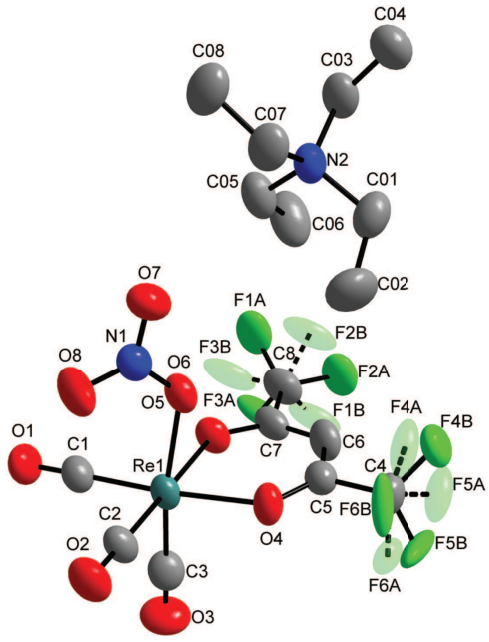
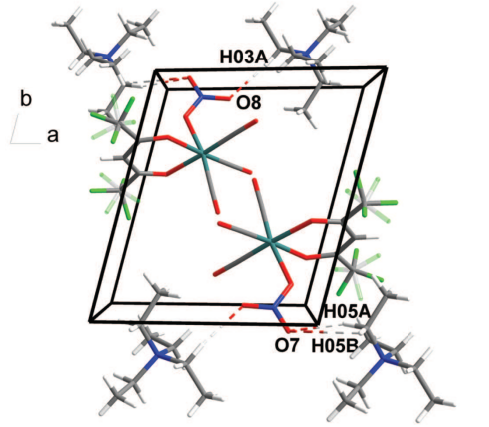
Open Access

Amanda-Lee Manicum*, Marietjie Schutte-Smith, Hendrik G. Visser, Carla Pretorius and Andreas Roodt

Crystal structure of tetraethylammonium *fac*-tricarbonyl(hexafluoroacetylacetonato-κ^2O,O′)-(nitrato-κO)rhenium(I), $C_{16}H_{21}O_8N_2F_6Re$





***Corresponding author: Amanda-Lee Manicum,** Department of Chemistry, University of the Free State, P.O. Box 339, Bloemfontein, 9300, South Africa, e-mail: volminkae@ufs.ac.za
Marietjie Schutte-Smith, Hendrik G. Visser, Carla Pretorius and Andreas Roodt: Department of Chemistry, University of the Free State, P.O. Box 339, Bloemfontein, 9300, South Africa

DOI 10.1515/ncrs-2015-0115
Received June 3, 2015; accepted January 18, 2016; available online February 11, 2016

Abstract

$C_{16}H_{21}O_8N_2F_6Re$, triclinic, $P\bar{1}$, $a = 9.161(5)$ Å, $b = 10.283(5)$ Å, $c = 12.974(5)$ Å, $\alpha = 87.739(5)°$, $\beta = 78.339(5)°$, $\gamma = 75.047(5)°$, $V = 1156.3(10)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.037$, $wR_{ref}(F^2) = 0.1012$, $T = 100(2)$ K.

CCDC no.: 1447936

Table 1: Data collection and handling.

Crystal:	Orange, plate, size 0.14×0.27×0.69 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	53.46 cm^{-1}
Diffractometer, scan mode:	Bruker APEX-II CCD, φ and ω scans
$2\theta_{max}$:	56°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	21687, 5560
$N(param)_{refined}$:	330
Programs:	Bruker data collection and reduction software [17], SHELX [18], Diamond [19]

The crystal structure is shown in the figure. Tables 1–3 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

