ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2019, Vol. 45, No. 5, pp. 326–332. © Pleiades Publishing, Ltd., 2019.
Russian Text © The Author(s), 2019, published in Koordinatsionnaya Khimiya, 2019, Vol. 45, No. 5, pp. 276–282.

The Structure of Monomeric Octahedral d^2-Rhenium(V) Monooxo Complexes $\left[\mathrm{ReO}\left(\mathrm{L}_{\mathrm{tri}}^{m}\right)\left(\mathrm{L}_{\mathrm{bi}}^{n}\right)\right]$, $\left[\mathrm{ReO}\left(\mathrm{L}_{\mathrm{tri}}^{m}\right)\mathrm{Cl}_2\right]$ with Oxygen Atoms of Tridentate Chelating (O,S,O and S,O,S) Ligands

V. S. Sergienko[a, b, *] **and A. V. Churakov**[a]

[a] *Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences*
Moscow, 119991 Russia
[b] *All-Russian Institute for Scientific and Technical Information, Russian Academy of Sciences*
Moscow, 125190 Russia
**e-mail: sergienko@igic.ras.ru*

Received June 20, 2018; revised August 16, 2018; accepted September 15, 2018

Abstract—The structural features of eleven mononuclear octahedral d^2-Re(V) monooxo complexes with tridentate chelating (O,S,O and S,O,S) ligands, $\left[\mathrm{ReO}\left(\mathrm{L}_{\mathrm{tri}}^{m}\right)\left(\mathrm{L}_{\mathrm{bi}}^{n}\right)\right]$, $\left[\mathrm{ReO}\left(\mathrm{L}_{\mathrm{tri}}^{m}\right)\mathrm{Cl}_2\right]$, are discussed. The $\mathrm{Re{-}O}\left(\mathrm{L}_{\mathrm{tri}}^{m}\right)_{trans}$ bond lengths (except for two cases) were shown to be similar to (or somewhat shorter than), the Re–O(L)$_{cis}$ or Re–O(ST) bond lengths, which is indicative of the presence of pseudo-dioxo $\mathrm{ReO_2}$ groups with increased bond orders for both *trans*-arranged Re–O bonds. In the structures of two compounds, the $\mathrm{Re{-}O}\left(\mathrm{L}_{\mathrm{tri}}^{m}\right)_{trans}$ bonds are, on average, 0.093 Å longer than the Re–O(ST) bonds, which is consistent with the structural requirements of the *trans*-effect of a multiply bonded oxo ligand.

Keywords: crystal structure, X-ray diffraction analysis, six-coordinate d^2-Re monooxo compounds, tridentate chelating (O,S,O and S,O,S) ligands

