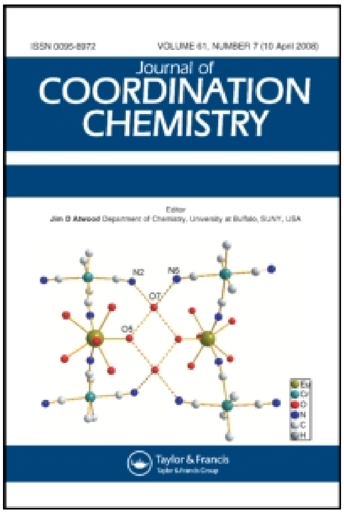

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Synthesis, spectroscopic characterization, crystal and molecular structure of *fac*-[ReO$_3$Br(phen)]

B. Machura[a]; J. O. Dzięgielewski[a]; R. Kruszynski[b]; T. J. Bartczak[b]

[a] Department of Inorganic and Radiation Chemistry, Institute of Chemistry, University of Silesia, 40-006 Katowice, Poland [b] X-Ray Crystallography and Crystal Chemistry Group, Institute of General and Ecological Chemistry, Technical University of Łódź, 90-924 Łódź, Poland

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SYNTHESIS, SPECTROSCOPIC CHARACTERIZATION, CRYSTAL AND MOLECULAR STRUCTURE OF *fac*-[$\mathbf{ReO_3Br(phen)}$]

B. MACHURA[a], J.O. DZIĘGIELEWSKI[a,*],
R. KRUSZYNSKI[b] and T.J. BARTCZAK[b]

[a]*Department of Inorganic and Radiation Chemistry, Institute of Chemistry,*
University of Silesia, 9th Szkolna St., 40-006 Katowice, Poland;
[b]*X-Ray Crystallography and Crystal Chemistry Group,*
Institute of General and Ecological Chemistry, Technical University of Łódź,
116 Żeromski St., 90-924 Łódź, Poland

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A new rhenium oxo-complex *fac*-[ReO_3Br(phen)] has been obtained in high yield from the direct reaction of ammonium perrhenate with 1,10-phenanthroline in hydrobromic acid and characterized by X-ray diffraction and IR and UV-Vis spectra.

Keywords: Rhenium complexes; Oxo-complexes; X-ray structure

INTRODUCTION

For many years transition metal-oxo complexes have been a focus of interest for scientists engaged both in basic research [1–5] and in trying to employ these compounds in many catalytic oxidation processes [6–8] and in oxygen atom transfer between substrates [9–11].

One of the most efficient homogenous oxidation catalysts for hydrogen peroxide in both aqueous and organic solvents is methylrhenium trioxide (MTO). With hydrogen peroxide as the oxidant, MTO catalyzes olefin epoxidations [12], conversion of thiolatocobalt to sulfenatocobalt [13], oxidations of organic sulfides [14], phosphines, triphenylarsine, triphenylstibine [15] and tertiary amines to the corresponding oxides and for the conversion of aniline to nitrosobenzene [16].

According to recent research the derivatives of halogenorhenium(VII) oxides also show considerable catalytic activity in these oxidation processes [17]. However,

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*Corresponding author. E-mail: jod@tc3.ich.us.edu.pl

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in contrast to organorhenium(VII) oxide complexes whose chemistry is relatively well developed, only a few derivatives of halogenorhenium(VII) oxides have been obtained and structurally characterized [17–21].

Here we present a one-pot synthesis of [ReO_3Br(phen)], together with its spectroscopic characterization, crystal and molecular structure.

EXPERIMENTAL

Reagents and Instrumentation

All synthetic manipulations were carried out open to the atmosphere. All solvents were of reagent grade and were used as received. 1,10-Phenanthroline and ammonium perrhenate were purchased from Aldrich Chemical Co. and used without further purification.

Infrared spectra were recorded on a Nicolet Magna 560 spectrophotometer in the spectral range 4000–400 cm^{-1} with the samples in the form of KBr pellets. Electronic spectra were measured on a Lab Alliance UV-VIS 8500 spectrophotometer in the range 800–220 nm in deoxygenated dichloromethane solution. Elemental analyses (C,H,N) were performed on a Perkin-Elmer CHN-2400 analyzer.

