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Synthesis and Structural Characterization of a Triply-bridged Binuclear Diazenido-complex of Rhenium, $(HNEt_3)[Re_2(NNC_6H_5)_2(SC_6H_5)_7]$

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Although there have been extensive studies of mononuclear diazenido complexes [1], there has been a single report of a binuclear metal–diazenido-species [2]. Furthermore, diazenido-complexes with thiolate donors as coligands are relatively rare as are coordination compounds of rhenium with thiolate ligands in general. As part of a systematic study of this chemistry [3], we have synthesized and structurally characterized a binuclear rhenium thiolato–diazenido-complex exhibiting a triple thiolato-bridge.

The complex $[ReCl(N_2C_6H_5)_2(PPh_3)_2]$, **I**, was prepared by reacting $[ReOCl_3(PPh_3)_2]$ with excess phenylhydrazine in methanol. Reaction of **I** with thiophenol and Et_3N in benzene yields bright red crystals of $(HNEt_3)[Re_2(NNC_6H_5)_2(SPh)_7]$, **II**, in quantitative yield. Complex **II** shows a strong infrared band at 1577 cm^{-1} characteristic of ν(N–N).

Crystals of **II** suitable for X-ray diffraction were grown from dichloromethane–diethylether. Crystal data: space group $P2_1/n$, a = 10.951(2) Å, b = 25.198(4) Å, c = 24.112(4) Å, β = 100.32(1)°, V = 6545.9(2) Å^3, Z = 4. Structure solution and refinement were based on 2984 reflections to give a final discrepancy factor of 0.056.

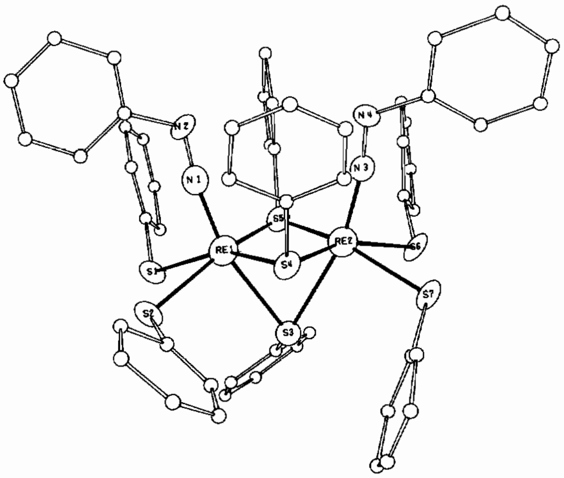

Fig. 1. ORTEP representation of the binuclear anion $[Re_2(NNC_6H_5)_2(SC_6H_5)_7]^-$ showing the atom labelling scheme. Selected bond lengths and angles: Re1–Re2, 2.747(2); Re1–S1, 2.451(9); Re1–S2, 2.438(8); Re1–S3, 2.539(7); Re1–S4, 2.374(7); Re1–S5, 2.404(7); Re2–S6, 2.459(8); Re–S7, 2.457(9); Re2–S3, 2.553(7); Re2–S4, 2.390(7); Re2–S5, 2.398(7), Re1–N1, 1.81(2); Re2–N3, 1.81(2); N1–N2, 1.23(3); N3–N4, 1.24(3); Re1–N1–N2, 170.0(18); Re2–N3–N4, 171.4(19); Re1–S3–Re2, 65.6(2); Re1–S4–Re2, 70.4(2); Re1–S5–Re2, 69.8(2); S3–Re1–N1, 164.0(7); S3–Re2–N3, 163.3(6).

The structure of **II** is shown in Fig. 1 with selected bond lengths and angles presented in the caption. The binuclear anion consists of two distorted octahedra sharing a face defined by the sulfur-donors of the bridging thiolate groups. Although many triply-bridged thiolates of molybdenum are known, examples in rhenium chemistry are comparatively rare, the only other example being $[Re_2(NO)_2(SC_6H_4Me)_7]^-$ [4]. In **II** the bridging thiolates are structurally non-equivalent with S4 and S5 coplanar with Re1 and Re2 and occupying positions *pseudo-trans* to the terminal thiolate donors, while S3 is

TABLE I. Comparison of Structural Parameters for Triply-bridged Thiolato-complexes with the $[(SR)_2ML(\mu\text{-}SR)_3ML(SR)_2]$ Core.^{b}

Complex	M–M	M–S_b	M–$S_b{}^a$	M–N	N–A(A)	M–S–M
$[Mo_2(NNPh)(NNHPh)(SCH_2CH_2S)_3(SCH_2CH_2SH)]^{2-}$	2.837(2)	2.433(7)	2.577(6)	1.767(8)	1.33(2)(N)	71.4(S_b) 66.9($S_b{}^a$)
$[Re_2(NO)_2(SC_6H_4Me)_7]^-$	2.783(1)	2.400(7)	2.564(7)	1.68(2)	1.25(3)(O)	70.9(2)(S_b) 65.7(2)($S_b{}^a$)
$[Re(NNC_6H_5)_2(SC_6H_5)_7]^-$	2.747(2)	2.392(9)	2.536(7)	1.81(1)	1.24(2)(N)	70.1(2)(S_b) 65.6(2)($S_b{}^a$)

^{b}Distances in Å, angles in degrees; standard deviations in the last quoted figure in parentheses. Abbreviations X_b, bridging thiolate sulfur in the M–S–S–M rhombus; $S_b{}^a$, bridging thiolate *trans* to the multiply-bonding terminal ligand L; A, group bonded to the metal-bound nitrogen.

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axially disposed to the Re_2S_6 unit and *trans* to the diazenido-group.

There is considerable multiple bond character in the rhenium–diazenido grouping as suggested by the short Re–N bonds, 1.81(2) Å, and the linear Re–N–N unit. A consequence of this strong interaction is a significant *trans* influence, lengthening the Re–S3 distances to 2.536(7) Å compared to an average of 2.392(9) Å for Re–S distances in the Re1–S4–S5–Re2 rhombus. The structural parameters observed for **II** exhibit pronounced similarities to those previously reported for $[Re_2(NO)_2(SC_6H_4Me)_7]^-$ and $[Mo_2(NNC_6H_5)(NNHC_6H_5)(SCH_2CH_2SH)(SCH_2CH_2S)_3]^{2-}$, as shown in Table I.

The structure of **II** provides further evidence for the versatility of the triply-bridged coordination mode. The 'diagonal relationship' between molybdenum and rhenium suggests that numerous examples of triply-bridged binuclear rhenium complexes may be accessible, with structural parallels to analogous molybdenum species. Finally, the structural similarity of **II** to the nitrosyl derivative $[Re_2(NO)_2(SC_6H_4Me)_7]^-$ reinforces the chemical relationship of the diazenido-grouping and the isoelectronic nitrosyl group as three-electron donor ligands with strong preference for linear geometries exhibiting extensive multiple bonding.

The synthetic precursor $[ReCl(N_2C_6H_5)_2(PPh_3)_2]$ reacts with a variety of thiolates to give products whose structures depend on the nature of the thiolate. While reaction with ethanedithiol yields mixtures of monomeric thiolates and $[ReCl_2(NNPh)(NNHPh)(PPh_3)_2]$, sterically-hindered thiols such as 2,4-diisopropylthiophenol react to give $[Re(NNC_6H_5)(TIPT)_4]$ in good yield. The contrasting characteristics of chelating, sterically-hindered, and sterically-innocent thiolates with rhenium–diazenido-precursors will be discussed in subsequent reports.

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