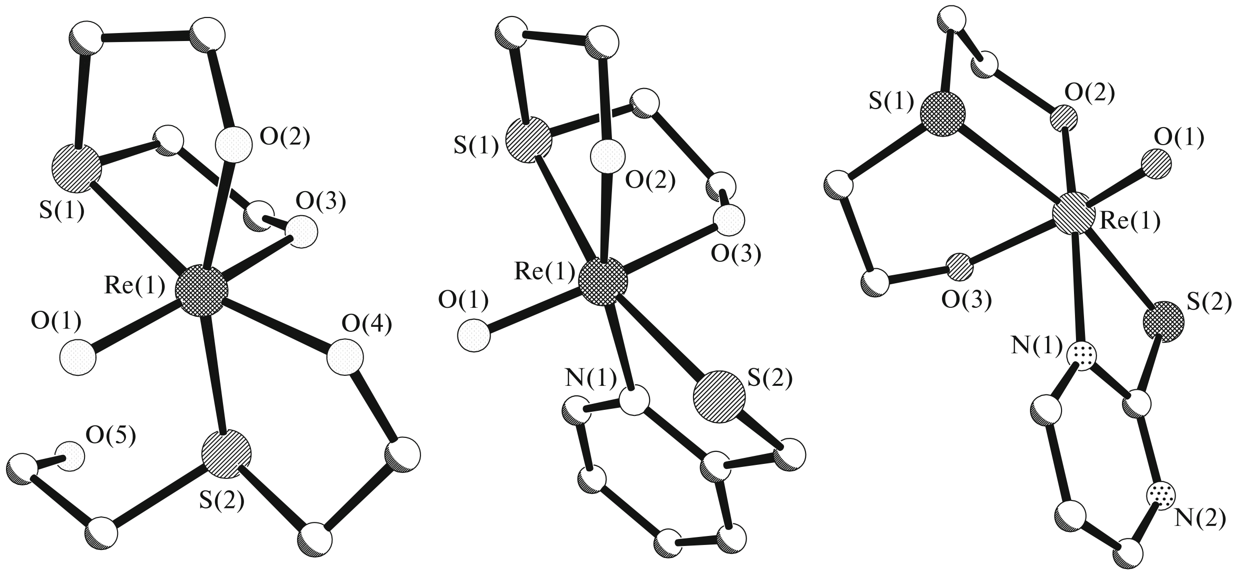
DOI: 10.1134/S1070328419030072

INTRODUCTION

The structures of monomeric octahedral complexes of Group 5–7 d^0- and d^2-metals (Nb, V, Mo, W, Re, Tc) with multiply bonded O(oxo) ligands are considered in detail in [1–7]. More than five hundred d^2-Re(V) compounds were studied by X-ray diffraction (see Cambridge Crystallographic Data Centre (CCDC), version 5.39, August 2018 [8]). Most of these complexes, $\mathrm{ReO_{oxo}O(Lig)}_{trans}$, contain oxygen atoms of mono- and polydentate ligands in the *trans*-positions to the oxo ligands. Previously, we published a number of integrating papers dealing with d^2-Re(V) monomeric octahedral complexes with ligands being represented by halogen, nitrogen, sulfur, or hydrogen atoms; oxygen atoms of monodentate anionic ligands (hydroxy, alkoxy (methoxy, ethoxy, propoxy), OR^{n-} (n = 1, 2; R = Ph, Cy, $\mathrm{C_6H_4OH}$, $\mathrm{C_6H_4OMe}$, $\mathrm{P(O)(OMe)_2}$, $\mathrm{C(O)(CF_3)}$, $\mathrm{OCMe(CF_3)_2}$, $\mathrm{BF_3}$), OER^{n-} (n = 1, 2; E = Si, B, S; R = $\mathrm{Me_3}$, $\mathrm{F_3}$, $\mathrm{O_2CF_3}$)); bidentate chelating (O,O), (O,S), (O,C), (O,P), and (O,N) singly charged ligands; singly and doubly charged tridentate chelating (O,N,O) [9] and (O,O,O) [10] ligands; and neutral oxygen-containing ligands (water molecules, phosphine oxide and arsine oxides $\mathrm{OER_3}$ (E = P, As; $\mathrm{R_3}$ = $\mathrm{Ph_3}$, $\mathrm{PhEt_2}$), OR' molecules: DMF, R''OH (R'' = Me, Et, Pr), L ($\mathrm{ON_4C_6 \cdot C_6H_{10}}$, $\mathrm{O^-(C_6H_3MeCH_2NH^+Et_2)}$, $\mathrm{O^-(NH^+C_5H_4)}$) located in the *trans*-position relative to the multiply bonded O(oxo) ligands. We also published reviews dealing with the structural details of d^0-Re(VII) [11] and d^0-, d^2-technetium(V, VII) [12] complexes.

A structural consequence of the *trans*-effect of the multiply bonded O(oxo) ligand, namely, elongation of the opposing Re–L$_{trans}$ bond, is characterized by the parameter Δ (the difference between the like bonds {[Re–L$_{trans}$] – [Re–L$_{cis}$]}). If the structure contains no ligands of the same sort in both *trans* and *cis* positions relative to O(oxo), we used the parameter {[Re–L$_{trans}$] – [Re–L(ST)]}, where ST is the statistical mean standard length of the Re(V) bond with the ligand of the same sort as L$_{trans.}$ As the Re–O(ST) value, we took (as previously [4]) 2.04 Å.

This communication discusses the structure of the monomeric octahedral monooxo complexes $\left[\mathrm{ReO}\left(\mathrm{L}_{\mathrm{tri}}^{m}\right)\left(\mathrm{L}_{\mathrm{bi}}^{n}\right)\right]$, and $\left[\mathrm{ReO}\left(\mathrm{L}_{\mathrm{tri}}^{m}\right)\mathrm{Cl}_2\right]$, containing



I **II** **IV**

Fig. 1. Structures of the complexes: $\left[\mathrm{ReO}\left(\mathrm{L}^1_{\mathrm{tri}}\right)\left(\mathrm{L}^1_{\mathrm{bi}}\right)\right]$ (**I**); $\left[\mathrm{ReO}\left(\mathrm{L}^1_{\mathrm{tri}}\right)\left(\mathrm{L}^2_{\mathrm{bi}}\right)\right]$ (**II**); $\left[\mathrm{ReO}\left(\mathrm{L}^1_{\mathrm{tri}}\right)\left(\mathrm{L}^4_{\mathrm{bi}}\right)\right]$ (**IV**).

tridentate chelating (O,S,O or S,O,S), bidentate chelating, or two monodentate (Cl) ligands.

Selected bond lengths for the eleven structurally studied complexes of the above-indicated types are summarized in Table 1.

