Rhenium complexes with pyrazoles. Synthesis and crystal structure of *trans*-$[Re(O)(OMe)L_4]Br_2 \cdot L \cdot 4H_2O$ (L is 3,5-dimethylpyrazole)

M. N. Sokolov,[a] N. E. Fedorova,[a] V. E. Fedorov,[a] A. V. Virovets,[a] and P. Nuñez[b]*

[a]*Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 3 prosp. Akad. Lavrent´eva, 630090 Novosibirsk, Russian Federation. Fax: +7 (383 2) 34 4489. E-mail: cluster@che.nsk.su*
[b]*Department of Inorganic Chemistry, University of La Laguna, 38200 La Laguna Canary Island, Spain*

The first mononuclear Re^V complex with four pyrazole ligands, *viz.*, $[Re(O)(OMe)L_4]Br_2$ (L is 3,5-dimethylpyrazole), and its molecular adduct with L, *viz.*, $[Re(O)(OMe)L_4]Br_2 \cdot L \cdot 4H_2O$, were synthesized. The complex is resistant to hydrolysis in a neutral aqueous solution. The structure of the adduct was established by X-ray diffraction analysis.

Key words: rhenium complexes, dimethylpyrazole, crystal structure, X-ray diffraction analysis.

Rhenium(v) compounds are among the most widespread and available compounds in the chemistry of this element. There is a wide range of ligands stabilizing rhenium(v), which is prone to disproportionation in aqueous solutions in the absence of additional ligands. The formation of the monooxo (ReO^{3+}) and *trans*-dioxo (ReO_2^+) groups is typical of rhenium in the oxidation state +5. Protonated and methylated derivatives of ReO_2^+, for example, the octahedral $[Re(O)(OR)L_4]^{2+}$ (R = H or Me) complexes, contain the $[(Re(O)(OH)]^{2+}$ and $[Re(O)(OMe)]^{2+}$ groups, respectively.[1] The *trans*-dioxorhenium(v) group imparts interesting electrochemical, photophysical, and photochemical properties to compounds.[2—6] The ability of the ReO_2^+ group to add two electrons and two protons (upon reduction) thus producing the $Re(OH)_2^{3+}$ gave impetus to investigations of the catalytic and electrocatalytic properties of systems containing the $[ReO_2L_4]^+$ fragment. The $[ReO(OMe)(4\text{-Mepy})_4]^{2+}$ complex can undergo reversible one-electron oxidation and can also be reversibly reduced (two one-electron processes) under conditions of cyclic voltammetry. However, only pyridine, imidazole, and their substituted derivatives were used as the ligands. The $[ReO_2L_4]^+$ complex (L is 7-azaindole) has also been described.[7—13] The data on the preparation of Re^V compounds with other heterocycles are lacking in the literature.

In the present study, we synthesized the mononuclear rhenium complex $[Re(O)(OMe)(3,5\text{-}Me_2C_3H_2N_2)_4]Br_2 \cdot Me_2C_3H_2N_2 \cdot 4H_2O$ (**1**) and established its molecular and crystal structure. This complex is an adduct with the free ligand molecule in which the linear $[Re(O)(OMe)]^{2+}$ group (the Re—O—C angle is 180°) is coordinated by four 3,5-dimethylpyrazole molecules.

Experimental

All operations were carried out in air. Ammonium perrhenate (NH_4ReO_4) (Novosibirsk rare metal plant), 48% HBr (Reakhim), and 3,5-dimethylpyrazole ($Me_2C_3H_2N_2$) (Aldrich) were used without additional purification. Elemental analysis was carried out at the Laboratory of Microanalysis of the N. N. Vorozhtsov Institute of Organic Chemistry of the Siberian Branch of the Russian Academy of Sciences (Novosibirsk). The electronic absorption spectra were recorded on a Shimazu UV 2101 PC spectrophotometer. The IR spectra were measured on a Bruker IFS-85 Fourier spectrometer. The FAB mass spectra were obtained on a high-resolution VG Auto Spec mass spectrometer.