Source of material

fac-$[NEt_4]_2[Re(CO)_3Br_3]$ (500 mg; 0.649 mmol) was dissolved in water (10 ml) at pH 2.2 and $AgNO_3$ (331 mg; 1.947 mmol) was added. The solution was stirred overnight for 16 hours at room temperature and the precipitated AgBr was filtered off and weighed (367 mg; 1.955 mmol). Hexafluoroacetylacetone (0.135 g; 0.649 mmol) was added to the solution and stirred for 24 hours at room temperature. The orange precipitate, *fac*-$[NEt_4]_2[Re(Hfaa)(CO)_3NO_3]$, was filtered off, washed, dried

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	Site	x	y	z	U_{iso}
H(01A)	2*i*	0.4537	0.9446	0.7245	0.084
H(01B)	2*i*	0.4703	0.7893	0.7027	0.084
H(02A)	2*i*	0.3258	0.9221	0.5921	0.156
H(02B)	2*i*	0.2039	0.9984	0.6911	0.156
H(02C)	2*i*	0.2202	0.8427	0.6695	0.156
H(03A)	2*i*	0.5235	0.9029	0.8876	0.072
H(03B)	2*i*	0.4348	0.8261	0.9783	0.072
H(04A)	2*i*	0.6784	0.6916	0.9126	0.114
H(04B)	2*i*	0.6423	0.6993	0.7965	0.114
H(04C)	2*i*	0.5524	0.6218	0.8868	0.114
H(05A)	2*i*	0.1275	0.9947	0.8666	0.079
H(05B)	2*i*	0.1934	0.9689	0.9724	0.079
H(6)	2*i*	1.1995	0.3337	0.5807	0.071
H(06A)	2*i*	0.1909	1.1849	0.9133	0.137
H(06B)	2*i*	0.2997	1.1261	0.8039	0.137
H(06C)	2*i*	0.3650	1.1007	0.9104	0.137
H(07A)	2*i*	0.1682	0.7703	0.8281	0.074
H(07B)	2*i*	0.3307	0.6637	0.8222	0.074
H(08A)	2*i*	0.1573	0.6306	0.9710	0.114
H(08B)	2*i*	0.1366	0.7806	1.0112	0.114
H(08C)	2*i*	0.2985	0.6716	1.0044	0.114

and weighed. (Yield: 274 mg; 86%). Crystals of the title complex was obtained from crystallization of the precipitate in MeOH. Yield = 148 mg; 40%. IR (KBr, cm^{-1}): ν_{CO} (2023, 1880).

Experimental details

In the structure all the H atoms were positioned geometrically and refined discernible using a riding model, with C—$H_{methine}$ = 0.98 Å; C—H_{methyl} = 0.96 Å; C—$H_{aromatic}$ = 0.93 Å. The H atom isotropic displacement parameters were fixed; $U_{iso}(H) = 1.2U_{eq}(C)$ for aromatic and methine and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl protons, allowing them to ride on the parent atom. The CF_3 substituents on the beta-diketone backbone are both structurally disordered, as manifested by the fluoro-atoms on both carbons (C4 and C8), occupying six positions on each carbon with occupancies of 0.181(16) (for F4A, F5A and F6A) and 0.819(16) (for F4B, F5B and F6B) on C4, and 0.724(13) (for F1A, F2A and F3A) and 0.276(13) (for F1B, F2B and F3B) on C8 [1]. In one case, F1A, F2A and F3A displays the dominant occupancy, and in the other case, F4B, F5B and F6B.

Discussion

Researchers are continually showing interest in the *fac*-$[M(CO)_3]^+$ [M = Re, Tc] synthon, particularly the *fac*-

