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Substitution reactions of rhenium–chloride bonds in $[Re_2(DMAA)_4Cl_2]$, (DMAA = 2′,6′-dimethylacetanilido); synthesis and characterisation of $[Re_2(DMAA)_4X_2]$ (X = NCO, NCS, N_3) and $[Re_2(DMAA)_4L_n][SbF_6]_2$ ($n = 2$, L = pyridine; $n = 1$, L = 4,4′-bipyridine)

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Abstract

Substitution of chloride ligands in $[Re_2(DMAA)_4Cl_2]$ (**1**), (DMAA = 2′,6′-dimethylacetanilido) in a mixture of dichloromethane–methanol affords $[Re_2(DMAA)_4X_2]$ complexes with X = $[N_3]^-$, **2**·CH_2Cl_2, $[SCN]^-$, **3**, or $[NCO]^-$, **4**·CH_2Cl_2 in yields of 84, 72 and 76%, respectively. The reaction of **1** and $Ag[SbF_6]$ in air affords $[Re_2(DMAA)_4(H_2O)_2][SbF_6]_2\cdot H_2O$, **5**·$H_2O$ (71%). The aquo ligands in **5** can be displaced by pyridine or 4,4′-bipyridine to produce $[Re_2(DMAA)_4(pyridine)_2][SbF_6]_2$ (**6**) (68%), and $[Re_2(DMAA)_4(4,4'\text{-bipyridine})][SbF_6]_2\cdot CH_2Cl_2$ (**7**) (42%). All new compounds were characterised with C, H and N chemical analysis, FTIR and, except for **7**, ^1H and ^{13}C NMR spectroscopies. Additionally, single crystal X-ray crystallography was used to establish the molecular structures of **2**·CH_2Cl_2 and **3**·$0.83CHCl_3$. Principal distances and angles are: rhenium–rhenium distances in **2** and **3** of 2.2477(3) and 2.2324(5) Å, respectively; rhenium to azido nitrogen distances in **2** of 2.158(5) and 2.166(6) Å, and rhenium to isothiocyanato nitrogen distances in **3** of 2.208(8) and 2.210(6) Å; essentially linear azido and isothiocyanato ligands with N–N–N angles of 178.4(10) and 179.1(9)° and N–C–S angles of 177.9(10) and 179.7(9)°, and Re–N–X angles (X = N for **2** and C for **3**) of the rhenium *pseudo*-halide bonds of 139.8(6) and 128.6(5)° in **2** and 151.9(7) and 169.1(9)° in **3**, respectively.

Keywords: Synthesis; Dirhenium; *Pseudo*-halides; Crystal structures; Di-cation; Amidato

1. Introduction

Dimers of the form $[Re_2(\mu\text{-lig})_4X_2]$ (Scheme 1(a) where lig = a bidentate bridging ligand, X = terminal ligand) which contain rhenium–rhenium multiply bonded cores are of interest as precursors to the formation of conducting molecular wires provided that the linear X–Re–Re–X sequence can be incorporated into a conjugated system, Scheme 1(b). Examples of such systems with dirhodium [1] and diruthenium [2] cores have been prepared and polymers of the general formula $[Re_2(RCOO)_2Cl_4(L)]_n$, where R = Me or Et, L = 4,4′-bipyridine or pyrazine have also been reported [3].

Dirhenium complexes with several types of bridging ligands are known including those with bridging carboxylato ligands, $[Re_2(RCOO)_4Cl_2]$ [4,5]. The carboxylato compounds have been studied extensively since the series of compounds with R = Me, Et, *n*-Bu, *iso*-Bu, *n*-C_7H_{15} was first described [5]. Complexes with other organic-based bidentate bridging ligands such as amidato, [6] 2-oxypyridinato, [7] amidinato [8] and adenato

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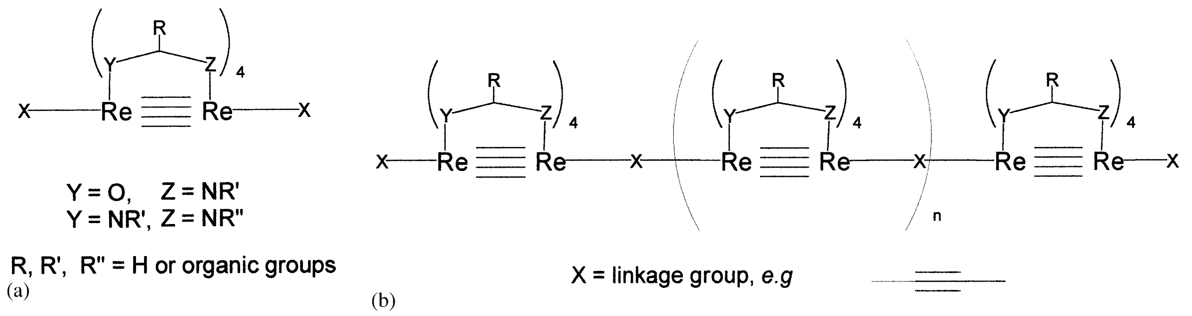


Scheme 1. (a) Dirhenium supported by bidentate bridging ligands; (b) dirhenium units joined by linkage groups.