I. STRUCTURE OF $\left[\mathrm{ReO}\left(\mathrm{L}^m_{\mathrm{tri}}\right)\left(\mathrm{L}^n_{\mathrm{bi}}\right)\right]\left(\mathrm{L}^m_{\mathrm{tri}}\right)$ = TRIDENTATE CHELATING (O,S,O) LIGAND)

Each of the six 3 + 2 type complexes considered in this chapter is based on doubly charged tridentate chelating bis(2-oxyethyl) sulfide ligand $\mathrm{S(CH_2CH_2O)_2^{2-}}\left(\mathrm{L}^1_{\mathrm{tri}}\right)$, in which all three atoms (O,S,O) are located in the common face of the rhenium octahedron (*fac*-isomer). The *trans*-position relative to the multiply bonded oxo ligand is always occupied by either of the two alkoxy oxygen atoms of $\mathrm{L}^1_{\mathrm{tri}}$. The coordination of $\mathrm{L}^1_{\mathrm{tri}}$ to rhenium is accompanied by closure of two similar five-membered $\mathrm{ReOC_2S}$ rings fused by the Re–S bond. The structure is completed by the bidentate chelating heteroatomic ligands that may have three different compositions (see below). All of the $\mathrm{L}^{n-}_{\mathrm{bi}}$ ligands are singly charged.

Structure of the $\left[\mathbf{ReO}\left(\mathbf{L}^1_{\mathbf{tri}}\right)\left(\mathbf{L}^1_{\mathbf{bi}}\right)\right]$ complex with the bidentate chelating (O,S) ligand $\mathbf{L}^1_{\mathbf{bi}}$. The crystal structure of $\left[\mathrm{ReO}\left(\mathrm{L}^1_{\mathrm{tri}}\right)\left(\mathrm{L}^1_{\mathrm{bi}}\right)\right]$ (**I**) [13] (Fig. 1a) comprises two ligands of the same type: the tridentate chelating $\left(\mathrm{L}^1_{\mathrm{tri}}\right)^{2-}$ and singly charged bidentate chelating (O,S) 2-hydroxyethyl(2-oxyethyl)thiolato ligand $\mathrm{OCH_2CH_2SCH_2CH_2OH^-}$ ($\mathrm{L}^1_{\mathrm{bi}}$) containing one pending branch with a terminal hydroxy group. The pending $\mathrm{CH_2CH_2OH}$ branch has a *syn*-orientation. The $\mathrm{L}^1_{\mathrm{bi}}$ coordination to the metal atom is accompanied by closure of the five-membered chelate ring $\mathrm{ReOC_2S}$. As usual, the rhenium atom is shifted from the equatorial plane of the $\mathrm{ONS_2}$ atoms towards the oxo ligand: Δ_{Re} = 0.259 Å.

Structure of the complex $\left[\mathbf{ReO}\left(\mathbf{L}^1_{\mathbf{tri}}\right)\left(\mathbf{L}^2_{\mathbf{bi}}\right)\right]$ with a bidentate chelating (NS) ligand. In the structure of $\left[\mathrm{ReO}\left(\mathrm{L}^1_{\mathrm{tri}}\right)\left(\mathrm{L}^2_{\mathrm{bi}}\right)\right]$ (**II**) [14] (Fig. 1b), the mercapromethylpyridyl ligand $\mathrm{SCH_2C_5H_4N}$ $\left(\mathrm{L}^2_{\mathrm{bi}}\right)$ is coordinated to Re to give a five-membered $\mathrm{ReNC_2S}$ ring. Note that two bonds, Re–S(1)$\left(\mathrm{L}^1_{\mathrm{tri}}\right)$ (2.530(2) Å) and Re–S(2)$\left(\mathrm{L}^2_{\mathrm{bi}}\right)$ (2.313(2) Å), with the sulfide and thiolate sulfur atoms, respectively, substantially differ in the length (for details, see below).

Structure of the complexes $\left[\mathbf{ReO}\left(\mathbf{L}^1_{\mathbf{tri}}\right)\left(\mathbf{L}^n_{\mathbf{bi}}\right)\right]$ (*n* = 3–6) with bidentate chelating (N,S) ligands. There are four known complexes similar in the composition $\left[\mathrm{ReO}\left(\mathrm{L}^1_{\mathrm{tri}}\right)\left(\mathrm{L}^n_{\mathrm{bi}}\right)\right]$ (*n* = 3–6) [13], but somewhat differing in the bidentate chelating (S,N) R-2-thiolato

Table 1. Selected geometric parameters (Å) in the monomeric octahedral complexes $\left[\mathrm{ReO}\left(\mathrm{L_{tri}}\right)\left(\mathrm{L_{bi}^{\mathit{n}}}\right)\right]$ with tridentate chelating (O,S,O and S,O,S) ligands*

