ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2019, Vol. 45, No. 9, pp. 651–666. © Pleiades Publishing, Ltd., 2019.
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Structural Features of Monomeric Octahedral d^2-Rhenium(V) Monooxo Complexes with Oxygen Atoms of Tridentate Chelating (O,N,S) Ligands

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Received November 13, 2018; revised December 11, 2018; accepted January 28, 2019

Abstract—The structural features of 31 mononuclear octahedral d^2-Re(V) monooxo complexes with tridentate chelating (O,N,S) ligands, $[\mathrm{ReO}\left(\mathrm{L}^m_{\mathrm{tri}}\right)\left(\mathrm{L}^n_{\mathrm{bi}}\right)]$ and $[\mathrm{ReO}\left(\mathrm{L}^m_{\mathrm{tri}}\right)(\mathrm{L}_{\mathrm{mono}})_2]$ ($\mathrm{L}_{\mathrm{mono}}$ = Cl, Br, OMe, $OPPh_3$, PPh_3) are considered. The $\mathrm{Re{-}O}\left(\mathrm{L}^m_{\mathrm{tri}}\right)_{trans}$, $\mathrm{Re{-}O}\left(\mathrm{L}^n_{\mathrm{bi}}\right)_{trans}$, and Re–O(OMe) bonds in 14 complexes were found to be commensurable in length with (or shorter than) analogous *cis*-bonds. This indicates the presence of pseudo-dioxo ReO_2 groups in these structures with increased orders of both Re–O bonds located in *trans*-positions relative to each other. In the structures of 12 compounds, the $\mathrm{Re{-}O}(\mathrm{L}_{\mathrm{tri}})_{trans}$, $\mathrm{Re{-}O}(\mathrm{L}_{\mathrm{bi}})_{trans}$, and $\mathrm{Re{-}O}(OPPh_3)$ bonds are markedly longer than analogous *cis*-bonds in accordance with the structural consequences 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,N,S) ligands

DOI: 10.1134/S1070328419080074

INTRODUCTION

The structures of monomeric octahedral complexes (MOCs) of Group 5–7 d^0- and d^2-metals (Nb, V, Mo, W, Re, Tc) with multiply bonded O(oxo) ligands were analyzed in detail in the literature [1–7]. More than five hundred d^2-Re(V) compounds were studied by X-ray diffraction (Cambridge Crystallographic Data Centre (CCDC), version 5.39, November 2017 [8]). In most of the $\mathrm{ReO_{oxo}O(L)}_{trans}$ complexes, the oxygen atoms of mono- and polydentate ligands are located in the *trans*-positions to the oxo ligands. Previously, we published a number of integrating papers considering d^2-Re(V) MOCs with ligands being represented by halogen, nitrogen, sulfur, and hydrogen atoms; oxygen atoms of monodentate anionic ligands (hydroxy, alkoxy (methoxy, ethoxy, propoxy), OR^{n-} (n = 1, 2; R = Ph, Cy, C_6H_4OH, C_6H_4OMe, $P(O)(OMe)_2$, $C(O)(CF_3)$, $OCMe(CF_3)_2$, BF_3), OER^- (n = 1, 2; E = Si, B, S; R = Me_3, F_3, O_2CF_3)); bidentate chelating singly charged (O,O), (O,S), (O,C), (O,P), and (O,N) ligands; tridentate chelating singly and doubly charged (O,N,O) [9], (O,O,O) [10], (O,S,O and S,O,S) [11], (O,P,O and O,P,N) [12], and (O,N,N) [13] ligands; and neutral oxygen-containing ligands (water molecules, phosphine oxides and arsine oxides OER_3 (E = P, As; R_3 = Ph_3, $PhEt_2$), OR' molecules (DMF, R"OH (R" = Me, Et, Pr), L = $\mathrm{O^-(C_6H_{3\text{-}}MeCH_2NH^+Et_2)}$, $\mathrm{O^-(NH^+C_5H_4)}$, located in *trans*-positions to the multiply bonded O(oxo) ligands. Reviews dealing with structural features of MOCs formed by d^0-Re(VII) [14] and d^0-, d^2-technecium(V, VII) [15] were published.

The structural consequence of the *trans*-effect of the multiply bonded O(oxo) ligand, namely, elongation of the opposing $\mathrm{Re{-}L}_{trans}$ bond, is characterized by the parameter Δ, that is, the difference between the lengths of like bonds: $[\mathrm{Re{-}L}_{trans}] - [\mathrm{Re{-}L}_{cis}]$. If no ligands of the same sort are present in both *trans* and *cis* positions to O(oxo), we use the parameter $\{[\mathrm{Re{-}L}_{trans}] - [\mathrm{Re{-}L(ST)}]\}$, where ST is the statistical mean standard length for Re(V) bond with the ligand of the same sort as $\mathrm{L}_{trans.}$ As previously [4], Re–O(ST) was taken to be 2.04 Å.

The present paper discusses the structures of the monomeric octahedral monooxo complexes, $[\mathrm{ReO}\left(\mathrm{L}^m_{\mathrm{tri}}\right)(\mathrm{L}_{\mathrm{mono}})_2]$ and $[\mathrm{ReO}\left(\mathrm{L}^m_{\mathrm{tri}}\right)\left(\mathrm{L}^n_{\mathrm{bi}}\right)]$, containing a tridentate chelating (O,N,S) ligand and two monodentate ligands or a bidentate chelating ligand.

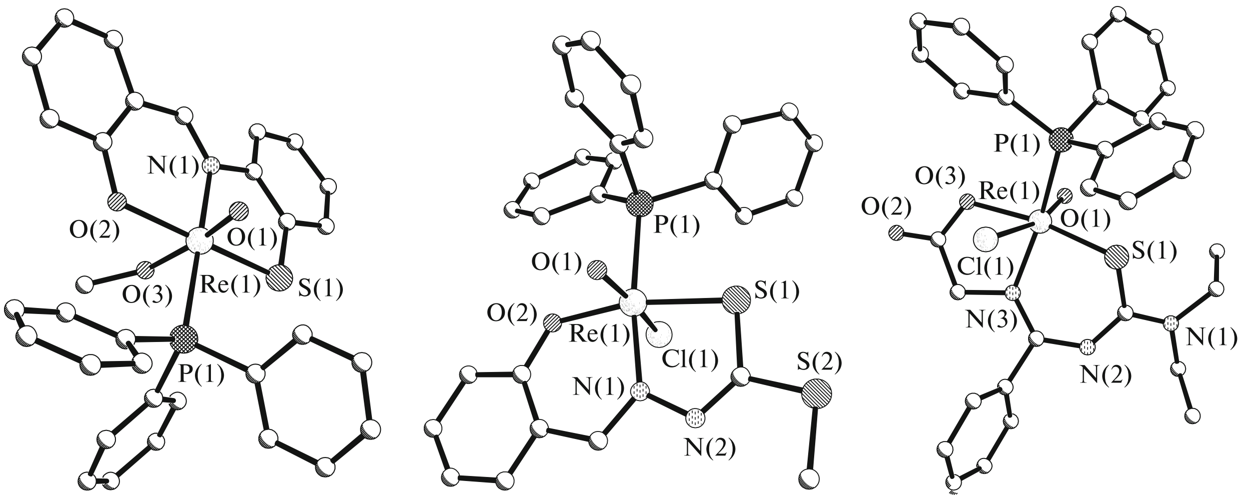

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Fig. 1. Structures of: $[\mathrm{ReO}(\mathrm{L}^1_{\mathrm{tri}})(\mathrm{OMe})(\mathrm{PPh}_3)]$ (**I**), $[\mathrm{ReO}(\mathrm{L}^2_{\mathrm{tri}})(\mathrm{OPPh}_3)\mathrm{Cl}]$ (**II**), and $[\mathrm{ReO}(\mathrm{L}^3_{\mathrm{tri}})\mathrm{Cl}_2]$ (**IV**).

Selected bond lengths for the 31 structurally studied complexes of the above-indicated type are summarized in Table 1.

STRUCTURE OF COMPLEXES $[\mathrm{ReO}(\mathrm{L}^m_{\mathrm{tri}})(\mathrm{L}_{\mathrm{mono}})_2]$ WITH A TRIDENTATE CHELATING (O,N,S) LIGAND AND TWO MONODENTATE LIGANDS LOCATED IN *cis*-POSITIONS RELATIVE TO EACH OTHER

Structures of $[\mathrm{ReO}(\mathrm{L}^m_{\mathrm{tri}})(\mathrm{L}_{\mathrm{mono}})_2]$ with two different monodentate ligands. Crystal structures are known for four complexes of the title type containing two different monodenatate ligands. The tridentate bis(chelating) doubly charged (with deprotonated O and S atoms) ligand $\left(\mathrm{L}^m_{\mathrm{tri}}\right)^{2-}$ always has a meridional (*mer*) geometry: the O and S atoms are located in the *trans*-positions relative to each other and the N atom is in the *cis*-position to them. The $\left(\mathrm{L}^m_{\mathrm{tri}}\right)^{2-}$ ligands are connected at the Re–N bonds by four different pairs of five- and six-membered rings (for details, see below).

In the $[\mathrm{ReO}(\mathrm{L}^1_{\mathrm{tri}})(\mathrm{OMe})(\mathrm{PPh}_3)]$ complex (**I**, Fig. 1), where $\mathrm{L}^1_{\mathrm{tri}}$ is salicylaldehyde-2-sulfonylanilato, $(\mathrm{OC}_6\mathrm{H}_4)\mathrm{CH{=}NC}_6\mathrm{H}_4\mathrm{S}$, the dianionic $\mathrm{L}^1_{\mathrm{tri}}$, ligand coordinates the rhenium atom, thus forming five- and six-membered metallacycles, ReNSC_2 and $\mathrm{ReNC}_3\mathrm{O}$ [16]. Two independent complex molecules have similar structures. The Re–O(OMe) bond with the single-charged monodentate methoxy ligand (1.901(9) ± 0.004 Å) located in the *trans*-position to Re–O(oxo) is shortened, on average, by 0.139 Å with respect to the standard Re–O(ST) bond (2.04 Å). The authors [16] note rather long Re–O, Re–N, and Re–S bonds with atoms of the $\mathrm{L}^1_{\mathrm{mono}}$, ligand (2.137 ± 0.023, 2.14 ± 0.01, and 2.309 ± 0.003 Å, respectively) as a result of steric strain.

In $[\mathrm{ReO}(\mathrm{L}^2_{\mathrm{tri}})(\mathrm{OPPh}_3)\mathrm{Cl}]$ (**II**, Fig. 1),where $\mathrm{L}^2_{\mathrm{tri}}$ is a Schiff base, S'-methyl-3-(salicylidene)dithiocarbazato, $\mathrm{OC}_6\mathrm{H}_4\mathrm{CH{=}NN{=}C(SMe)S}$, the *trans*-position to the oxo ligand is occupied by the $\mathrm{O(OPPh}_3)$ atom of neutral triphenylphosphine oxide ligand [17]. The bond to this ligand is elongated to 2.145 Å as a consequence of the *trans*-effect of the multiply bonded oxo ligand. The $\mathrm{Re{-}O(OPPh}_3)$ bond in **II** is substantially longer than analogous bonds in $[\mathrm{ReOX}_3(\mathrm{PR}_3)(\mathrm{OPR}_3)]$ (X = Cl, Br) (which are 2.053–2.082 Å long, e.g., [18]). The Re atom is displaced from the SNOCl equatorial plane towards the oxo ligand; $\Delta_{\mathrm{Re}} = 0.31$ Å.

