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# Monomeric/dimeric complexes of *fac*-[Re(CO)<sub>3</sub>]<sup>+</sup> with benzoylthiourea derivatives

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### ABSTRACT

The reactions of  $[Re(CO)_5Br]$  with the potentially bidentate ligands N,N-dialkylbenzoylthiourea (HL1) and its N, N-diphenyl derivative (HL2) were studied. In the complex *fac*- $[Re(CO)_3(HL1)_2Br]$  (1) the two neutral HL1 ligands are coordinated in a monodentate manner via the thiourea sulfur atom. Coordination of the monoanionic chelate L2 occurs through the neutral benzoyl oxygen atom and the anionic sulfur atom, which also acts as a bridge to the second metal centre, in the dimeric complex  $[Re_2(CO)_6(L2)_2]$  (2). The crystal structures of 1 and 2 were determined by X-ray single crystal diffraction. UV-vis absorption spectra of the complexes show the intraligand and MLCT transitions.

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The current interest in the coordination chemistry of rhenium and technetium is mainly the result of the application of their <sup>186/188</sup>Re and <sup>99m</sup>Tc radionuclides in radiopharmacy [1]. Since these two metals are congeners, rhenium is often used as a non-radioactive substitute for technetium in experiments. Metal-based radiopharmaceuticals require thermodynamically and kinetically stable complexes, and therefore the focus has recently mainly been on compounds containing the robust rhenium(I) (d<sup>6</sup>) core *fac*-[Re(CO)<sub>3</sub>]<sup>+</sup> with a large variety of ligands containing a combination of nitrogen, oxygen and sulfur donor atoms [2–4].

In the past few years there has been considerable interest in benzoylthiourea derivatives as ligands for transition metals in general [5], and also for rhenium and technetium in particular [6]. These derivatives have shown in vitro activity against a large range of tumours [7], and have exhibited antibacterial [8], antiviral [8], herbicidal [9] and antifungal [10] activities.

In this account the products of the reactions of the potentially bidentate ligands, N,N-dialkyl-(HL1) and N,N-diphenylbenzoylthiourea (HL2) with [Re(CO)<sub>5</sub>Br] are reported [11]. With HL1, the complex *fac*-[Re(CO)<sub>3</sub>(HL1)<sub>2</sub>Br] (1) was isolated, in which HL1 is coordinated as a neutral monodentate ligand with coordination via the thiocarbonyl sulfur atom. The reaction with HL2 led to the dimeric complex [Re<sub>2</sub>(CO)<sub>6</sub>(L2)<sub>2</sub>] (2), in which L2 acts as a monoanionic chelate with coordination via the benzoyl oxygen and the sulfur atoms as a bridge between the two rhenium(I) centres.



Both complexes were prepared by the heating under reflux of  $[Re(CO)_5Br]$  with a twofold molar excess of the ligands HL in toluene [12]. They were characterised by elemental analysis, FTIR, <sup>1</sup>H NMR and single crystal X-ray diffraction. All the data are consistent with their formulation.

The infrared spectrum of **1** displays three strong bands in the carbonyl stretching region at 2024, 1943 and 1884 cm<sup>-1</sup>. In **2** the corresponding absorptions are at 2050, 1932 and 1902 cm<sup>-1</sup>. This pattern is typical for three carbonyls in a *facial* isomer arrangement around the rhenium [13]. The  $\nu$ (C=O) of the ligands HL1 in **1** is assigned to the peak at 1703 cm<sup>-1</sup>, with  $\nu$ (C=S) and  $\nu$ (NH) at 1535 and 3119 cm<sup>-1</sup> respectively. For **2** the  $\nu$ (C=O) of L2 occurs as a medium intensity peak at 1697 cm<sup>-1</sup>, with a strong absorption at 1577 cm<sup>-1</sup> being assigned to  $\nu$ (C=N).

In the <sup>1</sup>H NMR spectrum of **1**, the signal of the N*H* proton occurs the furthest downfield as a singlet at 10.50 ppm, with the four protons on each phenyl ring appearing as two doublets at 7.77 and 7.58 ppm. The presence of the four ethyl chains in **1** is confirmed by four-proton quartets at 3.94 and 3.42 ppm and two triplets at 1.36 and 1.21 ppm. The spectrum of **2** is not informative, with a 26 proton multiplet in the range 7.11–7.83 ppm.

The electronic absorption and luminescence spectra of **1** and **2** were recorded at room temperature. The absorption spectra of both complexes exhibit two peaks. On the basis of previously reported

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Fig. 1. Emission spectra of complexes 1 (in acetone) and 2 (in dichloromethane) after equilibration under nitrogen.

spectroscopic studies of Re(I) tricarbonyl complexes [14], we assigned the intense absorption around 350 nm (355 nm for **1**, 343 nm for **2**) to the intraligand transition ( $\pi \rightarrow \pi^*$ ), since similar absorptions are observed for the uncoordinated ligands HL1 and HL2. The less intense and lower-energy absorptions around 445 nm (441 nm for **1**, 448 nm for **2**) are assigned to the metal-to-ligand charge transfer (MLCT) d $\pi$ (Re)  $\rightarrow \pi^*$  (ligand) transitions. The latter absorption is more intense for complex **2**, which is reasonable since it has a more conjugated  $\pi$  system.

