Rhenium(IV) and rhenium(V) complexes with 3,5-dimethylpyrazole

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Mono- and dinuclear Re^{IV} and Re^{V} complexes with 3,5-dimethylpyrazole (Me_2pzH) were synthesized. The *cis*-$[Re_2O_3Cl_4(3,5\text{-}Me_2pzH)_4]$ complex (*cis*-**1**) was prepared by the reaction of NH_4ReO_4 with $K[HB(Me_2pz)_3]$ in concentrated HCl or by refluxing of $[ReCl_3(MeCN)(PPh_3)_2]$ with Me_2pzH in air. The bromide complex *trans*-$[Re_2O_3Br_4(3,5\text{-}Me_2pzH)_4]$ (*trans*-**2**) was synthesized by passing dry HBr through a solution of $[Re_2O_3Br_2(\mu\text{-}3,5\text{-}Me_2pz)_2(3,5\text{-}Me_2pzH)_2]$ (**4**) in chloroform. The pyrazolate-bridged complex $[Re_2O_3Cl_2(\mu\text{-}3,5\text{-}Me_2pz)_2(3,5\text{-}Me_2pzH)_2]$ (**3**) was prepared from $(Et_4N)_2[ReOCl_5]$ or $Cs_2[ReOCl_5]$ and Me_2pzH. The corresponding bromide and iodide complexes $[Re_2O_3X_2(3,5\text{-}Me_2pz)_2(3,5\text{-}Me_2pzH)_2]\cdot C_6H_6$ (X = Br (**4**) or I (**5**)) were synthesized by the reactions of $(NH_4)_2[ReBr_6]$ or $K_2[ReI_6]$, respectively, with Me_2pzH. The $[ReO(OMe)(3,5\text{-}Me_2pzH)_4]Br_2\cdot 3,5\text{-}Me_2pzH\cdot 4H_2O$ complex (**6**) was obtained as a by-product in the synthesis of complex **4**. The reaction of $[ReNCl_2(PPh_3)_2]$ with Me_2pzH was accompanied by hydrolytic denitration giving rise to the mixed-ligand complex $[Re_2O_3Cl_2(\mu\text{-}3,5\text{-}Me_2pz)_2(3,5\text{-}Me_2pzH)(PPh_3)]$ (**7**). The reaction of $(NH_4)_2[ReBr_6]$ with a Me_2pzH melt gave the *trans*-$[ReBr_4(3,5\text{-}Me_2pzH)_2]\cdot Me_2CO$ complex (**8**). The structures of complexes **2** and **4**—**8** were established by X-ray diffraction. All compounds were characterized by elemental analysis, electronic absorption spectroscopy, ^1H NMR and IR spectroscopy, mass spectrometry, and cyclic voltammetry.

Key words: rhenium; 3,5-dimethylpyrazole; oxo complexes; structure.

Coordination chemistry of rhenium has been extensively developed in recent years due, to a large extent, to the fact that short-lived rhenium isotopes hold promise as β-emitters in radiotherapy.[1—3] Rhenium complexes with amines and derivatives of pyridine and imidazole are used for studying electron transfer, oxygen atom transfer, electrocatalysis, luminescence, and fluorescence.[4—8] Complexes with nitroimidazoles and nitropyrazoles have found application as markers for hypoxic tumor cells.[9,10] These aspects of the chemistry of rhenium complexes with pyridine and imidazole derivatives have been studied in depth.[11—20] Coordination compounds of rhenium with other heterocyclic ligands, such as pyrazoles and triazoles, have received attention only recently.[21—28] Rhenium complexes with poly(pyrazolyl)borates were studied in detail.[29] The first structurally characterized rhenium complex with the pyrazole ligand, $[Re_2O_3Cl_4(3,5\text{-}Me_2pzH)_4]\cdot(CH_3)_2CO$, was isolated in attempting to synthesize Re^{V} complexes with $[HB(3,5\text{-}Me_2pz)_3]^-$.[10] The aim of the present study was to investigate the reactions of Re^{V}, Re^{IV}, and Re^{III} complexes with 3,5-dimethylpyrazole.

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Experimental

All reactions were carried out in air in organic solvents, which were purified according to standard procedures. Commercial reagents were used without additional purification.

The IR spectra (4000—400 cm^{-1}) were measured on a Bruker IFS-85 Fourier-transform spectrometer in KBr pellets. The NMR spectra were recorded on a Bruker AC 250 spectrometer (250.13 MHz for ^1H and 101.26 MHz for ^{31}P) with the use of Me_4Si and 85% H_3PO_4 as the external standard. The electronic absorption spectra were measured on a Shimadzu UV 2101 PC instrument. The FAB mass spectra were obtained on a Finnigan MS 8230 instrument. Cyclic voltammetry experiments were carried out on a Potentiostat/Galvanostat Model 263 (EG&G INSTRUMENTS) instrument with the use of the Ag/AgCl electrode and 0.1 *M* Bu_4NClO_4 as the supporting electrolyte. Under these conditions, the potential of the standard Fc^+/Fc pair is 0.44 V. Thermogravimetric analysis was performed on a TA 7000 instrument. Elemental analyses were carried out in 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 starting compounds $[ReCl_3(CH_3CN)(PPh_3)_2]$, $(Et_4N)_2[ReOCl_5]$, $Cs_2[ReOCl_5]$, $[ReNCl_2(PPh_3)_2]$, $(NH_4)_2ReBr_6$, and K_2ReI_6 were synthesized according to

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known procedures. 3,5-Dimethylpyrazole (3,5-Me_2pzH) and K[HB(3,5-Me_2pz)$_3$] were purchased from Aldrich.