In the complex $[\mathrm{ReO}\left(\mathrm{L}^2_{\mathrm{tri}}\right)\mathrm{Cl}(\mathrm{PPh}_3)] \cdot \mathrm{H}_2\mathrm{O}$ (**III**), the *trans*-position to the oxo ligand is occupied by a chlorine atom [17]. The $\mathrm{Re{-}Cl}_{trans}$ bond (2.403 Å) is elongated because of the *trans*-effect; it is 0.048 Å longer than the $\mathrm{Re{-}Cl}_{cis}$ bond in complex **II**. The parameter Δ_{Re} for structure **III** is 0.20 Å. The $\mathrm{L}^2_{\mathrm{tri}}$ ligand in both **II** and **III** closes five- and six-membered rings, $\mathrm{ReN}_2\mathrm{CS}$ and $\mathrm{ReNC}_3\mathrm{O}$, upon coordination to rhenium. The five-membered ring in **III** has a *twist*-envelope conformation with torsion angles in the range from –8.1° to +10.9°. It was noted [17] that all three bonds with the donor atoms of the doubly charged $\mathrm{L}^2_{\mathrm{tri}}$ ligand (deprotonated O atoms and neutral N atom) are markedly longer in **II** than in **III** (Re–O, 2.18 and 1.99; Re–N, 2.05 and 1.99; Re–S, 2.372 and 2.268 Å).

Table 1. Selected geometric parameters (Å) of monomeric octahedral complexes with tridentate chelating (O,N,S) ligands*

Complex	Re=O	Re–L$_{cis}$	Re–L$_{trans}$	Δ (Δ)**	Ref
$[\mathrm{ReO}(\mathrm{L}^{1}_{\mathrm{tri}})(\mathrm{OMe})(\mathrm{PPh}_3)]$ **(I)**	1.707(8)	2.114(9) $\mathrm{O}(\mathrm{L}^{1}_{\mathrm{tri}})$ 2.13(1) $\mathrm{N}(\mathrm{L}^{1}_{\mathrm{tri}})$ 2.306(4) $\mathrm{S}(\mathrm{L}^{1}_{\mathrm{tri}})$ 2.473(4) $\mathrm{P}(\mathrm{PPh}_3)$	1.904(9) O(OMe)	(–0.136)	[16]
$[\mathrm{ReO}(\mathrm{L}^{2}_{\mathrm{tri}})(\mathrm{OPPh}_3)\mathrm{Cl}]$ **(II)**	1.666(7)	2.180(6) $\mathrm{O}(\mathrm{L}^{2}_{\mathrm{tri}})$ 2.051(10) $\mathrm{N}(\mathrm{L}^{2}_{\mathrm{tri}})$ 2.372(4) $\mathrm{S}(\mathrm{L}^{2}_{\mathrm{tri}})$ 2.355(3) Cl	2.145(11) $\mathrm{O}(\mathrm{OPPh}_3)$	(0.105)	[17]
$[\mathrm{ReO}(\mathrm{L}^{2}_{\mathrm{tri}})\mathrm{Cl}(\mathrm{PPh}_3)] \cdot \mathrm{H_2O}$ **(III)**	1.70(1)	1.99(1) $\mathrm{O}(\mathrm{L}^{2}_{\mathrm{tri}})$ 1.99(2) $\mathrm{N}(\mathrm{L}^{2}_{\mathrm{tri}})$ 2.268(5) $\mathrm{S}\ (\mathrm{L}^{2}_{\mathrm{tri}})$ 2.450(6) $\mathrm{P}(\mathrm{Ph}_3)$	2.403(1) Cl	(0.048) Cl	[17]
$[\mathrm{ReO}(\mathrm{L}^{3}_{\mathrm{tri}})\mathrm{Cl}(\mathrm{PPh}_3)] \cdot 0.25\mathrm{CH_3CN} \cdot 0.125\mathrm{H_2O}$ **(IV)**	1.682(7) ± 0.002	2.052(8) ± 0.017 $\mathrm{O}(\mathrm{L}^{3}_{\mathrm{tri}})$ 2.041(9) ± 0.001 $\mathrm{N}(\mathrm{L}^{3}_{\mathrm{tri}})$ 2.328(3) ± 0.003 $\mathrm{S}(\mathrm{L}^{3}_{\mathrm{tri}})$ 2.484(3) ± 0.008 $\mathrm{P}(\mathrm{Ph}_3)$	2.444(3) ± 0.001 Cl	(0.089) Cl	[19]
$[\mathrm{ReO}(\mathrm{L}^{4}_{\mathrm{tri}})\mathrm{Cl}_2] \cdot 2\mathrm{OC_4H_8}$ **(V)**	1.692(2)	2.235(2) $\mathrm{N}(\mathrm{L}^{4}_{\mathrm{tri}})$ 2.421(1) $\mathrm{S}(\mathrm{L}^{4}_{\mathrm{tri}})$ 2.390(1) ± 0.020 Cl	1.913(2) $\mathrm{O}(\mathrm{L}^{4}_{\mathrm{tri}})$	(–0.127)	[20]
$[\mathrm{ReO}(\mathrm{D,L}\text{-}\mathrm{L}^{5}_{\mathrm{tri}})\mathrm{Cl}_2]$ monoclinic **(VI)**	1.663(5) ± 0.005	2.147(5) ± 0.001 $\mathrm{N}(\mathrm{L}^{5}_{\mathrm{tri}})$ 2.415(2) ± 0.015 $\mathrm{S}(\mathrm{L}^{5}_{\mathrm{tri}})$ 2.349(2) ± 0.028 Cl	2.059(4) ± 0.003 $\mathrm{O}(\mathrm{L}^{5}_{\mathrm{tri}})$	(0.019)	[21]
$[\mathrm{ReO}(\mathrm{D}\text{-}\mathrm{L}^{5}_{\mathrm{tri}})\mathrm{Cl}_2]$ orthorhombic **(VII)**	1.673(4)	2.100(5) $\mathrm{N}(\mathrm{L}^{5}_{\mathrm{tri}})$ 2.421(2) $\mathrm{S}(\mathrm{L}^{5}_{\mathrm{tri}})$ 2.359(2) ± 0.023 Cl	2.049(5) $\mathrm{O}(\mathrm{L}^{5}_{\mathrm{tri}})$	(0.009)	[21]
$[\mathrm{ReO}(\mathrm{D,L}\text{-}\mathrm{L}^{5}_{\mathrm{tri}})\mathrm{Br}_2] \cdot 0.5\mathrm{MeOH}$ **(VIII)**	1.65(1) ± 0.01	2.17(1) ± 0.01 $\mathrm{N}(\mathrm{L}^{5}_{\mathrm{tri}})$ 2.426(4) ± 0.006 $\mathrm{S}(\mathrm{L}^{5}_{\mathrm{tri}})$ 2.509(2) ± 0.007 Br	2.06(1) ± 0.01 $\mathrm{O}(\mathrm{L}^{6}_{\mathrm{tri}})$	(0.02)	[21]
$[\mathrm{ReO}(\mathrm{D,L}\text{-}\mathrm{L}^{5}_{\mathrm{tri}})\mathrm{Br}_2] \cdot 0.5\mathrm{H_2O}$ **(IX)**	1.662(8) ± 0.005	2.146(8) ± 0.009 $\mathrm{N}(\mathrm{L}^{5}_{\mathrm{tri}})$ 2.432(3) ± 0.001 $\mathrm{S}(\mathrm{L}^{5}_{\mathrm{tri}})$ 2.495(1) ± 0.007 Br	2.066(7) ± 0.002 $\mathrm{O}(\mathrm{L}^{5}_{\mathrm{tri}})$	(0.026)	[21]
$[\mathrm{ReO}(\mathrm{L}^{6}_{\mathrm{tri}})\mathrm{Cl}_2]$ **(X)**	1.696(3)	2.082(6) $\mathrm{N}(\mathrm{L}^{6}_{\mathrm{tri}})$ 2.450(1) $\mathrm{S}(\mathrm{L}^{6}_{\mathrm{tri}})$ 2.39(1) ± 0.02 Cl	1.911(3) $\mathrm{O}(\mathrm{L}^{6}_{\mathrm{tri}})$	(–129)	[22]

Table 1. (Contd.)

Complex	Re=O	Re–L$_{cis}$	Re–L$_{trans}$	Δ (Δ)**	Ref
$[\mathrm{ReO}(\mathrm{L}^{6}_{\mathrm{tri}})\mathrm{Br}_2]$ **(XI)**	1.699(4)	2.095(4) N$(\mathrm{L}^{6}_{\mathrm{tri}})$ 2.456(1) S$(\mathrm{L}^{6}_{\mathrm{tri}})$ 2.5232(6) ± 0.092 Br	1.935(4) O$(\mathrm{L}^{6}_{\mathrm{tri}})$	(–0.105)	[23]
$[\mathrm{ReO}(\mathrm{L}^{1}_{\mathrm{tri}})(\mathrm{L}^{1}_{\mathrm{bi}})]$ **(XII)**	1.700(3)	2.076(3) O$(\mathrm{L}^{1}_{\mathrm{tri}})$ 2.050(4) N$(\mathrm{L}^{1}_{\mathrm{tri}})$ 2.312(1) S$(\mathrm{L}^{1}_{\mathrm{tri}})$ 2.140(4) N$(\mathrm{L}^{1}_{\mathrm{tri}})$	1.989(3) O$(\mathrm{L}^{1}_{\mathrm{bi}})$	(–0.051) (–0.087)***	[16]
$[\mathrm{ReO}(\mathrm{L}^{7}_{\mathrm{tri}})(\mathrm{L}^{2}_{\mathrm{bi}})]$ **(XIII)**	1.680(5)	2.029(5) O$(\mathrm{L}^{7}_{\mathrm{tri}})$ 1.989(5) N$(\mathrm{L}^{7}_{\mathrm{tri}})$ 2.348(2) S$(\mathrm{L}^{7}_{\mathrm{tri}})$ 2.189(6) N$(\mathrm{L}^{2}_{\mathrm{bi}})$	2.120(5) O$(\mathrm{L}^{2}_{\mathrm{bi}})$	(0.080) (0.091)***	[27]
$[\mathrm{ReO}(\mathrm{L}^{6}_{\mathrm{tri}})(\mathrm{L}^{3}_{\mathrm{bi}})]\mathrm{Cl} \cdot 2\mathrm{H}_2\mathrm{O}$ **(XIV)**	1.698(3)	2.106(3) N$(\mathrm{L}^{6}_{\mathrm{tri}})$ 2.475(1) S$(\mathrm{L}^{6}_{\mathrm{tri}})$ 1.960(3) O$(\mathrm{L}^{3}_{\mathrm{bi}})$ 2.087(3) N$(\mathrm{L}^{3}_{\mathrm{bi}})$	1.946(3) O$(\mathrm{L}^{6}_{\mathrm{tri}})$	(–0.094) (–0.016)***	[23]
$\{\mathrm{N(CH_2)_2Et}\}[\mathrm{ReO}(\mathrm{L}^{8}_{\mathrm{tri}})(\mathrm{L}^{4}_{\mathrm{bi}})]$ **(XV)**	1.692(5)	2.007(5) N$(\mathrm{L}^{8}_{\mathrm{tri}})$ 2.294(2) S$(\mathrm{L}^{8}_{\mathrm{tri}})$ 2.076(5) O$(\mathrm{L}^{4}_{\mathrm{bi}})$ 2.435(2) P$(\mathrm{L}^{4}_{\mathrm{bi}})$	2.126(4) O$(\mathrm{L}^{8}_{\mathrm{tri}})$	(0.086) (0.050)***	[28]
$[\mathrm{ReO}(\mathrm{L}^{1}_{\mathrm{tri}})(\mathrm{L}^{4}_{\mathrm{bi}})]$ **(XVI)**	1.696(3)	2.094(3) O$(\mathrm{L}^{1}_{\mathrm{tri}})$ 2.102(4) N$(\mathrm{L}^{1}_{\mathrm{tri}})$ 2.310(1) S$(\mathrm{L}^{1}_{\mathrm{tri}})$ 2.430(1) P$(\mathrm{L}^{4}_{\mathrm{bi}})$	2.047(3) O$(\mathrm{L}^{4}_{\mathrm{bi}})$	(0.007) (–0.047)***	[29]
$[\mathrm{ReO}(\mathrm{L}^{9}_{\mathrm{tri}})(\mathrm{L}^{5}_{\mathrm{bi}})]$ **(XVII)**	1.659(7)	2.043(5) O$(\mathrm{L}^{9}_{\mathrm{tri}})$ 2.041(7) N$(\mathrm{L}^{9}_{\mathrm{tri}})$ 2.313(2) S$(\mathrm{L}^{9}_{\mathrm{tri}})$ 2.391(2) S$(\mathrm{L}^{5}_{\mathrm{bi}})$	2.249(5) O$(\mathrm{L}^{5}_{\mathrm{bi}})$	(0.209) (0.206)***	[30]

Table 1. (Contd.)

