A novel trinuclear Re(I) complex containing 1,3,4-thiadiazole-2,5-dithiolate: structural and spectroscopic properties†

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In the title complex $[SSS(Re(CO)_5)_3](CF_3SO_3)$ (SSS = 1,3,4-thiadiazole-2,5-dithiolate), SSS adopts a two-S/one-N (κ_3) coordination form, representing an unprecedented coordination pattern for this ligand. In addition, its solid-state structure confirms that an interesting anion π-interaction (2.880 Å) between the *N*-heterocyclic ligand and the $CF_3SO_3^-$ anion is observed.

Supramolecular interactions are weak intermolecular forces that play a crucial role in both chemical and biological recognition.[1] To date, these interactions have been widely exemplified by hydrogen bonding, π···π interactions and other weak interactions, and their combination has been recognized as a very powerful and versatile strategy in material synthesis.[2] Among the various weak interactions, hydrogen bonding and cation π-interactions are of great importance for many biological systems and have been known for a long time.[3] However, in contrast, anion π-interactions are relatively unexplored.[4] This is most likely due to the electron-donating character of anions, which is expected to lead to repulsive interactions with aromatic π-electron clouds.[5] However, theoretical studies have demonstrated that there are potentially energetically favorable interactions between electron deficient π-systems (*i.e.*, hexafluorobenzene and benzene systems with strong electron-withdrawing groups, and 1,3,5-triazine- and pyrazine-based derivatives with *N*-heterocyclic systems) and anions (*i.e.*, halides, $N_3^-$and NO_3^-).[6] In 2004, Meyer *et al.* reported the first crystal structure, showing anion π-interactions between Cl^- and the 1,3,5-triazine ring in a carousel Cu(II)-triazine complex.[7] Recently, Reedijk and co-workers have designed a series of 1,3,5-triazine-based derivatives focusing on systematic anion π studies, and many crystal structures have since shown the existence of anion π-interactions.[8] In this context, the chemistry of anion π-interactions has become an area of growing interest as a branch of supramolecular chemistry. In the search for new crystallographic evidence for supramolecular non-covalent interactions, 1,3,4-thiadiazole-2,5-dithiolate (SSS) was chosen in this study for the design and synthesis of the target complex. We report herein the structural and spectroscopic properties of a novel trinuclear $[SSS(Re(CO)_5)_3](CF_3SO_3)$ complex, where an unprecedented tridentate (two-S/one-N) coordination form of the SSS ligand has been found. Notably, the title complex also shows an interesting anion π-interaction.

As a *N*-heterocyclic thiol, 1,3,4-thiadiazole-2,5-dithiol (H_2SSS) is particularly interesting, since the five donor sites in its deprotonated form enable coordination to two or more metal ions, leading to the anticipated formation of various structural motifs. Indeed, SSS has been shown to be a useful ligand in the construction of multifunctional metal complexes in several reports regarding Au(I),[9a] Pt(II),[9b] Sn(II)[9c,e,f] and Ru(II)[9d] complexes, and it can act as a mono-, bi- or tetradentate ligand with coordination to one or two metal ions. Surprisingly, there is no tridentate form reported so far, and this is most likely due to steric hindrance and unpredictability for this unsymmetrical bridging form.

Upon reacting Na_2SSS with three equivalents of $Re(CO)_5(CF_3SO_3)$, $\mathbf{1}\cdot CF_3SO_3$ can be isolated as a pale yellow and air stable solid in *ca.* 50% yield (Scheme 1).‡ $\mathbf{1}\cdot CF_3SO_3$ crystallized in the space group $P2_1/n$, involving nearly octahedral geometries for the three Re(I) environments. As shown in Fig. 1(a), the SSS ligand coordinates to three $Re(CO)_5^+$ through a novel two-S/one-N (κ_3) coordination form that is different from the previously reported one-S(κ_1),[9b] two-S(κ_2),[9a,b,d] two-N (κ_2)[9c] and two-S/two-N (κ_4)[9c,e,f] coordination forms. To the best of our knowledge, this (κ_3) coordination form for SSS is unprecedented. Additionally, the two S–$Re(CO)_5^+$ groups are in an *anti* conformation, and only one of the two nitrogen atoms in the thiadiazole ring coordinates to a $Re(CO)_5^+$, both of which are expected to be a consequence of steric interactions between the $Re(CO)_5^+$ groups. In fact, cation **1** is analogous to the SSS ligand protonated on two thiolates and one imine by three H^+ or the $SSSH_2$ ligand protonated on one imine by one H^+, where the $Re(CO)_5^+$ group is considered an isolobal analogue to H^+.[10] Another important feature of the solid-state structure is the fairly short anion···π distance (2.880 Å, the sum of van der Waal's radii is 3.220 Å) between the oxygen atom of the $CF_3SO_3^-$ and the midpoint of C(17)═N(1) bond in cation **1**. The packing diagram of the unit cell is shown in Fig. 1(b). The anion···π distance in cation **1** is well below the sum of van der Waal's radii, and is suggestive of the possible presence of an anion π-interaction. Moreover, it is truly remarkable that the C(17)═N(1) bond (1.317(8) Å) is significantly longer than the C(16)═N(2) bond (1.278(8) Å) by *ca.* 0.04 Å in the same thiadiazole ring. Thus, the anion π-interaction as well as coordination of N(1) to $Re(CO)_5^+$, resulting in a decrease in the π electron density of the C(17)═N(1) bond, may be