X-ray diffraction study. X-ray diffraction data sets were collected on Stoe IPDS1 (for **4**), Stoe IPDS2 (for *trans*-**2**, **7**, and **8**), and Nonius CAD-4 (for **5**) diffractometers (MoKα radiation, λ = 0.71073 Å). The structures were solved by direct methods and refined anisotropically by the full-matrix least-squares method against $|F|^2$ using the SHELXTL program package.[45] The positions of the hydrogen atoms were calculated geometrically. For compounds *trans*-**2**, **4**, **7**, and **8**, empirical absorption corrections were applied. The absorption correction for compound **5** was applied by the ψ-scan method. The crystallographic data were deposited with the Cambridge Structural Database (CCDC 265471-265474).

***cis*-Tetrakis(3,5-dimethylpyrazole)trioxotetrachlorodirhenium(v), $Re_2O_3Cl_4(3,5\text{-}Me_2pzH)_4$ (*cis*-1).** A mixture of [$ReCl_3(CH_3CN)(PPh_3)_2$] (200 mg, 0.23 mmol) and 3,5-dimethylpyrazole (45 mg, 0.46 mmol) was refluxed in a $CHCl_3$—$(CH_3)_2CO$ mixture (1 : 1, v/v) for 1 h. The solvent was evaporated, the precipitate was dissolved in chloroform, and the solution was stirred at ~20 °C for 4 h. Then the solution was filtered, the dark-yellow filtrate was concentrated, and the residue was dissolved in acetonitrile. An orange precipitate, which, most likely, has the structure [$ReCl_3(Me_2pzH)(PPh_3)_2$], was obtained by diethyl ether vapor diffusion into the solution, after which the solution gradually turned green, and crystals of complex *cis*-**1** precipitated. The yield was 16 mg (15%). IR (ν/cm^{-1}): 3553 s, 3474 s, 3416 s (NH), 3929 s, 3150 s (CH of the ring), 2934 w (CH_3), 1617 m, 1574 s, 1473 w, 1408 s, 1278 m, 1178 m, 1055 s, 969 m (Re=O), 904 s, 796 s, 756 s, 705 s (Re—O—Re), 616 m, 472 w. FAB-MS: *m/z* (I_{rel} (%)): 946 (10) $[M]^+$, 850 (100) $[M - 3,5\text{-}Me_2pzH]^+$, 719 (88) $[M - 3,5\text{-}Me_2pzH - Cl]^+$. EAS ($CHCl_3$), λ_{max}/nm (ε/L mol^{-1} cm^{-1}): 684 (394). ^{1}H NMR ($CDCl_3$), δ: 1.79, 2.28, 2.80, and 2.86 (all s, 6 H each, CH_3); 5.85 and 5.96 (both s, 2 H each, CH); 10.87 and 11.72 (both s, 2 H each, NH).

***trans*-Tetrakis(3,5-dimethylpyrazole)trioxotetrabromodirhenium(v), $Re_2O_3Br_4(3,5\text{-}Me_2pzH)_4$ (*trans*-2).** Dry HBr was passed through a boiling solution of complex **4** (30 mg) in chloroform (30 mL) for 1 h. The resulting green solution was concentrated to a minimum volume. The crystals were grown by diethyl ether vapor diffusion into the solution. The yield was 32 mg (90%). Found (%): C, 22.61; H, 2.89; N, 9.63; Br, 30.50. $C_{20}H_{32}Br_4N_8O_3Re_2$. Calculated (%): C, 21.36; H, 2.87; N, 9.96; Br, 28.42. IR (ν/cm^{-1}): 3227 s, 3130 sh, 1617 m, 1570 s, 1475 w, 1402 s, 1380 sh, 1300 m, 1180 m, 1150 w, 1062 s, 1030 w, 975 m (Re=O), 800 s, 780 s, 750 s, 680 s (Re—O—Re), 650 m, 600 m. ^{1}H NMR ($CDCl_3$), δ: 2.48 and 2.91 (both s, 12 H each, CH_3); 5.91 and 11.34 (both s, 4 H each, NH).

Bis(3,5-dimethylpyrazole)bis(μ-dimethylpyrazolato)trioxodichlorodirhenium(v), $Re_2O_3Cl_2(\mu\text{-}3,5\text{-}Me_2pz)_2(3,5\text{-}Me_2pzH)_2$ (3). A solution of the $(Et_4N)_2[ReOCl_5]$ complex (200 mg, 0.31 mmol) and 3,5-dimethylpyrazole (60 mg, 0.62 mmol) in ethanol (30 mL) was refluxed for 6.5 h, cooled to room temperature, and filtered. The green precipitate of complex **3** that formed was rapidly washed with ethanol and diethyl ether and dried in air. The yield was 120 mg (80%). Found (%): C, 28.68; H, 2.98; N, 10.23; Cl, 8.25. $C_{20}H_{30}Cl_2N_8O_3Re_2$. Calculated (%): C, 27.49; H, 3.46; N, 12.82; Cl, 8.11. IR (ν/cm^{-1}): 3424 m, 2926 w, 2831 w, 1605 s, 1569 sh, 1532 s, 1487 m, 1451 s, 1416 s, 1365 s, 1214 m, 1148 m, 1053 m, 962 s (Re=O), 760 s, 688 sh, 661 sh, 631 s (Re—O—Re), 480 m, 444 m. FAB-MS: *m/z* (I_{rel} (%)): 874 (28) $[M]^+$, 840 (29) $[M - Cl]^+$, 774 (14) $[M - 3,5\text{-}Me_2pzH]^+$, 682 (40) $[M - 2\ (3,5\text{-}Me_2pzH)]^+$. ^{1}H NMR ($CDCl_3$), δ: 2.19, 2.43, 2.73, and 2.83 (all s, 6 H each, CH_3); 5.83 and 6.03 (both s, 2 H each, CH).