No.	Complex	Re=O	Re–L$_{cis}$	Re–O(L$_{\mathrm{tri}}$)$_{trans}$	Δ	Refs
I	$\left[\mathrm{ReO}\left(\mathrm{L_{tri}^1}\right)\left(\mathrm{L_{bi}^1}\right)\right]$	1.703(5)	1.951(5) O$\left(\mathrm{L_{tri}^1}\right)$ 1.964(5) O$\left(\mathrm{L_{bi}^1}\right)$ 2.477(2) S$\left(\mathrm{L_{tri}^1}\right)$ 2.465(2) S$\left(\mathrm{L_{bi}^1}\right)$	2.007(5)	0.056	[13]
II	$\left[\mathrm{ReO}\left(\mathrm{L_{tri}^1}\right)\left(\mathrm{L_{bi}^2}\right)\right]$	1.711(4)	1.965(5) O$\left(\mathrm{L_{tri}^1}\right)$ 2.530(2) S$\left(\mathrm{L_{tri}^1}\right)$ 2.312(2) S$\left(\mathrm{L_{bi}^2}\right)$ 2.158(6) N$\left(\mathrm{L_{bi}^2}\right)$	1.966(4)	0.001	[14]
III	$\left[\mathrm{ReO}\left(\mathrm{L_{tri}^1}\right)\left(\mathrm{L_{bi}^3}\right)\right]$	1.700(6)	1.977(6) O$\left(\mathrm{L_{tri}^1}\right)$ 2.502(2) S$\left(\mathrm{L_{tri}^1}\right)$ 2.397(2) S$\left(\mathrm{L_{bi}^3}\right)$ 2.167(7) N$\left(\mathrm{L_{bi}^3}\right)$	1.968(6)	–0.009	[13]
IV	$\left[\mathrm{ReO}\left(\mathrm{L_{tri}^1}\right)\left(\mathrm{L_{bi}^4}\right)\right]$	1.698(5)	1.974(4) O$\left(\mathrm{L_{tri}^1}\right)$ 2.496(2) S$\left(\mathrm{L_{tri}^1}\right)$ 2.391(2) S$\left(\mathrm{L_{bi}^4}\right)$ 2.158(5) N$\left(\mathrm{L_{bi}^4}\right)$	1.971(4)	–0.003	[13]
V	$\left[\mathrm{ReO}\left(\mathrm{L_{tri}^1}\right)\left(\mathrm{L_{bi}^5}\right)\right]$	1.702(5)	1.965(4) O$\left(\mathrm{L_{tri}^1}\right)$ 2.492(2) S$\left(\mathrm{L_{tri}^1}\right)$ 2.374(2) S$\left(\mathrm{L_{bi}^5}\right)$ 2.164(5) N$\left(\mathrm{L_{bi}^5}\right)$	1.963(4)	–0.002	[13]
VI	$\left[\mathrm{ReO}\left(\mathrm{L_{tri}^1}\right)\left(\mathrm{L_{bi}^6}\right)\right]$	1.710(3)	1.957(3) O$\left(\mathrm{L_{tri}^1}\right)$ 2.471(1) S$\left(\mathrm{L_{tri}^1}\right)$ 2.384(1) S$\left(\mathrm{L_{bi}^6}\right)$ 2.186(3) N$\left(\mathrm{L_{bi}^6}\right)$	1.963(3)	0.006	[13]
VII	$\left[\mathrm{ReO}\left(\mathrm{L_{tri}^2}\right)\left(\mathrm{HL_{bi}^2}\right)\right]$	1.680(3)	2.287(1) S$\left(\mathrm{L_{tri}^2}\right)$ 2.440(1) S$\left(\mathrm{L_{tri}^2}\right)$ 2.304(1) S$\left(\mathrm{HL_{bi}^2}\right)$ 2.532(1) S$\left(\mathrm{HL_{bi}^2}\right)$	2.134(3)	0.094	[15]

Table 1. (Contd.)

No.	Complex	Re=O	Re–L$_{cis}$	Re–O(L$_{\text{tri}}$)$_{trans}$	Δ	Refs
VIII	$\left[\mathrm{ReO}\left(\mathrm{L}_{\text{tri}}^{2}\right)\left(\mathrm{L}_{\text{bi}}^{7}\right)\right]$	1.693(4)	2.276(2) $\mathrm{S}\left(\mathrm{L}_{\text{tri}}^{2}\right)$ 2.427(1) $\mathrm{S}\left(\mathrm{L}_{\text{tri}}^{2}\right)$ 2.313(2) $\mathrm{S}\left(\mathrm{L}_{\text{bi}}^{7}\right)$ 2.554(1) $\mathrm{S}\left(\mathrm{L}_{\text{bi}}^{7}\right)$	2.132(3)	0.092	[15]
IX	$\left[\mathrm{ReO}\left(\mathrm{L}_{\text{tri}}^{3}\right)\mathrm{Cl}_2\right]$	1.692(9)	2.472(3) ± 0.010 $\mathrm{S}\left(\mathrm{L}_{\text{tri}}^{3}\right)$ 2.367(4) ± 0.040 Cl	1.953(8)	–0.087	[16]
X	$\left[\mathrm{ReO}\left(\mathrm{L}_{\text{tri}}^{4}\right)\mathrm{Cl}_2\right]$	1.71(2)	2.434(7) ± 0.006 $\mathrm{S}\left(\mathrm{L}_{\text{tri}}^{4}\right)$ 2.431(6) ± 0.025 Cl	1.92(2)	–0.12	[16]
XI	$\left[\mathrm{ReO}\left(\mathrm{L}_{\text{tri}}^{5}\right)\mathrm{Cl}_2\right]$	1.686(6)	2.425(3) ± 0.003 $\mathrm{S}\left(\mathrm{L}_{\text{tri}}^{5}\right)$ 2.383(3) ± 0.023 Cl	1.917(6)	–0.123	[16]