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† The HTML version of this article has been enhanced with colour images.

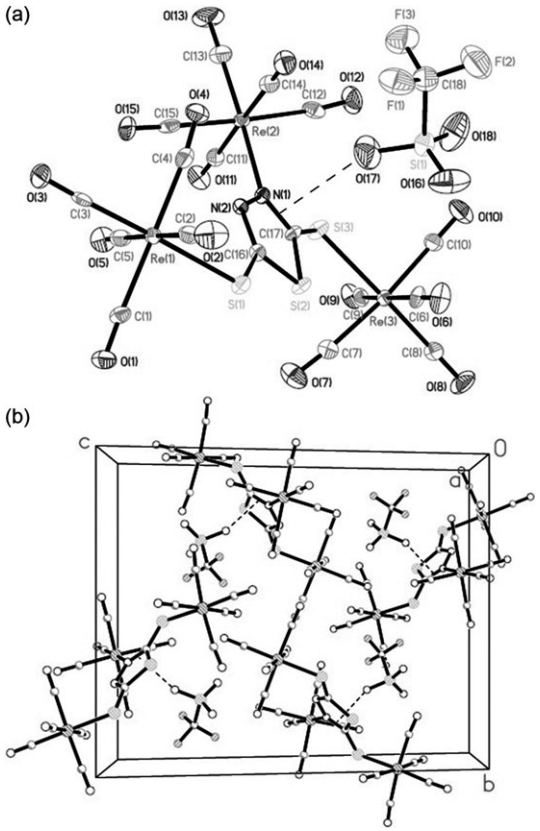
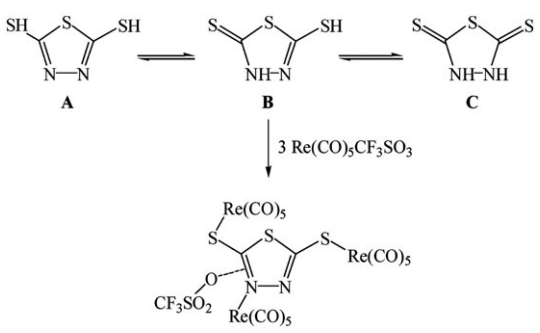


Fig. 1 (a) A perspective view of cation **1**. Selected bond lengths (Å) and angles (°): Re(1)–S(1) 2.5083(18), Re(3)–S(3) 2.5022(18), Re(2)–N(1) 2.162(6), N(1)–C(17) 1.317(8), N(1)–N(2) 1.400(7), N(2)–C(16) 1.278(8); C(4)–Re(1)–C(1) 179.4(3), C(3)–Re(1)–C(5) 89.9(3), C(3)–Re(1)–S(1) 177.8(2), C(2)–Re(1)–S(1) 87.0(2), C(13)–Re(2)–N(1) 177.5(3), C(15)–Re(2)–N(1) 88.3(2), C(17)–S(2)–C(16) 88.4(3). The ORTEP diagram shows 50% probability ellipsoids. (b) The packing diagram of the unit cell showing anion π-interactions.

anticipated as responsible for this significant π bond lengthening. With reference to the literature, the average C═N distance for Au(I)-,[9a] Pt(II)-[9b] and Ru(II)-SSS[9d] complexes (SSS as a κ_2 (two-S) form) is 1.292 Å, which is only slightly shorter than that of 1.305 Å for Sn(II)-SSS complexes[9c,e,f] (SSS as a κ_4 (two-S/two-N) form). In this context, coordination of N to metal ions typically causes an increase in the C═N distance of *ca.* 0.01 Å, and hence an increase of *ca.* 0.04 Å from C(16)═N(2) to C(17)═N(1) is unlikely to be a simple consequence of the coordination effect. We reasoned that this lengthening of the C(17)═N(1) distance could be strong evidence of the presence of anion π-interactions and a consequence of the combination of coordination and anion···π effects, instead of simply being due to coordination and/or crystal packing.