Bis(3,5-dimethylpyrazole)bis(μ-dimethylpyrazolato)trioxodibromodirhenium(v) benzene monosolvate, $Re_2O_3Br_2(\mu\text{-}3,5\text{-}Me_2pz)_2(3,5\text{-}Me_2pzH)_2\cdot C_6H_6$ (4). A mixture of $(NH_4)_2ReBr_6$ (200 mg, 0.29 mmol) and 3,5-dimethylpyrazole (240 mg, 2.5 mmol) (or K[HB(Me_2pz)$_3$] (98 mg, 0.29 mmol)) in methanol (30 mL) was refluxed for 4 h. The brown solution was filtered and slowly concentrated. After several days, the green crystals of complex **4** that formed were filtered off, washed with ethanol, and dried in air. The yield was 46 mg (34%). Crystals suitable for X-ray diffraction were prepared by recrystallization from a benzene—*n*-hexane mixture. Found (%): C, 24.93; H, 3.12; N, 11.86; Br, 16.26. $C_{20}H_{30}Br_2N_8O_3Re_2$. Calculated (%): C, 24.95; H, 3.14; N, 11.64; Br, 16.60. IR (ν/cm^{-1}): 3320 sh, 3288 s, 2980 m, 2933 m, 2857 m, 1570 s, 1535 s, 1475 w, 1420 s, 1384 m, 1350 m, 1288 m, 1180 sh, 1150 m, 1120 m, 1058 s, 968 s (Re=O), 825 m, 814 m, 788 m, 750 w, 670 sh, 638 s (Re—O—Re), 600 m, 580 m, 500 m, 480 w, 449 w. EAS ($CHCl_3$), λ_{max}/nm (ε/L mol^{-1} cm^{-1}): 714 (328). ^{1}H NMR ($CDCl_3$), δ: 2.29, 2.47, 2.80, and 2.82 (all s, 6 H each, CH_3); 5.84 and 6.05 (both s, 2 H each, CH); 9.96 (s, 2 H, NH). FAB-MS: *m/z* (I_{rel} (%)): 962 (100) $[M]^+$, 867 (18) $[M - 3,5\text{-}Me_2pzH]^+$, 785 (26) $[M - 3,5\text{-}Me_2pzH - Br]^+$.

Bis(3,5-dimethylpyrazole)bis(μ-dimethylpyrazolato)trioxodiiododirhenium(v) benzene monosolvate, $Re_2O_3I_2(\mu\text{-}3,5\text{-}Me_2pz)_2(3,5\text{-}Me_2pzH)_2\cdot C_6H_6$ (5). Complex **5** was synthesized in 26% yield analogously to complex **4** (see above) with the use of $K_2[ReI_6]$ as a source of rhenium. Crystals suitable for X-ray diffraction were prepared by recrystallization from a benzene—*n*-hexane mixture. Found (%): C, 27.19; H, 2.84; N, 9.76; I, 23.30. $C_{26}H_{36}I_2N_8O_3Re_2$. Calculated (%): C, 27.52; H, 3.20; N, 9.87; I, 22.37. IR (ν/cm^{-1}): 3286 s, 2920 m, 2853 w, 1567 s, 1530 m, 1474 w, 1413 s, 1380 m, 1340 m, 1281 m, 1148 m, 1049 s, 960 s (Re=O), 913 s, 784 m, 666 sh, 624 s (Re—O—Re), 487 w, 443 w. EAS ($CHCl_3$), λ_{max}/nm (ε/L mol^{-1} cm^{-1}): 726 (277). ^{1}H NMR ($CDCl_3$), δ: 2.29, 2.53, 2.80, and 2.84 (all s, 6 H each, CH_3); 5.84 and 6.05 (both s, 2 H each, CH); 10.05 (s, 2 H, NH). FAB-MS: *m/z* (I_{rel} (%)): 1056 (100) $[M]^+$, 833 (18) $[M - 3,5\text{-}Me_2pzH - I]^+$, 739 (26) $[M - (3,5\text{-}Me_2pzH) - I]^+$, 610 (23) $[M - 2\ (3,5\text{-}Me_2pzH) - 2\ I]^+$, 425 (79) $[Re_2O_3]^+$.