Complex	Re=O	Re–L_{cis}	Re–L_{trans}	Δ (Δ)**	Ref
[ReO$(\mathrm{L}^{9}_{\mathrm{tri}})(\mathrm{L}^{6}_{\mathrm{bi}})$] (**XVIII**)	1.644(8)	2.052(7) O$(\mathrm{L}^{9}_{\mathrm{tri}})$ 2.020(9) N$(\mathrm{L}^{9}_{\mathrm{tri}})$ 2.327(3) S$(\mathrm{L}^{9}_{\mathrm{tri}})$ 2.403(3) S$(\mathrm{L}^{6}_{\mathrm{bi}})$	2.204(7) O$(\mathrm{L}^{6}_{\mathrm{bi}})$	(0.144) (0.152)***	[30]
[ReO$(\mathrm{L}^{10}_{\mathrm{tri}})(\mathrm{L}^{5}_{\mathrm{bi}})$] (**XIX**)	1.662(4)	1.968(5) O$(\mathrm{L}^{10}_{\mathrm{tri}})$ 2.009(6) N$(\mathrm{L}^{10}_{\mathrm{tri}})$ 2.360(2) S$(\mathrm{L}^{10}_{\mathrm{tri}})$ 2.399(2) S$(\mathrm{L}^{5}_{\mathrm{bi}})$	2.196(4) O$(\mathrm{L}^{5}_{\mathrm{bi}})$	(0.156) (0.208)***	[31]
[ReO$(\mathrm{L}^{10}_{\mathrm{tri}})(\mathrm{L}^{6}_{\mathrm{bi}})$] (**XX**)	1.681(2)	1.996(2) O$(\mathrm{L}^{10}_{\mathrm{tri}})$ 2.028(2) N$(\mathrm{L}^{10}_{\mathrm{tri}})$ 2.354(1) S$(\mathrm{L}^{10}_{\mathrm{tri}})$ 2.408(1) S$(\mathrm{L}^{6}_{\mathrm{bi}})$	2.158(2) O$(\mathrm{L}^{6}_{\mathrm{bi}})$	(0.118) (0.162)***	[31]
[ReO$(\mathrm{L}^{11}_{\mathrm{tri}})(\mathrm{L}^{7}_{\mathrm{bi}})$] (**XXI**)	1.686(5)	2.125(6) N$(\mathrm{L}^{11}_{\mathrm{tri}})$ 2.333(2) S$(\mathrm{L}^{11}_{\mathrm{tri}})$ 2.227(4) N$(\mathrm{L}^{7}_{\mathrm{bi}})$ 2.322(2) S$(\mathrm{L}^{7}_{\mathrm{bi}})$	2.034(5) O$(\mathrm{L}^{11}_{\mathrm{tri}})$	(–0.006)	[32]
[ReO$(\mathrm{L}^{12}_{\mathrm{tri}})(\mathrm{L}^{8}_{\mathrm{bi}})$] (**XXII**)	1.692(4)	2.078(5) N$(\mathrm{L}^{12}_{\mathrm{tri}})$ 2.311(2) S$(\mathrm{L}^{12}_{\mathrm{tri}})$ 2.219(4) N$(\mathrm{L}^{8}_{\mathrm{bi}})$ 2.331(3) S$(\mathrm{L}^{8}_{\mathrm{bi}})$	2.084(4) O$(\mathrm{L}^{12}_{\mathrm{tri}})$	(0.044)	[32]
[ReO$(\mathrm{L}^{13}_{\mathrm{tri}})(\mathrm{L}^{9}_{\mathrm{bi}})$] (**XXIII**)	1.687(6)	2.214(7) N$(\mathrm{L}^{13}_{\mathrm{tri}})$ 2.296(2) S$(\mathrm{L}^{13}_{\mathrm{tri}})$ 2.186(6) N$(\mathrm{L}^{9}_{\mathrm{bi}})$ 2.286(2) S$(\mathrm{L}^{9}_{\mathrm{bi}})$	2.184(6) O$(\mathrm{L}^{13}_{\mathrm{tri}})$	(0.146)	[34]
[ReO$(\mathrm{L}^{13}_{\mathrm{tri}})(\mathrm{L}^{9}_{\mathrm{bi}})$] (**XXIV**)	1.663(5)	2.194(6) N$(\mathrm{L}^{13}_{\mathrm{tri}})$ 2.300(2) S$(\mathrm{L}^{13}_{\mathrm{tri}})$ 2.162(6) N$(\mathrm{L}^{10}_{\mathrm{bi}})$ 2.280(2) S$(\mathrm{L}^{10}_{\mathrm{bi}})$	2.179(4) O$(\mathrm{L}^{13}_{\mathrm{tri}})$	(0.139)	[34]

Table 1. (Contd.)

Complex	Re=O	Re–L_{cis}	Re–L_{trans}	Δ (Δ)**	Ref
$[\mathrm{ReO}(\mathrm{L}^{14}_{\mathrm{tri}})(\mathrm{L}^{11}_{\mathrm{bi}})]$ (**XXV**)	1.670(4)	2.202(5) $\mathrm{N}(\mathrm{L}^{14}_{\mathrm{tri}})$ 2.305(1) $\mathrm{S}(\mathrm{L}^{14}_{\mathrm{tri}})$ 2.158(4) $\mathrm{N}(\mathrm{L}^{11}_{\mathrm{bi}})$ 2.290(1) $\mathrm{S}(\mathrm{L}^{11}_{\mathrm{bi}})$	2.159(4) $\mathrm{O}(\mathrm{L}^{14}_{\mathrm{tri}})$	(0.119)	[36]
$[\mathrm{ReO}(\mathrm{L}^{14}_{\mathrm{tri}})(\mathrm{L}^{11a}_{\mathrm{bi}})]$ (**XXVI**)	1.660	2.200 $\mathrm{N}(\mathrm{L}^{14}_{\mathrm{tri}})$ 2.286 $\mathrm{S}(\mathrm{L}^{14}_{\mathrm{tri}})$ 2.180 $\mathrm{N}(\mathrm{L}^{11a}_{\mathrm{bi}})$ 2.284 $\mathrm{S}(\mathrm{L}^{11a}_{\mathrm{bi}})$	2.150 $\mathrm{O}(\mathrm{L}^{14}_{\mathrm{tri}})$	(0.110)	[36]
$[\mathrm{ReO}(\mathrm{L}^{13}_{\mathrm{tri}})(\mathrm{L}^{12}_{\mathrm{bi}})]$ (**XXVII**)	1.680(6)	2.189(6) $\mathrm{N}(\mathrm{L}^{13}_{\mathrm{tri}})$ 2.305(3) $\mathrm{S}(\mathrm{L}^{13}_{\mathrm{tri}})$ 2.171(7) $\mathrm{N}(\mathrm{L}^{12}_{\mathrm{bi}})$ 2.291(2) $\mathrm{S}(\mathrm{L}^{12}_{\mathrm{bi}})$	2.177(5) $\mathrm{O}(\mathrm{L}^{13}_{\mathrm{tri}})$	(0.137)	[37]
$[\mathrm{ReO}(\mathrm{L}^{15}_{\mathrm{tri}})(\mathrm{L}^{13}_{\mathrm{bi}})]$ (**XXVIII**)	1.664(5)	2.130(5) $\mathrm{N}(\mathrm{L}^{15}_{\mathrm{tri}})$ 2.337(2) $\mathrm{S}(\mathrm{L}^{15}_{\mathrm{tri}})$ 2.162(6) $\mathrm{N}(\mathrm{L}^{13}_{\mathrm{bi}})$ 2.321(2) $\mathrm{S}(\mathrm{L}^{13}_{\mathrm{bi}})$	2.005(5) $\mathrm{O}(\mathrm{L}^{15}_{\mathrm{tri}})$	(–0.035)	[38]
$[\mathrm{ReO}(\mathrm{L}^{16}_{\mathrm{tri}})(\mathrm{L}^{14}_{\mathrm{bi}})] \cdot (\mathrm{Py})$ (**XXIXa**)	1.690(6)	2.049(6) $\mathrm{O}(\mathrm{L}^{16}_{\mathrm{tri}})$ 1.973(6) $\mathrm{N}(\mathrm{L}^{16}_{\mathrm{tri}})$ 2.308(2) $\mathrm{S}(\mathrm{L}^{16}_{\mathrm{tri}})$ 2.146(7) $\mathrm{N}(\mathrm{L}^{14}_{\mathrm{bi}})$	2.267(7) $\mathrm{N}(\mathrm{L}^{14}_{\mathrm{bi}})$	0.121 N_{bi}	[39]
$[\mathrm{ReO}(\mathrm{L}^{16}_{\mathrm{tri}})(\mathrm{L}^{14}_{\mathrm{bi}})] \cdot (\mathrm{imino})$ (**XXIXb**)	1.678(6)	2.048(5) $\mathrm{O}(\mathrm{L}^{16}_{\mathrm{tri}})$ 1.977(6) $\mathrm{N}(\mathrm{L}^{16}_{\mathrm{tri}})$ 2.304(2) $\mathrm{S}(\mathrm{L}^{16}_{\mathrm{tri}})$ 2.180(7) $\mathrm{N}(\mathrm{L}^{14}_{\mathrm{bi}})$	2.261(6) $\mathrm{N}(\mathrm{L}^{14}_{\mathrm{bi}})$	0.081 N_{bi}	[39]
$[\mathrm{ReO}(\mathrm{L}^{16}_{\mathrm{tri}})(\mathrm{L}^{15}_{\mathrm{bi}})]$ (**XXX**)	1.670(5)	2.058(5) $\mathrm{O}(\mathrm{L}^{16}_{\mathrm{tri}})$ 1.967(6) $\mathrm{N}(\mathrm{L}^{16}_{\mathrm{tri}})$ 2.299(2) $\mathrm{S}(\mathrm{L}^{16}_{\mathrm{tri}})$ 2.127(6) $\mathrm{N}(\mathrm{L}^{15}_{\mathrm{bi}})$	2.281(6) $\mathrm{N}(\mathrm{L}^{15}_{\mathrm{bi}})$	0.154 N_{bi}	[39]

Table 1. (Contd.)