[9] have also been reported but, in general, there has been less work on these species.

Some studies of $[Re_2(\mu\text{-lig})_4Cl_2]$ dimers concerning the reactivity of the rhenium chloride bonds have been published. Substitutions of the chloride by iodide, thiocyanate and aquo ligands in $[Re_2(RCOO)_4Cl_2]$ have been reported [5,10]. Furthermore, the reaction between $[Re_2Cl_8]^{2-}$ and mixtures of H_2SO_4–$[SO_4]^{2-}$ affords [11] the species $[Re_2(SO_4)_4]^{2-}$ while the octamethyl complex $[Re_2(Me)_8]^{2-}$ is formed from $[Re_2(PhCOO)_4Cl_2]$ by reaction with methyllithium [12]. Kühn et al. have replaced the chloride ligands in $[Re_2(Bu^tCOO)_4Cl_2]$ by the moiety $[(CO)_5M(CN)]^-$ (where M = Cr, Mo, W) [13]. It has also been reported that the chloride ligands in the amidinato complex $[Re_2(DFM)_4Cl_2]$ (where HDFM = di-*p*-toylformamidine) have been replaced by methoxy groups [14].

We have used the complex $[Re_2(DMAA)_4Cl_2]$ (**1**) (where HDMAA = 2′,6′-dimethylacetanilide) to prepare a number of compounds by substituting chloride ligands with the *pseudo*-halide species $[N_3]^-$, $[SCN]^-$ and $[NCO]^-$. In addition, we report the synthesis of the dicationic dirhenium complexes $[Re_2(DMAA)_4(H_2O)_2][SbF_6]_2$, $[Re_2(DMAA)_4(pyridine)_2][SbF_6]_2$ and $\{[Re_2(DMAA)_4L'][SbF_6]_2\}_n$ where L′ = 4,4′-bipyridine. The $[Re_2(DMAA)_4Cl_2]$ complex was chosen for this work partly because Cotton et al. [6] reported it to be a single isomer with virtual D_{2d} symmetry in the central $[Re_2(N–C–O)_4]$ part of the molecule.

2. Results and discussion

Neutral *pseudo*-halide complexes $[Re_2(DMAA)_4X_2]$ where X = $[N_3]^-$ (**2**), $[SCN]^-$ (**3**) or $[NCO]^-$ (**4**) were prepared from the reactions between $[Re_2(DMAA)_4Cl_2]$ and the *pseudo*-halide salts $Na[N_3]$, $[NH_4]SCN$ or K[NCO], respectively. The reactions were carried out in mixtures of dichloromethane–methanol and were heated at reflux temperature for 16 h. The products isolated were **2**·CH_2Cl_2, **3** and **4**·CH_2Cl_2 in yields of 77, 72 and 71%, respectively, Table 1. Complexes **2** and **4** were red and **3** was orange.

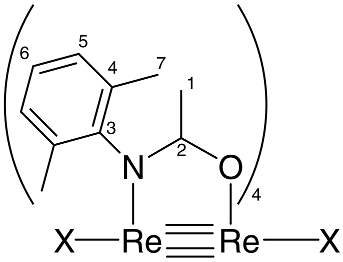
The IR spectrum of the diazido complex, $[Re_2(DMAA)_4(N_3)_2]$ (**2**) shows very strong bands at 2064 and 2042 cm^{-1} which are assigned to the $\nu(N_3)$ stretches. The spectrum of complex **3** shows a very strong $\nu(CN)$ band at 2015 cm^{-1} which, since it is closer to 2000 than 2100 cm^{-1}, is indicative of an isothiocyanato Re–NCS bonded species [15]. The band at 801 cm^{-1} in the spectrum of **3** can be assigned as the $\nu(CS)$ vibration. Complex **4** shows very strong bands of almost equal intensity at 2183 and 2168 cm^{-1} which are assigned to the $\nu(CN)$ stretches of rhenium-bonded –NCO or –OCN groups.

The general features of the ^1H NMR spectra of **2**–**4** are similar to those reported for the chloride complex $[Re_2(DMAA)_4Cl_2]$ (**1**) suggesting that the complexes have similar structures in solution, Table 2. However, whereas compounds **2** and **3** are present as single