Tetrakis(3,5-dimethylpyrazole)oxo(methoxo)rhenium(v) dibromide 3,5-dimethylpyrazole tetrahydrate, $[ReO(OMe)(3,5\text{-}Me_2pzH)_4]Br_2\cdot 3,5\text{-}Me_2pzH\cdot 4H_2O$ (6). The filtrate obtained after separation of the green crystals of compound **4**, was concentrated to dryness, and the residue was extracted with water. Slow evaporation of the filtrate in air afforded violet crystals of complex **6**. The yield was 17 mg (7%). Found (%): C, 32.98; H, 4.80; N, 14.13; Br, 16.80. $C_{20}H_{30}Cl_2N_8O_3Re_2$. Calculated (%): C, 32.16; H, 5.51; N, 15.00; Br, 17.11. IR (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 (Re=O), 813 m, 712 w. EAS (H_2O), λ_{max}/nm (ε/L mol^{-1} cm^{-1}): 543 (605). ^{1}H NMR ($CDCl_3$), δ: 1.75 (s, 12 H, CH_3); 2.26 (s, 6 H, CH_3); 2.36 (12 H, CH_3); 3.74 (s, 3 H, OCH_3); 5.84 (s, 1 H, CH); 6.18 (s, 4 H, CH); 11.2 (s, 4 H, NH). FAB-MS: *m/z* (I_{rel} (%)): 617 (100%) $[M - H]^+$.

(3,5-Dimethylpyrazole)(triphenylphosphine)bis(μ-dimethylpyrazolato)trioxodichlorodirhenium(v), $Re_2O_3Cl_2(\mu\text{-}3,5\text{-}Me_2pz)_2(3,5\text{-}Me_2pzH)(PPh_3)$ (7). A mixture of the $[ReNCl_2(PPh_3)_2]$ complex (200 mg, 0.025 mmol) and 3,5-dimethylpyrazole (97 mg, 0.1 mmol) in methanol (30 mL) was refluxed for 3 h. Then methylene chloride (20 mL) was added and the mixture was refluxed for 16 h. The hot solution was filtered and slowly evaporated in air. After three days, the green crystals of complex **7** that formed were filtered off, washed with acetone, and dried in air. The yield was 15 mg (12%). Found (%): C, 37.95; H, 3.32; N, 8.02; Cl, 6.70. $C_{33}H_{37}Cl_2N_6PO_3Re_2$. Calculated (%): C, 38.11; H, 3.59; N, 8.08; Cl, 6.82. IR (ν/cm^{-1}): 3300 m, 1560 w, 1525 w, 1480 w, 1433 sh, 1408 m, 1343 m, 1280 w, 1158 w, 1100 w, 1050 m, 960 s (Re=O), 820 w, 780 w, 753 m, 747 w, 695 m, 664 m, 635 s (Re—O—Re), 590 m, 533 w, 510 w, 480 w. $^{31}P\{^1H\}$ NMR ($CDCl_3$), δ: 7.07 (s). EAS, λ_{max}/nm (ε/L mol^{-1} cm^{-1}): 704 (304).

***trans*-Bis(3,5-dimethylpyrazole)tetrabromorhenium(iv) acetone monosolvate, $ReBr_4(3,5\text{-}Me_2pzH)_2 \cdot Me_2CO$ (8).** The salt $(NH_4)_2ReBr_6$ (62 mg, 0.09 mmol) was melted with a sixfold molar excess of 3,5-dimethylpyrazole (51 mg, 0.53 mmol). The reaction mixture was kept at 100 °C for 3 days and then at 200 °C for 2 days. The solidified melt was extracted with acetone and the solution was filtered. Large red crystals of complex **8** suitable for X-ray diffraction were grown by slow evaporation of the filtrate in air. The yield was 8 mg (13%). FAB-MS, *m/z* (I_{rel} (%)): 699 (39) $[M]^+$, 506.5 (22) $[ReBr_4]^+$, 442 (47) $[M - 2\,Br - (3,5\text{-}Me_2pzH)]^+$. EAS, λ_{max}/nm (ε/L mol^{-1} cm^{-1}): 524 (107).

