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Preparation and characterization of dirhenium complex anions of the type $[Re_2Cl_7(dithioether)]^-$ with Re–Re quadruple bonds ☆

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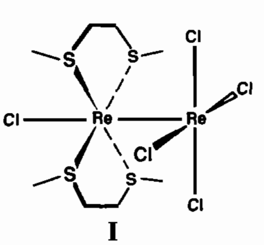
Abstract

Two dirhenate(III) anions containing dithioether ligands and Re–Re quadruple bonds have been synthesized and characterized by X-ray crystallography. Under mild reaction conditions, both 3,6-dithiaoctane ($CH_3CH_2SCH_2CH_2SCH_2CH_3$ or dto) and 2,5-dithiahexane ($CH_3SCH_2CH_2SCH_3$ or dth) displace a single chloride ligand from $[Re_2Cl_8]^{2-}$ to yield $[Re_2Cl_7(dto)]^-$ and $[Re_2Cl_7(dth)]^-$, respectively. The tetra-n-butylammonium (Bu_4N) salts of these complex ions have been isolated and found to react with additional dithioether to produce the unsymmetrical compounds $Re_2Cl_5(dto)_2$ and $Re_2Cl_5(dth)_2$ with Re–Re triple bonds. The complex $(Bu_4N)[Re_2Cl_7(dto)]$ crystallizes in the triclinic space group $P\bar{1}$ with $a=11.299(3)$, $b=11.552(4)$, $c=14.654(4)$ Å, $\alpha=108.19(2)$, $\beta=104.07(2)$, $\gamma=88.65(3)°$ and $Z=2$, while $(Bu_4N)[Re_2Cl_7(dth)]$ crystallizes in the monoclinic space group $P2_1$ with $a=10.361(2)$, $b=15.567(4)$, $c=11.663(3)$ Å, $\beta=117.01(2)°$ and $Z=2$. The Re–Re bond distances are 2.248(1) and 2.257(1) Å for the dto and dth complexes, respectively.

Keywords: Crystal structures; Rhenium complexes; Quadruple bond complexes; Dithioether ligand complexes; Dinuclear complexes

1. Introduction

The first example of a compound containing a metal–metal triple bond was synthesized many years ago by the prolonged heating of a mixture of the $[Re_2Cl_8]^{2-}$ anion with an excess of 2,5-dithiahexane ($CH_3SCH_2CH_2SCH_3$ or dth) [1,2]. This compound, $Re_2Cl_5(dth)_2$, possesses an unusual structure (represented by I) that consists of four chloride ligands coordinated to one Re atom, a single axial chloride ligand and two dth ligands coordinated to the other Re atom, and a staggered rotational conformation about the central Re_2 unit [3]. Only recently, as a result of our investigations into the reactivity of $[Re_2X_8]^{2-}$ (X = Cl or Br) with 3,6-dithiaoctane ($CH_3CH_2SCH_2CH_2SCH_2CH_3$ or dto), have additional examples of this type of molecule been isolated, namely $Re_2Cl_5(dto)_2$ and $Re_2Br_5(dto)_2$ [4].



I

At the same time that $Re_2Cl_5(dth)_2$ was first prepared, several other dirhenium complexes containing dth were synthesized but not structurally characterized [2]. Their proposed molecular formulas are $Re_2Cl_6(dth)_2$, $Re_2Br_6(dth)_2$ and $Re_2Br_4(dth)_2$. In our efforts to prepare the dto analogs of these compounds, we have instead isolated the dirhenium monoanion $[Re_2Cl_7(dto)]^-$ with only one chelating dithioether ligand. Under similar conditions, we were also able to prepare $[Re_2Cl_7(dth)]^-$. These anions react with additional dithioether (SS) to yield the neutral compounds $Re_2Cl_5(SS)_2$ with structures as noted above, and are therefore proposed to be intermediates in the formation of triply bonded compounds from quadruply bonded starting materials.

Recently, several monoanionic complexes of the type $[Re_2Cl_7L]^-$, where L is a large monodentate tertiary phosphine ligand, have been prepared and structurally characterized [5–7]. These react with additional phosphine to give the neutral compounds $Re_2Cl_6L_2$ with eclipsed conformations, quadruple Re–Re bonds, and *trans* phosphine ligands coordinated to different Re atoms [5,8]. The structures of the $[Re_2Cl_7(SS)]^-$ com-

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☆ This paper is dedicated to Professor F.A. Cotton on the occasion of his 65th birthday.