Synthesis of *trans*-tetrakis(3,5-dimethylpyrazole)methoxyoxorhenium(v) dibromide tetrahydrate (adduct with 3,5-dimethylpyrazole). A 48% HBr solution (10 mL) was added to NH_4ReO_4 (0.5 g, 1.86 mmol), and the reaction mixture was carefully concentrated until a crystalline brown product was formed and the acid was completely removed. Then a solution of 3,5-dimethylpyrazole (0.24 g, 2.50 mmol) in methanol (30 mL) was added to the product (0.20 g) and the mixture was refluxed for 4 h. The resulting brown solution was allowed to crystallize in an open beaker for 12 h. The crystalline green $Re_2O_3(\mu\text{-}O)(\mu\text{-}3,5\text{-}Me_2C_3HN_2)_2Br_2$ complex was isolated in a yield of 0.046 g.[14] The mother liquor was concentrated to dryness and the residue was dissolved in water. The resulting violet solution was slowly concentrated to obtain large well-faceted violet single crystals

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in a yield of 0.017 g. Found (%): C, 32.98; H, 4.80; Br, 16.80; N, 14.13. $C_{26}H_{51}Br_2N_{10}O_6Re$. Calculated (%): C, 32.16; H, 5.51; Br, 17.11; N, 15.00. IR (KBr), ν/cm^{-1}: 3400 (m), 3132 (s), 2926 (s), 2360 (m), 2337 (m), 1699 (w), 1649 (m), 1573 (s), 1503 (m), 1418 (m), 1294 (m), 1151 (m), 1120 (m), 1062 (m), 1027 (m), 948 (m), 908 (s, ν(Re=O)), 813 (m), 712 (w). FAB-MS (*m/z*): 617 $[Re(O)(OMe)L_4 - H]^+$, 100%. The electronic absorption spectrum (300—900 nm, MeCN): $\lambda = 533$ ($\varepsilon = 560$ $mmol^{-1}$ cm^{-1}). ^1H NMR (CD_3CN, 298 K), δ: 1.75 (s, 12 H, $CC\underline{H}_3$); 2.26 (s, 6 H, $CC\underline{H}_3$); 2.36 (s, 12 H, $CC\underline{H}_3$); 3.74 (s, 3 H, $OC\underline{H}_3$); 5.84 (s, 1 H, C<u>H</u>); 6.18 (s, 4 H, C<u>H</u>); 11.2 (s, 4 H, N<u>H</u>).

X-ray diffraction study. The structure of $[Re(O)(OMe)(Me_2C_3H_2N_2)_4]Br_2 \cdot Me_2C_3H_2N_2 \cdot 4H_2O$ (**1**) was established by X-ray diffraction analysis. The crystallographic characteristics and details of X-ray diffraction study are given in Table 1. The structure was solved by the direct method and refined by the full-matrix least-squares method using the SHELX-97 program package.[15] The bromide anions were found to be disordered over two closely spaced positions with equal occupancies. In addition, the crystal structure contains a noncoordinated 3,5-dimethylpyrazole molecule disordered over two positions, which are related by a twofold axis; the molecules in two orientations being partially overlapped. The hydrogen atoms of the ligands were placed in geometrically calculated positions. The hydrogen atoms of only one methyl group of the disordered noncoordinated $Me_2C_3H_2N_2$ molecule were included in the refinement because the second methyl group overlaps with the molecule in another position. The hydrogen atoms of the coordinated methoxy group were not located. The atomic coordinates were deposited with the Cambridge Structural Database (CCDC code is 177282). The principal bond lengths and bond angles are given in Table 2.

Table 1. Crystallographic characteristics of compound **1**

Parameter	Characteristic
Molecular formula	$C_{26}H_{51}Br_2N_{10}O_6Re$
Molecular weight	945.79
Crystal system	Tetragonal
Space group	*I*4/*m*
Z	4
a/Å	14.912(3)
c/Å	17.108(4)
V/Å^3	3804.3(13)
ρ_{calc}/g cm^{-3}	1.651
μ/mm^{-1}	5.344
Diffractometer	Bruker APEX CCD
Temperature	298 K
Radiation,	Mo-Kα
λ/Å	0.71073
θ_{max}	28.62
Number of reflections measured/independent	9624/2355
R_{int}	0.0897
Observed reflections ($F_{hkl} \geq 4\sigma(F)$)	1774
R_1	0.0427
wR_2 for $F_{hkl} \geq 4\sigma(F)$	0.0940
R_1	0.0573
wR_2 for all reflections	0.0978
GOF for all reflections	0.921

Table 2. Selected bond lengths (*d*) and bond angles (ω) in the cation of complex **1**