Table 1
Characterisation of compounds **2**–**7**

Complex (lig = DMAA)	M.p. (°C)	Yield (%)	IR	Analysis (theoretical values)		
				C	H	N
$Re_2(lig)_4\{N_3\}_2\cdot CH_2Cl_2$	288 [a]	77	2064 s, 2042 vs, 1326 m	41.5 (41.4)	4.3 (4.2)	11.6 (11.8)
$Re_2(lig)_4\{SCN\}_2$	320 [a]	72	2016 vs, 801 m	44.7 (44.4)	4.6 (4.3)	7.0 (7.4)
$Re_2(lig)_4\{NCO\}_2\cdot CH_2Cl_2$	196 [a]	71	2183 vs, 2168 vs	43.6 (43.4)	4.5 (4.2)	6.8 (7.1)
$[Re_2(lig)_4(H_2O)_2][SbF_6]_2\cdot H_2O$ [b]	255 [a]	71	659 vs	30.5 (31.1)	3.5 (3.5)	3.5 (3.6)
$[Re_2(lig)_4(py_2)][SbF_6]_2$	264 [a]	68	1604 m, 659 vs	36.3 (36.4)	3.8 (3.4)	4.9 (4.9)
$[Re_2(lig)_4bipy][SbF_6]_2\cdot CH_2Cl_2$	270 [a]	42	659 vs	34.6 (34.3)	3.3 (3.3)	4.7 (4.6)

[a] Melting with decomposition.
[b] The compound $[Re_2(lig)_4(H_2O)_2][SbF_6]_2\cdot H_2O$ analysed 0% for chlorine.



Scheme 2. dirhenium complexes labelling ^{1}H and ^{13}C NMR nuclei.

isomers, complex **4** shows three sets of resonances due to three isomers in solution. One set of resonances is twice the intensity of the other two. This may be rationalised on the basis that complex **4** exists as a mixture of three isomers in solution i.e. the $(OCNRe)_2$, (OCN)Re-Re(OCN) and $(NCORe)_2$ bonded species with a statistical distribution of 1:2:1, respectively. This suggestion is supported by the ^{13}C NMR spectrum of **4**, Table 2, but, since there appears to be accidental overlap of the resonances for the C(3)/O*C*N sites in the isomer mixture, the signals at 145.9 and 145.3 ppm can only be assigned tentatively. The ^{13}C NMR spectrum of **3** shows a resonance at 151.2 ppm, which is attributed to the carbon atom in the SCN ligand. The observation of a single isomer for complex **3** is in contrast to the three isomers observed for complex **4** and this may be a consequence of both the preference of rhenium for the distinctly 'harder' donor properties of N compared with S in **4** and the smaller size of the nitrogen donor atom compared with the sulfur atom. Whereas, for complex **4**, there is less to choose between the N and O donor sites of NCO on both electronic and size grounds.

The yellow dicationic dirhenium complex $[Re_2(DMAA)_4(H_2O)_2][SbF_6]_2 \cdot H_2O$, **5**·$H_2O$ was formed by the addition in air of silver hexafluoroantimonate to a dichloromethane solution of $[Re_2(DMAA)_4Cl_2]$ at room temperature and subsequent work-up in air. The yellow product was isolated in 71% yield, Table 1. The IR spectrum of **5** confirmed the presence of the hexafluoroantimonate anion with a single very strong band at 659 cm^{-1}. ^{1}H and ^{13}C NMR spectra were similar to those observed for complexes **1**–**3**, Table 2. Unfortunately crystals of **5** suitable for an X-ray structural determination, could not be obtained.

Two other yellow dicationic dirhenium complexes were prepared from complex **5**, i.e. $[Re_2(DMAA)_4(pyridine)_2][SbF_6]_2$ (**6**) and $\{[Re_2(DMAA)_4L'][SbF_6]_2\}_n$, (**7**) (L′ = 4,4′-bipyridine). Reaction in dichloromethane solution at room temperature between **5** and 2 equiv. of pyridine afforded the bispyridine dicationic complex $[Re_2(DMAA)_4(pyridine)_2][SbF_6]_2$ (**6**) in 68% yield. The IR spectrum of **6** confirms the presence of the hexafluoroantimonate anion with a very strong band at 659 cm^{-1}. The ^{1}H NMR spectrum exhibits three multiplet signals between 8.08 and 6.98 ppm that can be attributed to the pyridine ligand. The aromatic protons on the bridging DMAA ligand occur at 6.78 ppm, and the aliphatic protons at 3.36 and 2.32 ppm. A similar

Table 2
^{1}H and ^{13}C NMR spectroscopic data for compounds **1**–**6**

Nucleus	Signal intensity	Compound					
		1	**2**	**3**	**4** [a]	**5** [b]	**6** [c]
H(5,6) [d]	1H	7.04	7.05	7.04	7.04	7.16	6.78
H(1)	1H	2.86	2.85	2.92	2.86	3.01	3.37
H(7)	2H	2.22	2.23	2.23	2.21	2.21	2.32
C(2)		185.2	184.3	184.7	184.7	187.6	188.8
C(8) [e]				151.2	145.3 [f]		
C(9)							147.7
C(3)		147.4	145.8	144.8	145.9 [f]	140.8	142.5
C(11)							141.2
C(4)		132.5	131.8	131.8	131.9	132.9	133.1
C(5)		129.1	129.3	129.3	129.1	130.5	130.5
C(6)		127.3	127.0	127.6	127.2	129.4	129.4
C(10)							126.6
C(1)		21.8	21.0	21.1	21.2	21.6	21.1
C(7)		18.9	18.4	18.4	18.4	18.4	18.8

[a] Less abundant isomers of NCO had the following ^{13}C NMR signals C_2 185.3, 185.0; C_4 131.9, 131.7; C_5 130.0, 129.3; C_6 128.1, 127.6; C_1 21.4, 21.0; C_7 18.6, 18.4.

