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Note

Two diphenylformamidinate compounds of the quadruply-bonded Re_2^{6+} core

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Abstract

The compounds $\text{Re}_2(\text{DPhF})_3\text{Cl}_3$ and $\text{Re}_2(\text{DPhF})_2\text{Cl}_4$ have been prepared and structurally characterized (DPhF = anion of *N*,*N*-diphenylformamidine). The former has three bridging DPhF ligands, two equatorial Cl ligands and one axial Cl ligand. The Re–Re distances in two different crystallographic forms are 2.2318(8) Å and 2.2288(9) Å. The second compound has two *trans* DPhF ligands and the Re₂Cl₄ unit is planar with Re–Re = 2.177(1) Å, Re–Cl(av) = 2.319(5) Å, Re–N(av) = 2.06(1) Å and Cl–Re–Cl(av) = 106.0(1)°. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Rhenium complexes; Quadruply-bonded complexes; Diphenylformadinate complexes; Dinuclear complexes

1. Introduction

In recent years, work in this laboratory has shown that the diarylformamidinate ions, PhNC(H)NPh⁻ (DPhF) and (*p*-tol)NC(H)N(*p*-tol)⁻ (DtolF), have great utility for the stabilization of M_2^{n+} cores [1]. Most commonly the compounds are of the type $M_2(DArF)_4$ or $M_2(DArF)_4X_2$ but other compounds occur. We report here two such cases obtained with Re_2^{6+} .

2. Experimental

The starting materials, $Re_2Cl_5(PMePh_2)_3$ [2] and $Re_2Cl_4(PEt_3)_4$ [3] were prepared by literature methods. Diphenylformamidine (HDPhF) was purchased from Aldrich. Solvents were freshly distilled under N_2 from suitable drying agents. All operations were carried out under argon in standard Schlenkware.

2.1. Preparation of Re₂(DPhF)₃Cl₃

A suspension of $Re_2Cl_5(PMePh_2)_3$ (0.50 g, 0.43 mmol) and HDPhF (0.34 g, 1.7 mmol) in 10 ml of toluene was

refluxed for 24 h producing an orange precipitate. The reaction was cooled and filtered in air. The orange solid was washed repeatedly with hot hexanes (5 \times 20 ml). The product was recrystallized by dissolution in methylene chloride followed by slow addition of diethyl ether. The resulting solid was collected by filtration, washed with diethyl ether $(4 \times 20 \text{ ml})$ and dried under vacuum; yield 0.32 g (69%). IR (Nujol, cm⁻¹): 1703(s), 1700(s), 1591(m), 1531(m), 1516(s), 1487(s), 1355(m), 1342(m), 1321(s), 1212(s), 1078(w), 1027(m), 937(m), 850(w), 780(w), 757(m), 695(m), 502(w), and 415(w). Electronic absorption spectrum (λ_{max} , CH₂Cl₂, nm): 510. C.V. (200 mV s⁻¹, CH₂-Cl₂, tetrabutylammonium hexafluorophosphate): $E_{1/2,red} =$ -0.97 V versus Ag/AgCl ($\Delta E = 102$ mV). This compound may also be prepared from Re₂Cl₄(PEt₃)₄ using excess formamidine under similar conditions.

The crystals obtained as above were solvent-free. When 20 mg of $Re_2(DPhF)_3Cl_3$ was dissolved in 5 cm³ of hot acetonitrile in an open vial and this solution was set aside to cool and partially evaporate, a crop of orange crystals of composition $Re_2(DPhF)_3Cl_3 \cdot 2CH_3CN$ was obtained.

2.2. Preparation of trans-Re₂Cl₄(DPhF)₂

A solution of $Re_2(DPhF)_3Cl_3$ (0.025 g, 0.002 mmol) in 1 ml of CH₃CN and 3 ml CH₂Cl₂ was treated with 0.2 ml of 85% HBF₄·Et₂O. The resulting red solution was layered

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Table 2

with diethyl ether to produce a small crop of dark red crystals. The yield was not established.

2.3. X-ray crystallography

Methods and instruments regularly used in this laboratory and previously described [4] were employed. Because the crystals of Re2(DPhF)3Cl3·2CH3CN and Re2(DPhF)2Cl4 were very thin plates, the quality of the data obtained was relatively poor, the structures are not of high quality, and they will not be reported in detail.