Complex	Re=O	Re–L_{cis}	Re–L_{trans}	Δ (Δ)**	Ref
$[ReO(L_{tri}^{17})(L_{bi}^{16})]$ (**XXXI**)	1.702(5)	2.086(4) $O(L_{tri}^{17})$ 1.914(5) $N(L_{tri}^{17})$ 2.295(2) $S(L_{tri}^{17})$ 2.201(5) $N(L_{bi}^{16})$	2.266(5) $N(L_{bi}^{16})$	0.065 N_{bi}	[40]

* L_{tri}^{1} = $OC_{6\,4}CH{=}\ NC_6H_4S$; L_{tri}^{2} = $OC_6H_4CH{=}NN{=}C(SMe)S$; L_{tri}^{3} = $OC({=}O)CH_2NC(Ph)N{=}C(NEt_2)S$; L_{tri}^{4} = OC_6H_2 · *tert*-$Bu_2CH_2N(Me)(CH_2)_2SEt$; L_{tri}^{5} = $OC({=}O)C(NH_2)(CH_2)_2SMe$; L_{tri}^{6} = $O(CH_2)_2SCH_2\{CN(Me)CH)_2N\}$; L_{tri}^{7} = $OC_6H_4NC(Ph)NC(NEt_2)S$; L_{tri}^{8} = $OC({=}O)CH_2NC({=}O)C(Me)S$; L_{tri}^{9} = $OC(Ph){=}NN{=}C(Ph)N{=}C(NEt_2)CS$; L_{tri}^{10} = $OC_6H_5N{=}C(Ph)N{=}C(NEt_2)S$; L_{tri}^{11} = $OC_6H_4C(H){=}NN{=}C(Ph)S$; L_{tri}^{12} = $OC(Ph){=}C(H)C(Me){=}NN{=}C(Ph)S$; L_{tri}^{13} = $OC({=}O)C(NH_2)C(Me_2)S$; L_{tri}^{14} = $OC({=}O)CH(NH_2)CH_2S$; L_{tri}^{15} = $OC_6H_4C{=}NNH{=}C(SMe)S$; L_{tri}^{16} = $OC({=}O)CH_2NC({=}O)CH_2S$; L_{tri}^{17} = $OC({=}O)CH_2N(CH_2)_2S$; L_{bi}^{1} = $OC_6H_4C{=}NC_6H_4S$; L_{bi}^{2} = $OC({=}O)CH_2NH_2$; L_{bi}^{3} = $OCH_2CN(Me)(CH)_2N$; L_{bi}^{4} = $OC_6H_4PPh_2$; L_{bi}^{5} = $O{=}C(Ph)N{=}C(NPh_2)S$; L_{bi}^{6} = $O{=}C(Ph)N{=}C(NC_4OH_4)S$; L_{bi}^{7} = $HOC_6H_4C(H){=}NN{=}C(Ph)S$; L_{bi}^{8} = $O{=}C(Ph)CH_2C(Me){=}NN{=}C(Ph)S$; L_{bi}^{9} = $SC(Me_2)C(COOH)NH_2$; L_{bi}^{10} = $SC(Me_2)C\{C(OOMe)NH_2\}$; L_{bi}^{11} = $SCH_2CH(NH_2)C({=}O)OMe$; L_{bi}^{12} = $S(CH_2)NH_2$; L_{bi}^{13} = $HOC_6H_4C{=}NNH{=}C(SMe)S$; L_{bi}^{m} = $NC_6H_4CH{=}NR$, R = Ph ($m = 14$), $N(CH_2)_3{-}NC_4NH_4{-}C_6H_4(MeO)$ ($m = 15$); L_{bi}^{16} = $(NC_5H_4)_2$.

** By default, the parameters Δ, (Δ) refer to the Re–O bonds; (Δ) = (Re–O_{trans}) – (Re–Re(ST)).

*** (Δ) = {Re–$O(L_{tri}^{m})$ – Re–$O(L_{bi}^{n})$} or {Re–$O(L_{bi}^{n})$ – Re–$O(L_{tri}^{m})$}.

In the complex $[ReO(L_{tri}^{3})Cl(PPh_3)] \cdot 0.25\ MeCN \cdot 0.125H_2O$ (**IV**, Fig. 1), where L_{tri}^{3} is the doubly charged *N*-(((diethylamino)sulfanylmethylene)amino)(phenyl)methylene)glycinato ligand, a thiourea derivative of the α-amino acid, $OC({=}O)CH_2N{=}C(Ph)N{=}C(NEt_2)S$, like in complex **II**, the *trans*-position to the oxo ligand is occupied by chlorine [19]. The Re–Cl_{trans} bond in **III** (2.444 ± 0.001 Å) is elongated due to the *trans*-effect of a multiply bonded oxo ligand to even a greater extent than that in **II** (Δ = 0.089 Å). The structure of **III** has two similar independent molecules. The coordination of L_{tri}^{3} to the metal atom is accompanied by closure of five- and six-membered $ReNC_2O$ and ReSCNCN rings.

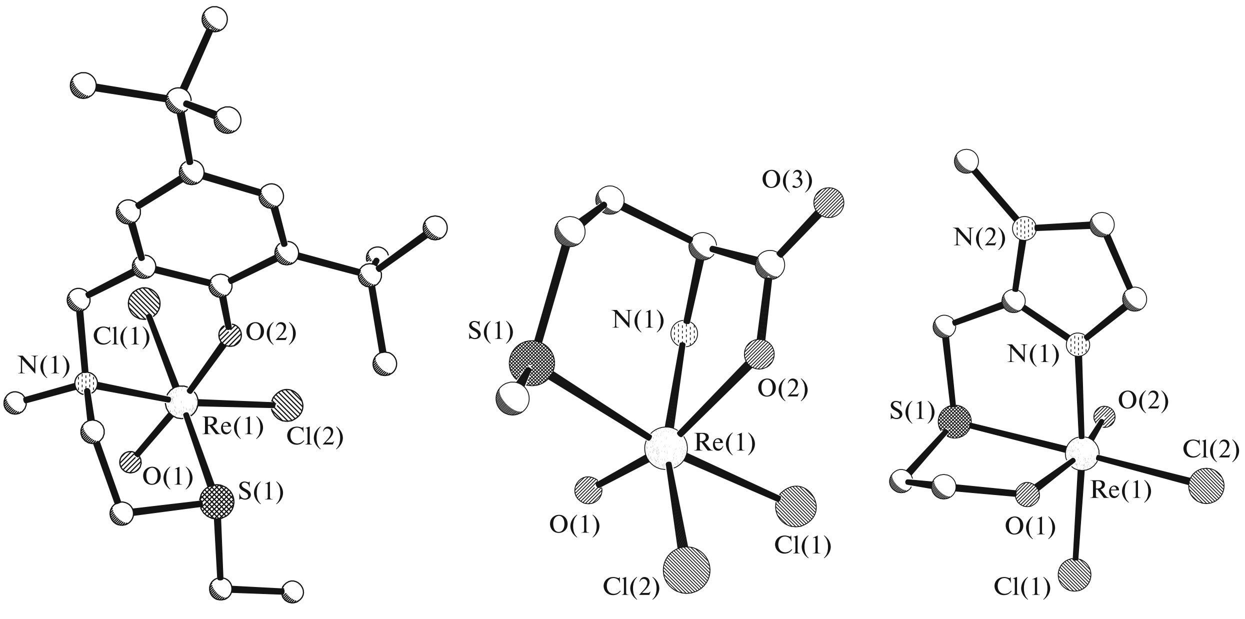
Structure of $[ReO(L_{tri}^{m})(Hal)_2]$ (Hal = Cl, Br). Structures are known for seven complexes corresponding to the title formula. Unlike the four above-described $[ReO(L_{tri}^{m})(L_{mono})_2]$ complexes with two different monodentate ligands, in these compounds, the singly charged $(L_{tri}^{m})^{-}$ ligands have a *fac* (rather than *mer*) geometry the O, N, and S donor atoms being in the *cis*-positions. In all seven complexes, the *trans*-positions relative to O(oxo) are occupied by the $O(L_{tri}^{m})$ atoms.

In compounds **V–IX**, two different metallacycles in the L_{tri}^{m} ligand are fused at the Re–N bonds; those in **X** and **XI** are fused at the Re–S bonds.

In $[ReO(L_{tri}^{4})Cl_2] \cdot 2OC_4H_8$ (**V**, Fig. 2), rhenium coordination of the $(L_{tri}^{4})^{2-}$, ligand, 2,4-di-*tert*-butyl-6-(2-(ethylsulfanyl)ethyl(methyl)(amino)methyl)-phenolato, OC_6H_2-*tert*-Bu-$CH_2N(Me)(CH_2)_2SEt$, is accompanied by closure of five- and six-membered rings, $ReNC_2S$ and $ReNC_3O$ [20]. The first one has an envelope conformation with one C atom being deviated from the ReNCS plane of four atoms by 0.734 Å

.

In four compounds described as $[ReO(L_{tri}^{5})\ (Hal)_2]$, where Hal is Cl (**VI**, monoclinic, Fig. 2) and (**VII**, orthorhombic); Br (**VIII**, 2 : 1 solvate with MeOH, or **IX**, 2 : 1 hydrate with H_2O), the ligand L_{tri}^{5} = methioninato, $OC({=}O)(CN_2)(CH_2)_2SMe$, occurs as two different diastereomers: D,L in **VI**, **VIII**, and **IX** and D in **VII** [21]. In the former case, the *syn*-isomer is formed (the S–C(Me) bond is on the same side as Re=O(oxo)), while in the latter case, there is *anti* isomer (the S–C(Me) bond deviates from the Re=O(oxo) bond). In the D,L isomers, the S_RC_R and S_SC_S chirality is observed for the sulfur atom and cen-



(V) **(VI)** **(X)**

Fig. 2. Structures of: $[\mathrm{ReO}\left(\mathrm{L}^4_{\mathrm{tri}}\right)\mathrm{Cl}_2]$ **(V)**, monoclinic $[\mathrm{ReO}(\mathrm{D,L}\text{-}\mathrm{L}^5_{\mathrm{tri}})\mathrm{Cl}_2]$ **(VI)**, and $[\mathrm{ReO}\left(\mathrm{L}^6_{\mathrm{tri}}\right)\mathrm{Cl}_2)]$ **(X)**.

tral carbon atom of the amino acid, while in the D form, only the S_RC_R enantiomer is present. In all independent molecules of the complexes (three molecules in **VI**, two molecules in each of **VIII** and **IX**, and one molecule in **VII**), the $\mathrm{L}^5_{\mathrm{tri}}$ ligand coordination to rhenium is accompanied by closure of five- and six-membered $\mathrm{ReNC_2J}$ (A) and $\mathrm{ReNC_3S}$ (B) rings at the Re–N bonds. In **VII**, five-membered chelate rings A of the three D molecules have an envelope conformation with a 0.52 Å average deviation of one of the C atoms from the plane through the other four atoms. In all six-membered rings B of D-molecules occurring in the chair conformation, two atoms (Re,C; S,C; or N, C) deviate from the plane of other four atoms by 0.59–1.20 Å to different directions. In all D,L-molecules of complexes **VI**, **VIII**, and **IX**, the configuration of both chiral rings differs from that of the rings in D-molecules of **VII**: half-chair for rings A and boat for ring B (with N atom and one C atom deviating by 0.71–0.86 Å, in the same direction, from the plane of nearly coplanar (within ±0.12–0.20 Å) ReSOC atoms). The parameter Δ_{Re} for complexes **VI**–**IX** is in the range of 0.24–0.30 Å. Note that in all six compounds, two Re–Hal bonds have different lengths, the Re–Hal(1) bond in the *trans*-position to Re–S is regularly longer than the Re–Hal(2) bond in the *trans* position to Re–N: in **VI** and **VII**, Re–Cl(1), 2.361 ± 0.016, 2.378; Re–Cl(2), 2.341 ± 0.003, 2.333 Å; in **VIII** and **IX**, Re–Br(1), 2.509 ± 0.007, 2.507 ± 0.001; Re–Br(2), 2.486 ± 0.005, 2.485 ± 0.004 Å.

In the crystals of two structurally similar complexes, $[\mathrm{ReO}\left(\mathrm{L}^6_{\mathrm{tri}}\right)(\mathrm{Hal})_2]$, where Hal is Cl (**X**, Fig. 2) [22] and Br (**XI**) [23], the $\left(\mathrm{L}^6_{\mathrm{tri}}\right)^-$, [2-(2-oxyethylthiomethyl)-1-methylimidazole ligand, $\mathrm{O(CH_2)_2}$-$\mathrm{SCH_2\{CN(Me)(CH_2)_2N\}}$], is coordinated to the metal, thus closing two five-membered rings, $\mathrm{ReNC_2S}$ and $\mathrm{ReOC_2S}$, through the Re–S bond. The $\mathrm{N_2C_3}$ imidazole rings are planar, which is typical of aromatic systems. The Re–Hal(1) bonds located in the *trans*-positions to Re–N are longer than Re–Hal(2) bonds in the *trans* positions to Re–S (Re–Cl(1), 2.41; Re–Cl(2), 2.37 Å in **X**; Re–Br(1), 2.5324; Re–Br(2), 2.5140 Å in **XI**). In the opinion of the authors [22], this is caused by greater *trans*-effect of the Im ring compared with the S atom. The parameters Δ_{Re} for **X** and **XI** are 0.152 and 0.185 Å. The $\mathrm{Re{-}O1}\left(\mathrm{L}^6_{\mathrm{tri}}\right)$ bonds located in the *trans*-positions to O(oxo) (1.911 and 1.935 Å in **X** and **XI**, respectively) are somewhat longer than the Re–O(ethoxide) bonds (1.880–1.896 Å) [24] and are markedly shorter than the Re–O single bonds (2.00–2.08 Å) [25, 26]. The partial double-bond nature of the $\mathrm{Re{-}O(1)}\left(\mathrm{L}^6_{\mathrm{tri}}\right)$ bonds in **X** and **XI** is confirmed by the size of ReO(1)C angles (129.6° in **X** and 127.6° in **XI**), which exceed the standard value of 120° and rule out intramolecular non-bonding contacts.