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plexes presented herein are compared with the structures of the $[Re_2Cl_7L]^-$ complexes in an effort to explain the difference in their reactivity. A portion of this work has been previously published in a preliminary communication [9].

2. Experimental

All reactions were carried out in a nitrogen atmosphere with air-free techniques employed prior to isolation of final products. Anhydrous HPLC-grade solvents were used as obtained from Aldrich Chemical Co. The reagent 3,6-dithiaoctane (dto) was purchased from Pfaltz and Bauer, while 2,5-dithiahexane (dth) was purchased from Columbia Organic Chemical Co. These dithioethers were also used as received. The compound $(Bu_4N)_2Re_2Cl_8$, in which Bu_4N = tetra-n-butylammonium, was prepared using a published procedure [10].

2.1. Preparation of $(Bu_4N)[Re_2Cl_7(dto)]$ (1)

Ethanol (25 ml) was added to a flask containing 0.50 g (0.44 mmol) $(Bu_4N)_2Re_2Cl_8$. Next, 0.15 ml (0.98 mmol) 3,6-dithiaoctane (dto) was added. The resulting mixture was stirred and heated at 55 °C for 6 h. A green precipitate was then collected, washed with ethanol and diethyl ether, and dried under vacuum; yield 0.36 g (82%). *Anal.* Found: C, 26.3; H, 5.2; N, 1.2. Calc. for $C_{22}H_{50}NS_2Cl_7Re_2$: C, 26.1; H, 5.0; N, 1.4%. δ–δ^* CH_2Cl_2 solution: 732 nm ($\epsilon = 1350$).

Single crystals of $(Bu_4N)[Re_2Cl_7(dto)]$ suitable for analysis by X-ray diffraction were obtained by dissolving the compound in dichloromethane, then carefully layering this solution with hexane. Slow diffusion produced many well-shaped dark green crystals.

2.2. Preparation of $(Bu_4N)[Re_2Cl_7(dth)]$ (2)

Methanol (10 ml) was added to 0.10 g (0.088 mmol) $(Bu_4N)_2Re_2Cl_8$ in a round-bottom flask equipped with a stir bar. Next, 0.5 ml conc. HCl and 0.25 ml (1.8 mmol) 2,5-dithiahexane (dth) were added. The mixture was stirred and heated at 60 °C for 0.5 h. The resulting green solid was filtered off and washed with methanol and diethyl ether, and dried under vacuum. Yield 0.080 g (92%). *Anal.* Found: C, 24.6; H, 4.6; N, 1.3. Calc. for $C_{20}H_{46}NS_2Cl_7Re_2$: C, 24.4; H, 4.8; N, 1.1%. δ–δ^* CH_2Cl_2 solution: 734 nm ($\epsilon = 1510$).

Large, green–brown crystals of $(Bu_4N)[Re_2Cl_7(dth)]$ suitable for X-ray diffractometry were grown by slow diffusion of hexane into a CH_2Cl_2 solution of the complex.

2.3. Conversion of $[Re_2Cl_7(dto)]^-$ to $Re_2Cl_5(dto)_2$

Ethanol (25 ml) was added to a flask containing 0.10 g (0.099 mmol) $(Bu_4N)[Re_2Cl_7(dto)]$. A portion of dto (0.40 ml, 2.6 mmol) was then added and the mixture was refluxed for 72 h. $Re_2Cl_5(dto)_2$ was filtered off and washed with methanol and diethyl ether. Yield 0.076 g (90%).

2.4. Conversion of $[Re_2Cl_7(dth)]^-$ to $Re_2Cl_5(dth)_2$

Methanol (20 ml) was added to a flask containing 0.031 g (0.031 mmol) $(Bu_4N)[Re_2Cl_7(dth)]$. A portion of dth (0.18 ml, 1.3 mmol) was then added and the mixture was refluxed for 56 h. The resulting insoluble solid was filtered off and washed with methanol and diethyl ether. Yield 0.018 g (73%).