* Designations of the ligands: $\left(\mathrm{L}_{\text{tri}}^{1}\right)^{2-}$ = $\mathrm{S(CH_2CH_2O)_2}$; $\left(\mathrm{L}_{\text{tri}}^{2}\right)^{2-}$ = $\mathrm{SCH_2CH_2SCH_2COO}$; $\left(\mathrm{L}_{\text{tri}}^{3}\right)^{-}$ = $\mathrm{OCH(CH_2S\text{-}Bu^{\mathit{t}})_2}$; $\left(\mathrm{L}_{\text{tri}}^{n}\right)^{-}$ = $\mathrm{O(CH_2)_2S(CH_2)_2C(CH_2)R}$, R = OH ($n = 4$), OEt ($n = 5$); $\left(\mathrm{L}_{\text{bi}}^{1}\right)^{-}$ = $\mathrm{OCH_2CH_2SCH_2CH_2OH}$; $\left(\mathrm{L}_{\text{bi}}^{2}\right)^{-}$ = $\mathrm{SCH_2C_5H_4N}$; $\left(\mathrm{L}_{\text{bi}}^{3}\right)^{-}$ = $\mathrm{SC_5H_4N}$; $\left(\mathrm{L}_{\text{bi}}^{4}\right)^{-}$ = $\mathrm{SC_4H_3N_2}$; $\left(\mathrm{L}_{\text{bi}}^{5}\right)^{-}$ = $\mathrm{SC_4H_2N_2\text{-}4\text{-}CH_3}$; $\left(\mathrm{L}_{\text{bi}}^{6}\right)^{-}$ = $\mathrm{SC_9H_6N}$; $\left(\mathrm{L}_{\text{bi}}^{7}\right)^{-}$ = $\mathrm{S(CH_2)_2SCH_2C({=}O)OMe}$.

ligand SR: R = pyridine $\mathrm{C_5H_4N}$ (**III**, n = 3); R = pyrimidine $\mathrm{C_4H_3N_2}$ (**IV**, n = 4; Fig. 1c); R = methylpyrimidine $\mathrm{C_4H_2N_2CH_3}$ (**V**, n = 5); and R = quinoline $\mathrm{C_9H_6N}$ (**VI**, n = 6). The coordination of $\left(\mathrm{L}_{\text{tri}}^{n}\right)$ to rhenium in **III**–**VI** is accompanied by closure of the four-membered chelate rings ReNCS. The parameters Δ_{Re} in **III**–**VI** are in the range of 0.204–0.224 Å.

II. STRUCTURE OF COMPLEXES $\left[\mathrm{ReO}\left(\mathrm{L}_{\text{tri}}^{m}\right)\left(\mathrm{L}_{\text{bi}}^{n}\right)\right]$, $\left[\mathrm{ReO}\left(\mathrm{L}_{\text{tri}}^{m}\right)\mathrm{Cl}_2\right]$ $\left(\mathrm{L}_{\text{tri}}^{m}\right)$ = TRIDENTATE CHELATING (S,O,S) LIGAND)

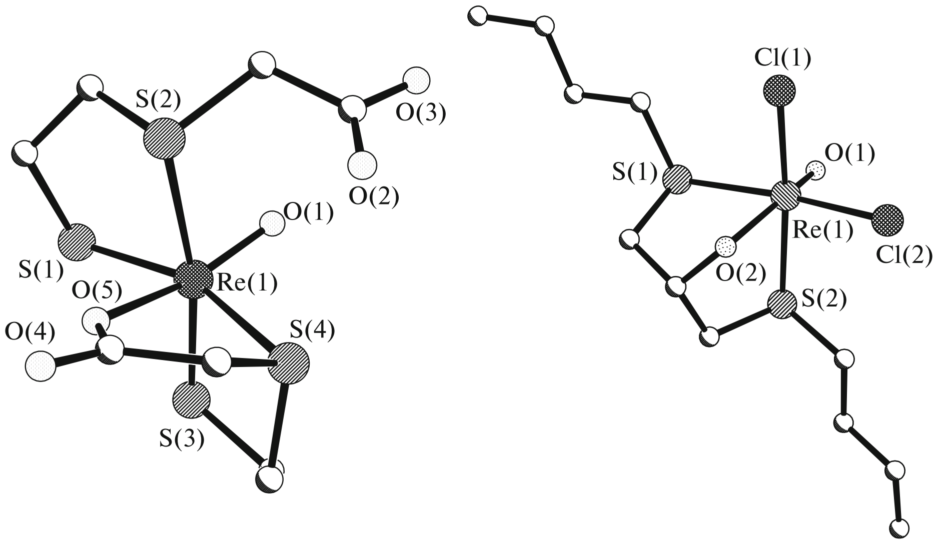
In the five title complexes, all three S,O,S atoms in each tridentate bis(chelating) ligand have a *fac* (facial) configuration in the coordination octahedra of rhenium. The *trans*-position relative to the multiply bonded oxo ligand is always occupied by the alkoxy oxygen atom of $\mathrm{L}_{\text{tri}}^{m}$.