STRUCTURES OF $[\mathrm{ReO}(\mathrm{L}^m_{\mathrm{tri}})(\mathrm{L}^n_{\mathrm{bi}})]$ COMPLEXES WITH BIDENTATE CHELATING (O,N; O,P; O,S; N,S; N,N) LIGANDS $\mathrm{L}^n_{\mathrm{bi}}$

Structural features of monooctahedral monooxo $[\mathrm{ReO}(\mathrm{L}^m_{\mathrm{tri}})(\mathrm{L}^n_{\mathrm{bi}})]$ complexes containing a tridentate (O,N,S) bis(chelating) $\mathrm{L}^m_{\mathrm{tri}}$ ligand and a bidentate (X,Y; X = O, N; Y = N, P, S) chelating $\mathrm{L}^n_{\mathrm{bi}}$ ligand are considered. The *trans*-positions relative to the oxo groups are occupied by the anionic oxygen atoms of $\mathrm{L}^m_{\mathrm{tri}}$ or $\mathrm{L}^n_{\mathrm{bi}}$. All complexes have a typical 3 + 2 coordination based on ReO^{3+}.

Structures of $[\mathrm{ReO}(\mathrm{L}^m_{\mathrm{tri}})(\mathrm{L}^n_{\mathrm{bi}})]$ complexes with bidentate chelating (O,N) ligands $(\mathrm{L}^n_{\mathrm{bi}})$. Structures of three complexes of the indicated composition are known. The tridentate bis(chelating) $\mathrm{L}^m_{\mathrm{tri}}$ ligands are doubly charged (the O and S atoms are deprotonated), while the bidentate ligands are singly charged (the O atom is deprotonated).

Two complexes, $[\mathrm{ReO}(\mathrm{L}^1_{\mathrm{tri}})(\mathrm{L}^1_{\mathrm{bi}})]$ (**XII**) [16] and $[\mathrm{ReO}(\mathrm{L}^7_{\mathrm{tri}})(\mathrm{L}^2_{\mathrm{bi}})]$ (**XIII**) [27], have *mer*-configuration, which the *trans*-positions to O(oxo) being occupied by oxygens of bidentate chelating (O,N) ligands rather than tridentate (O,N,S) bis(chelating) $\mathrm{L}^m_{\mathrm{tri}}$, ligands (Fig. 3). In complex **XII**, the bidentate chelating $\mathrm{L}^1_{\mathrm{bi}}$, ligand, $\mathrm{OC_6H_4C{=}NC_6H_4S}$, exists in the oxidized 2-(2-hydroxyphenyl)benzothiazole form with sp^2-hybridized N(3) atom. The Re–O(3)$(\mathrm{L}^1_{\mathrm{bi}})_{trans}$ bond in this complex (1.989 Å) is markedly (by 0.087 Å) shorter than the equatorial Re–O(2)$(\mathrm{L}^1_{\mathrm{tri}})_{cis}$ bond, while the Re–N(3)$(\mathrm{L}^1_{\mathrm{bi}})$, bond is, conversely, 0.090 Å longer than Re–N(1)$(\mathrm{L}^1_{\mathrm{tri}})$ (two Re–N bonds are located in *trans*-positions relative to each other). In **XIII** ($\mathrm{L}^7_{\mathrm{tri}}$ = *N'*-(diethylcarbamothioyl)-*N*-(2-oxyphenylbenzylcarboximidate, $\mathrm{OC_6H_4NC(Ph)\text{-}NC(NEt_2)S}$; $\mathrm{L}^2_{\mathrm{bi}}$ = glycinato, $\mathrm{OC({=}O)CH_2NH_2}$), like in **XII**, the Re–N(4)$(\mathrm{L}^2_{\mathrm{bi}})$ bond is longer (by 0.200 Å) than Re–N(2)$(\mathrm{L}^7_{\mathrm{tri}})$ (2.189 and 1.989 Å), but the Re–O(3) $(\mathrm{L}^2_{\mathrm{bi}})_{trans}$ bond (2.120 Å) is, as usual, longer (by 0.091 Å) rather than shorter than Re–O(4)$(\mathrm{L}^1_{\mathrm{tri}})_{cis}$ (2.029 Å). In both complexes, the coordination of the $\mathrm{L}^m_{\mathrm{tri}}$ ligands to rhenium gives rise to five- and six-membered rings, $\mathrm{ReNC_2S}$ and $\mathrm{ReNC_3O}$ in **XII** and $\mathrm{ReNC_2O}$ and ReNCNCS in **XIII**, fused at the R–N bond.

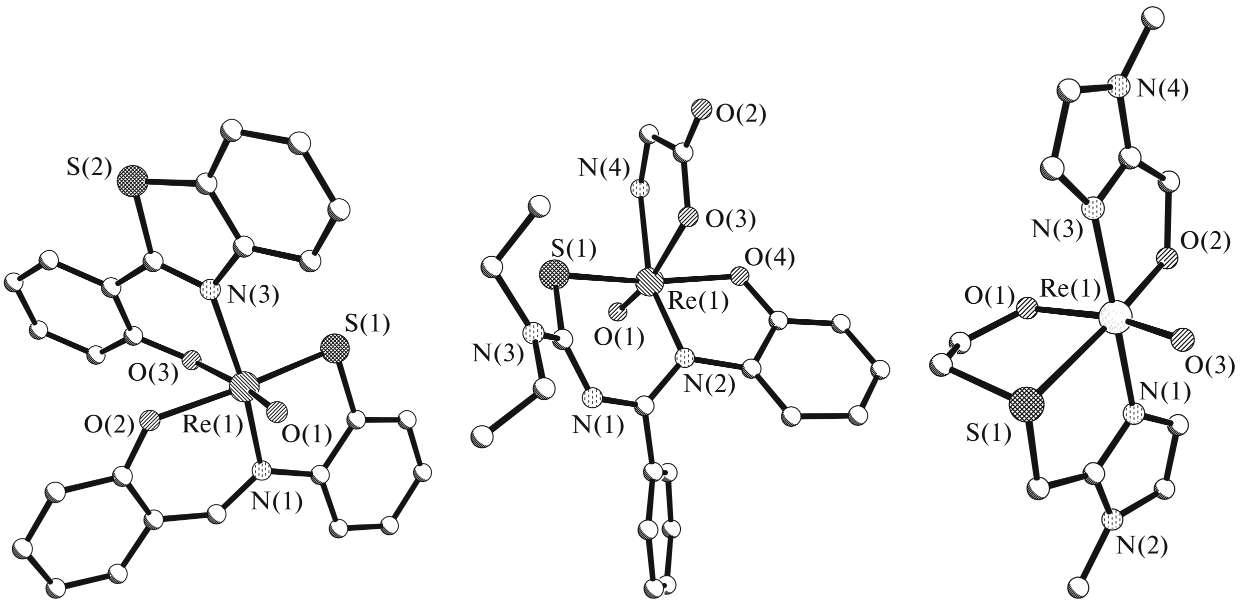
In $[\mathrm{ReO}(\mathrm{L}^6_{\mathrm{tri}})(\mathrm{L}^3_{\mathrm{bi}})]\mathrm{Cl}\cdot 2\mathrm{H_2O}$ (**XIV**, Fig. 3), where $(\mathrm{L}^3_{\mathrm{bi}})^-$ is 2-(oxymethyl)-1-(methylimidazole), $\mathrm{OCH_2\text{-}CN(Me)(CH)_2N}$, unlike **XII** and **XIII**, the facial *fac* (rather than the meridional, *mer*) geometry is present; the five-membered $\mathrm{ReSC_2O}$ and $\mathrm{ReSC_2N}$ chelate rings in $\mathrm{L}^6_{\mathrm{tri}}$ are fused at the Re–S (instead of Re–N) bond, and the $\mathrm{L}^6_{\mathrm{tri}}$ ligand is singly rather than doubly charged [23]; Δ = 0.170 Å. The Im ring is not strictly planar; the C–N(4)–C–C and N(3)–C–C–N(2) torsion angles are 0.1° and –0.6°, respectively. The N(3)–C–N(4) group is delocalized, the N–C bond length being 1.337 ± 0.002 Å. The authors of [23] noted the unusual fact that the Re–O(1)$_{trans}$ bond (1.946 Å) is not longer, but somewhat shorter (by 0.014 Å) than Re–O(2)$_{cis}$ (1.960 Å).

Structure of the $[\mathrm{ReO}(\mathrm{L}^m_{\mathrm{tri}})(\mathrm{L}^4_{\mathrm{bi}})]$ complexes with bidentate chelating (O,P) ligands. In both compounds of the title type, the $\mathrm{L}^m_{\mathrm{tri}}$ ligands form five-membered $\mathrm{ReNC_2S}$ rings fused at the Re–N bonds and either five-membered $\mathrm{ReNC_2O}$ chelate ring (in **XV**) or six-membered $\mathrm{ReNC_3O}$ ring (in **XVI**). The $\mathrm{L}^8_{\mathrm{tri}}$ ligand has the *fac*-geometry.

In $\{\mathrm{N(CH_2Et)_4}\}[\mathrm{ReO}(\mathrm{L}^8_{\mathrm{tri}})(\mathrm{L}^4_{\mathrm{bi}})]$ (**XV**, Fig. 4), where $(\mathrm{L}^8_{\mathrm{tri}})^{3-}$ is thiopropyne, $\mathrm{OC({=}O)CH_2N(Me)S}$, in the triply charged $\mathrm{L}^8_{\mathrm{tri}}$ ligand of the anionic complex, the Re–O(3)$(\mathrm{L}^8_{\mathrm{tri}})$ bond (2.126 Å) located in the *trans*-position to Re=O(1) (0.050 Å) is longer than Re–O(2)$(\mathrm{L}^4_{\mathrm{bi}})$ (2.076 Å) [28]; Δ_{Re} = 0.30 Å. All three five-membered metallacycles have an envelope conformation, with the Re ($\mathrm{RePC_2O}$), S ($\mathrm{ReSC_2O}$), and N ($\mathrm{ReSC_2N}$) atoms deviating from the tetraatomic planes by 0.35, 0.46, and 0.06 Å. The dihedral angle between the O(2)NSP (equatorial) and O(2)CCP planes is 75.7°.