2.5. Reaction of $[Re_2Cl_7(dithioether)]^-$ with $PMePh_2$

Both $(Bu_4N)[Re_2Cl_7(dto)]$ and $(Bu_4N)[Re_2Cl_7(dth)]$ react with methyldiphenylphosphine ($PMePh_2$) to produce $Re_2Cl_6(PMePh_2)_2$. In a typical reaction, 10 ml CH_2Cl_2 were added to 0.10 g (0.099 mmol) $(Bu_4N)[Re_2Cl_7(dto)]$, followed by 0.039 g (0.20 mmol) $PMePh_2$. The mixture was then stirred at 25 °C for 3 h. The solvent was removed by vacuum distillation and the residue was washed with ethanol, leaving green $Re_2Cl_6(PMePh_2)_2$. Yield 0.051 g (64%). δ–δ^* CH_2Cl_2 solution: 722 nm ($\epsilon = 3600$). At the time that this reaction was carried out, the crystal structure of the product had not been published, so we grew single crystals of this compound by slow diffusion of hexane into a dichloromethane solution. While we were collecting X-ray data on a single crystal, we were made aware of a new publication describing the crystal structure of $Re_2Cl_6(PMePh_2)_2$ [8]. The unit cell parameters of our crystal ($a = 10.247$, $b = 11.753$, $c = 15.258$ Å, $\alpha = 90$, $\beta = 100.16$, $\chi = 90°$) matched those of the sample in the published report.

2.6. X-ray crystallography

2.6.1. Data collection

All X-ray crystallographic data were obtained by Crystalytics Co. on a Syntex automated four-circle diffractometer. For each data set, six check reflections monitored throughout data collection showed no significant loss or gain in intensity. Empirical absorption corrections using psi scans for four or five reflections were also applied to each data set, followed by standard Lorentz and polarization corrections. Pertinent crystallographic parameters for the structures are given in Table 1.

Table 1
Crystallographic data for $(Bu_4N)[Re_2Cl_7(dto)]$ (**1**) and $(Bu_4N)[Re_2Cl_7(dth)]$ (**2**)

	Compound 1	Compound 2
Formula	$Re_2Cl_7S_2NC_{22}H_{50}$	$Re_2Cl_7S_2NC_{20}H_{46}$
Formula weight	1013.4	985.3
Space group	$P\bar{1}$	$P2_1$
Systematic absences	none	$0k0$, $k=2n+1$
a (Å)	11.299(3)	10.361(2)
b (Å)	11.552(4)	15.567(4)
c (Å)	14.645(4)	11.663(3)
α (°)	108.19(2)	90.00
β (°)	104.07(2)	117.01(2)
γ (°)	88.65(3)	90.00
V (Å^3)	1759	1676
Z	2	2
D_{calc} (g cm^{-3})	1.913	1.952
μ (cm^{-1})	190.08	80.12
Radiation, λ (Å)	Cu Kα, 1.54184	Mo Kα, 0.71073
Temperature (°C)	20 ± 1	20 ± 1
Scan method	θ–2θ	ω
No. unique data with $F_o^2 > 3\sigma(F_o^2)$	3324	2697
No. parameters refined	307	289
Transmission factors: max., min.	0.292, 1.00	0.445, 1.00
R [a]	0.04771	0.03611
R_w [b]	0.05829	0.03869
Quality-of-fit indicator [c]	1.157	1.237
Largest shift/e.s.d, final cycle	0.02	0.21
Largest peak, e Å^{-3}	1.02	0.726

[a] $R=\Sigma||F_o|-|F_c||/\Sigma|F_o|$.
[b] $R_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w=1/\sigma^2(|F_o|)$.
[c] Quality-of-fit $=[\Sigma w(|F_o|-|F_c|)^2/(N_{obs}-N_{para})]^{1/2}$.

Table 2
Positional and isotropic equivalent thermal parameters for $(Bu_4N)[Re_2Cl_7(dto)]$ (**1**) [a]