[b] In CD_3CN; broad signal centred at 2.27 ppm due to H_2O.

[c] In acetone-d_6; resonances for pyridine ligands: 8.08 2H m (J^3 4.8 Hz, J^4 2.3 Hz) *ortho*, 7.53 1H m (J^3 7.5 Hz, J^4 1.5 Hz) *para*, 6.98 2H m (J^3 6.3 Hz, J^4 1.3 Hz) *meta*. Relative intensities of proton signals for two pyridine: four DMAA was 10:48. C(9), C(10) and C(11) refer to carbon atoms *ortho*, *meta* and *para* to the heteroatom on pyridine, respectively.

[d] See Scheme 2 above for positions of nuclei.

[e] C(8), carbon nucleus on *pseudo*-halide group.

[f] Tentative assignments see text.

reaction to that affording **6**, i.e. reaction between **5** and either one or two equiv. of 4,4′-bipyridine, produced the insoluble, possibly polymeric, complex {[Re_2(DMAA)$_4$L′][SbF_6]$_2$}$_n$ (**7**). The IR spectrum of **7** was very similar to that of **6** and was characterised by bands due to the organic ligand and the hexafluoroantimonate anion.

3. X-ray crystallographic studies of the structures of 2 and 3

In order to establish the structural details of these compounds, single crystal structure studies were undertaken. Suitable crystals were obtained by evaporation of dichloromethane–ether solution of compound **2** and a chloroform solution of **3**. Data collection and structure refinement details are given in the Section 4 below. The molecular structures of **2** and **3** are depicted in Figs. 1 and 2 and important distance and angle data are given in Tables 3 and 4, respectively.

Compound **2** appears to be the first dirhenium(III) azide-containing structure to be studied and compound **3** is the first dirhenium(III) isothiocyanate with a linear N–Re–Re–N grouping. In general, each rhenium atom is octahedrally coordinated being bonded to two *trans*-located nitrogen and two *trans*-located oxygen atoms from the bridging DMAA ligands, a nitrogen atom from the *pseudo*-halide and the other rhenium atom. Although the mean values of the rhenium to nitrogen distances in **2** and **3** for nitrogen in the bridging DMAA ligands are similar at 2.096(5) and 2.096(6) Å, respectively, there are significant differences within each set of Re–N(amidato) distances in each molecule, e.g. in **3** the Re(2)–N(21) distance is 2.079(6) Å whereas the Re(2)–N(41) distance is 2.130(6) Å. Significant differences also exist in the Re–O(amidato) distances in **2** but this is not observed in the molecular structure of **3**. The mean Re–O values are 2.012(4) and 2.013(5) Å for **2** and **3**, respectively.

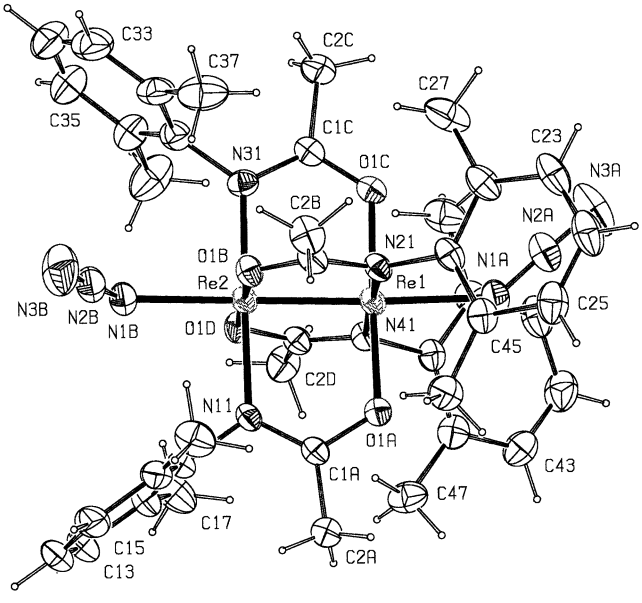


Fig. 1. View of [Re_2(DMAA)$_4$(N_3)$_2$], with numbering scheme.

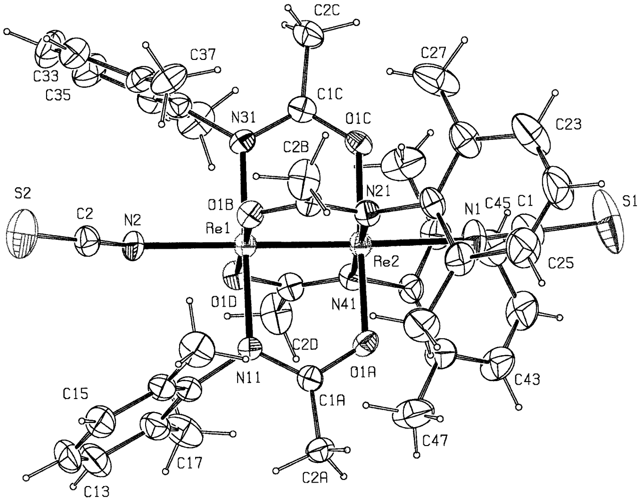


Fig. 2. View of [Re_2(DMAA)$_4$(SCN)$_2$], with numbering scheme.