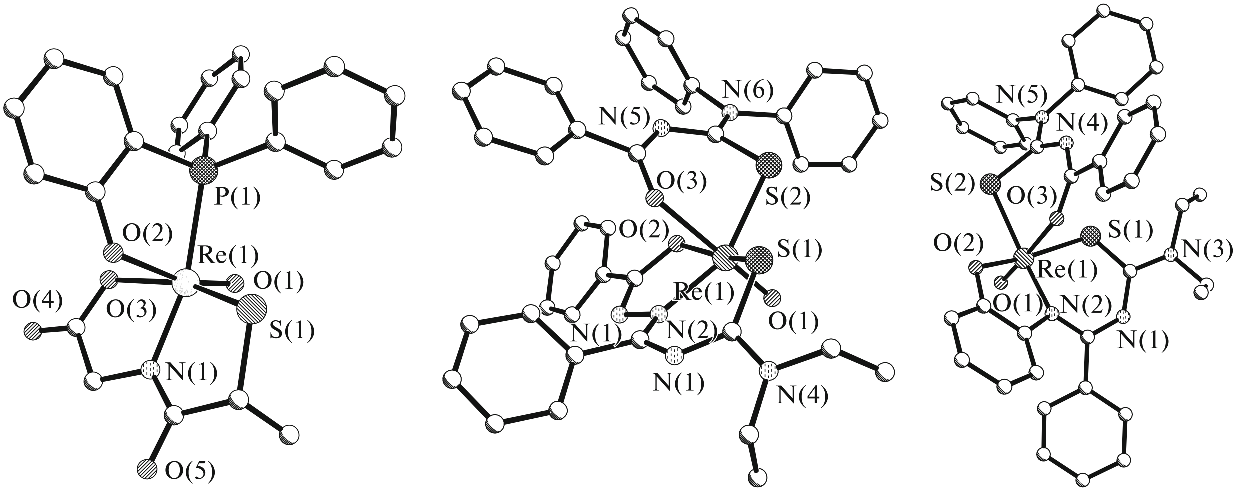
In the $[\mathrm{Re}(\mathrm{L}^1_{\mathrm{tri}})(\mathrm{L}^4_{\mathrm{bi}})]$ complex (**XVI**), the *trans*-position to the oxo ligand is occupied by O atom of the bidentate chelating singly charged $\mathrm{L}^4_{\mathrm{bi}}$, ligand, with the Re–O bond to this atom (2.047 Å) being somewhat shorter (by 0.047 Å) rather than longer than the Re–O$(\mathrm{L}^1_{\mathrm{tri}})_{cis}$ bond (2.094 Å) to oxygen of the doubly charged Schiff base [29].

Structure of the $[\mathrm{ReO}(\mathrm{L}^m_{\mathrm{tri}})(\mathrm{L}^n_{\mathrm{bi}})]$ complexes with bidentate chelating (O,S) ligands. The structures are known for four title complexes; they are similar and contain tridentate benzamidine type $(\mathrm{L}^{9,10}_{\mathrm{tri}})$ ligands



(XII) **(XIII)** **(XIV)**

Fig. 3. Structures of: $[\mathrm{ReO}(\mathrm{L}^1_{\mathrm{tri}})(\mathrm{L}^1_{\mathrm{bi}})]$ **(XII)**, $[\mathrm{ReO}(\mathrm{L}^7_{\mathrm{tri}})(\mathrm{L}^2_{\mathrm{bi}})]$ **(XIII)**, and $[\mathrm{ReO}(\mathrm{L}^6_{\mathrm{tri}})(\mathrm{L}^3_{\mathrm{bi}})]$ **(XIV)**.



(XV) **(XVII)** **(XIX)**

Fig. 4. Structures of: $[\mathrm{ReO}(\mathrm{L}^8_{\mathrm{tri}})(\mathrm{L}^4_{\mathrm{bi}})]^-$ **(XV)**, $[\mathrm{ReO}(\mathrm{L}^9_{\mathrm{tri}})(\mathrm{L}^5_{\mathrm{bi}})]$ **(XVII)**, and $[\mathrm{ReO}(\mathrm{L}^{10}_{\mathrm{tri}})(\mathrm{L}^5_{\mathrm{bi}})]$ **(XIX)**.

and bidentate benzoylthiourea type $(\mathrm{L}^{5,6}_{\mathrm{bi}})$ ligands. In all cases, the $\mathrm{L}^m_{\mathrm{tri}}$ ligands have *mer*-geometry (the O and S atoms located opposite to each other), while the bicyclic system conjugated at the Re–N bond contains six-membered ReNCNCS rings and either five-membered $\mathrm{ReN_2CO}$ ring (**XVII**, **XVIII**) or $\mathrm{ReNC_2O}$ ring (**XIX**, **XX**). The *trans*-position to the oxo ligands is occupied by the O atoms of bidentate chelating $\mathrm{L}^{5,6}_{\mathrm{bi}}$ ligands.

Two compounds with a similar composition $[\mathrm{ReO}(\mathrm{L}^9_{\mathrm{tri}})(\mathrm{L}^n_{\mathrm{bi}})]$ differ only by the substituents R_1, R_2 of the $\mathrm{L}^n_{\mathrm{bi}}$, ligands $\mathrm{SC(NR_1R_2)NC(Ph)O}$: $R_1 = R_2 = \mathrm{Ph}$ (**XVII**, $n = 5$, Fig. 4) and $\mathrm{NR_1R_2}$ = morpholine (**XVIII**, $n = 6$) [30]. All three atoms (O, N, S) of the $(\mathrm{L}^9_{\mathrm{tri}})^{2-}$ ligand, *N*-[((diethylimino)(sulfido)(methylidene)amino)(phenyl)methylidene]benzenecarbohydrazonate, $\mathrm{SC(NEt_2){=}NC(Ph){=}NN{=}C(Ph)O}$, are located in the equatorial plane of the $\mathrm{ReO_3NS_2}$ octahedron, like the $\mathrm{S(2)}\left(\mathrm{L}^{n}_{\mathrm{bi}}\right)$, atoms, in the *trans* position to $\mathrm{N(2)}\left(\mathrm{L}^{9}_{\mathrm{tri}}\right)$. The parameters Δ_{Re} are 0.410 and 0.381 Å in **XVII** and **XVIII**, respectively. The $\mathrm{Re{-}O(3)}\left(\mathrm{L}^{n}_{\mathrm{bi}}\right)$ bonds in **XVII**, **XVIII** (2.219, 2.249 Å) are among the longest found in the metallacycles of Re(V) complexes. The $\mathrm{Re{-}S(1)}\left(\mathrm{L}^{9}_{\mathrm{tri}}\right)$ bonds in these two structures (2.313, 2.327 Å) are noticeably (by 0.078, 0.076 Å) shorter than $\mathrm{Re{-}S(2)}\left(\mathrm{L}^{n}_{\mathrm{bi}}\right)$ (2.391, 2.403 Å). The five- and six-membered $\mathrm{ReN_2CO}$ and ReNCNCS rings formed by the $\mathrm{L}^{9}_{\mathrm{tri}}$, ligands are nearly planar in both structures. The six-membered ReOCNCS chelate rings with the $\mathrm{L}^{n}_{\mathrm{bi}}$ ligands have a highly distorted sofa conformation with rhenium atoms deviating from the planes of other five ring atoms by 1.448 and 1.483 Å in **XVII** and **XVIII**, respectively. The authors of [30] noted a substantial delocalization of the π-electron density over each of the six-membered rings, which is manifested as averaging of all N–C bonds, which are intermediate between a single and a double bond (1.31–1.36 Å) in both complexes.

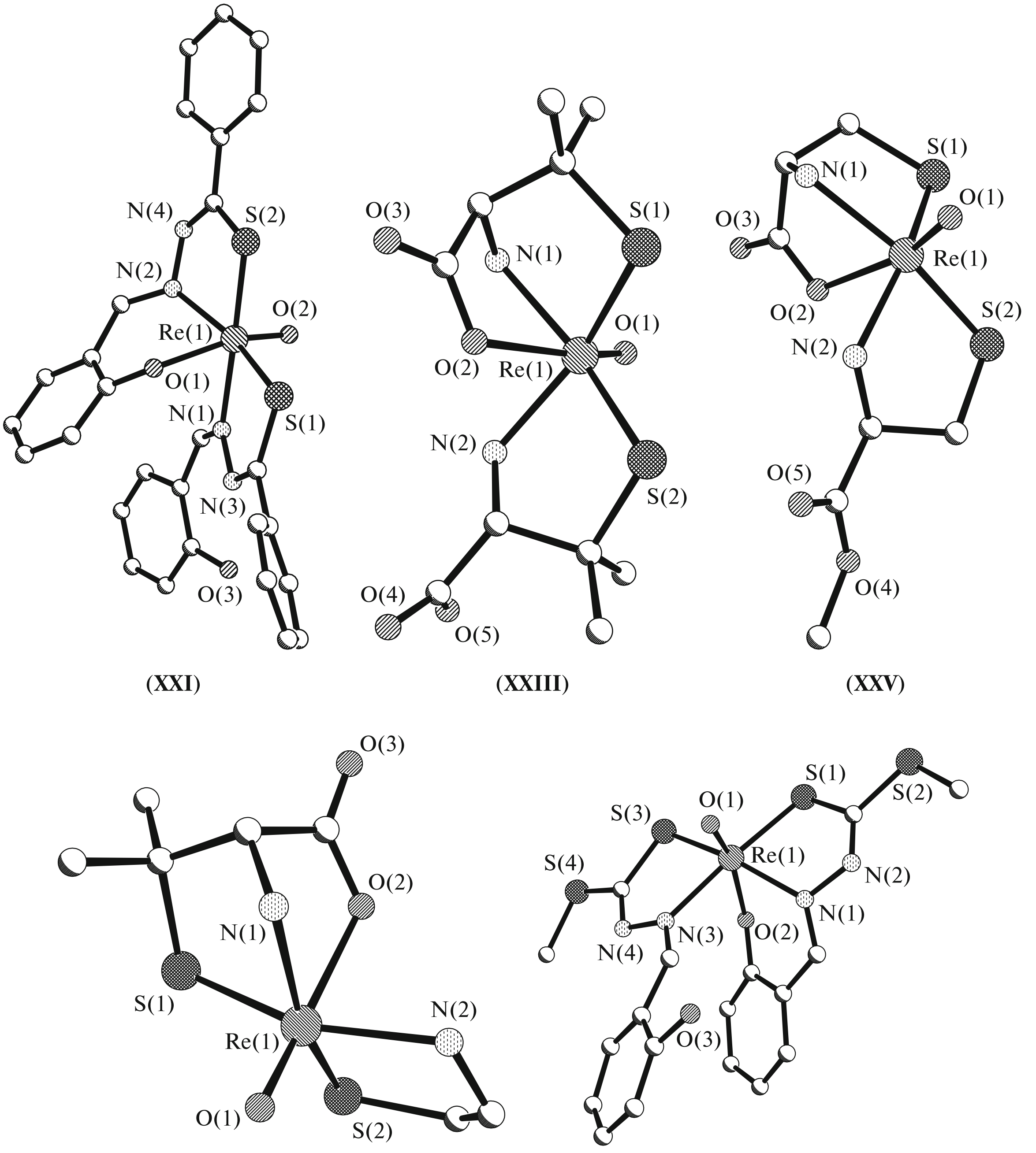
Two $\left[\mathrm{ReO}\left(\mathrm{L}^{10}_{\mathrm{tri}}\right)\left(\mathrm{L}^{n}_{\mathrm{bi}}\right)\right]$ complexes, like the two previous ones, have similar composition: $n = 5$ (**XIX**, Fig. 4) and $n = 6$ (**XX**) [31]. The structure is similar to that of **XVII**, **XVIII**: (a) all three donor atoms of $\left(\mathrm{L}^{10}_{\mathrm{tri}}\right)^{2-}$, $\mathrm{SC(NEt_2){=}NC(Ph){=}NC_6H_4O}$, are located in the equatorial plane of the $\mathrm{ReO_3NS_2}$ octahedron, like the $\mathrm{S(2)}\left(\mathrm{L}^{n}_{\mathrm{bi}}\right)$, atoms, in the *trans* position to $\mathrm{N2}\left(\mathrm{L}^{10}_{\mathrm{tri}}\right)$; (b) $\mathrm{Re{-}O(3)}\left(\mathrm{L}^{n}_{\mathrm{bi}}\right)$ bonds in **XIX**, **XX** (2.196, 2.158 Å) are relatively long; (c) $\mathrm{Re{-}S(1)}\left(\mathrm{L}^{10}_{\mathrm{tri}}\right)$ bonds in these two structures (2.360, 2.354 Å) are shorter by 0.039, 0.054 Å than $\mathrm{Re{-}S(2)}\left(\mathrm{L}^{n}_{\mathrm{bi}}\right)$ (2.399, 2.408 Å). The five- and six-membered $\mathrm{ReNC_2O}$ and ReNCNCS rings formed by $\mathrm{L}^{10}_{\mathrm{tri}}$, are nearly planar in both structures. The six-membered ReOCNCS chelating rings with the $\mathrm{L}^{n}_{\mathrm{bi}}$ ligands in **XIX**, **XX**, like in **XVII**, **XVIII**, have a highly distorted sofa conformation with rhenium atoms deviating from the planes of the five roughly coplanar (±0.175 and 0.097 Å) atoms of the rings by 1.157 and 1.093 Å in **XIX** and **XX**, respectively.