Atom	x	y	z	B (Å^2)
Re(1)	0.68219(7)	0.95761(5)	0.87215(6)	2.91(1)
Re(2)	0.89065(7)	1.000	0.87250(6)	2.84(1)
Cl(1)	0.5084(5)	0.9976(4)	0.6692(4)	5.0(1)
Cl(2)	0.6504(5)	0.8196(3)	0.7930(4)	4.1(1)
Cl(3)	0.7590(5)	0.8989(4)	1.0756(4)	4.5(1)
Cl(4)	0.5994(6)	1.0730(3)	0.9460(5)	5.5(1)
Cl(5)	1.0552(5)	0.9572(4)	1.0797(4)	4.7(1)
Cl(6)	0.9452(6)	0.8802(3)	0.7821(5)	5.6(1)
Cl(7)	0.8055(6)	1.0724(3)	0.6761(4)	5.0(1)
S(1)	0.8877(5)	1.1471(3)	0.9504(4)	3.5(1)
S(2)	1.1695(6)	1.0555(3)	0.9087(5)	4.6(1)
C(1)	1.039(2)	1.203(1)	0.941(2)	4.8(6)
C(2)	1.187(2)	1.154(1)	0.997(2)	4.9(5)
C(3)	0.946(2)	1.146(1)	1.122(2)	4.6(5)
C(4)	1.170(2)	1.094(2)	0.764(2)	7.8(7)
N	0.472(1)	0.8407(8)	0.324(1)	3.2(3)
C(11)	0.482(2)	0.803(1)	0.207(2)	4.2(5)
C(12)	0.391(2)	0.849(1)	0.081(1)	3.5(4)
C(13)	0.406(2)	0.800(1)	−0.023(2)	4.6(5)
C(14)	0.327(2)	0.846(1)	−0.157(2)	4.9(5)
C(21)	0.477(2)	0.941(1)	0.325(1)	4.3(5)
C(22)	0.623(2)	0.973(1)	0.333(2)	5.4(5)
C(23)	0.612(2)	1.075(1)	0.317(2)	6.2(6)
C(24)	0.746(3)	1.112(2)	0.333(2)	9.3(9)
C(31)	0.593(2)	0.806(1)	0.454(2)	4.7(5)
C(32)	0.575(3)	0.711(1)	0.469(2)	7.9(8)
C(33)	0.717(3)	0.675(1)	0.574(2)	6.4(6)
C(34)	0.822(3)	0.659(2)	0.533(2)	10.0(1)
C(41)	0.319(2)	0.816(1)	0.312(2)	3.9(4)
C(42)	0.280(2)	0.857(1)	0.415(2)	5.0(5)
C(43)	0.132(2)	0.825(1)	0.394(2)	5.4(6)
C(44)	0.074(3)	0.873(2)	0.475(2)	8.1(8)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $4/3[a^2\beta_{11}+b^2\beta_{22}+ab(\cos\gamma)\beta_{12}+ac(\cos\beta)\beta_{13}+bc(\cos\alpha)\beta_{23}]$.

2.6.2. Structure solution and refinement

Solution and refinement of both structures were carried out using SDP-VAX software (from Enraf-Nonius) running on a VAX 11/785 computer at Abilene Christian University.

2.6.3. $(Bu_4N)[Re_2Cl_7(dto)]$ (1)

A Patterson map was used to find the positions of the two Re atoms. Successful location and anisotropic refinement of all non-hydrogen atoms proceeded smoothly in space group $P\bar{1}$. Full-matrix least-squares refinement of 307 parameters using 3324 reflections gave residuals of $R=0.048$ and $R_w=0.058$. Fractional atomic coordinates and isotropic equivalent thermal parameters are given in Table 2. Selected bond distances and angles are listed in Table 3.

2.6.4. $(Bu_4N)[Re_2Cl_7(dth)]$ (2)

From systematic absences, the space group was determined to be either $P2_1$ or $P2_1/m$. $P2_1$ was verified as the correct choice through successful refinement of the structure. The positions of the two rhenium atoms were determined from a Patterson map. All remaining non-hydrogen atoms were located by a sequence of alternating least-squares refinements and difference Fourier maps. Upon convergence of the R factors using isotropic thermal parameters, the coordinates of all atoms were changed to correspond to the other enantiomorph and this resulted in lower values for R and R_w. Consequently, the second enantiomorph was chosen and refined anisotropically, resulting in residuals of $R=0.0361$ and $R_w=0.0387$. Fractional atomic coordinates and isotropic equivalent thermal parameters are listed in Table 4, while selected bond distances and angles are given in Table 5.