Preparation of [ReO_3Br(phen)]

A solution of NH_4ReO_4 (0.54 g, 2 mmol) in concentrated HBr (5 cm^3) was added to the stirred solution of 1,10-phenanthroline (1 g, 8. mmol) in acetic acid (29 cm^3). A yellow precipitate of [ReO_3Br(phen)] formed after a few seconds. The reaction mixture was stirred for 2 h, the yellow precipitate was filtered, washed with ethanol and cold ether and dried *in vacuo*. Crystals suitable for X-ray structure determination were obtained by slow evaporation of an acetonitrile solution of [ReO_3Br(phen)]. Yield 60%. IR (KBr, cm^{-1}) 3060 (w), 3034 (w), 2993 (w), 1626 (m), 1582 (m), 1521 (s), 1486 (m), 1313 (w), 1290 (w), 1223 (m), 1146 (m), 1114 (m), 1033 (w) 942 (s), 924 (s), 906 (vs), 876 (m), 853 (s), 784 (m), 743 (m), 725 (s), 656 (m), 430 (m).

Anal. Calcd. for $C_{12}H_8N_2Br_3ORe$ (%): C, 29.16; H, 1.63; N, 5.67. Found: C, 29.20; H, 1.69; N, 5.60.

X-ray Determination of Crystal Structure

A needle crystal of approximate dimensions 0.051 × 0.079 × 0.252 mm was mounted on a KM-4-CCD automatic diffractometer equipped with CCD detector, and used for data collection. X-ray intensity data were collected with graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) at 289.0(2) K in ω scan mode. A 37 s exposure time was used. The whole Ewald sphere up to $2\theta = 57.30°$ was collected. The unit cell parameters were determined from least-squares refinement of the setting angles of the 3198 strongest reflections. Crystal data and refinement details are given in Table I.

Examination of two reference frames monitored after each 50 frames measured showed 6.71% loss of the intensity. During the data reduction decay correction coefficient was applied. The pale-yellow, transparent crystal used for data collection did

TABLE I Crystal data and structure refinement for [ReO_3Br(phen)]

Empirical formula	$C_{12}H_8N_2BrO_3Re$
Formula weight	494.31
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P1$
Unit cell dimensions (Å,°)	$a = 7.8092(4)$ $\alpha = 105.626(5)$
	$b = 8.7986(5)$ $\beta = 92.006(4)$
	$c = 9.9862(5)$ $\gamma = 99.901(4)$
Volume ($Å^3$)	648.5(3)
Z	2
Calculated density ($Mg\,m^{-3}$)	2.531
Absorption coefficient (mm^{-1})	12.453
$F(000)$	456
Crystal size (mm)	0.25 × 0.08 × 0.05
θ range for data collection	3.54–28.65
Index ranges	$-10 \leq h \leq 10, -11 \leq k \leq 11, -13 \leq l \leq 13$
Reflections collected/unique	7443/3096 [$R_{(int)} = 0.0348$]
Max. and min. transmission	0.5748 and 0.1468
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3096/0/173
Goodness-of-fit on F^2	1.149
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0304$, $wR2 = 0.0605$
R indices (all data)	$R1 = 0.0343$, $wR2 = 0.0624$
Largest diff. peak and hole ($e\,Å^{-3}$)	1.291 and −1.157

not change its appearance. Lorentz and polarization corrections were applied to the intensity data. A numerical absorption correction was used [22]. The maximum and minimum transmission factors were 0.5748 and 0.1468. The structure was solved by direct methods. All the non-hydrogen atoms were refined anisotropically using full-matrix, least-squares technique on F^2. All the hydrogen atoms were found from difference Fourier synthesis after four cycles of anisotropic refinement, and refined as "riding" on the adjacent carbon atom with individual isotropic temperature factors 1.2 times the value of the equivalent temperature factor of the parent carbon atom. The solution and refinements were performed with SHELXS97 [23] and SHELXL97 [24]. Graphical manipulations were performed using the XP routine of SHELXTL [25]. Atomic scattering factors were those incorporated in the computer programs.