As is shown in Fig. 1, the photo-excitation of the complexes at 422 nm (for **1** in acetone) and 420 nm (for **2** in dichloromethane) leads to ligand-centred emissions at 503 and 489 nm respectively. In fact, both ligands HL1 and HL2 exhibit an emission at 501 nm after being excited at 425 nm (for HL1 in acetone) and 420 nm (for HL2 in chloroform). The nitrogen-equilibrated samples of 1 and 2 gave quantum yields of 0.012 and 0.008 respectively. The lifetimes of the complexes could not be measured due to the limitations of the spectrofluorometer. A comparison of the photophysical data of the complexes with other  $[Re(CO)_3]^+$  complexes containing thiourea derivatives as ligands was not possible, since no such data were reported [6a,15,16]. However, for the complexes fac-[Re(CO)<sub>3</sub>N<sub>3</sub>], containing the tridentate derivatives of benzimidazole, quinoline and tryptophan  $(N_3)$ , emission lifetimes of the order of 16 µs were found for MLCT emissions [17]. Interestingly, for complexes in which the emissions are not related to MLCT, the lifetimes were also too short to be measured [17].

#### Structure of fac- $[Re(CO)_3(HL1)_2Br]$ (1)

Crystals of **1** were obtained from the slow evaporation of the preparative solution at room temperature. The packing in the unit cell shows discrete monomeric and neutral units, with no intermolecular contacts shorter than the Van Der Waals' radii sum [18]. Each rhenium(I) atom lies in a distorted octahedral environment, with the bromide and two sulfur atoms in a facial arrangement, imposed by the *fac*-[Re(CO)<sub>3</sub>]<sup>+</sup> core (Fig. 1). Both HL1 ligands are neutral and are coordinated monodentately through the thiocarbonyl sulfur atoms. The three Re – C bond distances [average 1.910(3) Å] fall in the range observed [1.900(2)–1.928(2) Å] for similar complexes



**Fig. 2.** ORTEP diagram of the molecular structure of *fac*-[Re(CO)<sub>3</sub>(HL1)<sub>2</sub>Br] (1). Thermal ellipsoids are drawn at 40% probability. Selected bond lengths [Å]: Re–Br(3) 2.6690(3), Re–S(1) 2.5027(7), Re–S(2) 2.5234(8), Re–C(92) 1.890(3), Re–C(90) 1.922(3), Re–C(91) 1.919(3), C(1)–S(1) 1.703(3), C(3)–S(2) 1.709(3), O(1)–C(2) 1.210(4), O(2)–C(4) 1.211(3), C(1)–N(2) 1.324(4), C(3)–N(4) 1.320(4), C(3)–N(3) 1.382(4). Bond angles [°]: S(1)–Re–S(2) 85.63(3), Br(3)–Re–S(1) 92.99(2), Br(3)–Re–S(2) 93.91(2), Br(3)–Re–C(91) 90.00(9), S(1)–Re–C(90) 175.4(1), C(1)–S(1)–Re 115.22(8), N(1)–C(1)–N(2) 119.2(3).



**Fig. 3.** Molecular diagram and atom numbering scheme for [Re<sub>2</sub>(CO)<sub>6</sub>(L2)<sub>2</sub>] (**2**). Selected bond lengths [Å]: Re–S(1) 2.514(2), Re–S(1<sup>i</sup>) 2.530(2), Re–O(1) 2.154(2), Re–C(43) 1.901(4), C(1)–O(1) 1.251(4), S(1)–C(2) 1.782(4), N(1)–C(2) 1.308(4), N(1)–C(1) 1.333(4), C(2)–N(2) 1.354(5). Bond angles [°]: Re(1)–S(1)–Re(1<sup>i</sup>) 97.89(3), Re–S(1)–C(2) 98.8(1), S(1)–Re–O(1) 85.61(6), C(1)–N(1)–C(2) 127.5(3), O(1)–Re–C(42) 174.9(1), S(1)–Re–C(43) 175.1(1), S(1)–Re–C(41) 91.9(1).

[14,19]. The two Re-S bond lengths are similar [average of 2.5131(8) Å] and are typical for Re(I)-thiocarbonyl bonds [19,20]. The distortion from octahedral ideality is mainly the result of the *trans* angles S(1)-Re-C(90) = 175.4(1)°, S(2)-Re-C(91) = 176.09(9)° and Br(3)-Re-C(92) = 178.3(1)°.