Results and Discussion

Syntheses and interconversions of complexes

The green *cis*-$[Re_2O_3Cl_4(3,5\text{-}Me_2pzH)_4]$ complex (*cis*-**1**) was prepared in low yield by the reaction of NH_4ReO_4 with $K[HB(Me_2pz)_3]$ in concentrated HCl or by refluxing of $[ReCl_3(MeCN)(PPh_3)_2]$ with 3,5-Me_2pzH in air. The latter procedure afforded also another product as an orange precipitate. According to elemental analysis, the composition of the latter is $[ReCl_3(Me_2pzH)(PPh_3)_2]$. The IR spectrum of this complex shows bands of both PPh_3 and 3,5-Me_2pzH. However, the FAB-mass spectrum has only the ion peaks $[PPh_3]^+$ (100%), $[Me_2pzH]^+$ (100%), $[ReCl_3(Me_2pzH)]^+$ (1.5%), and $[ReCl_4(Me_2pzH)_2]^+$ (1.8%). Single crystals of this complex suitable for X-ray diffraction were not obtained because of low solubility of this product in most organic solvents. Recently, the red-orange $[ReCl_3(Me_2pzH)_2(PPh_3)]$ complex has been synthesized[25] in 85% yield under similar conditions with the only exception that the Re : 3,5-Me_2pzH molar ratio of 1 : 6.6 has been used in the cited study, whereas we used the 1 : 2 ratio. Apparently, oxo complex **1** was formed as a result of hydrolysis and oxidation of the intermediate Re^{III} complex with 3,5-Me_2pzH. The reaction of $[ReOCl_3(OAsPh_3)(AsPh_3)]$ with 3,5-Me_2pzH afforded complex **1** in higher yield (42%).[24] Its bromide analog, *viz.*, *cis*-$[Re_2O_3Br_4(3,5\text{-}Me_2pzH)_4]$ (*cis*-**2**), was synthesized[24] from $[ReOBr_3(OAsPh_3)(AsPh_3)]$ and 3,5-Me_2pzH in 40% yield along with a small amount of the complex with the deprotonated bridging pyrazolate ligand, $[Re_2O_3Br_2(\mu\text{-}3,5\text{-}Me_2pz)_2(3,5\text{-}Me_2pzH)_2]$ (**4**). Attempts to efficiently separate the mixture of these compounds failed. The corresponding chloride complex $[Re_2O_3Cl_2(\mu\text{-}3,5\text{-}Me_2pz)_2(3,5\text{-}Me_2pzH)_2]$ (**3**) was prepared by the reaction of $(Et_4N)_2[ReOCl_5]$ or $Cs_2[ReOCl_5]$ with 3,5-dimethylpyrazole in 80% and 10% yields, respectively. In the reaction with $Cs_2[ReOCl_5]$, $K[HB(3,5\text{-}Me_2pzH)_3]$ can serve as a source of dimethylpyrazole (the yield of complex **3** was 9%). The yield is low because of very poor solubility of $Cs_2[ReOCl_5]$. Earlier,[21] this complex has been structurally characterized as the $[Re_2O_3Cl_2(\mu\text{-}3,5\text{-}Me_2pz)_2(3,5\text{-}Me_2pzH)_2] \cdot 2[3,5\text{-}Me_2pzH_2]Cl$ compound (**3a**). We found that both complex **4** and its previously unknown iodide analog **5** can be selectively prepared in satisfactory yields by the reaction of $(NH_4)_2[ReBr_6]$ or $K_2[ReI_6]$ with 3,5-dimethylpyrazole. These complexes crystallize as benzene solvates $[Re_2O_3X_2(\mu\text{-}3,5\text{-}Me_2pz)_2(3,5\text{-}Me_2pzH)_2] \cdot C_6H_6$. In these reactions, Re^{IV} is oxidized to Re^{V}. In the reaction with the bromide, the purple $[Re(O)(OCH_3)(3,5\text{-}Me_2pzH)_4]Br_2 \cdot [3,5\text{-}Me_2pzH] \cdot 4H_2O$ complex was isolated in 7% yield.[22] The coordinated methoxy group is formed as a result of the nucleophilic attack of methanol on the rhenium atom. It should be emphasized that earlier all known $[ReO(OCH_3)L_4]^{2+}$ complexes (L are pyridines or imidazoles) have been synthesized by the reaction of the dioxo complexes $[ReO_2L_4]^{2+}$ with methyl triflate.[43,46]

The treatment of complex **4** with dry HBr in $CHCl_3$ led to cleavage of the pyrazolate bridges due to protonation of the ligand with the resulting selective formation of the *trans* isomer (*trans*-**2**).

$$\underset{\mathbf{4}}{[Re_2O_3Br_2(\mu\text{-}3,5\text{-}Me_2pz)_2(3,5\text{-}Me_2pzH)_2]} + 2\ HBr = \underset{trans\text{-}\mathbf{2}}{[Re_2O_3Br_4(3,5\text{-}Me_2pzH)_4]} \quad (1)$$

Our attempts to perform the reverse reaction by deprotonation of $[Re_2O_3X_4(3,5\text{-}Me_2pzH)_4]$ (X = Cl or Br) with such bases as pyridine (pK_a 5.20) or 3,5-dimethylpyrazole (pK_a 4.38) failed. The reaction (1) should lead to cleavage of the Re—N bond in the *trans* position with respect to the Re—Br bond because this bond is the longest one (X-ray diffraction data). It is the selective cleavage of this bond that gives rise to the *trans* isomer.

The reaction of $[ReNCl_2(PPh_3)_2]$ with 3,5-dimethylpyrazole unexpectedly led to hydrolytic denitration giving rise to the mixed-ligand complex $[Re_2O_3Cl_2(\mu\text{-}3,5\text{-}Me_2pz)_2(3,5\text{-}Me_2pzH)(PPh_3)]$ (**7**) in 12% yield as one of products. This compound and its bromide analogs were prepared in good yields (40%) by the reactions of

$[ReO(OEt)X_2(PPh_3)_2]$ with the ligand in ethanol.[24] The symmetric $[Re_2O_3X_2(\mu\text{-}3,5\text{-}Me_2pz)_2(PPh_3)_2]$ complexes (X = Cl or Br) can be prepared by performing the reaction of $[ReOX_3(PPh_3)_2]$ with a larger amount of the ligand.[24] We failed to replace dimethylpyrazole in $[Re_2O_3Cl_2(\mu\text{-}3,5\text{-}Me_2pz)_2(3,5\text{-}Me_2pzH)_2]$ with PPh_3 even after prolonged refluxing in chloroform (^{31}P NMR monitoring).