Bond	*d*/Å	Angle	ω/deg
Re(1)—O(1)	1.735(8)	O(1)—Re(1)—O(2)	180.0
Re(1)—O(2)	1.843(7)	O(1)—Re(1)—N(1)	91.33(12)
Re(1)—N(1)	2.114(4)	O(2)—Re(1)—N(1)	88.67(12)
O(2)—C(6)	1.402(12)	N(1)$^{\#1}$—Re(1)—N(1)	177.3(2)
N(1)—C(1)	1.339(7)	N(1)—Re(1)—N(1)$^{\#2}$	89.969(6)
N(1)—N(2)	1.364(6)	C(6)—O(2)—Re(1)	180.0
N(2)—C(3)	1.353(7)	C(1)—N(1)—N(2)	106.6(5)
C(1)—C(2)	1.386(10)	C(1)—N(1)—Re(1)	132.1(4)
C(1)—C(4)	1.479(9)	N(2)—N(1)—Re(1)	120.8(3)
C(2)—C(3)	1.322(11)	C(3)—N(2)—N(1)	109.7(5)
C(3)—C(5)	1.506(10)	N(1)—C(1)—C(2)	107.8(7)
		N(1)—C(1)—C(4)	122.6(6)
		C(2)—C(1)—C(4)	129.6(6)
		C(3)—C(2)—C(1)	108.8(6)
		C(2)—C(3)—N(2)	107.1(6)
		C(2)—C(3)—C(5)	132.7(6)
		N(2)—C(3)—C(5)	120.1(7)

Note. The hydrogen atoms are generated from the basis atoms by the symmetry transformations: $^{\#1}$ $-x - 1, -y - 1, z$; $^{\#2}$ $y, -x - 1, z$.

Results and Discussion

The reaction of $ReBr_6^{2-}$ with 3,5-dimethylpyrazole in methanol in air afforded two products, *viz.*, the green binuclear compound $[Re_2O_3(\mu\text{-}O)(\mu\text{-}3,5\text{-}Me_2C_3HN_2)_2Br_2]$ (the major product) and the pink-violet complex $[Re(O)(OMe)(3,5\text{-}Me_2C_3H_2N_2)_4]Br_2$ (the minor product). The latter was isolated as the molecular adduct $[Re(O)(OMe)(3,5\text{-}Me_2C_3H_2N_3)_4]Br_2 \cdot Me_2C_3H_2N_2 \cdot 4H_2O$ (**1**). The green binuclear complex is structurally similar to the chloride obtained by us previously[14] and is not considered in the present study. It is remarkable that the $[Re(O)(OMe)(3,5\text{-}Me_2C_3H_2N_3)_4]^{2+}$ cation is resistant to hydrolysis in a neutral aqueous solution, whereas the pyridine and imidazole derivatives of $[ReO_2L_4]^{2+}$ readily lose at least one of the ligands under these conditions to form, for example, $[ReO_2(py)_3(H_2O)]^+$.[11,16] The resistance of the methoxy group in complex **1** to hydrolysis is also worthy of note taking into account that the pyridine complexes $ReO(OR)Cl_2py_2$ are readily hydrolyzed with elimination of ROH followed by condensation to give $Re_2O_2(\mu\text{-}O)Cl_4py_4$.[17] Solubility of complex **1** in water and its hydrolytic stability are of great interest in connection with the potential use of ^{186}Re and ^{188}Re β-emitters in radiotherapy.[18]

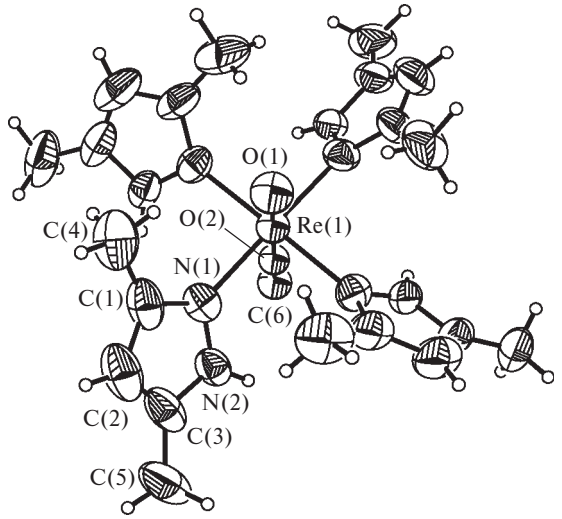

Fig. 1. Overall view of the cation of compound **1** (thermal ellipsoids with the 50% probability).