Table 3: Atomic displacement parameters (Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	2*i*	0.5582(6)	0.3619(5)	0.8038(5)	0.043(3)	0.048(3)	0.063(4)	−0.017(2)	−0.009(2)	0.000(2)
C(01)	2*i*	0.3963(8)	0.8743(7)	0.7315(5)	0.074(4)	0.073(4)	0.056(4)	−0.019(3)	0.007(3)	0.000(3)
C(02)	2*i*	0.276(1)	0.913(1)	0.6653(6)	0.109(6)	0.142(8)	0.057(5)	−0.021(6)	−0.026(4)	0.010(5)
C(2)	2*i*	0.5836(6)	0.2237(6)	0.6348(5)	0.038(2)	0.057(3)	0.054(3)	−0.012(2)	−0.011(2)	−0.010(2)
C(3)	2*i*	0.6244(7)	0.4713(6)	0.6171(5)	0.060(3)	0.056(3)	0.062(4)	−0.021(3)	−0.010(3)	−0.013(3)
C(03)	2*i*	0.4746(7)	0.8269(7)	0.9015(6)	0.048(3)	0.071(4)	0.067(4)	−0.026(3)	−0.008(3)	−0.007(3)
C(04)	2*i*	0.5976(7)	0.6988(8)	0.8718(6)	0.055(3)	0.085(5)	0.083(5)	−0.008(3)	−0.015(3)	0.003(4)
C(4)	2*i*	1.1449(6)	0.1871(6)	0.4436(5)	0.052(3)	0.097(5)	0.049(4)	−0.022(3)	0.003(3)	−0.005(3)
C(5)	2*i*	1.0367(6)	0.2566(6)	0.5414(5)	0.043(3)	0.060(3)	0.051(3)	−0.014(2)	−0.008(2)	0.004(2)
C(05)	2*i*	0.2219(6)	0.9826(6)	0.8958(6)	0.045(3)	0.070(4)	0.078(4)	−0.013(3)	−0.002(3)	−0.017(3)
C(6)	2*i*	1.0955(6)	0.3294(6)	0.6025(5)	0.042(3)	0.068(4)	0.073(4)	−0.026(3)	−0.003(3)	−0.001(3)
C(06)	2*i*	0.2739(8)	1.1095(7)	0.8794(8)	0.071(4)	0.056(4)	0.137(7)	−0.014(3)	0.005(4)	−0.017(4)
C(07)	2*i*	0.2597(7)	0.7437(6)	0.8612(5)	0.061(3)	0.070(4)	0.064(4)	−0.035(3)	−0.011(3)	−0.004(3)
C(7)	2*i*	1.0102(6)	0.3960(5)	0.6936(5)	0.040(2)	0.044(3)	0.074(4)	−0.020(2)	−0.020(2)	0.004(2)
C(8)	2*i*	1.0844(6)	0.4718(5)	0.7556(5)	0.053(3)	0.066(4)	0.090(5)	−0.028(3)	−0.028(3)	−0.002(3)
C(08)	2*i*	0.2087(8)	0.7032(7)	0.9714(6)	0.077(4)	0.090(5)	0.071(4)	−0.048(4)	−0.007(3)	0.008(4)
O(1)	2*i*	0.4603(5)	0.3911(4)	0.8766(3)	0.052(2)	0.076(3)	0.058(3)	−0.009(2)	0.002(2)	−0.010(2)
O(2)	2*i*	0.4997(5)	0.1721(4)	0.6065(4)	0.054(2)	0.076(3)	0.081(3)	−0.030(2)	−0.023(2)	−0.011(2)
O(3)	2*i*	0.5665(6)	0.5684(5)	0.5790(5)	0.103(4)	0.055(3)	0.098(4)	−0.021(3)	−0.043(3)	0.012(2)
O(4)	2*i*	0.9038(4)	0.2418(4)	0.5546(3)	0.044(2)	0.065(2)	0.053(2)	−0.026(2)	0.003(2)	−0.011(2)
O(5)	2*i*	0.8730(4)	0.4011(4)	0.7371(3)	0.047(2)	0.057(2)	0.063(2)	−0.021(2)	−0.017(2)	−0.010(2)
O(6)	2*i*	0.8553(4)	0.1418(4)	0.7514(3)	0.036(2)	0.059(2)	0.066(3)	−0.019(2)	−0.009(2)	−0.002(2)
O(7)	2*i*	0.8915(5)	−0.0401(4)	0.8417(4)	0.061(2)	0.074(3)	0.071(3)	−0.008(2)	−0.023(2)	0.010(2)
O(8)	2*i*	0.6642(5)	0.0597(5)	0.8210(5)	0.045(2)	0.087(3)	0.143(5)	−0.031(2)	−0.016(3)	0.048(3)
Re(1)	2*i*	0.71603(2)	0.31160(2)	0.68294(2)	0.0353(1)	0.0490(1)	0.0498(2)	−0.01844(9)	−0.00744(9)	−0.00651(9)
N(1)	2*i*	0.8010(5)	0.0508(5)	0.8057(4)	0.046(2)	0.054(3)	0.051(3)	−0.015(2)	−0.009(2)	−0.004(2)
N(2)	2*i*	0.3380(5)	0.8555(4)	0.8471(4)	0.042(2)	0.047(2)	0.051(3)	−0.015(2)	−0.002(2)	−0.006(2)
F(4A)	2*i*	1.214(2)	0.066(1)	0.462(2)	0.12(2)	0.09(2)	0.11(2)	−0.05(1)	0.06(2)	−0.02(1)
F(5A)	2*i*	1.250(2)	0.248(2)	0.407(2)	0.12(2)	0.09(2)	0.11(2)	−0.05(1)	0.06(2)	−0.02(1)