Table 3
Selected bond distances (Å) and angles (°) in [Re_2(DMAA)$_4$(N_3)$_2$] (**2**)

Atom labels		Atom labels	
Bond distances			
Re(1)–Re(2)	2.2477(3)	Re(2)–O(1D)	1.987(4)
Re(1)–O(1A)	2.001(4)	Re(2)–O(1B)	2.037(4)
Re(1)–O(1C)	2.025(4)	Re(2)–N(31)	2.098(5)
Re(1)–N(41)	2.111(4)	Re(2)–N(11)	2.104(5)
Re(1)–N(21)	2.070(5)	Re(2)–N(1B)	2.166(6)
Re(1)–N(1A)	2.158(5)	N(2A)–N(3A)	1.145(9)
N(1A)–N(2A)	1.185(8)	N(2B)–N(3B)	1.136(10)
N(1B)–N(2B)	1.214(9)		
Bond angles			
O(1A)–Re(1)–N(1A)	90.7(2)	O(1D)–Re(2)–N(1B)	96.95(19)
O(1C)–Re(1)–N(1A)	87.1(2)	O(1B)–Re(2)–N(1B)	81.86(19)
N(21)–Re(1)–N(1A)	92.2(2)	N(31)–Re(2)–N(1B)	91.2(2)
N(41)–Re(1)–N(1A)	89.0(2)	N(11)–Re(2)–N(1B)	90.1(2)
O(1A)–Re(1)–Re(2)	92.70(11)	O(1B)–Re(2)–Re(1)	89.18(11)
O(1C)–Re(1)–Re(2)	89.39(12)	O(1D)–Re(2)–Re(1)	92.04(11)
N(21)–Re(1)–Re(2)	90.92(13)	N(31)–Re(2)–Re(1)	90.77(14)
N(41)–Re(1)–Re(2)	87.83(13)	N(11)–Re(2)–Re(1)	87.81(13)
N(1A)–Re(1)–Re(2)	175.31(16)	N(1B)–Re(2)–Re(1)	170.79(16)
N(2A)–N(1A)–Re(1)	139.8(6)	N(2B)–N(1B)–Re(2)	128.6(5)
N(3A)–N(2A)–N(1A)	178.4(10)	N(3B)–N(2B)–N(1B)	179.1(9)
O(1A)–C(1A)–N(11)	119.6(5)	O(1B)–C(1B)–N(21)	119.7(5)
O(1C)–C(1C)–N(31)	120.6(6)	O(1D)–C(1D)–N(41)	119.9

In **2**, the rhenium to azido nitrogen distances Re–N(1), Table 3, are slightly longer at 2.158(5) and 2.166(6) Å than the longest Re–N(amidato) distance

Table 4
Selected bond distances (Å) and angles (°) in $[Re_2(DMAA)_4(NCS)_2]$ (**3**)

Atom labels		Atom labels	
Bond distances			
Re(1)–Re(2)	2.2324(5)	Re(1)–O(1D)	1.997(5)
Re(2)–O(1A)	2.008(5)	Re(1)–O(1B)	2.021(5)
Re(2)–O(1C)	2.027(5)	Re(1)–N(31)	2.079(6)
Re(2)–N(21)	2.079(6	Re(1)–N(11)	2.094(6
Re(2)–N(41)	2.130(6)	Re(1)–N(2)	2.210(6)
Re(2)–(N1)	2.208(8)	S(1)–C(1)	1.617(11)
S(2)–C(2)	1.623(9)	C(1)–N(1)	1.095(12)
C(2)–N(2)	1.146(10)		
Bond angles			
O(1D)–Re(1)–N(2)	94.9(2)	O(1A)–Re(2)–N(1)	91.4(3)
O(1B)–Re(1)–N(2)	82.7(2)	O(1C)–Re(2)–N(1)	87.1(3)
N(31)–Re(1)–N(2)	91.8(2)	N(21)–Re(2)–N(1)	92.6(3)
N(11)–Re(1)–N(2)	88.9(2)	N(41)–Re(2)–N(1)	88.3(3)
O(1D)–Re(1)–Re(2)	92.78(15)	O(1A)–Re(2)–Re(1)	91.57(14)
O(1B)–Re(1)–Re(2)	89.60(14)	O(1C)–Re(2)–Re(1)	90.01(14)
N(31)–Re(1)–Re(2)	90.35(17)	N(21)–Re(2)–Re(1)	91.16(17)
N(11)–Re(1)–Re(2)	88.75(16)	N(41)–Re(2)–Re(1)	87.98(17)
N(2)–Re(1)–Re(2)	171.95(19)	N(1)–Re(2)–Re(1)	175.2(2)
N(1)–C(1)–S(1)	177.9(10)	N(2)–C(2)–S(2)	179.7(9)
C(1)–N(1)–Re(2)	169.1(9)	C(2)–N(2)–Re(1)	151.9(7)
O(1A)–C(1A)–N(11)	118.6(7)	O(1C)–C(1C)–N(31)	119.2(7)
O(1B)–C(1B)–N(21)	119.8(7)	O(1D)–C(1D)–N(41)	120.6(7)