Scheme 1

The distance between the oxygen atom of the $CF_3SO_3^-$ and the centroid of the thiadiazole ring has been calculated as 3.126 Å in $\mathbf{1}\cdot CF_3SO_3$. Though most observed anion π-interactions exist in aromatic systems, they have also been seen in olefinic systems.[5g] Although the H_2SSS ligand has three forms (A, B and C forms in Scheme 1), SSS is known to prefer a thiolate form rather than a thione form.[9b] As a matter of fact, the distances of 1.717(7) and 1.736(7) Å for the C(17)–S(3) and C(16)–S(1) bonds, respectively, coincide with the thiolate form.

As shown in Fig. 2, the absorption spectrum of $\mathbf{1}\cdot CF_3SO_3$, measured in CH_3CN, shows absorption bands at *ca.* 333 and 380 nm. Since the absorption spectrum of H_2SSS also shows an absorption band at *ca.* 340 nm, the *ca.* 333 nm absorption in $\mathbf{1}\cdot CF_3SO_3$ is tentatively assigned to an intraligand transition. The *ca.* 380 nm absorption is red-shifted towards that of H_2SSS by *ca.* 40 nm, and thus it could quite impossibly be ascribed to an intraligand transition. Due to the strong σ-donating strength of thiolates, a ligand-to-metal charge-transfer (LMCT) transition may be anticipated based on previous studies of metal thiolates.[11]

In this study, a Re(I) complex showing interesting anion π-interactions (2.880 Å) has been serendipitously isolated and characterized by X-ray diffraction, suggesting that such interactions are energetically favorable between electron deficient π-systems and anions. Although the SSS ligand has been shown to act as a mono-, bi- or tetradentate ligand in the literature, the SSS ligand in cation **1** coordinates to three $Re(CO)_5^+$ groups in a novel unprecedented two-S/one-N (κ_3) coordination form. We anticipate that this Re(I) complex containing the electron-deficient SSS ligand may find useful applications in anion recognition studies through diagnostic anion π-interactions.

Acknowledgements

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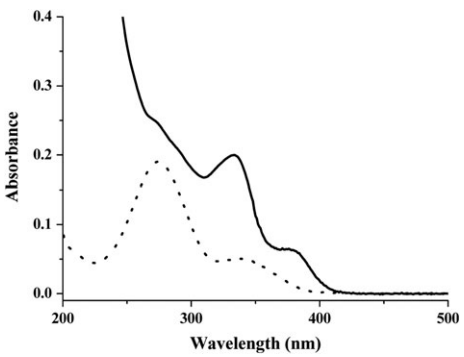

Fig. 2 Absorption spectra of $\mathbf{1}\cdot CF_3SO_3$ (solid line) and H_2SSS (dotted line) measured in CH_3CN at a concentration of 10^{-5} M.

References

‡ $[SSS(Re(CO)_5)_3]\cdot CF_3SO_3$ ($\mathbf{1}\cdot CF_3SO_3$): The reaction of Na_2SSS (15 mg, 0.1 mmol) with $Re(CO)_5CF_3SO_3$ (144 mg, 0.3 mmol) in CH_2Cl_2 (20 ml) at room temperature for 48 h gave a pale yellow solution. The solution was filtered off and the filtrate concentrated to *ca.* 5 mL. Addition of diethyl ether yielded a pale yellow precipitate. Single crystals of **1** were grown from acetone/hexane with a 50% yield. FT-IR: $\nu_{C\equiv O}$ = 2155, 2097 and 2029 cm^{-1}, $\nu_{C\equiv N}$ = 1635 cm^{-1}. ESI-MS: m/z = 1126.81, 100% $[M - CF_3SO_3]^+$. Anal. calc. (%) for $C_{18}F_3N_2O_{18}Re_3S_4$: C, 16.94; N, 2.20. Found (%): C, 16.87; N, 1.87. Crystal data for $\mathbf{1}\cdot CF_3SO_3$: $C_{18}F_3N_2O_{18}Re_3S_4$, M = 1276.04, monoclinic, space group $P2_1/n$, T = 150(1) K, a = 9.2003(4), b = 16.5780(8), c = 20.4180(10) Å, β = 101.307(1)°, V = 3053.8(2) $Å^3$, Z = 4, μ = 12.236 mm^{-1}, $F(000)$ = 2328, 23266 reflections collected, 7002 independent, R_{int} = 0.0653, final residuals $R1$ = 0.0383, w$R2$ = 0.0692 [$I > 2\sigma(I)$]; $R1$ = 0.0509, w$R2$ = 0.0728 (all data). CCDC 622767. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b616122g

1 E. A. Meyer, R. K. Castellano and F. Diederich, *Angew. Chem., Int. Ed.*, 2003, **42**, 1210.

2 (*a*) D. Braga, F. Grepioni and G. R. Desiraju, *Chem. Rev.*, 1998, **98**, 1375; (*b*) A. D. Burrows, C.-W. Chan, M. W. Chowdhry, J. E. McGrady and D. M. P. Mingos, *Chem. Soc. Rev.*, 1995, **24**, 329; (*c*) C. Janiak, *Dalton Trans.*, 2003, 2781.