RESULTS AND DISCUSSION

The [ReO_3Br(phen)] complex has been obtained in high yield from the direct reaction of ammonium perrhenate with 1,10-phenanthroline in hydrobromic acid:

$$NH_4ReO_4 + \text{phen} + 2HBr \rightarrow [ReO_3Br(\text{phen})] + H_2O + NH_4Br$$

Previously characterized [ReO_3XL_2] complexes with N-donor ligands (L) were isolated from the reactions of ReO_3X with the corresponding ligands [17–19]. Indeed halogenorhenium(VII) oxides were among the first reported rhenium complexes, but most of the published synthetic methods for rhenium(VII) oxohalides lead to impure products or mixtures of products [4].

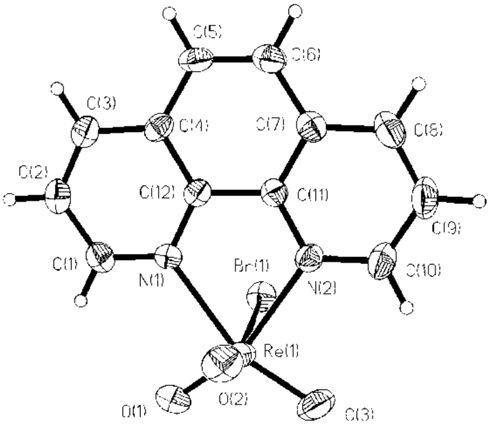

FIGURE 1 The molecular structure of the [ReO_3Br(phen)] complex. The thermal ellipsoids are drawn at 50% probability level.

The [ReO_3Br(phen)] complex crystallizes in the triclinic space group $P1$ and its crystal structure is composed of discrete monomers with all atoms located in general positions. Accurate cell parameters, crystal data and details of the structure of [ReO_3Br(phen)] are given in Table I.

The perspective view of the compound, together with the atom numbering scheme, is shown in Fig. 1.

Three oxo ligands are in a pyramidal *facial* arrangement. The bidentate 1,10-phenanthroline ligand and two oxygen atoms O(1) and O(3) occupy the equatorial positions, while the bromine ion and the remaining oxygen occupy the apical sites in *trans* positions. The pseudooctahedral environment of the Re center in [ReO_3Br(phen)] shows clear distortions, induced mainly by the narrow bite angle of chelating 1,10-phenanthroline and the strong repulsion of the electron pairs of the three oxo ligands. Consequently, the angles N–Re–N and N–Re–O are considerably smaller than the ideal octahedral angle of 90° [e.g., N(1)–Re(1)–N(2) is 72.08(15)°] and the O–Re–O bond angles of the terminal oxo groups are larger than 90° [104.2(2)–106.6(2)°]. The most important angles and bond lengths for [ReO_3Br(phen)] are reported in Table II.

The Re–O bond distances of the terminal oxo groups are in good agreement with those reported for similar complexes such as [ReO_3Cl(bipy)] [19], [$(C_5H_4Me)ReO_3$] [26] or [(bdmpza)ReO_3] [27]. The double-bond character of these bonds is indicated by their average length of 1.709 Å. The bond valences were computed as $\nu_{ij} = \exp \times [(R_{ij} - d_{ij})/B]$ [28,30,31], where R_{ij} is the bond-valence parameter (in the formal sense R_{ij} is the single-bond length between atoms i and j) [29]. $R_{\text{Re–O}}$, $R_{\text{Re–N}}$, $R_{\text{Re–Br}}$ were taken as 1.97, 2.06 and 2.45 [29] respectively and the value of B was taken as 0.37 [30]. The computed bond valences of the rhenium are $\nu_{\text{Re–O}} = 1.99$, 2.00, 2.07 (which also confirms the double bond character of these bonds); $\nu_{\text{Re–Br}} = 0.57$; $\nu_{\text{Re–N}} = 0.57$, 0.59 v.u. (valence units). The Re–N bond lengths of 2.263(4) and 2.257(4) Å are quite long compared with those observed in [$Re(CO)_3$(phen)(imidiazole)]: 2.182(4) and 2.167(4) Å [31]. This is caused by the *trans* influence of the terminal oxo groups and it indicates a weak N→Re bonding interaction. As a result of strong *trans* influence of the terminal oxo ligand considerable elongation of the Re–Br bond