Structure of the complexes $\left[\mathbf{ReO}\left(\mathbf{L}_{\textbf{tri}}^{2}\right)\left(\mathbf{L}_{\textbf{bi}}^{n}\right)\right]$ with bidentate chelating (S,S) ligands. In the two complexes indicated in the subheading, the octahedral coordination of the metal atoms is completed by bidentate chelating singly charged (S,S) ligands. In the structure of $\left[\mathrm{ReO}\left(\mathrm{L}_{\text{tri}}^{2}\right)\left(\mathrm{HL}_{\text{bi}}^{2}\right)\right]$ (**VII**) [15] (Fig. 2a), the bidentate-chelating 2-dithiacyclohexanecarboxylic acid ligand $\mathrm{SCH_2CH_2SCH_2COOH}$ $\left(\mathrm{HL}_{\text{bi}}^{2}\right)$ is analogous to the doubly charged 2-dithiacyclohexanecarboxylate tridentate chelating $\mathrm{L}_{\text{tri}}^{2}$ ligand. In the latter case, the carboxylate group is deprotonated, while in the former case, the COOH group is terminal (does not coordinate rhenium).

The crystal structure of $\left[\mathrm{ReO}\left(\mathrm{L}_{\text{tri}}^{2}\right)\left(\mathrm{L}_{\text{bi}}^{2}\right)\right]$ (**VIII**) [15] resembles that of **VII**, differing by the terminal ester (rather than carboxylate) group of the bidentate chelating methyl 3,6-dithiahexanoate ligand $\mathrm{SCH_2CH_2SCH_2C({=}O)OMe}$ $\left(\mathrm{L}_{\text{bi}}^{7}\right)$. In both structures, the O(carbonyl) atoms of the uncoordinated carboxylate or ester group are in the *anti*-conformation relative to O(oxo). The coordination of L_{tri} to rhenium in both compounds leads to closure of five-membered rings fused by the Re–S bond, which have different compositions: $\mathrm{ReOC_2S}$ and $\mathrm{ReSC_2S}$.

The $\mathrm{Re{-}O}\left(\mathrm{L}_{\text{tri}}^{2}\right)_{trans}$ bonds in **VII** and **VIII** are elongated to 2.132 and 2.134 Å due to the *trans*-effect of the multiply bonded oxo ligand. Note that in **VII** and **VIII**, two bond lengths in each $\mathrm{Re{-}S}\left(\mathrm{L}_{\text{tri}}^{2}\right)$ and $\mathrm{Re{-}S}\left(\mathrm{L}_{\text{bi}}^{2}\right)$ pair are considerably different (Table 1; for details of this difference, see chapter III).

In **VI**, the oxygen atoms of the coordinated and uncoordinated carboxylate groups are connected by a short O(3)–H···O(4) hydrogen bond (O(3)–H, 0.78; H···O, 1.88; O(3)···O(4), 2.605 Å; OHO angle, 155°).



(VII) **(IX)**

Fig. 2. Structures of the complexes: $\left[\mathrm{ReO}\left(\mathrm{L}^{2}_{\mathrm{tri}}\right)\left(\mathrm{HL}^{2}_{\mathrm{bi}}\right)\right]$ (**VII**); $\left[\mathrm{ReO}\left(\mathrm{L}^{4}_{\mathrm{tri}}\right)\mathrm{Cl}_2\right]$ (**IX**).

Structure of the complexes [ReO(L^n_{tri})Cl$_2$]. The crystal structure was determined for three complexes with singly charged tridentate chelating L^m_{tri} ligands. The general formula of the complexes is [ReO$\left(L^m_{tri}\right)$-Cl$_2$] [16]; L^m_{tri} = 5,9-dithiotridecan-7-olato, OCH(CH$_2$S-Bu^t)$_2$ (*m* = 3) (**IX**) (Fig. 2b); 8-hydroxy-3,6-dithiaoctan-1-olato O(CH$_2$)$_2$S(CH$_2$)$_2$C(CH$_2$)OH (*m* = 4) (**X**); and 3,6-dithia-9-oxaundecan-1-olato O(CH$_2$)$_2$S(CH$_2$)$_2$C(CH$_2$)OEt (*m* = 5) (**XI**). The two last-mentioned structures are equivalent, differing only in the terminal groups in the pending SCH$_2$CH$_2$R branches: R = OH in **X** and Et in **XI**.

In all three structures, the Re–O(L^m_{tri}) bonds (1.917–1.953 Å) are markedly shorter than the standard single Re–O(ST) bond (2.04 Å), while all Re–S bonds (average, 2.472, 2.434, and 2.425 Å in **IX**, **X**, and **XI**, respectively) have commensurable and expected lengths (see, for example, [17–19]). The L^m_{tri} ligands are coordinated to rhenium atoms, each closing two five-membered metallacycles fused by the Re–S bonds, symmetrical rings ReSC$_2$O in **IX** and asymmetrical rings ReSC$_2$S and ReSC$_2$O in **X** and **XI**.