3 J. C. Ma and D. A. Dougherty, *Chem. Rev.*, 1997, **97**, 1303.

4 (*a*) P. D. Beer and P. A. Gale, *Angew. Chem., Int. Ed.*, 2001, **40**, 487; (*b*) R. Vilar, *Angew. Chem., Int. Ed.*, 2003, **42**, 1460; (*c*) B. L. Schottel, H. T. Chifotides, M. Shatruk, A. Chouai, L. M. Pérez, J. Bacsa and K. R. Dunbar, *J. Am. Chem. Soc.*, 2006, **128**, 5895; (*d*) R. M. Fairchild and K. T. Holman, *J. Am. Chem. Soc.*, 2005, **127**, 16364; (*e*) K. T. Holman, M. M. Halihan, J. W. Steed, S. S. Jurisson and J. L. Atwood, *J. Am. Chem. Soc.*, 1995, **117**, 7848.

5 (*a*) C. Garau, A. Frontera, D. Quinonero, P. Ballester, A. Costa and P. M. Deya, *ChemPhysChem*, 2003, **4**, 1344; (*b*) D. Quinonero, C. Garau, C. Rotger, A. Frontera, P. Ballester, A. Costa and P. M. Deya, *Angew. Chem., Int. Ed.*, 2002, **41**, 3389; (*c*) D. Quinonero, C. Garau, A. Frontera, P. Ballester, A. Costa and P. M. Deya, *Chem. Phys. Lett.*, 2002, **359**, 486; (*d*) M. Mascal, A. Armstrong and M. D. Bartberger, *J. Am. Chem. Soc.*, 2002, **124**, 6274; (*e*) C. Garau, D. Quinonero, A. Frontera, A. Costa, P. Ballester and P. M. Deya, *Chem. Phys. Lett.*, 2003, **370**, 7; (*f*) C. Garau, A. Frontera, D. Quinonero, P. Ballester, A. Costa and P. M. Deya, *Chem. Phys. Lett.*, 2003, **382**, 534; (*g*) Y. S. Rosokha, S. V. Lindeman and J. K. Kochi, *Angew. Chem., Int. Ed.*, 2004, **43**, 4650.

6 I. Alkorta, I. Rozas and J. Elguero, *J. Org. Chem.*, 1997, **62**, 4687.

7 S. Demeshko, S. Dechert and F. Meyer, *J. Am. Chem. Soc.*, 2004, **126**, 4508.

8 (*a*) P. de Hoog, P. Gamez, I. Mutikainen, U. Turpeinen and J. Reedijk, *Angew. Chem., Int. Ed.*, 2004, **43**, 5815; (*b*) T. J. Mooibroek, S. J. Teat, C. Massera, P. Gamez and J. Reedijk, *Cryst. Growth Des.*, 2006, **6**, 1569; (*c*) H. Casellas, C. Massera, P. Gamez, A. M. M. Lanfredi and J. Reedijk, *Eur. J. Inorg. Chem.*, 2005, 2902; (*d*) P. U. Maheswari, B. Modec, A. Pevec, B. Kozlevčar, C. Massera, P. Gamez and J. Reedijk, *Inorg. Chem.*, 2006, **45**, 6637; (*e*) H. Casellas, C. Massera, F. Buda, P. Gamez and J. Reedijk, *New J. Chem.*, 2006, **30**, 1561.

9 (*a*) J. D. Wilton-Ely, A. Schier and H. Schmidbaur, *Organometallics*, 2001, **20**, 1895; (*b*) H. Tannai, K. Tsuge, Y. Sasaki, O. Hatozaki and N. Oyama, *Dalton Trans.*, 2003, 2353; (*c*) C. Ma, J. Zhang, F. Li and R. Zhang, *Eur. J. Inorg. Chem.*, 2004, **12**, 2775; (*d*) H. Tannai, K. Tsuge and Y. Sasaki, *Inorg. Chem.*, 2005, **45**, 6637; (*e*) C. Ma, F. Li, Q. Jiang and R. Zhang, *J. Organomet. Chem.*, 2004, **689**, 96; (*f*) C. Ma, F. Li, D. Wang and H. Ying, *J. Organomet. Chem.*, 2003, **667**, 5.

10 R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 711.

11 P. Pyykkö, J. Li and N. Runberg, *Chem. Phys. Lett.*, 1994, **218**, 133.