3. Results and discussion

The compound Re₂(DPhF)₃Cl₃ is the third example of this sort of stoichiometry and structure, the previous ones being Re₂(O₂CCMe₃)₃Cl₃ [5] and Re₂(O₂CC₂H₅)(mhp)₂Cl₃ [6]. We have prepared it from two different starting materials and determined its structure in two crystalline forms. One of these, containing no solvent of crystallization, gave a good quality structure. The crystallographic parameters are summarized in Table 1 and selected metric parameters of the molecule are collected in Table 2. A labeled drawing is

Selected bond lengths (Å) and angles (°) for Re2(DPhF)3Cl3			
Re(1)–N(1)	2.103(7)	N(1)–C(2)	1.44(1)
Re(1)–N(3)	2.105(6)	N(2)–C(1)	1.32(1)
Re(1)–N(5)	2.121(6)	N(2)–C(8)	1.43(1)
$\operatorname{Re}(1)$ - $\operatorname{Re}(2)$	2.2318(8)	N(3)-C(14)	1.30(1)
Re(1)-Cl(1)	2.368(2)	N(3)-C(15)	1.47(1)
Re(1)–Cl(3)	2.446(2)	N(4)-C(14)	1.33(1)
Re(2)–N(4)	2.035(6)	N(4)–C(21)	1.44(1)
Re(2)–N(6)	2.052(7)	N(5)-C(27)	1.30(1)
Re(2)–N(2)	2.066(7)	N(5)-C(28)	1.46(1)
Re(2)-Cl(2)	2.357(2)	N(6)-C(27)	1.34(1)
N(1)–C(1)	1.34(1)	N(6)-C(34)	1.44(1)
N(1)-Re(1)-N(3)	90.8(3)	Cl(1)-Re(1)-Cl(3)	85.63(7)
N(1)-Re(1)-N(5)	173.8(3)	N(4)-Re(2)-N(6)	87.8(3)
N(3)-Re(1)-N(5)	94.6(3)	N(4)-Re(2)-N(2)	91.1(3)
N(1)-Re(1)-Re(2)	89.6(2)	N(6)-Re(2)-N(2)	172.6(3)
N(3)-Re(1)-Re(2)	88.0(2)	N(4)-Re(2)-Re(1)	93.3(2)
N(5)-Re(1)-Re(2)	87.7(2)	N(6)-Re(2)-Re(1)	94.5(2)
N(1)-Re(1)-Cl(1)	86.3(2)	N(2)-Re(2)-Re(1)	92.9(2)
N(3)-Re(1)-Cl(1)	168.8(2)	N(4)-Re(2)-Cl(2)	160.3(2)
N(5)-Re(1)-Cl(1)	89.0(2)	N(6)-Re(2)-Cl(2)	90.1(2)
Re(2)–Re(1)–Cl(1)	102.69(5)	N(2)-Re(2)-Cl(2)	88.4(2)
N(1)-Re(1)-Cl(3)	94.5(2)	Re(1)-Re(2)-Cl(2)	106.38(5)
N(3)-Re(1)-Cl(3)	83.9(2)	N(2)-C(1)-N(1)	122.7(7)
N(5)-Re(1)-Cl(3)	89.0(2)	N(3)-C(14)-N(4)	121.5(8)
Re(2)–Re(1)–Cl(3)	170.97(5)	N(5)-C(27)-N(6)	121.8(8)

Table 1

Crystal data and structure refinement for Re2(DPhF)3Cl3, Re2(DPhF)3Cl3.2CH3CN and Re2(DPhF)2Cl4