of 2.111(4) Å. The rhenium–azide moieties in **2** are typical of metal–azide groups with the N(1)–N(2) bonds slightly, but not significantly, shorter than the N(2)–N(3) bonds.

The distances are 1.185(8) and 1.214(9) Å, and 1.145(9) and 1.136(10) Å, respectively. Both azido ligands are essentially linear with N–N–N angles of 178.4(10) and 179.1(9)°. These data can be compared with those from the only other rhenium azide complexes reported in the Cambridge Crystallographic Database. These compounds contain single rhenium centres and neither contains rhenium in oxidation state +III. The compounds are the Re(I) complex *trans*-$[Re(N_3)(N_2)(Ph_2PCH_2CH_2PPh_2)_2]$ [16] and the Re(V) complex $[ReN(N_3)(Me_2PhP)_2(Et_2tcb)]$, [17] where Et_2tcb = *N*-(*N*,*N*-diethylthiocarbonylbenzamidine). These molecules contain Re–N(1), N(1)–N(2), N(2)–N(3) distances of 2.058(3), 1.199(10) and 1.200(13) Å and 2.323(9), 1.23(1) and 1.08(1) Å, respectively, and the azide groups are linear.

The rhenium to isothiocyanato nitrogen distances in **3** are much longer at 2.208(8) and 2.210(6) Å than the longest Re–N(amidato) distance in **3** of 2.130(6) Å. The isothiocyanate groups in **3** have N–C distances of 1.095(12) and 1.146(10) Å and C–S distances of 1.617(11) and 1.623(9) Å, respectively. The N–C–S groups are essentially linear as expected with angles of 177.9(10) and 179.7(9)°. Of the 32 reported compounds with Re–NCS bonds in the Cambridge Crystallographic Database, only five of these contain rhenium in the +III oxidation state. Of these, the only quadruply bonded rhenium dimers are $[Re_2(NCS)_8L_2]^{2-}$ with L = acetone **8a** or pyridine **8b** ligands [18]. In both **8a** and **8b** there is a linear X–Re–Re–X sequence with X being either the O atom of acetone or the N atom of pyridine and the isothiocyanate ligands occupying the positions taken by the amidato ligands in **3** [18]. Other rhenium compounds of relevance in the Cambridge Crystallographic Database were *cis*- and *trans*-$[Re(NCS)(Cl_2)(PMe_2Ph)_3]$ (**9a**) and (**9b**), respectively [19] and *mer*-$[Re(NCS)_3(PEt_2Ph)(Ph_2PCH_2CH_2PPh_2)]$ (**10**) [20]. Comparison of the Re–N–C–S distances in **3** with those in the other compounds shows in general that (i) the Re–N bonds in **3** are significantly longer (mean 2.209(8) Å compared with a range of 1.992(8) Å in **10**–2.071(4) Å in **9b**), (ii) the N–C distances are shorter (mean 1.121(12) Å in **3**, compared with a range of 1.09(1) Å in **9a**–1.18(2) Å in **8a**), and (iii) the C–S distances are longer (mean 1.620(11) Å in **3**, compared with a range of 1.560(13) Å in **8a**–1.64(2) Å in **9a**). Overall this suggests that the bonding in **3** may be represented as $Re{-}N^{\delta+}{\equiv}C{-}S^{\delta-}$ with the possibility that the sulfur atom is available for bonding to another metal centre.

It is noteworthy that the Re–N–N angles in **2** are quite different from 120° and also different within the molecule being 139.8(6) and 128.6(5)°. The Re–N–N angles in the Re(I) complex *trans*-$[Re(N_3)(N_2)(Ph_2PCH_2CH_2PPh_2)_2]$ [16] and the Re(V) complex $[ReN(N_3)(Me_2PhP)_2(Et_2tcb)]$, [17] are notably larger at 150.3(5) and 151.6(7)°, respectively. The Re–N–C angles in **3** are 151.9(7) and 169.1(9)° which are more typical of those observed in previously studied rhenium–isothiocyanate complexes where a range of values from 162(1)° in **8b** to 174.3(9)° in **10** have been reported. Both the ReN_3 sections in **2** are almost co-planar with planes containing the adjacent set of $(O)_2ReRe'$ atoms, see Fig. 1, with torsional angles O(1A)–Re(1)–N(1A)–N(2A) and O(1C)–Re(1)–N(1A)–N(2A) of 172.2(8) and 8.7(8)° and O(1D)–Re(2)–N(1B)–N(2B) and O(1B)–Re(2)–N(1B)–N(2B) of 179.1(6) and 0.2(6)°. However, co-planarity of the related sections in molecule **3** only occurs in one part of the molecule, see Fig. 2, i.e. in the sections containing Re(1)–N(2)–C(2)–S(2) and Re(1), O(1B), O(1D) and Re(2) where the relevant torsional angles O(1D)–Re(1)–N(2)–C(2) and O(1B)–Re(1)–N(2)–C(2) are 173.5(14) and 6.5(14)°.