In structure **IX**, the Re atom is shifted from the equatorial S$_2$Cl$_2$ plane towards the oxo ligand by 0.198 Å. The chloro ligands in all three compounds are located in the *cis*-positions relative to each other.

III. STRUCTURAL FEATURES OF MONOMERIC OCTAHEDRAL RHENIUM(V) MONOOXO COMPLEXES $\left[\mathrm{ReO}\left(\mathrm{L}^{m}_{\mathrm{tri}}\right)\left(\mathrm{L}^{n}_{\mathrm{bi}}\right)\right]$, $\left[\mathrm{ReO}\left(\mathrm{L}^{m}_{\mathrm{tri}}\right)\mathrm{Cl}_2\right]$ WITH TRIDENTATE CHELATING (O,S,O AND S,O,S) LIGANDS

Table 2 summarizes the average values for the key geometric parameters of **I**–**IX**.

Note two stereochemical features of octahedral monooxo complexes of Group 5–7 metals (in particular, rhenium):

(1) choice of the *trans*-partner (in the presence of competing ligands) is determined by the “self-consistency rule” [2]: the *trans*-position relative to the multiply bonded O(oxo) ligand is usually occupied by the least polarizable neutral σ-donor ligand (atom), the bond to which is weakened more easily, rather than by a negatively charged ligand (atom);

(2) the Re–L bonds in the *trans* position to O(oxo) are elongated because of the *trans*-effect of the multiply bonded oxo ligand.

The first rule does not hold in any of the eleven complexes considered in the paper: in compounds **I**–**XI**, the *trans*-positions to O(oxo) are occupied by anionic oxygen atoms of the L$_{tri}$ ligands. The Re–O$\left(L^m_{tri}\right)_{trans}$ bond lengths (1.917–2.007 Å; average, 1.959 Å) in nine of the eleven complexes (except for **VII** and **VIII**) are commensurable with the Re–O$\left(L^m_{tri}\right)_{cis}$ bond lengths in **I**–**VI** (1.951–1.977 Å; average, 1.965 Å), but they are not longer (due to the *trans*-

Table 2. Selected geometric parameters (Å) of the monomeric octahedral d^2-Re(V) monooxo complexes with tridentate chelating (O,S,O and S,O,S) ligands*

Parameter	Value (Å)
Re–O(oxo)	1.680–1.711 {11} (1.699 ± 0.019)
$\text{Re-O}\left(\text{L}^{m}_{\text{tri}}\right)_{trans}$	1.917–2.007 {9} (1.959 ± 0.048) 2.132, 2.134 {2} (2.133 ± 0.001)
$\text{Re–O}\left(\text{L}^{m}_{\text{tri}}\right)_{cis}$	1.951–1.977 {6} (1.965 ± 0.014)
$\Delta\left\{\text{Re–O}\left(\text{L}^{m}_{\text{tri}}\right)\right\}$	–0.009...+0.056 {6} (0.008 ± 0.048)
$\Delta\left\{\text{Re–O}\left(\text{L}^{m}_{\text{tri}}\right)\right\}$	–0.087...–0.123 {3} (–0.110 ± 0.023) 0.092–0.094 {2} (0.093 ± 0.001)
$\text{Re–O}\left(\text{L}^{n}_{\text{bi}}\right)_{cis}$	1.964 {1}
$\Delta\left\{\text{Re–O}\left(\text{L}^{n}_{\text{bi}}\right)\right\}$	0.009
$\text{Re–N}\left(\text{L}^{n}_{\text{bi}}\right)_{cis}$	2.158–2.186 {5} (2.164 ± 0.022)
Re–Cl	2.367–2.413 {3} (2.388 ± 0.025)

* The presented data include the ranges of values, the number of examples (in braces), and the average values with the scatter (in parentheses).

effect), as for most octahedral d^2-Re(V) monooxo complexes. It may seem that this fact is at variance with the "self-consistency rule" [2]. However, actually, the Re–O(L_{tri}) bond lengths in the *trans*-positions relative to the oxo ligands in **I–VI**, **IX–XI** can be considered as having a higher order, as they are markedly shorter than the Re–O(ST) value (2.04 Å) [4]. In this case, one deals with pseudo-dioxo complexes containing two multiply bonded ligands (O(oxo) and O(L)_{trans}). Recall that in the Group 5–7 d^2 metal dioxo complexes, two multiply bonded ligands are always located in *trans*-positions to each other. As opposed to the nine compounds mentioned above, in the two complexes **VII** and **VIII**, the $\text{Re–O}\left(\text{L}^{m}_{\text{tri}}\right)_{trans}$ bonds (2.132 and 2.134 Å) are markedly elongated (average Δ = 0.093 Å) because of the *trans*-effect.