The structure of the $[Re(O)(OMe)(3,5\text{-}Me_2C_3H_2N_3)_4]^{2+}$ cation is shown in Fig. 1. The principal bond lengths and bond angles are given in Table 1. The cation is located on a fourfold axis, which passes through the C and O atoms of the methoxy group, the Re atom, and the terminal O atom, and the angles are equal to 180°. The hydrogen atoms of the Me group are disordered to meet the requirements of the crystallographic symmetry. The Re—O and Re—OMe bond lengths are 1.735(8) and 1.843(7) Å, respectively. These distances are shorter than those expected for the double and single Re—O bonds, respectively (1.77 and 2.04 Å).[9] Similar bond lengths were found in the $[Re(O)(OMe)(4\text{-}Mepy)_4](CF_3SO_3)_2$ complex (Re—O, 1.693(7) Å; Re—OMe, 1.829(7) Å). It was suggested[9] that the order of the bond between Re and the terminal oxo ligand is larger than double and the bond between Re and the methoxy group is stronger than single. This is confirmed by the linearity of the Re—OMe group and its high hydrolytic stability. Complexes containing the linear methoxy group are few in number. Analysis of the data available in the Cambridge Structural Database demonstrated that the Re—O—C angles in three of 16 structurally characterized complexes containing the O=Re—OMe group are in the range of 170—180°, whereas this angle in the remaining complexes are in the range of 120—145°. In one complex, *viz.*, $[Re(O)(OMe)(1\text{-methylimidazole})_4](PF_6)_2$, the Re—O—C angle is exactly equal to 180°.[12] The complex cation in the latter compound, like that in **1**, is located on a fourfold axis passing through the O=Re—OMe group. The Re—N distances (2.114(4) Å) are typical of Re^V complexes with other nitrogen-containing heterocycles.[7—13] The coordination environment about the Re atom is an octahedron (the angles differ only slightly from 90°).

The orientations of the heterocycles in compound **1** are, apparently, determined by the necessity of minimizing repulsions between the Me substituents in the pyrazole ring. The mutual orientation of the rings can be described as nearly propeller-like with the O(1)—Re—N(1)—C(1) and O(1)—Re—N(1)—N(2) torsion angles of +36.8° and −133.4°, respectively. Systematic analysis of the orientations of the ligands in the $[ReO_2Im_4]^+$ complexes (Im is methyl-substituted imidazole) demonstrated that the propeller conformation occurs if the imidazole fragment contains the Me group at position 2, *i.e.*, at the C atom adjacent to the coordinated N atom. Otherwise, the planes of the imidazole rings are arranged virtually parallel to the O—Re—O direction.[11]

The crystal packing of compound **1** is shown in Fig. 2. In the crystal, the disordered Br^- ions, the N atoms of the ligands, and the water molecules of crystallization are linked *via* a system of hydrogen bonds. The complex cations form a rather loose packing with the cavities whose sizes are larger than the size of the 3,5-dimethylpyrazole molecule, which, apparently, leads to disorder of the latter.

In complex **1**, the pyrazole ligands are unsymmetrical and two different substituents (O and OMe) are located in the *trans* positions with respect to the Re atom. As a result, several rotamers can exist due to rotation about the Re—N bonds. In the crystal of **1**, all rings are oriented in a similar fashion so that the second N atom of each ring and the MeO group are located on the same side of the ReN_4 plane. According to the data from

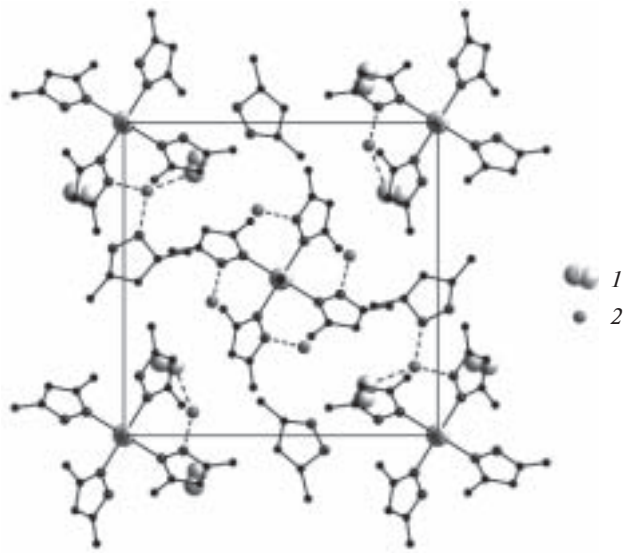

Fig. 2. Crystal packing of compound **1** projected along the *z* axis (only one of the disordered 3,5-dimethylpyrazole molecules is shown): *1*, disordered Br^- anions; *2*, water molecules of crystallization.