Red crystals of *trans*-$[ReBr_4(3,5\text{-}Me_2pzH)_2] \cdot Me_2CO$ (**8**) were isolated in 13% yield from the solution, which was obtained in the reaction of $(NH_4)_2[ReBr_6]$ with 3,5-dimethylpyrazole performed in the absence of a solvent by melting with a large excess of the ligand (200 °C, 2 days) followed by extraction of the solidified melt with acetone. This is the only known Re^{IV} complex with a pyrazole-type ligand. The formation of the *trans* isomer can easily be attributed to the steric requirements of the bulky ligand. The reaction can proceed either as the direct attack of the ligand on $[ReBr_6]^{2-}$ or through the initial elimination of ammonia to form $(3,5\text{-}Me_2pzH_2)_2[ReBr_6]$. The latter undergoes the Anderson rearrangement to give complex **8**. It is noteworthy that Re^{IV} is only partially reduced to Re^{III} under these drastic conditions. In turn, the Re^{III} complexes $[ReCl_3(pzH)_2(PPh_3)]$ and $[ReCl_3(pzH)_3]$ can easily be prepared from $[ReOCl_3(PPh_3)_2]$ by prolonged refluxing with an excess of the ligand. Apparently, these reactions occur due to the presence of PPh_3, which can act as an oxygen acceptor.[25,27]

Crystal structures

The characteristics of X-ray diffraction study are summarized in Table 1. The geometric parameters of the *cis*-$[Re_2O_3Cl_4(3,5\text{-}Me_2pzH)_4]$ molecule (*cis*-**1**) determined in three independent studies[10,21,24] agree well with each other and are not discussed in the present study. The molecular structure of *trans*-$[Re_2O_3Br_4(3,5\text{-}Me_2pzH)_4]$ (*trans*-**2**) is shown in Fig. 1. Selected distances and bond angles are given in Table 2. In both complexes, the rhenium atom is in a distorted octahedral environment, two oxygen atoms are in *trans* positions with respect to each other, and the Re=O and Re—O bond lengths have standard values. The *cis* and *trans* isomers differ in the mutual orientation of the halide and pyrazole ligands. The central Re—O—Re fragment is almost linear in *cis*-**2** (angle is 178.7° (2)) and is strictly linear in *trans*-**2**. In the latter complex, the geometry is strictly linear because the molecules have the crystallographic symmetry C_2.

Numerous complexes containing the linear $Re_2O_3^{4+}$ fragment were described in the literature: $[Re_2O_3Cl_4(py)_4]$ (both *cis* and *trans* isomers are known),[11,12] *cis*-$[Re_2O_3Cl_4(C_4H_4N_2)_4]$ ($C_4H_4N_2$ is pyrazine),[17] *trans*-$[Re_2O_3Cl_4(1\text{-}MeIm)_4]$ (1-MeIm is 1-methylimidazole),[30] *cis*-$[Re_2O_3Cl_4(Me_3Bzm)_4]$ (Me_3Bzm is 1,5,6-trimethylbenzimidazole), *symm*,*cis*-$[Re_2O_3Cl_4(Me_3Bzm)_2(py)_2]$,[13,31] and *cis*-$[Re_2O_3Cl_4(Haza)_4]$ (Haza

Table 1. Crystallographic parameters for complexes **2**, **4**, **5**, and **8**

Parameter	**2**	**4**	**5**	**8**
Molecular formula	$C_{20}H_{32}Br_4N_8O_3Re_2$	$C_{26}H_{36}Br_2N_8O_3Re_2$	$C_{26}H_{36}I_2N_8O_3Re_2$	$C_{13}H_{22}Br_4N_4ORe$
Molecular weight	1124.58	1040.85	1040.85	814.26
T/K	203(2)	203(2)	293(2)	100(2)
Space group	*Pccn*	*C*2/*c*	*C*2/*c*	$P2_1/c$
a/Å	11.322(2)	27.573(6)	27.718(4)	13.366(3)
b/Å	12.507(3)	15.521(3)	15.786(2)	9.285(2)
c/Å	21.651(4)	15.486(3)	15.860(2)	19.346(4)
α/deg	90	90	90	90
β/deg	90	94.67(3)	94.33(1)	93.79(3)
γ/deg	90	90	90	90
V/Å^3	3065.9(11)	6605(2)	6919.8(2)	2395.7(8)
Z	4	8	8	4
d_{calc}/g cm^{-3}	2.436	2.093	2.179	2.252
μ/mm^{-1}	13.139	9.783	8.814	11.762
Number of reflections				
measured	22088	8412	5057	14453
independent	3400	5120	4946	4960
GOOF	1.149	1.069	0.977	1.175
R factors				
for reflections with $I > 2\sigma(I)$:				
R_1	0.0666	0.0468	0.0375	0.0372
wR_2	0.1777	0.1237	0.1207	0.0997
for all reflections:				
R	0.0779	0.0504	0.0604	0.0380
wR_2	0.1891	0.1302	0.1260	0.1004

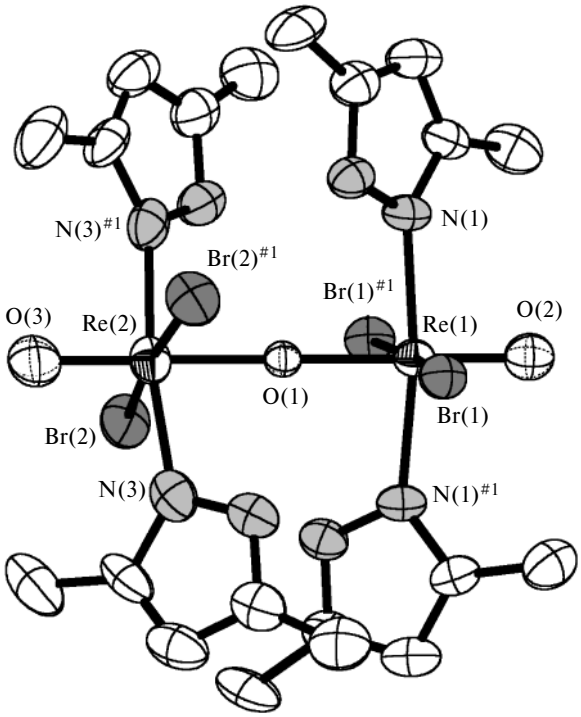

Fig. 1. Molecular structure of *trans*-**2**. The atoms are represented by anisotropic displacement ellipsoids drawn at the 50% probability level. The hydrogen atoms are omitted.