In **II–VI**, two types of rhenium–sulfur bonds with the sulfide $\left(\text{L}^{m}_{\text{tri}}\right)$ and thiolate $\left(\text{L}^{n}_{\text{bi}}\right)$ sulfur atoms have substantially different lengths. The former type bonds, $\left(\text{Re–S}\left(\text{L}^{m}_{\text{tri}}\right)\right.$, 2.471–2.530 Å; average, 2.496 Å) are noticeably (on average, by 0.108 Å) shorter than the latter type bonds $\left(\text{Re–S}\left(\text{L}^{n}_{\text{bi}}\right)\right.$, 2.312–2.465 Å; average, 2.387 Å). In structure **I**, these bonds are commensurable in the length (2.477 and 2.465 Å, respectively, see Table 1). A different situation is observed for **VII** and **VIII**. In these compounds, the tridentate chelating ligands $\text{L}^{m}_{\text{tri}}$, like the bidentate chelating ligands L^{n}_{bi}, form two substantially nonequivalent Re–S bonds, one long bond $\left(\text{Re–S}\left(\text{L}^{m}_{\text{tri}}\right)\right.$, 2.434 ± 0.007; $\text{Re–S}\left(\text{L}^{n}_{\text{bi}}\right)$, 2.543 ± 0.011 Å) and one short bond $\left(\text{Re–S}\left(\text{L}^{m}_{\text{tri}}\right)\right.$, 2.296 ± 0.009; Re–S($\text{L}_{\text{bi}}$), 2.295 ± 0.019 Å). The authors of [15] attributed the presence of longer Re–S(L_{bi}) bonds to the absence of chelation of the carboxylic group. Meanwhile, two $\text{Re–S}\left(\text{L}^{m}_{\text{tri}}\right)$ bonds in each of the three complexes **IX–XI** have commensurable lengths (average, 2.434–2.472 Å to within ±0.003–0.010 Å). Because of large scatter of the Re–S distances in the crystal structures of the compounds, we do not give the data for these bonds in Table 2.

In all of the discussed structures, the Re–O(oxo), $\text{Re–N}\left(\text{L}^{n}_{\text{bi}}\right)$, and Re–Cl bond lengths are commensurable in the length, the average values being 1.704 ± 0.007, 2.164 ± 0.022, and 2.388 ± 0.025 Å, respectively (Table 2).

REFERENCES

1. Porai-Koshits, M.A. and Gilinskaya, E.A., *Kristallokhimiya* (Crystallochemistry), Moscow: VINITI, 1966, p. 126.
2. Porai-Koshits, M.A. and Atovmyan, L.O., *Koord. Khim.*, 1975, vol. 1, p. 1271.
3. Griffith, F. and Wicing, C., *J. Chem. Soc. A*, 1968, p. 379.
4. Porai-Koshits, M.A., *Izv. Yugoslav. Kristallogr. Tsentra*, 1974, vol. 9, p. 19.

5. Porai-Koshits, M.A. and Atovmyan L.O., *Kristallokhimiya koordinatsionnykh soedinenii molibdena* (Crystal Chemistry of Coordination Compounds of Molybdenum), Moscow: Nauka, 1974.
6. Shustorovich, E.M., Porai-Koshits, M.A., and Buslaev, Yu.A., *Coord. Chem. Rev.*, 1975, vol. 17, p. 1.
7. Porai-Koshits, M.A. and Sergienko, V.S., *Usp. Khim.*, 1990, vol. 59, p. 86.
8. Allen, F.H., *Acta Crystallogr., Sect. B: Struct. Sci.*, 2002, vol. 58, p. 380.
9. Sergienko, V.S., *Russ. J. Inorg. Chem.*, 2018, vol. 63, no. 14, p. 1757. doi 10.1134/S0036023618140048
10. Sergienko, V.S., *Russ. J. Inorg. Chem.*, 2016, vol. 61, p. 1408. doi 10.1134/S0036023616110188
11. Sergienko, V.S. and Churakov, A.V., *Crystallogr. Rep.*, 2014, vol. 59, no. 3, p. 300. doi 101134/S106377451140301711
12. Sergienko, V.S. and Churakov, A.V., *Crystallogr. Rep.*, 2013, vol. 58 no. 1, p. 5. doi 10.1134/S1063774513010112
13. Femia, F.J., Babich, J.W., and Zubieta, J., *Inorg. Chim. Acta*, 2000, vols. 300–302, p. 462.
14. Babich, J.W., Graham, W., Femia, F.J., et al., *Inorg. Chim. Acta*, 2001, vol. 323, p. 23.
15. Al-Jeboori, M.J., Dilworth, J.R., and Hiller, W., *Inorg. Chim. Acta*, 1999, vol. 285, p. 76.
16. Pietzsch, H.-J., Reisgys, M., Spis, H., et al., *Chem. Ber.*, 1997, vol. 130, p. 357.
17. Pietzsch, H.T., *Polyhedron*, 1995, vol. 14, p. 1849.
18. Reo, T.N., Adhikesovaly, D., Camerman, A., and Fitzkerg, A.R., *J. Chem. Soc.*, 1990, vol. 112, p. 5798.
19. Powell, J.L., *Inorg. Chim. Acta*, 1995, vol. 229, p. 241.

Translated by Z. Svitanko