TABLE II Selected bond lengths (Å) and angles (°) for $[ReO_3Br(phen)]$

Re(1)–O(1)	1.701(4)	O(1)–Re(1)–O(3)	106.6(2)
Re(1)–O(3)	1.713(4)	O(1)–Re(1)–O(2)	103.9(2)
Re(1)–O(2)	1.715(4)	O(3)–Re(1)–O(2)	104.2(2)
Re(1)–N(2)	2.258(4)	O(1)–Re(1)–N(2)	158.43(18)
Re(1)–N(1)	2.266(4)	O(3)–Re(1)–N(2)	90.06(18)
Re(1)–Br(1)	2.6549(6)	O(2)–Re(1)–N(2)	84.58(18)
N(1)–C(1)	1.321(6)	O(1)–Re(1)–N(1)	88.69(18)
N(1)–C(12)	1.357(6)	O(3)–Re(1)–N(1)	159.18(18)
N(2)–C(10)	1.325(7)	O(2)–Re(1)–N(1)	85.11(18)
N(2)–C(11)	1.355(6)	N(2)–Re(1)–N(1)	72.08(15)
		O(1)–Re(1)–Br(1)	88.37(15)
		O(3)–Re(1)–Br(1)	88.50(16)
		O(2)–Re(1)–Br(1)	158.65(14)
		N(2)–Re(1)–Br(1)	78.24(11)
		N(1)–Re(1)–Br(1)	77.65(10)
		C(1)–N(1)–C(12)	118.4(4)
		C(1)–N(1)–Re(1)	124.7(3)
		C(12)–N(1)–Re(1)	116.8(3)
		N(1)–C(1)–C(2)	122.2(5)
		N(2)–C(10)–C(9)	121.8(5)
		C(10)–N(2)–C(11)	119.1(5)
		C(10)–N(2)–Re(1)	123.8(4)
		C(11)–N(2)–Re(1)	117.0(3)
		N(2)–C(11)–C(7)	122.7(4)
		N(2)–C(11)–C(12)	117.1(4)
		N(1)–C(12)–C(4)	123.6(4)
		N(1)–C(12)–C(11)	116.9(4)

in $[ReO_3Br(phen)]$ is also observed. The covalent Re–Br bond distance is expected to be $\sim$2.50 Å [32]. The measured Re–Br bond distance in $[ReO_3Br(phen)]$ is significantly longer at 2.6546(11) Å, indicating a weaker interaction. It has been stated that the bond valence represents a measure of the strength of a bond that is independent of the atomic size [33]. The application of this correlation implies that Re–Br and Re–N bonds have almost the same strength and are distinctly weaker than Re–O bonds.

The conformation of the molecule is stabilized by two weak intramolecular hydrogen bonds [34] C(1)–H(1A)···O(1) and C(10)–H(10A)···O(3) (D···A distances 3.048(7) and 3.069(7) Å, D–H···A angles 111.3 and 111.8° respectively). The molecules of the title compound are assembled in a two-dimensional hydrogen-bonded chain (Fig. 2) *via* repeating weak intermolecular interactions [35,36] C(9)–H(9A)···Br(1) and C(10)–H(10A)···O(2), (D···A distances 3.782(6) and 3.052(7) Å, D–H···A angles 163.3 and 124.4° respectively). In the structure there are two multistacking interactions (Table III) linking molecules obtained via $-x,-y,-z+1$ and $-x+1,-y,-z+1$ symmetry transformations, which, together with hydrogen bonds, create a three-dimensional hydrogen-bonded/stacked network. In addition, the structure contains one more short intermolecular distance linking the central benzene ring of phenanthroline with a second obtained via $-x+1$, $-y$, $-z$ symmetry transformations, which can be considered as a weak stacking interaction [37,38].

The infrared spectrum of $[ReO_3Br(phen)]$ shows the absorptions associated with the coordinated 1,10-phenanthroline and several bands assignable as ν(Re=O): 942 (s), 924 (s) and 906 (s). These bands are found in similar positions in $[(bdmpza)ReO_3]$: 945 (m), 925 (s) and 913 (s) [27].