Table 3 Continued

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
F(6A)	2*i*	1.072(2)	0.185(2)	0.371(1)	0.09(2)	0.07(2)	0.04(1)	−0.02(1)	0.01(1)	−0.01(1)
F(4B)	2*i*	1.2884(6)	0.1452(8)	0.4508(6)	0.064(3)	0.140(7)	0.104(5)	0.004(3)	0.004(3)	−0.030(5)
F(5B)	2*i*	1.145(1)	0.267(1)	0.3644(6)	0.21(1)	0.22(1)	0.067(5)	0.069(9)	0.040(6)	0.059(6)
F(6B)	2*i*	1.1100(9)	0.083(1)	0.4175(8)	0.135(8)	0.25(1)	0.21(1)	−0.134(8)	0.104(7)	−0.18(1)
F(1A)	2*i*	1.0885(8)	0.4265(9)	0.8521(6)	0.089(4)	0.177(7)	0.130(5)	−0.075(4)	−0.032(3)	−0.039(4)
F(2A)	2*i*	1.2252(7)	0.4748(9)	0.7140(6)	0.089(4)	0.177(7)	0.130(5)	−0.075(4)	−0.032(3)	−0.039(4)
F(3A)	2*i*	1.0077(7)	0.5976(5)	0.7744(7)	0.090(5)	0.042(3)	0.21(1)	−0.006(3)	−0.091(6)	−0.026(4)
F(1B)	2*i*	1.120(1)	0.570(1)	0.701(1)	0.12(1)	0.097(9)	0.23(2)	−0.016(8)	−0.13(1)	−0.016(9)
F(3B)	2*i*	0.986(1)	0.522(1)	0.8428(9)	0.12(1)	0.097(9)	0.23(2)	−0.016(8)	−0.13(1)	−0.016(9)
F(2B)	2*i*	1.206(1)	0.401(2)	0.7858(9)	0.12(1)	0.097(9)	0.23(2)	−0.016(8)	−0.13(1)	−0.016(9)

$[Re(CO)_3(OH_2)_3]^+$ moiety, primarily because of its potential use in the design of new diagnostic and therapeutic radiopharmaceuticals [2–4]. A considerable amount of work, involving the rhenium tricarbonyl core has already been published from our group, and this study forms part of on-going research, aimed at studying the chelation behaviour and structure and reactivity of the rhenium(I) metal centre and other middle and late transition metal complexes' behaviour when coordinated to β-diketone types of ligands [5–15].