is 7-azaindole).[32,33] Bidentate 2,2′-bis(1*H*-imidazole) ($biimH_2$) forms the $[Re_2O_3Cl_4(biimH_2)_2]$, $[Re_2O_3Cl_4(biimH_2)_4]Cl_4$, and $[Re_2O_3(biimH)_4]$ complexes.[34,35] The $[Re_2O_3Cl_4(2,2'\text{-bipy})_2]$ complex was characterized in the study.[36] 4,6-Dimethylpyrimidine-2(1*H*)-thione (Me_2pymSH) forms the neutral *cis*-$[Re_2O_3(Me_2pymS)_4]$ complex.[37] As can be seen from the above-mentioned examples, almost all $[Re_2O_3X_4L_4]$ complexes (in which L is a monodentate ligand) were prepared as *cis* isomers. The only exceptions are the $[Re_2O_3Cl_4py_4]$ complex, for which both isomers were synthesized (*trans* isomer was prepared 34 years later than the *cis* isomer!),[11,12] and the $[Re_2O_3Cl_4(MeIm)_4]$ complex, which exists only as the *trans* isomer.[30] A comprehensive analysis of the possible conformations and nonbonded contacts in the $[Re_2O_3Cl_4py_4]$ complex did not provide an explanation for this seemingly preferential formation of the *cis* isomer.[11,12] On the whole, the geometric parameters of the complexes *trans*-**2**, *trans*-$[Re_2O_3X_4py_4]$, and *trans*-$[Re_2O_3Cl_4(1\text{-}MeIm)_4]$ are very similar. The conformations of all three molecules can be described as intermediate between eclipsed and staggered because both ReX_2L_2 planes are twisted about the Re—O—Re axis by 29.5° (*trans*-**2**), 27.5° (*trans*-$[Re_2O_3X_4py_4]$), and 28.5° (*trans*-$[Re_2O_3Cl_4(1\text{-}MeIm)_4]$) (0° corresponds to the completely eclipsed conformation). The planes of the heterocycles are inclined with respect to the ReX_2N_2 planes by 50.0° (*trans*-**2**), 40.9° (*trans*-$[Re_2O_3X_4py_4]$), and 37.1° (*trans*-$[Re_2O_3Cl_4(1\text{-}MeIm)_4]$), as is evident from the O=Re—N—C_{ortho} torsion angles. This conformation can be considered as a compromise between the necessity to avoid too close contacts between the substituents in the ring and the *cis*-ligands (which do not allow the rings to lie in a single plane), between two rings in the eclipsed configuration (resulting in the twist of the ReN_2X_2 planes about the O=Re—O—Re=O axis), and the tendency to retain stabilizing stacking interactions between the π orbitals of the heterocycles.[12]

In the $[ReOBr_3(OAsPh_3)(pzH)]$ complex with unsubstituted pyrazole,[38] the Re—N distance is 2.09(2) Å and the Re—Br distances are 2.496(2) and 2.542(2) Å.

In complexes **3a**, **4** (Fig. 2), and **5**, the central $Re_2O_3^{4+}$ fragment is nonlinear due to the contracting effect of two

Table 2. Bond lengths (*d*) and bond angles (ω) in complex *trans*-**2**

Bond	*d*/Å
Re(1)—O(2)	1.689(14)
Re(1)—O(1)	1.929(9)
Re(1)—N(1)	2.111(10)
Re(1)—N(1)#1	2.111(10)
Re(1)—Br(1)	2.5504(13)
Re(1)—Br(1)#1	2.5504(13)
Re(2)—O(3)	1.698(14)
Re(2)—O(1)	1.944(9)
Re(2)—N(3)	2.114(11)
Re(2)—N(3)#1	2.114(11)
Re(2)—Br(2)	2.5520(13)
Re(2)—Br(2)#1	2.5520(13)

Angle	ω/deg
Re(1)—O(1)—Re(2)	180.0
O(2)—Re(1)—O(1)	180.000(1)
O(2)—Re(1)—N(1)	94.0(3)
O(1)—Re(1)—N(1)	86.0(3)
O(2)—Re(1)—N(1)#1	94.0(3)
O(1)—Re(1)—N(1)#1	86.0(3)
N(1)—Re(1)—N(1)#1	172.1(5)
O(2)—Re(1)—Br(1)	92.54(3)
O(1)—Re(1)—Br(1)	87.46(3)
N(1)—Re(1)—Br(1)	88.6(3)
N(1)#1—Re(1)—Br(1)	88.6(3)
O(2)—Re(1)—Br(1)#1	92.54(3)
O(1)—Re(1)—Br(1)#1	87.46(3)
N(1)—Re(1)—Br(1)#1	87.46(3)
Br(1)—Re(1)—Br(1)#1	174.93(6)

Angle	ω/deg
O(3)—Re(2)—O(1)	180.000(2)
O(3)—Re(2)—N(3)#1	94.2(3)
O(1)—Re(2)—N(3)#1	85.8(3)
O(3)—Re(2)—N(3)	94.2(3)
O(1)—Re(2)—N(3)	85.8(3)
N(3)#1—Re(2)—N(3)	171.5(5)
O(3)—Re(2)—Br(2)	92.87(3)
O(1)—Re(2)—Br(2)	87.13(3)
N(3)#1—Re(2)—Br(2)	91.6(3)
N(3)—Re(2)—Br(2)	91.6(3)
O(3)—Re(2)—Br(2)#1	92.87(3)
O(1)—Re(2)—Br(2)#1	87.13(3)
N(3)—Re(2)—Br(2)#1	91.6(3)
Br(2)—Re(2)—Br(2)#1	174.25(6)

Note. The symmetry code: #1 $-x + 1/2, -y + 1/2, z$.