3. Results and discussion

The reactions of the quadruply bonded dirhenate(III) ion $[Re_2Cl_8]^{2-}$ with the dithioethers $EtSCH_2CH_2SEt$ (dto) and $MeSCH_2CH_2SMe$ (dth) in alcohol yield very different products depending upon the reaction conditions. With gentle heating for a short period of time,

Table 3
Selected bond distances (Å) and angles (°) for $(Bu_4N)[Re_2Cl_7(dto)]$ (1)

Re(1)–Re(2)	2.248(1)
Re(1)–Cl(1)	2.318(5)
Re(1)–Cl(2)	2.330(5)
Re(1)–Cl(3)	2.323(5)
Re(1)–Cl(4)	2.299(4)
Re(2)–Cl(5)	2.336(4)
Re(2)–Cl(6)	2.322(4)
Re(2)–Cl(7)	2.326(4)
Re(2)–S(1)	2.455(3)
Re(2)–S(2)	2.906(5)
S(1)–C(1)	1.83(2)
S(1)–C(3)	1.83(2)
S(2)–C(2)	1.81(2)
S(2)–C(5)	1.85(2)
Re(2)–Re(1)–Cl(1)	103.1(1)
Re(2)–Re(1)–Cl(2)	106.4(1)
Re(2)–Re(1)–Cl(3)	103.6(1)
Re(2)–Re(1)–Cl(4)	102.8(2)
Cl(1)–Re(1)–Cl(2)	87.1(2)
Cl(1)–Re(1)–Cl(4)	87.5(2)
Cl(2)–Re(1)–Cl(3)	85.7(2)
Cl(3)–Re(1)–Cl(4)	86.3(2)
Re(1)–Re(2)–Cl(5)	100.5(1)
Re(1)–Re(2)–Cl(6)	101.8(2)
Re(1)–Re(2)–Cl(7)	101.5(1)
Re(1)–Re(2)–S(1)	95.3(2)
Re(1)–Re(2)–S(2)	172.3(1)
Cl(5)–Re(2)–Cl(6)	90.9(2)
Cl(5)–Re(2)–S(1)	91.1(1)
Cl(5)–Re(2)–S(2)	73.8(1)
Cl(6)–Re(2)–Cl(7)	89.2(1)
Cl(6)–Re(2)–S(2)	83.6(1)
Cl(7)–Re(2)–S(1)	82.2(1)
Cl(7)–Re(2)–S(2)	83.9(1)
S(1)–Re(2)–S(2)	80.0(1)
C(1)–S(1)–C(3)	103.7(9)
C(2)–S(2)–C(5)	100.1(8)

Table 4
Positional and isotropic equivalent thermal parameters for $(Bu_4N)[Re_2Cl_7(dth)]$ (2) [a]

Atom	x	y	z	B (Å^2)
Re(1)	0.68219(7)	0.95761(5)	0.87215(6)	2.91(1)
Re(2)	0.89065(7)	1.000	0.87250(6)	2.84(1)
Cl(1)	0.5084(5)	0.9976(4)	0.6692(4)	5.0(1)
Cl(2)	0.6504(5)	0.8196(3)	0.7930(4)	4.1(1)
Cl(3)	0.7590(5)	0.8989(4)	1.0756(4)	4.5(1)
Cl(4)	0.5994(6)	1.0730(3)	0.9460(5)	5.5(1)
Cl(5)	1.0552(5)	0.9572(4)	1.0797(4)	4.7(1)
Cl(6)	0.9452(6)	0.8802(3)	0.7821(5)	5.6(1)
Cl(7)	0.8055(6)	1.0724(3)	0.6761(4)	5.0(1)
S(1)	0.8877(5)	1.1471(3)	0.9504(4)	3.5(1)
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C(3)	0.946(2)	1.146(1)	1.122(2)	4.6(5)
C(4)	1.170(2)	1.094(2)	0.764(2)	7.8(7)
N	0.472(1)	0.8407(8)	0.324(1)	3.2(3)
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C(13)	0.406(2)	0.800(1)	−0.023(2)	4.6(5)
C(14)	0.327(2)	0.846(1)	−0.157(2)	4.9(5)
C(21)	0.477(2)	0.941(1)	0.325(1)	4.3(5)
C(22)	0.623(2)	0.973(1)	0.333(2)	5.4(5)
C(23)	0.612(2)	1.075(1)	0.317(2)	6.2(6)
C(24)	0.746(3)	1.112(2)	0.333(2)	9.3(9)
C(31)	0.593(2)	0.806(1)	0.454(2)	4.7(5)
C(32)	0.575(3)	0.711(1)	0.469(2)	7.9(8)
C(33)	0.717(3)	0.675(1)	0.574(2)	6.4(6)
C(34)	0.822(3)	0.659(2)	0.533(2)	10(1) [b]
C(41)	0.319(2)	0.816(1)	0.312(2)	3.9(4)
C(42)	0.280(2)	0.857(1)	0.415(2)	5.0(5)
C(43)	0.132(2)	0.825(1)	0.394(2)	5.4(6)
C(44)	0.074(3)	0.873(2)	0.475(2)	8.1(8)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $4/3[a^2\beta_{11}+b^2\beta_{22}+ab(\cos\gamma)\beta_{12}+ac(\cos\beta)\beta_{13}+bc(\cos\alpha)\beta_{23}]$.