Structures of $\left[\mathrm{ReO}\left(\mathrm{L}^{m}_{\mathrm{tri}}\right)\left(\mathrm{L}^{n}_{\mathrm{bi}}\right)\right]$ complexes with bidentate chelating (N,S) ligands. Crystal structures are known for nine title complexes. In these compounds, the *trans*-positions relative to oxo ligands are occupied by O atoms of $\mathrm{L}^{m}_{\mathrm{tri}}$. In all nine complexes, the tridentate bis(chelating) $\mathrm{L}^{m}_{\mathrm{tri}}$ ligand has the *fac*-geometry: the O, S, N atoms are located in the *cis*-positions relative to each other on the common octahedron face. In all compounds, two metallacycles are connected at the Re–N bonds, while N atoms, like S atoms, are arranged in pairs in the *cis*-positions. In all nine complexes, the $\mathrm{L}^{m}_{\mathrm{tri}}$ ligands are doubly charged, while $\mathrm{L}^{n}_{\mathrm{bi}}$ are singly charged.

Two complexes of a similar composition, $\left[\mathrm{ReO}\left(\mathrm{L}^{m}_{\mathrm{tri}}\right)\left(\mathrm{L}^{n}_{\mathrm{bi}}\right)\right]$, where $\mathrm{L}^{11}_{\mathrm{tri}}$ is salicylaldehyde-thiobenzoylhydrazonato, $\mathrm{OC_6H_4C(H){=}NN{=}C(Ph)S}$ (**XXI**, $m = 11$, Fig. 5) and $\mathrm{L}^{12}_{\mathrm{tri}}$ is benzoylacetone-thiobenzoylhydrazonato, $\mathrm{OC(Ph){=}C(H)C(Me){=}NN{=}C(Ph)S}$ (**XXII**, $m = 12$), contain five- and six-membered ReNNCS and $\mathrm{ReOC_3N}$ rings fused at the Re–N bonds in the $\mathrm{L}^{m}_{\mathrm{tri}}$ ligands [32]. In the $\mathrm{HL}^{n}_{\mathrm{bi}}$ ligands ($\mathrm{HOC_6H_4C(H){=}NN{=}C(Ph)S^-}$; $m = 7$ in **XXI** and $\mathrm{O{=}C(Ph)CH_2C(Me){=}NN{=}C(Ph)S^-}$; $m = 8$ in **XXII**), similar to $\mathrm{L}^{m}_{\mathrm{tri}}$, five-membered chelate rings, $\mathrm{ReNC_2S}$, are formed. In **XXI**, the terminal O(3)H group forms an intramolecular hydrogen bond with the $\mathrm{N}\left(\mathrm{L}^{7}_{\mathrm{bi}}\right)$ atom (O···N, 2.60; H···N, 1.47 Å; NHO, 178°). In both compounds, the Re–S bonds to the sulfur atoms of $\mathrm{L}^{m}_{\mathrm{tri}}$, $\mathrm{L}^{n}_{\mathrm{bi}}$ are similar in length, while the $\mathrm{R{-}N}\left(\mathrm{L}^{m}_{\mathrm{tri}}\right)$ bonds are markedly shorter (by 0.102 and 0.141 Å in the two structures) than $\mathrm{L}^{n}_{\mathrm{bi}}$; this has been attributed [32] to higher steric strain in the two fused metallacycles of the tridentate bis(chelate) $\mathrm{L}^{m}_{\mathrm{tri}}$ ligand. The structures of both compounds are similar to that of analogous $\mathrm{TcO^{3+}}$ complexes [33].

In five complexes, the $\mathrm{L}^{m}_{\mathrm{tri}}$ ligands, when coordinated to Re atoms, close two five-membered metallacycles differing in composition at the Re–N bond. In the four of these compounds (**XXIII**–**XXVI**), these are $\mathrm{ReNC_2S}$ and $\mathrm{ReNC_2O}$ chelate rings.

Two $\left[\mathrm{ReO}\left(\mathrm{L}^{13}_{\mathrm{tri}}\right)\left(\mathrm{L}^{n}_{\mathrm{bi}}\right)\right]$ complexes, where $\left(\mathrm{L}^{13}_{\mathrm{tri}}\right)^{2-}$ is the D-penicillaminato, $\mathrm{SC(Me_2)CH(COO)NH_2}$, have fairly similar composition, crystallize in orthorhombic space group $P2_12_12_1$, $Z = 4$, and slightly differ in the $\left(\mathrm{L}^{n}_{\mathrm{bi}}\right)^{-}$ ligands containing, unlike $\mathrm{L}^{13}_{\mathrm{tri}}$, open-chain protonated COOR branches (R = H (**XXIII**, Fig. 5) or R = Me (**XXIV**)) [34]. In these complexes, as in **XXII**, the $\mathrm{Re{-}O}_{trans}$ bonds are highly elongated (up to 2.177–2.194 Å), because of the *trans*-effect of the multiply bonded O(oxo) ligand. Unlike the two preceding cases **XXI** and **XXII**, in the compounds considered in this chapter, two Re–N bonds in the bi- and



(XXI) **(XXIII)** **(XXV)**

(XXVII) **(XXVIII)**

Fig. 5. Structures of: [ReO$\left(\mathrm{L}^{13}_{\mathrm{tri}}\right)\left(\mathrm{L}^{7}_{\mathrm{bi}}\right)$] (**XXI**), [ReO$\left(\mathrm{L}^{13}_{\mathrm{tri}}\right)\left(\mathrm{L}^{9}_{\mathrm{bi}}\right)$] (**XXIII**), [ReO$\left(\mathrm{L}^{14}_{\mathrm{tri}}\right)\left(\mathrm{L}^{11}_{\mathrm{bi}}\right)$] (**XXV**), [ReO$\left(\mathrm{L}^{13}_{\mathrm{tri}}\right)\left(\mathrm{L}^{12}_{\mathrm{bi}}\right)$] (**XXVII**), and [ReO$\left(\mathrm{L}^{15}_{\mathrm{tri}}\right)\left(\mathrm{L}^{13}_{\mathrm{bi}}\right)$] (**XXVIII**).

tridentate rings, as well as the pairs of Re–S distances, have comparable lengths. The structure of compound **XXIII** is comparable with the structure of the analogous Tc^{5+} complex [35].

In two compounds, [ReO$\left(\mathrm{L}^{14}_{\mathrm{tri}}\right)\left(\mathrm{L}^{n}_{\mathrm{bi}}\right)$] (**XXV**, $n = 11$, Fig. 5) [36] and (**XXVI**, $n = 11a$) [36], the $\left(\mathrm{L}^{14}_{\mathrm{tri}}\right)^{2-}$ ligand, penicillamino, $\mathrm{SCH_2(Me)CH\text{-}(COO)NH_2}$, resembles in composition the $\mathrm{L}^{11a}_{\mathrm{bi}}$ ligand, while in $\mathrm{L}^{11}_{\mathrm{bi}}$ = $\mathrm{SCH_2C(NH_2)\{C(=O)OMe\}}$, the terminal O atom is linked to the Me group. The Re–O$\left(\mathrm{L}^{14}_{\mathrm{tri}}\right)$ bond in these two complexes, like in the above three complexes, is markedly elongated (up to 2.159 and 2.150 Å), because of the *trans*-effect of the multiply bonded oxo ligand, and the Re–N$\left(L^{14}_{\text{tri}}\right)$ bonds (2.202 and 2.200 Å) are somewhat longer than Re–N$\left(L^{m}_{\text{bi}}\right)$ (2.158 and 2.180 Å), with the two Re–S bond lengths in different rings being virtually equal (see Table 1).

In the case of [ReO$\left(L^{13}_{\text{tri}}\right)\left(L^{12}_{\text{bi}}\right)$] (**XXVII**, Fig. 5) with L^{13}_{tri} and L^{12}_{bi} = 2-aminoethanethiolato, $S(CH_2)_2NH_2$, the Re–N and Re–S pairs of bonds have comparable lengths, while the Re–O$\left(L^{13}_{\text{tri}}\right)_{trans}$ bond (2.177 Å), as in the three above structures, is markedly elongated because of the *trans*-effect of the multiply bonded oxo ligand [37]. The parameter Δ_{Re} = 0.40 Å.

In [ReO$\left(L^{15}_{\text{tri}}\right)\left(L^{13}_{\text{bi}}\right)$] (**XXVIII**, Fig. 5), the ligand L^{15}_{tri} = 5-methyl-β-*N*-(2-hydroxyphenyl)methylidenedithiocarbazato, $OC_6H_4C{=}NNH{=}C(SMe)S$, forms five- and six-membered ReN_2CS and $ReNC_3O$ rings fused at the Re–N bond [38]. The second (bidentate) ligand, Schiff base, has a composition similar to that of the tridentate $\left(L^{15}_{\text{tri}}\right)^{2-}$ ligand: $\left(L^{13}_{\text{bi}}\right)^{-} = \left(HL^{15}_{\text{tri}}\right)^{-}$ = $HOC_6H_4C{=}NNH{=}C(SMe)S$, but differs from the latter by the protonated oxygen atom and open Re–O bond; Δ_{Re} = 0.128 Å. The OReO angle is reduced to 158.0°.

Structure of the [ReO$\left(L^{m}_{\text{tri}}\right)\left(L^{n}_{\text{bi}}\right)$] complexes with bidentate chelating (N,N) ligands. Crystal structures are known for four title complexes. In all of these structures, (a) the L^{m}_{tri} ligands are coordinated to the metal atoms in the meridional (*mer*) fashion; (b) *trans*-positions to the oxo ligands are occupied by N$\left(L^{m}_{\text{bi}}\right)$ (c) coordination of two chelating ligands to Re is accompanied by closure of three five-membered metallacycles: $ReNC_2S$ (A) and $ReNC_2O$ (B), fused at the Re–N $\left(L^{n}_{\text{tri}}\right)$ bond, and $ReNC_2N$ $\left(L^{m}_{\text{bi}}\right)$ (C).

The monoclinic structure of [ReO$\left(L^{16}_{\text{tri}}\right)\left(L^{14}_{\text{bi}}\right)$] (**XXIX**) ($L^{16}_{\text{tri}}$ = *N*-(2-mercaptoacetyl)glycinato, $OC({=}O)CH_2NC({=}O)CH_2S$; L^{14}_{bi} = *N*-phenylpyridin-2-ylaldemine, $N(C_6(H_4)CH_2{=}NPh)$ (space group $P2_1/n$, $Z = 8$) contains two independent molecules, geometric isomers (**a** and **b**) [39]. The *trans*-position relative to the oxo ligand is occupied by the N(Py)$\left(L^{14}_{\text{bi}}\right)$ atom in isomer **XXIXa** and by the N(imino) atom in **XXIXb** $\left(L^{14}_{\text{bi}}\right)$.

The [ReO$\left(L^{16}_{\text{tri}}\right)\left(L^{15}_{\text{bi}}\right)$] complex (**XXX**, Fig. 6), which differs from **XXIX** by the substituent at one nitrogen atom (L^{15}_{bi} = *N*-{3-[4-(2-methoxyphenyl)piperazin-1-yl]propyl}piridin-2-ylaldimine, $N(C_6(H_4)CH_2{=}NCH{=}N(CH_2)_3\text{-}NC_4NH_4\text{-}C_6H_4(MeO))$, exists as isomer **a** (with the N(Py)$\left(L^{14}_{\text{bi}}\right)$ atom in the *trans*-position to O(oxo)) [39]. The parameters Δ_{Re} in **XXIXa**, **XXIXb**, and **XXX** are 0.36, 0.37, and 038 Å, respectively. In all three molecules, two five-membered rings (B and C) are planar, while the third one (A) has an envelope conformation with the sulfur atom as the flap deviating from the other four coplanar atoms by 0.64, 0.54, and 0.26 Å in **XXIXa**, **XXIXb**, and **XXX**, respectively.