The rhenium–rhenium distances in **2** and **3** of 2.2477(3) and 2.2324(5) Å, respectively, are typical of quadruply bonded rhenium atoms and may be compared with 2.2364(5) Å reported in the dichloro derivative $[Re_2(DMAA)_4Cl_2]^6$ or values of 2.270(1) and 2.296(1) Å in compounds **8a** and **8b**, respectively. The Re–Re distances in the four DMAA complexes reported by Cotton et al. [6] were in the range 2.2181(6)–

2.2364(5) Å. There are no unusual distances or angles within the bridging amidato ligands.

4. Experimental

4.1. General

All preparative experiments and crystallisation were carried out in an inert atmosphere except in the case of the preparation of **5**. Compounds 2′,6′-dimethylacetanilide, 4,4′-bipyridine, pyridine, silver hexafluoroantimonate, ammonium thiocyanate, potassium cyanate, and sodium azide were obtained from Aldrich Chem. Co. and used without further purification. Potassium perrhenate was obtained from Alfa Aesar. Synthesis of [$Re_2(DMAA)_4Cl_2$] was carried out as described in the literature [6]. IR spectra of compounds **2**–**7** were recorded from a KBr disc on a Perkin–Elmer Paragon FT spectrometer. Carbon, hydrogen, nitrogen and chlorine analyses were performed at University College Cork. NMR spectra were recorded on a Bruker AM 300 spectrometer. Solvents for NMR spectra were $CDCl_3$ for **1**–**4**, CD_3CN for **5**, and acetone-d_6 for **6**. Chemical shifts (δ) are expressed in parts per million (ppm) and are relative to internal $SiMe_4$ (^1H) and ^{13}C, positive values represent shifts to high frequency (‘low-field’) of the standards.

4.2. Crystal structure analysis for compound **2**

A suitable crystal was obtained from CH_2Cl_2 solution—Crystal data $C_{41}H_{50}Cl_2N_{10}O_4Re_2$, $M = 1190.21$, monoclinic, $P2_1/n$, $Z = 4$, $a = 11.7316(10)$ Å, $b = 13.9957(11)$ Å, $c = 27.513(3)$ Å, $\beta = 96.743(6)^\circ$, $U = 4486.2(7)$ Å^3, $D_{calc} = 1.762$ g cm^{-3}, $F(000) = 2328$, λ(Mo Kα) = 0.71073 Å, $\mu = 5.562$ mm^{-1}, $T = 293(1)$ K, $R = 0.0384$ for 7585 data with $I > 2\sigma(I)$, $R_w(F^2) = 0.0970$ for all 8792 measured data. A disordered dichloromethane solvent molecule of crystallisation is located in the lattice.

4.3. Crystal structure analysis for compound **3**

A suitable crystal was obtained from $CHCl_3$ solution—Crystal data $C_{42.83}H_{48.83}Cl_{2.48}N_6O_4$ Re_2S_2, $M = 1235.95$, monoclinic, $P2_1/c$, $Z = 4$, $a = 20.099(3)$ Å, $b = 11.5911(17)$ Å, $c = 22.461(4)$ Å, $\beta = 110.233(12)^\circ$, $U = 4909.9(12)$ Å^3, $D_{calc} = 1.672$ g cm^{-3}, $F(000) = 2416$, λ(Mo Kα) = 0.71073 Å, $\mu = 5.191$ mm^{-1}, $T = 293$ K, $R = 0.0464$ for 7485 data with $I > 2\sigma(I)$, $R_w(F^2) = 0.1088$ for all 9568 measured data. A disordered partial occupancy (0.83) chloroform solvent molecule of crystallisation is located in the lattice.

4.4. Structure determination

For both **2** and **3** accurate cell dimensions and the crystal orientation matrix were determined by a least-squares treatment of the setting angles of 67 and 38 reflections, respectively, for **2** and **3**. Data were collected on a Bruker P-4 diffractometer using graphite-monochromatised (Mo Kα) radiation. Intensities of four reflections measured every 296 reflections showed no significant decay for **2** but a 3% decay was detected in the intensity controls for **3**. Data were corrected for Lorentz, polarisation and absorption effects (Ψ-scans). The coordinates of the heavy atoms and remaining non-hydrogen atoms were located via the heavy-atom method in SHELXS-97 [21]. Refinement was by full-matrix least-squares calculations with the SHELXL-97 [21], initially, with isotropic and later with anisotropic displacement parameters for all of the non-hydrogen atoms [22]. Hydrogen atoms were visible in difference maps and were allowed for as riding atoms in the final refinement cycles.