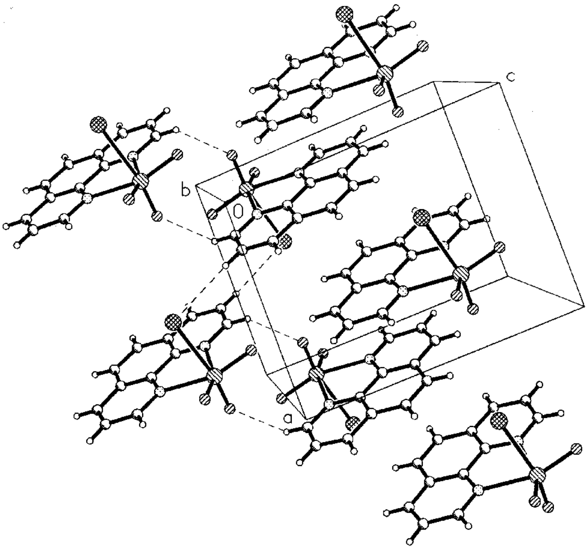

FIGURE 2 The packing diagram for [ReO_3Br(phen)].

TABLE III Stacking interaction characteristics for [ReO_3Br(phen)]

Ring A	*Ring B*	*Ring centroids distance* (Å)	*Dihedral angle between planes* (°)	*Angle between vector AB and normal to plane* (°)		*Perpendicular distance of ring* (Å)	
				A	*B*	*A on ring B*	*B on ring A*
Cg(1)	Cg(1) #1	3.8955	0.00	26.11	26.11	3.498	3.498
Cg(1)	Cg(2) #1	4.7872	1.58	41.88	43.26	3.486	3.564
Cg(1)	Cg(3) #1	3.6379	1.37	14.05	15.14	3.512	3.529
Cg(2)	Cg(1) #1	4.7872	1.58	43.26	41.88	3.564	3.486
Cg(3)	Cg(1) #1	3.6379	1.37	15.14	14.05	3.529	3.512
Cg(3)	Cg(3) #1	4.7876	0.03	43.27	43.27	3.486	3.486
Cg(1)	Cg(2) #2	4.8893	1.58	46.79	46.94	3.338	3.347
Cg(1)	Cg(3) #2	4.5242	1.37	41.62	42.96	3.311	3.382
Cg(2)	Cg(1) #2	4.8893	1.58	46.94	46.79	3.347	3.338
Cg(2)	Cg(3) #2	4.6053	0.85	43.00	43.85	3.321	3.368
Cg(3)	Cg(1) #2	4.5242	1.37	42.96	41.62	3.382	3.311
Cg(3)	Cg(2) #2	4.6053	0.85	43.85	43.00	3.368	3.321
Cg(2)	Cg(2) #3	5.4483	0.00	55.93	55.93	3.052	3.052

Symmetry transformations used to generate equivalent rings: #1: $-x,-y,-z+1$; #2: $-x+1,-y,-z+1$; #3: $-x+1,-y,-z$.

The positions (cm^{-1}) and molar absorption coefficients ($dm^3\,mol^{-1}\,cm^{-1}$) of electronic bands for [ReO_3Br(phen)] are as follows: 33 500 (4775), 36 040 (9640) and 42 645 (8400). The absorption bands at 33 500 and 36 040 cm^{-1} correspond to the electron transitions $\pi_{\mathrm{o}}^{\circ} \rightarrow 5d_{\mathrm{Re}}$ and $\pi \rightarrow \pi^*_{\mathrm{phen}}$ respectively, whereas the band at 42 645 cm^{-1} is a result of two transitions $\pi^{\mathrm{b}}_{\mathrm{Re=O}} \rightarrow \pi^*$ and $\pi \rightarrow \pi^*_{\mathrm{phen}}$. Both the absorption bands and their assignments show that in L → Re(VII) charge transfer only electrons from the oxygen atoms participate. That the Br^- ion does not show donor ability is shown by the significant elongation of the Re–Br bond. The lack of Re → L-type transitions is the cause of higher Re–N bond lengths.

Supplementary Data

Supplementary data are available from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK on request, quoting the deposition number 201890.

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