The title compound, *fac*-$[NEt_4][Re(CO)_3(Hfaa)(NO_3)]$, consists of three facial coordinated carbonyl ligands, a fluorinated β-diketone ligand (hexafluoroacetylacetonate-Hfaa) in the axial position, a nitrate ligand in the equatorial plane, as well as a counterion, tetraethylammonium (NEt_4), in the asymetric unit (see the figure, upper part). The coordination at Re(I) is a distorted octahedron, as seen in the C3—Re1—O6 (170.30(19)°) angle which deviates from 180°. The O4—Re1—O5 bite angle of 84.14(15)° correlates well with a similar hexafluoroacetylacetonate coordinated Re(I) complex, 84.56(8)° [6]. The bond distances in the coordination polyhedron, are within normal range when compared to a similar structure, ranging from 1.892(6) to 2.157(4) Å [16]. The molecules within the unit cell are packed in horizontal layers, in a head-to-head manner, when viewed along the *c*-axis. These layers are stabilised by intermolecular C—H···O bonds (see the figure, lower part).

Acknowledgements: Financial assistance from the University of the Free State is gratefully acknowledged. We also express our gratitude towards NTeMBI, PETLabs Pharmaceuticals, SASOL and the South African National Research Foundation (SA-NRF/THRIP). This work is based on the research supported in part by the National Research Foundations of South-Africa and the Thuthuka programme (Grant specific unique reference numbers (UID) 84913 and 94142). The Grant holders acknowledge that opinions, findings and conclusions or recommendations expressed in any publication generated by the NRF supported research are that of the author(s) and that the NRF accepts no liability whatsoever in this regard.

References

1. Viljoen, J. A.; Visser, H. G.; Roodt, A.; Steyn, M.: Di-μ-hydroxido-bis[tris(1,1,1,5,5,5-hexafluoroacetylacetonato-κ^{2}O,O′)-hafnium(IV)] acetone solvate. Acta Crystallogr. **E65** (2009) m1367–m1368.
2. Papagiannopoulou, D.; Triantis, C.; Vassileiadis, V.; Raptopoulou, C. P.; Psycharis, V.; Terzis, A.; Pirmettis, I.; Papadopoulous, M. S.: Synthesis, structural characterisation and radiochemistry of di- and tricarbonyl Re(I) and ^{99m}Tc(I) complexes with 8-hydroxy quinolone or 8-mercaptoquinoline and triphenylphosphine. Polyhedron. **68** (2014) 46–52.
3. Vassileiadis, V.; Triantis, C.; Raptopoulou, C. P.; Psycharis, V.; Pirmettis, I.; Papadopoulous, M. S.; Papagiannopoulou, D.: Synthesis, structural characterisation and radiochemistry of "2+1" *fac*-[^{99m}Tc/Re(CO)$_3$(L)(2-mercaptopyridine)] complexes, where L is phosphine or isocyanide. Polyhedron. **81** (2014) 511–516.
4. Triantis, C.; Tsotakos, T.; Tsoukalas, C.; Sagnou, M.; Raptopoulou, C.; Terzis, A.; Psycharis, V.; Pelecanou, M.; Pirmettis, I.; Papadopoulos, M.: Synthesis and characterization of *fac*-[M(CO)$_3$(P)(OO)] and *cis-trans*-[M(CO)$_2$(P)(OO)] complexes (M = Re, ^{99m}Tc) with acetylacetone and curcumin as OO donor bidentate ligands. Inorg. Chem. **52** (2013) 12995–13003.
5. Visser, H. G.; Roodt, A.; Volmink, A.; Kemp, G.: *fac*-Tricarbonyl-(pyridine-κ*N*)(1,1,1-trifluoroacetylacetone-κ^2*O,O′*)rhenium(I). Acta Crystallogr. **E67** (2011) m1631–m1631.
6. Manicum, A.; Schutte-Smith, M.; Kemp, G.; Visser, H. G.: Illustration of the electronic influence of coordinated β-diketone type ligands: A kinetic and structural study. Polyhedron. **85** (2015) 190–195.
7. Manicum, A.; Visser, H. G.; Engelbrecht, I.; Roodt, A: Crystal structure of *fac*-(acetylacetonato-κ^{2}O,O′)\ tricarbonyl(cyclohexyldiphenylphosphine-κP) rhenium(I), $C_{26}H_{28}O_5PRe$. Zeits. Z. Kristallogr. NCS. **230** (2015) 150–152.
8. Schutte, M.; Roodt, A.; Visser, H. G.: Coordinated aqua vs methanol substitution kinetics in *fac*-Re(I) tricarbonyl tropolonato complexes. Inorg. Chem. **51** (2012) 11996–12006.
9. Schutte, M.; Kemp, G.; Visser, H. G.; Roodt, A.: Tuning the reactivity in classic low-spin d^6 rhenium(I) tricarbonyl radiopharmaceutical synthon by selective bidentate ligand variation (L,L′-Bid; L,L′ = N,N′, N,O and O,O′ donor atom sets) in *fac*-[Re(CO)$_3$(L,L′-Bid)(MeOH)]^n complexes. Inorg. Chem. **50** (2011) 12486–12498.
10. Brink, A.; Roodt, A.; Steyl, G.; Visser, H. G.: Steric *vs* electronic anomaly observed from iodomethane oxidative