4.5. Preparation of [dirhenium-tetra(2,6-dimethylacetanilide){diazide}] (**2**)

To [Re_2(2′,6′-dimethylacetanilide)$_4Cl_2$] [6] (0.100 g, 0.092 mmol) dissolved in a mixture of dichloromethane–methanol (4/1) (50 ml), was added sodium azide (0.026 g, 0.400 mmol). The reaction mixture was heated at reflux temperature (16 h). A colour change from orange to red was observed. The reaction mixture was allowed to cool to room temperature (r.t.) and the solvent was removed under reduced pressure. The crude product was re-dissolved in dichloromethane, filtered and layered with ether. Crystallisation from dichloromethane afforded dark red crystals of **2** as the mono CH_2Cl_2 solvate, [$Re_2(C_{10}H_{12}NO)_4(N_3)_2$]·$CH_2Cl_2$, (0.085 g, 0.077 mmol, 84%), **2**·CH_2Cl_2.

The isothiocyanate, [$Re_2(C_{10}H_{12}NO)_4(NCS)_2$] (**3**), (yield 0.104 g, 0.092 mmol, 72%) and dicyanate, [$Re_2(C_{10}H_{12}NO)_4(NCO)_2$]·$CH_2Cl_2$, **4**·$CH_2Cl_2$, (yield 0.120 g, 0.109 mmol 76%) complexes were similarly prepared from reactions between Re_2[(2′,6′-dimethylacetanilide)$_4$]Cl_2 and ammonium thiocyanate and potassium cyanate, respectively.

Carbon, H and N analyses, ^1H and ^{13}C NMR spectroscopic data for **2**, **3** and **4** are listed in Tables 1 and 2, respectively.

4.6. Preparation of [dirhenium-tetra(2′,6′-dimethylacetanilide)(diaquo)] bis{hexafluoroantimonate} (**5**)

To [Re_2(2′,6′-dimethylacetanilide)$_4Cl_2$] (0.100 g, 0.092 mmol) dissolved in dichloromethane (50 ml), was added a solution of silver hexafluoroantimonate (0.063 g, 0.182

mmol) in dichloromethane (10 ml). The reaction mixture was stirred in air for 30 min at r.t. and the reaction solution changed colour from orange to yellow. A white precipitate was filtered from the reaction mixture. Removal of the solvent yielded a yellow solid $[Re_2(C_{10}H_{12}NO)_4(H_2O)_2][SbF_6]_2$ (**5**) as the monohydrate (0.102 g, 0.068 mmol 71%). Carbon, hydrogen and nitrogen analyses, ^1H and ^{13}C NMR spectroscopic data are listed in Tables 1 and 2, respectively. The ^1H spectrum showed a broad signal centred at 2.27 ppm due to water. The intensity ratio of this signal to the ^1H signals from the 2′,6′-dimethylacetanilide ligand showed that three water molecules were present in the rhenium complex i.e. it was $[Re_2(C_{10}H_{12}NO)_4(H_2O)_2][SbF_6]_2 \cdot H_2O$.

*4.7. Preparation of [dirhenium-tetra(2,6-dimethylacetanilide)]bis-pyridine-bis{hexafluoroantimonate} (**6**)*

To $[Re_2(2,6\text{-dimethylacetanide})_4Cl_2]$ (0.100 g, 0.092 mmol) dissolved in dichloromethane (50 ml), a solution of silver hexafluoroantimonate (0.063 g, 0.182 mmol) in dichloromethane (10 ml) was added. The reaction mixture was stirred (30 min). A colour change from orange to bright yellow solution was observed, together with a white precipitate. To the filtered solution, pyridine (0.016 g, 0.200 mmol) was added and the yellow colour of the solution intensified. The solvent was removed yielding $[Re_2(C_{10}H_{12}NO)_4(\text{pyridine})_2][SbF_6]_2$ (**6**) as a yellow solid (0.103 g, 0.062 mmol 68%). Similarly, a 4,4′-bipyridine adduct, $\{[Re_2(C_{10}H_{12}NO)_4(4,4'\text{-bipyridine})]\ [SbF_6]_2 \cdot (CH_2Cl_2)\}_n$ (**7**) was prepared using the same procedure. Results of C, H, N analyses, ^1H and ^{13}C NMR spectroscopic data are listed in Tables 1 and 2, respectively. Results of C, H, N analyses, ^1H and ^{13}C NMR spectroscopic data are listed in Tables 1 and 2, respectively. Attempts to prepare the bis 4,4′-bipyridine complex $[Re_2(C_{10}H_{12}NO)_4(4,4'\text{-bipyridine})_2][SbF_6]_2$ from the reaction between $[Re_2(2,6\text{-dimethylacetanide})_4Cl_2]$ and 4,4′-bipyridine in a 1:2 stoichiometric ratio yielded **7**.

5. Supplementary material

Supplementary data are available from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk); on request quoting the deposition numbers 169082 and 169083.

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