^{1}H NMR spectroscopy, this geometry is retained in solution. The protons of the methoxy group give only one signal at δ 3.74, which rules out the existence of several long-lived (within the NMR time scale) rotamers in solution. The presence of two Me groups in the pyrazole ligand must substantially increase the barrier to rotation about the Re—N bond to the extent that this rotation can become impossible. In the ^{1}H NMR spectrum of free 3,5-dimethylpyrazole, both methyl groups are equivalent at ~20 °C (singlet at δ 2.26) due to rapid interconversions of the tautomeric forms. Upon coordination, these groups become nonequivalent (two singlets δ 2.36 and 1.75).

In the region of 300—900 nm of the electronic absorption spectrum, only one band is observed at 533 nm (ε = 560). Both the position and intensity of this band are typical of $[Re(O)(OR)L_4]^{2+}$ (R = H or Me; L is a pyridine or imidazole derivative) and the band belongs to d—d transitions.[9—11]

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References

1. K. Conner and R. A. Walton, in *Comprehensive Coordination Chemistry*, Vol. **4**, Eds. G. Wilkinson, R. D. Gillard, and J. A. McCleverty, Pergamon Press, 1987, pp. 125—213.
2. D. W. Pipes and T. J. Meyer, *Inorg. Chem.*, 1986, **25**, 3256.
3. M. S. Ram, C. S. Johnson, R. L. Blackbourn, and J. T. Hupp, *Inorg. Chem.*, 1990, **29**, 238.
4. W. Lin, T. W. Welch, and H. H. Thorp, *Inorg. Chem.*, 1992, **31**, 4044.
5. M. S. Ram, L. M. Jones, H. J. Ward, Y. H. Wong, C. S. Johnson, P. Subramanian, and J. T. Hupp, *Inorg. Chem.*, 1991, **30**, 2928.
6. H. H. Thorp, J. Van Houten, and H. B. Gray, *Inorg. Chem.*, 1989, **28**, 889.
7. J. C. Brewer and H. B. Gray, *Inorg. Chem.*, 1989, **28**, 3344.
8. M. S. Ram and J. T. Hupp, *Inorg. Chem.*, 1991, **30**, 130.
9. M. S. Ram, L. M. Skeens-Jones, C. S. Johnson, X. L. Zhang, C. Stern, D. I. Yoon, D. Selmarten, and J. T. Hupp, *J. Am. Chem. Soc.*, 1995, **117**, 1411.
10. A.-M. Lebuis, J. M. C. Young, and A. L. Beauchamp, *Can. J. Chem.*, 1993, **71**, 2070.
11. S. Belanger and A. L. Beauchamp, *Inorg. Chem.*, 1996, **35**, 7836.
12. S. Belanger and A. L. Beauchamp, *Inorg. Chem.*, 1997, **36**, 3640.
13. A.-M. Lebuis and A. L. Beauchamp, *Can. J. Chem.*, 1993, **71**, 2060.
14. N. V. Pervukhina, M. N. Sokolov, N. E. Fedorova, and V. E. Fedorov, *Zh. Strukt. Khim.,* 2001, **42**, 993 [*Russ. J. Struct. Chem.*, 2001, **42** (Engl. Transl.)].
15. G. M. Sheldrick, *SHELX97 Release 97-2*, Göttingen University, Göttingen (Germany), 1998.
16. F. F. Kashani and R. K. Murmann, *Int. J. Chem. Kinet.*, 1985, **17**, 1007.
17. N. P. Johnson, F. I. M. Taha, and G. W. Wilkinson, *J. Chem. Soc.*, 1964, 2614.
18. *Technetium and Rhenium in Chemistry and Nuclear Medicine*, Eds. M. Nicolini, G. Baudoli, U. Mazzi, and S. G. Editoriali, Padova, Italy, 1995.

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