	Re ₂ (DPhF) ₃ Cl ₃	Re2(DPhF)3Cl3·2CH3CN	Re2(DPhF)2Cl4
Formula	C39H33Cl3N6Re2	C43H39Cl3N8Re2	$C_{26}H_{22}Cl_4N_4Re_2$
Formula weight	1064.46	1146.57	904.68
Space group	$P2_1/n$	$P2_1/c$	<i>P</i> 1
a (Å)	11.060(2)	15.305(3)	9.256(3)
b (Å)	13.622(1)	10.093(2)	9.646(2)
<i>c</i> (Å)	24.722(8)	28.106(6)	15.352(3)
α (°)	90	90	91.29(1)
β (°)	99.09(1)	102.81(3)	105.13(1)
γ (°)	90	90	90.92(1)
$V(Å^3)$	3678(1)	4234(2)	1322.5(6)
Ζ	4	4	2
$d_{\rm calc} ({\rm g}{\rm cm}^{-3})$	1.922	1.799	2.272
Crystal size (mm)	0.10 imes 0.05 imes 0.03	$0.40\times0.10\times0.05~mm$	0.50 imes 0.35 imes 0.10
μ (Mo $K\alpha$) (mm ⁻¹)	6.832	5.944	9.573
Data collection instrument	Nonius FAST	Nonius FAST	Nonius CAD4
Radiation (monochromated in incident beam)	Μο <i>Κ</i> α	Μο Κα	Μο Κα
Orientation reflections, number, range (2θ)	250, 9.1–20.8	250, 8–20	25, 20–23.5
Temperature (K)	183(2)	213(2)	123(2)
Scan method	ω	ω	ω -2 $ heta$
Data collected range, θ (°)	2.16-25.00	1.78-22.50	2.11-23.98
No. of unique data, total:	6471	5414	3824
No. of parameters refined	451	300	325
Transition factors, max., min.	0.818, 0.576	0.750, 0.460	0.8039, 0.3528
Final <i>R</i> indices $(I > 2\sigma(I)]^{a,b}$	R1 = 0.041, wR2 = 0.098	R1 = 0.066, wR2 = 0.140	R1 = 0.056, wR2 = 0.146
R indices (all data)	R1 = 0.053, wR2 = 0.109	R1 = 0.099, wR2 = 0.154	R1 = 0.066, wR2 = 0.154
Quality-of-fit indicator ^c	1.155	1.058	1.189
Weight parameters, a, b^{b}	0.04, 40.0	0.055, 125.0	0.11, 0.0
Largest shift/esd, final cycle	0.003	0.001	0.002
Largest peak, (e Å ⁻³)	3.2(2)	3.1(3)	4.4(5)

 ${}^{\mathrm{a}}R1 = \sum ||F_{\mathrm{o}}| - |F_{\mathrm{c}}|| / \sum |F_{\mathrm{o}}|.$

 ${}^{b}wR2 = [\sum_{v}^{\infty} (F_{o}^{2} - F_{c}^{2})^{2} / \sum_{v}^{\infty} (F_{o}^{2})^{2}] 1/2, w = 1/[\sigma^{2}(F_{o}^{2}) + (a \cdot p)^{2} + b \cdot p, p = [\max(F_{o}^{2} \text{ or } 0) + 2(F_{c}^{2})]/3.$ ${}^{c}\text{Quality-of-fit} = [\sum_{v} (|F_{o}^{2}| - |F_{o}^{2}|)^{2} / (N_{obs} - N_{param})]^{1/2}.$



Fig. 1. The $Re_2(DPhF)_3Cl_3^-$ molecules, with thermal displacement ellipsoids at the 30% probability level. The numbering scheme is the one used in Table 2.



Fig. 2. The two independent $Re_2(DPhF)_2Cl_4$ molecules. The principal dimensions, averaged over both and over chemically equivalent ones are: $Re-Re = 2.177(1)\text{\AA}$, $Re-N = 2.06(1)\text{\AA}$, $Re-Cl = 2.319(5)\text{\AA}$, $Cl-Re-Cl = 106.0(1)^{\circ}$.

given in Fig. 1. The Re–Re distance found is 2.2318(8) Å while that in the less satisfactory structure of the acetonitrile solvate is the same within experimental error, 2.2288(9) Å. The mean, 2.230 Å, is the same as that in Re₂(O₂CC-

 $Me_3)_3Cl_3$, 2.229(2) Å, and similar to that in $Re_2(O_2CC_2H_5)$ -(mph)₂Cl₃, 2.2041(6) Å.

The third crystal structure determined in this work is that of trans-Re₂(DPhF)₂Cl₄. This is a type of structure frequently seen in this area of chemistry. In this case the unit cell contains two independent centrosymmetric molecules, shown in Fig. 2. The bond distances and angles are normal and the average values of the principal ones are given in the caption to the figure.

The previously reported rhenium compounds of the DArF⁻ type of ligand and several with DTolF⁻, are all of the paddlewheel type with a Re₂(DTolF)₄ core [7]. For three with an Re₂⁶⁺ unit and Cl or OMe axial ligands the Re–Re distances are in the range 2.271–2.305 Å.

4. Supplementary material

Tables of atomic coordinates and additional data for all the three structures are available from the corresponding author on request.

Acknowledgements

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