_{28}H_{20}Cl_2F_6N_8PRe$, $M = 870.59$, were collected using a dark red-brown, prismatic crystal having dimensions $0.20 \times 0.10 \times 0.08$ mm. The crystal system was monoclinic, space group $P2_1/c$, $a = 10.1292(2)$, $b = 14.92310(10)$, $c = 20.6924(4)$ Å, $\beta = 92.4560(10)°$, $U = 3124.97(9)$ Å^3, $Z = 4$, $\mu = 4.181$ mm^{-1}, the extinction coefficient = 0.000 14(11), $D_c = 1.850$ g cm^{-3}, $F(000) = 1688$. The data were obtained at 183(2) K in the θ range 1.68–23.28° with limiting indices $-11 \leqslant h \leqslant 11$, $-16 \leqslant k \leqslant 16$, $-14 \leqslant l \leqslant 22$. Of the 12 536 reflections collected, 4472 were independent ($R_{int} = 0.0871$). The structure was solved by direct methods.[29] Full-matrix least-squares refinement based upon F^2 with 4467 data, zero restraints, and 444 parameters converged with final residuals: $R1 = 0.0604$, $wR2 = 0.1094$ and $S = 1.272$ based upon $I > 2\sigma(I)$. All non-hydrogen atoms were refined anisotropically with the exception of the fluorines of the chelated diazene, which displayed a site disorder. Two complete sets of fluorines were refined isotropically with 50% occupancy per set.

CCDC reference number 186/612.

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