[b] Refined isotropically.

compounds **1** and **2** with the formula $(Bu_4N)[Re_2Cl_7(SS)]$, in which SS = dto (**1**) or dth (**2**), are produced with retention of the quadruple bond. Under more forcing conditions (extended reflux), a redox reaction occurs to produce the compounds $Re_2Cl_5(SS)_2$ with Re–Re triple bonds and the structural arrangement $Cl_4ReRe(SS)_2Cl$ [2,4]. Complexes **1** and **2** are apparently intermediates in the formation of these latter compounds, since $(Bu_4N)[Re_2Cl_7(dto)]$ (**1**) reacts with dto to produce $Re_2Cl_5(dto)_2$, while $(Bu_4N)[Re_2Cl_7(dth)]$ (**2**) reacts with dth to give $Re_2Cl_5(dth)_2$. These intermediates are unusually stable; even after 10 h of reflux with excess dithioether, about half of the $[Re_2Cl_7(SS)]^-$ anion remains unchanged. Nevertheless, the reaction of compound **1** or **2** with $PMePh_2$ at room temperature results in loss of dithioether ligand to yield the known quadruply bonded compound $Re_2Cl_6(PMePh_2)_2$ [8]. It was our hope that a complete structural analysis of **1** and **2** would yield clues as to the reason why both SS ligands end up coordinated to the same Re atom in the $Re_2Cl_5(SS)_2$ compounds.

The structures of compounds **1** and **2** were determined by X-ray crystallography and views of the dirhenate anions appear in Figs. 1 and 2, respectively. These complex ions are very similar in every respect, and bear a close resemblance to the $[Re_2Cl_8]^{2-}$ ion from which they are derived. The seven chloride ligands along with sulfur atom S(1) occupy equatorial sites, while S(2) binds in an axial position to give a distorted octahedral coordination geometry for Re(2) and a distorted square-pyramidal geometry for Re(1). The dithioether ligands dto and dth are unsymmetrically chelated in an axial-equatorial fashion to rhenium atom Re(2). The axial coordination is significantly weaker than the equatorial, since the axial Re–S bond distance is 0.45 Å longer than the equatorial Re–S bond distance in the case of

Table 5
Selected bond distances (Å) and angles (°) for $(Bu_4N)[Re_2Cl_7(dth)]$ (**2**)

Re(1)–Re(2)	2.257(1)
Re(1)–Cl(1)	2.316(4)
Re(1)–Cl(2)	2.303(4)
Re(1)–Cl(3)	2.320(5)
Re(1)–Cl(4)	2.318(6)
Re(2)–Cl(5)	2.334(4)
Re(2)–Cl(6)	2.334(6)
Re(2)–Cl(7)	2.337(4)
Re(2)–S(1)	2.469(4)
Re(2)–S(2)	2.857(6)
S(1)–C(1)	1.84(2)
S(1)–C(3)	1.81(2)
S(2)–C(2)	1.81(2)
S(2)–C(4)	1.80(3)
Re(2)–Re(1)–Cl(1)	102.9(1)
Re(2)–Re(1)–Cl(2)	103.7(2)
Re(2)–Re(1)–Cl(3)	103.3(1)
Re(2)–Re(1)–Cl(4)	106.7(1)
Cl(1)–Re(1)–Cl(2)	86.4(2)
Cl(1)–Re(1)–Cl(4)	85.7(2)
Cl(2)–Re(1)–Cl(3)	87.9(2)
Cl(3)–Re(1)–Cl(4)	86.5(2)
Re(1)–Re(2)–Cl(5)	99.6(1)
Re(1)–Re(2)–Cl(6)	101.2(1)
Re(1)–Re(2)–Cl(7)	101.8(1)
Re(1)–Re(2)–S(1)	95.8(1)
Re(1)–Re(2)–S(2)	172.5(1)
Cl(5)–Re(2)–Cl(6)	91.6(2)
Cl(5)–Re(2)–S(1)	90.5(1)
Cl(5)–Re(2)–S(2)	73.7(2)
Cl(6)–Re(2)–S(2)	82.6(2)
Cl(6)–Re(2)–Cl(7)	90.2(2)
Cl(7)–Re(2)–S(1)	81.4(2)
Cl(7)–Re(2)–S(2)	84.6(2)
S(1)–Re(2)–S(2)	81.1(2)
Re(2)–S(1)–C(1)	105.2(7)
Re(2)–S(1)–C(3)	110.2(6)
Re(2)–S(2)–C(2)	99.8(8)
Re(2)–S(2)–C(4)	113.4(7)