In the neutral coordinated ligands HL1 the oxygen atoms O(1) and O(2) are not coordinated, and are doubly bonded to C(2) and C(4) respectively [O(1)-C(2)=1.210(4) Å, O(2)-C(4)=1.211(3) Å]. Enolisation of HL1 has not occurred. The C(1)–S(1) and C(3)–S(2) bonds are double [1.706(3) Å average], and all the C–N bonds are single. The coordinated bromide Br(3) is involved in intramolecular hydrogen bonds with N(1)H and N(3)H.

In a previous study the complex salt *fac*-[Re(CO)<sub>3</sub>(tu)<sub>3</sub>](NO<sub>3</sub>) was isolated from the reaction of *fac*-[Re(CO)<sub>3</sub>Br<sub>3</sub>]<sup>2-</sup> and thiourea (tu) [20]. The three tu ligands are coordinated monodentately via the neutral sulfur atoms, with an average Re-S bond length of 2.529(2) Å.

Structure of  $[\operatorname{Re}_2(\operatorname{CO})_6(\operatorname{L2})_2]$  (2)

Yellow crystals with the formulation **2** toluene were obtained by the slow evaporation of the preparative solution [21]. The dimer is produced by inversion, of which the centre is positioned in the centre of the nearly square  $\text{Re}_2\text{S}_2$  ring. Each rhenium(I) atom lies in a distorted octahedral environment, with an oxygen and two bridging thiolic sulfur atoms coordinated in a *facial* arrangement to the *fac*-[Re(CO)<sub>3</sub>]<sup>+</sup> moiety (Fig. 2). Both L2 ligands act as monoanionic tridentate ligands with coordination through a neutral carbonyl oxygen and an anionic bridging thiolate sulfur atom.

The dinuclear molecule is characterised by a rhombic  $(\mu$ -S)<sub>2</sub>Re<sub>2</sub> unit at the centre. Each sulfur-bridge is practically symmetrical, with very similar Re–S distances [Re(1)–S(1)=2.514(2) Å, Re(1)–S(1')=2.530(2) Å]

(Fig. 3). These distances fall in the range normally observed for thiolate sulfur atoms coordinated to a fac-[Re(CO)<sub>3</sub>]<sup>+</sup> core [22]. The Re–Re distance across the rhombus is 3.803(2) Å, implying no Re–Re bonding. The Re–C(carbonyl) distances [1.905(4) Å] fall in the observed range. The Re–O(1) distance [2.154(2) Å] is considerably longer than the observed distance of a Re–O(alcoholate) bond, which occurs around 2.00(2) Å [22], implying that O(1) is a neutral benzoyl oxygen atom.

The distortion from an ideal octahedral geometry around the rhenium is mainly the result of the constraints imposed by the coordination of the ligand L2, which forms a five-membered chelate ring with  $Re(1) [O(1)-Re(1)-S(1)=85.61(6)^{\circ}]$ .

The bonding parameters in the ligand L2 indicate that it is coordinated in the deprotonated enolate form. The C(1)–O(1) bond is double, the C(2)–S(1) bond is single and C(2)–N(1) is a methinyl double bond [C=N=1.308(4) Å], compared to the single C(2)–N(2) bond with a length of 1.354(5) Å.

In a previous study the rhenium(I) complex fac- $[Re(CO)_3Br_3]^{2-}$  has been reacted with thiourea (tu) to produce the complex salt fac- $[Re(CO)_3(tu)_3](NO_3)$ , in which each tu ligand is coordinated monodentately via the neutral sulfur atom, with a mean Re–S bond length of 2.529(2) Å [16]. With N,N-diethylbenzoylthiourea (Hbtu), the monomeric complex fac- $[Re(CO)_3(Hbtu)Br]$  was isolated, in which Hbtu acts as a neutral bidentate chelate with an oxygen and sulfur as donor atoms [16]. With the related ligand N,N-diethylthiocarbamoylbenzamidine (Htcb) the dimeric complex  $[Re_2(CO)_6(tcb)_2]$  was formed, with bridging through the neutral sulfur atom and coordination via the deprotonated aminate nitrogen atom [16]. The rhenium(V) compound *trans*- $[ReOCl_3(PPh_3)_2]$  reacts with Hbtu to form the complex  $[ReOCl_2(PPh_3)(btu)]$ , in which the benzoyl oxygen is coordinated *trans* to the oxo oxygen atom [6c].

The different coordination behaviour of the two ligands used in this study, HL1 and HL2, is peculiar. The only structural difference between the two chelates is the substituents on the terminal amino nitrogen. The greater spatial and steric requirements of the two phenyl substituents on N(2) would seemingly not permit the close approach of S(1) to the metal for monodentate coordination in a monomeric complex as observed in complex **1**.

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#### Appendix A. Supplementary material

Supplementary data for **1** (CCDC 879917) and **2** (CCDC 879918) are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam. ac.uk/data\_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.inoche.2012.08.008.

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