addition to tertiary phosphine modified rhodium (I) acetylacetonato complexes following progressive phenyl replacement by cyclohexyl [PR(3) = PPh(3), PPh(2)Cy, PPhCy(2) and PCy(3)]. Dalt. Trans. **39** (2010) 5572–5578.
11. Roodt, A.; Basson S. S.; Leipoldt, J. G.: Studies on the substitution reactions of dioxotetracyanometalate systems with bidentate ligands: kinetics of the reaction between aquaoxotetracyanotungstate(IV) and 2-pyridinecarboxylate ions. Polyhedron. **13** (1994) 599–607.
12. Van Aswegen, K. G.; Leipoldt, J. G.; Potgieter, I. M.; Lamprecht,G. J.; Roodt, A.; van Zyl, G. J.: The crystal structure of the acetone adduct of *trans*-methyliodo-8 hydroxyquinolinatocarbonyltriphenylphosphinerhodium(III). Transit. Met. Chem. **16** (1991) 369–371.
13. Kemp, G.; Roodt, A.; Purcell, W.; Koch, K. R.: Unprecedented N,S,O co-ordination of the doubly deprotonated anion of *N*-benzoyl-*N*′-phenylthiourea (H_2L^2) bridging two rhodium(I) centres: crystal structure of the acetone solvate of [$(PPh_3)_2$(CO)Rh(μ-L^2-κ*N*′:κ*O*,*S*)Rh(PPh_3)(CO)]. J. Chem. Soc. Dalton Trans. **23** (1997) 4481–4484.
14. Sacht, C.; Datt, M. S.; Otto,S.; Roodt, A.: Synthesis, characterisation and coordination chemistry of novel chiral *N*,*N*-dialkyl-*N*′-menthyloxycarbonylthioureas. Crystal and molecular structures of *N*,*N*-diethyl-*N*′-(-)-(3*R*)-menthyloxycarbonylthiourea and *cis*-(S,S)-[Pt(L)Cl(DMSO)] [where HL = *N*-(+)-(3*R*)-menthyloxycarbonyl-*N*′-morpholinothiourea or *N*-benzoyl-*N*′, *N*′-diethylthiourea]. J. Chem. Soc. Dalton Trans. (2000) 4579–4586.
15. Erasmus, J. J. C.; Lamprecht, G. J.; Swarts, J. C.; Roodt, A.; Oskarsson, A.: (E)-1,3-Diferrocenyl-2-buten-1-one-water (4–1). Acta Crystallogr. **52** (1996) 3000–3002.
16. Brink, A.; Visser, H. G.; Roodt, A.: Tetraethylammonium (acetylacetonenato)bromidotricarbonylrhenate(I). Acta Crystallogr. **E67** (2011) m34–m35.
17. Bruker SAINT-Plus (Version 7.12) and SADABS (Version 2004/1). Bruker AXS Inc., Madison, Wisconsin, USA 2004.
18. Sheldrick, G. M.: A short history of SHELX. Acta Crystallogr. **A64** (2008) 112–122.
19. Brandenburg, K.; Putz, H. DIAMOND. Visual crystal structure information system. Version 3.2i. Crystal Impact, Bonn, Germany 2012.