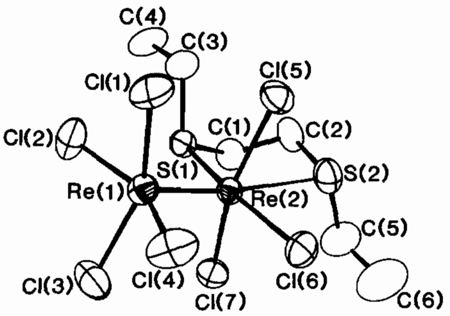


Fig. 1. An ORTEP drawing of $[Re_2Cl_7(dto)]^-$, the anion in compound **1**.

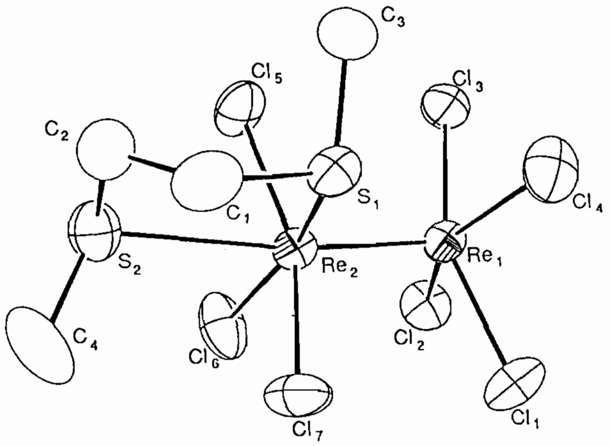


Fig. 2. An ORTEP drawing of $[Re_2Cl_7(dth)]^-$, the anion in compound **2**.

Table 6
Comparison of important bond distances and angles for compounds **1** and **2**

Bond distance (Å) or angle (°)	$(Bu_4N)[Re_2Cl_7(dto)]$ (**1**)	$(Bu_4N)[Re_2Cl_7(dth)]$ (**2**)
Re(1)–Re(2)	2.248(1)	2.257(1)
Re(2)–S(1)	2.455(3)	2.469(3)
Re(2)–S(2)	2.906(5)	2.857(5)
Re(1)–Cl (av.)	2.318(9)	2.314(6)
Re(2)–Cl (av.)	2.328(7)	2.335(6)
Re(1)–Re(2)–S(1)	95.3(1)	95.8(1)
Re(1)–Re(2)–S(2)	172.3(1)	172.5(1)
Re(1)–Re(2)–Cl (av.)	101.3(8)	100.9(9)
Re(2)–Re(1)–Cl (av.)	104(2)	104(1)

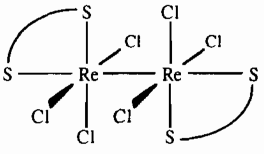
dto and 0.39 Å longer in the case of dth. A comparison of important bond distances and angles for complexes **1** and **2** appears in Table 6.