The structure of [ReO$\left(L^{17}_{\text{tri}}\right)\left(L^{16}_{\text{bi}}\right)$] · H_2O (**XXXI**, Fig. 6), where L^{17}_{tri} is 2-mercaptoethyl-N-glycinato, $OC({=}O)CH_2N(CH_2)_2S$; L^{16}_{bi} = Bipy, $(NC_5H_4)_2$, is similar to the structures of **XXIX** and **XXX** [40]; Δ_{Re} = 0.33 Å. Two complex molecules are hydrogen-bonded, via the solvation water molecule, to the terminal carboxylate oxygen atoms of L^{17}_{tri}: (H···O, 1.54 and 1.64; O···O, 2.787 and 2.820 Å; OHO, 158° and 164°). In all of the four above-described molecules, the Re–N$\left(L^{16}_{\text{bi}}\right)_{trans}$ bonds are markedly (by 0.065–0.154 Å) longer than the Re–N$\left(L^{16}_{\text{bi}}\right)_{cis}$ bonds because of the *trans*-effect of the multiply bonded oxo ligand. However, the Re–N(Py, imino) $\left(L^{16}_{\text{bi}}\right)_{cis}$ bonds are substantially (by 0.160–0.287 Å) longer than Re–N(amino) $\left(L^{17}_{\text{bi}}\right)_{cis}$ (see Table 1).

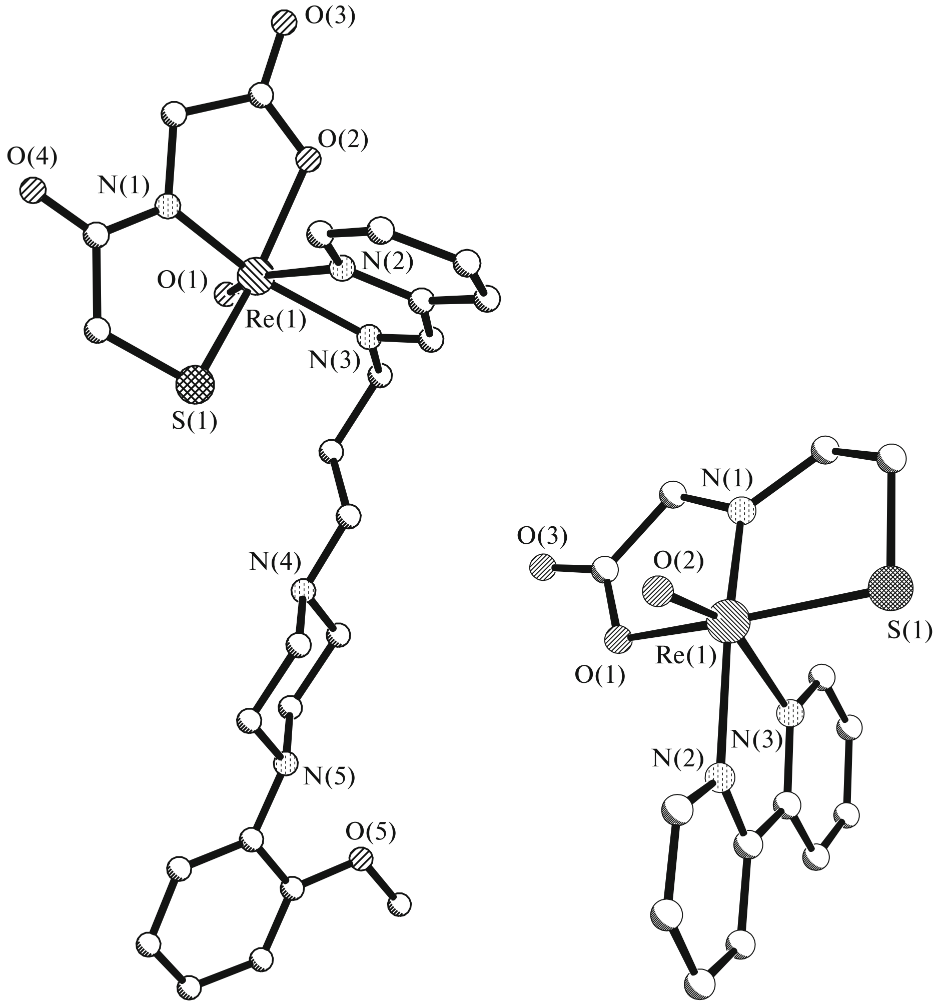
STRUCTURAL FEATURES OF MONOMERIC OCTAHEDRAL RHENIUM(V) MONOOXO COMPLEXES WITH TRIDENTATE CHELATING (O, N, S) LIGANDS

Table 2 presents the average values of the key geometric parameters for **I**–**XXXI**. Two specific structural features of octahedral monooxo complexes of Group 5–7 metals (including rhenium) are noteworthy.

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

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

The second rule holds for 12 compounds considered in this review (see Table 2). In these complexes, the Re–O$\left(L^{m}_{\text{tri}}\right)$ (2.126–2.184), Re–O$\left(L^{n}_{\text{bi}}\right)$ (2.120–2.249), and Re–O($OPPh_3$) (2.245 Å) bonds are elon-



(XXX) **(XXXI)**

Fig. 6. Structures of: $[\mathrm{ReO}\left(\mathrm{L}^{16}_{\mathrm{tri}}\right)\left(\mathrm{L}^{15}_{\mathrm{bi}}\right)]$ (**XXX**) and $[\mathrm{ReO}\left(\mathrm{L}^{17}_{\mathrm{tri}}\right)\left(\mathrm{L}^{16}_{\mathrm{bi}}\right)]$ (**XXXI**).

gated to different extents $((\Delta)\mathrm{Re}-\left(\mathrm{L}^{m}_{\mathrm{tri}}\right)$ 0.080–0.209 Å) (Table 2) in comparison with the Re–O(ST) bond (2.04 Å) [4] because of the *trans*-effect of the multiply bonded oxo ligand.

For 14 complexes considered in the review, neither of the above rules holds. The *trans*-positions to O(oxo) are occupied by anionic rather than neutral oxygen atoms of the $\mathrm{L}_{\mathrm{tri}}$ and L_{bi} ligands, while in one case, by O(OMe). The $\mathrm{Re{-}O(L_{tri})}_{trans}$ (1.911–2.084), $\mathrm{Re{-}O(L_{bi})}_{trans}$ (1.989 and 2.047), and Re–O(OMe) (1.904 Å) bonds ((Δ)Re–O(Lig) = –0.136...+0.044 Å) are commensurable in their length with the $\mathrm{Re{-}O(Lig)}_{cis}$ bonds (1.934–2.042 Å)(rather than longer than these bonds due to the *trans*-effect). This fact seemingly contradicts the "self-consistency" rule [2]. However, in reality, the Re–O(Lig) bonds in *trans*-positions relative to the oxo ligands in these 14 complexes can be considered as having a higher order, as they are markedly shorter than Re–O(ST) (2.04 Å) [4]. Hence, these complexes can be classified as pseudo-dioxo complexes containing two multiply bonded ligands (O(oxo) and $\mathrm{O(L)}_{trans}$). Recall that in Group 5–7 d^2 metal dioxo compounds, two multiply bonded ligands are always located in *trans*-positions to each other.

In four structures (see Table 2), the *trans*-positions to the oxo ligands are occupied by neutral nitrogen atoms of the $\mathrm{L}^{m}_{\mathrm{bi}}$ ligands, while the $\mathrm{Re{-}N}_{trans}$ bonds (2.261–2.281 Å; average, 2.269 Å) are longer by 0.065–0.151 Å (on average, by 0.105 Å) than the $\mathrm{Re{-}N}_{cis}$ bonds (2.087–2.227 Å) because of the *trans*-effect of the multiply bonded oxo ligand.

Also, the $\mathrm{Re{-}Cl}_{trans}$ bonds (2.403, 2.444 Å) are shorter (by 0.013–0.089; on average, by 0.055 Å) than the $\mathrm{Re{-}Cl}_{cis}$ bonds (2.355–2.390 Å; average, 2.369Å).

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

Parameter	Ranges of values, number of cases (in brackets), average values (in parentheses), Å*
Re–O(oxo)	1.644–1.707, {32}, (1.680 ± 0.037)
Re–O$\left(\mathrm{L}_{\mathrm{bi}}^{n}\right)_{trans}$	(b) 1.989; 2.047, {2}, (2.019 ± 0.029) (c) 2.120–2.249, {5}, (2.185 ± 0.065)
Re–O$\left(\mathrm{L}_{\mathrm{tri}}^{m}\right)_{trans}$	(a) 1.911–1.946, {4}, (1.926 ± 0.020) (b) 2.005–2.084, {7}, (2.052 ± 0.047) (c) 2.126–2.184, {6}, (2.162 ± 0.040)
Re–O(OMe)$_{trans}$	1.904, {1}
Re–O(OPPh$_3$)$_{trans}$	2.245, {1}
Re–O$\left(\mathrm{L}_{\mathrm{tri}}^{m}\right)_{cis}$	1.934{1}–2.042, {7}, (1.969 ± 0.073)
Re–O$\left(\mathrm{L}_{\mathrm{bi}}^{n}\right)_{cis}$	1.939–2.042, {8}, (1.989 ± 0.053)
(Δ){Re–$\left(\mathrm{L}_{\mathrm{tri}}^{m}\right)$}	(a) (–0.129...–0.094), {4}, (–0.114 ± 0.020) (b) (–0.035...+0.044), {7}, (0.012 ± 0.047) (c) (0.086–0.144), {6}, (0.122 ± 0.036)
(Δ){Re–O$\left(\mathrm{L}_{\mathrm{bi}}^{n}\right)$}	(a) (–0.087, –0.047, {2}, (–0.067 ± 0.020) (c) (0.091–0.208), {5} (0.164 ± 0.073)
(Δ){Re–O (OMe)}	(–0.136)
(Δ){Re–O (OPPh$_3$)}	(0.105)
Re–N$\left(\mathrm{L}_{\mathrm{bi}}^{n}\right)_{trans}$	2.261–2.281, {4}, (2.269 ± 0.012)
Re–N$\left(\mathrm{L}_{\mathrm{bi}}^{n}\right)_{cis}$	2.087–2.227, {14}, (2.169 ± 0.082)
Re–N$\left(\mathrm{L}_{\mathrm{tri}}^{m}\right)_{cis}$	1.914–2.235, {32}, (2.094 ± 0.180)
Δ{Re–N$\left(\mathrm{L}_{\mathrm{bi}}^{n}\right)$}	0.065–0.151, {4}, (0.105 ± 0.046)
Re–Cl$_{trans}$	2.403, 2.444, {2}, (2.424 ± 0.020)
Re–Cl$_{cis}$	2.355–2.390, {5}, (2.369 ± 0.021)
(Δ)(Re–Cl)	(0.013–0.089), {7}, (0.055 ± 0.038)
Re–Br$_{cis}$	2.495–2.523, {3}, (2.509 ± 0.014)
Re–S$\left(\mathrm{L}_{\mathrm{tri}}^{m}\right)_{cis}$	2.268–2.475, {32}, (2.347±0.128)
Re–S$\left(\mathrm{L}_{\mathrm{bi}}^{n}\right)_{cis}$	2.286–2.408, {12}, (2.334 ± 0.074)
Re–P$\left(\mathrm{L}_{\mathrm{bi}}^{n}\right)_{cis}$	2.430, 2.435, {2}, (2.433 ± 0.003)
Re–P(Ph$_3$)$_{cis}$	2.450–2.484, {3}, (2.469 ± 0.019)

* Different types of the parameter (Δ)$\left(\mathrm{L}_{\mathrm{bi,\ tri}}^{m}\right)$: (a) negative, (b) neutral, and (c) positive.

The Re–S_{cis} bonds in the bidentate and tridentate ligands (L_{tri} and L_{bi}) are comparable in length: 2.268–2.408 and 2.286–2.408 Å (average, 2347 and 2.334 Å).

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Translated by Z. Svitanko