To our knowledge, these are the first examples of quadruply bonded dirhenium compounds with no bridging ligands and only one axial ligand. One effect of axial coordination is a slight weakening of the Re–Re quadruple bond. This bond weakening is evident from the observation that the Re–Re bond distances (2.248(1) Å for **1** and 2.257(1) Å for **2**) are somewhat longer than the Re–Re bond length of 2.222(2) Å in $(Bu_4N)_2[Re_2Cl_8]$ [11], and also longer than the Re–Re distances (<2.222 Å) in the $[Re_2Cl_7L]^-$ anions where L is the large tertiary phosphine PBu_3, PBu_2Ph or $PBuPh_2$ (Bu = n-butyl and Ph = phenyl) [6,7]. There is an inverse correlation between Re–Re bond length and axial Re–S bond length. In compound **1**, the Re–Re bond is shorter and the axial Re–S bond longer than the corresponding bonds in compound **2**. Further evidence of Re–Re bond weakening is provided by a shift to longer wavelength in the δ–δ^* transition energies for **1** (732 nm) and **2** (734 nm) as compared to $(Bu_4N)_2[Re_2Cl_8]$ (685 nm).

Coordination of a single chelating dithioether in complexes **1** and **2** results in non-zero L–Re–Re–L torsion angles, as opposed to the totally eclipsed conformation observed for the $[Re_2Cl_8]^{2-}$ ion. In the dto case, each of the four independent torsion angles are different, ranging from 1.3 to 3.8° with an average of 2.3°. In the dth case, the range is 0.2–5.9° and the average is 2.4°. Such small twisting does not significantly weaken the δ component of the quadruple bond even though maximum δ overlap occurs with a torsion angle of zero [12].

It is logical to assume that in the formation of $Re_2Cl_5(SS)_2$ from $[Re_2Cl_7(SS)]^-$ a second dithioether ligand coordinates to the same Re atom to which the first dithioether is already bonded. As mentioned previously, in the case of the $[Re_2Cl_7L]^-$ complexes, a second phosphine ligand coordinates to a different Re atom. For these complexes, Re–Cl bond lengths were used as the primary structural clue to locate the most likely chloride ligand to be replaced by phosphine, and it was suggested that rotation about the Re–Re bond and possibly rotation (internal flip) of the Re_2 dimetal unit must occur to result in the observed $Re_2Cl_6L_2$ compounds with the P atoms *trans* across the Re–Re bond [6]. The longest Re–Cl distance in the $[Re_2Cl_7L]^-$ complexes almost always corresponds to the Re–Cl bond *trans* (on the same Re atom) to the phosphine ligand. By contrast, in compounds **1** and **2**, the longest Re–Cl bond distance is associated with a Cl atom *cis* to the equatorial sulfur atom S(1), while the shortest Re–Cl bond length is that associated with the Cl atom that is positioned the farthest from S(1) and on the other Re atom. Also, the average Re–Cl distance for Re(2), to which the dithioether is coordinated, is longer than the average Re(1)–Cl distance in both $[Re_2Cl_7(SS)]^-$ anions. It would appear that the coordination of the first dithioether ligand to one Re atom labilizes one or more chloride ligands on that same Re atom so that the second dithioether ligand coordinates adjacent to the first when $Re_2Cl_5(SS)_2$ is formed.

The structural characterization of compound **2** also sheds light on the nature of $Re_2Cl_6(dth)_2$, which was originally reported at the same time as $Re_2Cl_5(dth)_2$ and is believed to have the structure indicated by **II**



II

with an Re–Re quadruple bond [13]. The similarity of **II** to the structure of the $[Re_2Cl_7(dth)]^-$ anion suggests that it probably represents the correct molecular geometry for $Re_2Cl_6(dth)_2$. Repeated attempts in our lab to prepare the analogous complex $Re_2Cl_6(dto)_2$ have so far been unsuccessful.

We are continuing to study the reactivity of dithioethers toward binuclear complexes with multiple metal–metal bonds. Recently, it was shown that 4,7-dithiadecane ($C_3H_7SCH_2CH_2SC_3H_7$ or dtd) reacts with quadruply bonded $[Mo_2Cl_8]^{4-}$ to produce several dimolybdenum complexes [14], but our attempts to synthesize another new dirhenium complex by the reaction of dtd with $[Re_2Cl_8]^{2-}$ have only resulted in essentially quantitative recovery of starting material. It would appear that the extra steric bulk of the terminal propyl groups versus methyl and ethyl groups for dth and dto render this reagent inactive with respect to chloride substitution in this case.

4. Supplementary material

Structure factors, anisotropic thermal parameters, and complete listings of bond distances and angles are available from author G.L.P.

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