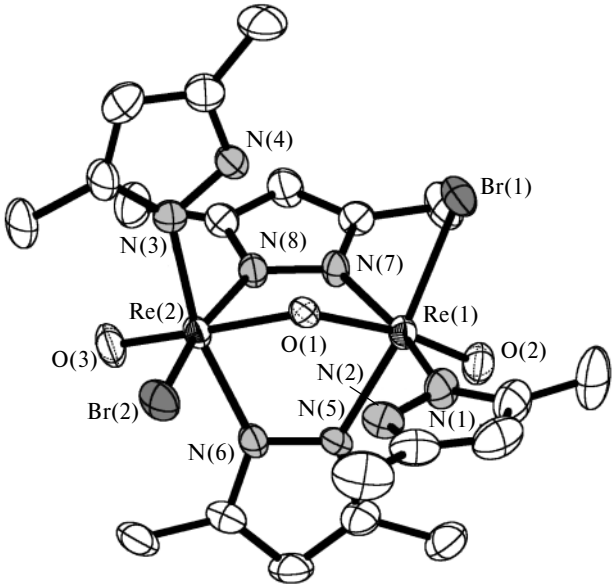

Fig. 2. Molecular structure of the $[Re_2O_3Br_2(\mu\text{-}3,5\text{-}Me_2pz)_2(3,5\text{-}Me_2pzH)_2]$ complex in the crystals of **4**. The atoms are represented by anisotropic displacement ellipsoids drawn at the 50% probability level. The hydrogen atoms are omitted.

bridging pyrazolate ligands. These fragments are additionally coordinated by two neutral pyrazole molecules and two halogen atoms. The structure of **3a** has been discussed in detail in the study.[30] Complexes **4** and **5** crystallize as isostructural benzene solvates. The structural data for complexes **4** and **5** are given in Table 3. The Re—O—Re angles are only slightly different (122.7° in **3a** and **4** and 125.6° in **5**). The Re=O and Re—O bond lengths in the linear $Re_2O_3^{4+}$ group differ insignificantly from those in the nonlinear fragment. However, the terminal Re=O bond in complex **5** is one of the shortest bonds found in compounds containing the $Re_2O_3^{4+}$ fragment.[39] The Re—N bonds in *trans* positions with respect to the coordinated halogen atoms are slightly longer than those in *cis* positions. Apparently, this is responsible for the formation of complex *trans*-**2** in the reaction of complex **4** with dry HBr. The μ-benzotriazolate complexes $[Re_2O_3X_4(\mu\text{-}C_6H_4N_3)_2(Ph_3P)_2]$ (X = Cl or Br) prepared from $[ReOX_3(PPh_3)_2]$ and benzotriazole are the closest structural analogs of the bridged pyrazolate complexes. The Re—O—Re angles in these complexes have very similar values (125—126°). The Re—N distances in both types of complexes are virtually equal.[26] The $[ReO\{\eta^2\text{-}Bpz_4\}(\eta\text{-}pz)]_2(\mu\text{-}O)$ and $[Re_2O_3Cl_4(\mu\text{-}Me_2biimz)_2]$ complexes also contains the nonlinear central fragment.[34,35,39]

Let us note the interesting common features of the chemistry of pyrazole and pyrazolate complexes of ReO^{3+} and $Ru(NO)^{3+}$. The *trans*-$[Ru_2(NO)_2(\mu\text{-}O)Cl_4(3,5\text{-}Me_2pzH)_4]$ complex has the linear $\{(NO)Ru—O—Ru(NO)\}^{4+}$ fragment, whereas the nonlinear $\{(NO)Ru—O—Ru(NO)\}^{4+}$ fragment is present in the $[Ru_2(NO)_2(\mu\text{-}O)(\mu\text{-}3,5\text{-}Me_2pzH)_2(3,5\text{-}Me_2pzH)_2Cl_2]$ complex, which is an analog of complex **3**. The $\{(NO)Ru—O—Ru(NO)\}^{4+}$ and $Re_2O_3^{4+}$ groups can be considered as isoelectronic if the terminal oxygen atoms in the rhenium complex are considered as donors of four electrons.[40]

The crystal structure of the solvate $[ReBr_4(3,5\text{-}Me_2pzH)_2]\cdot Me_2CO$ (**8**) contains two crystallographically

Table 3. Bond lengths (*d*) and bond angles (ω) in molecules **4** and **5** (X = Br or I)

Parameter	**4** (X = Br)	**5** (X = I)
Bond	*d*/Å	
Re(1)—O(2)	1.682(5)	1.688(12)
Re(1)—O(1)	1.935(4)	1.915(10)
Re(1)—N(1)	2.127(8)	2.130(14)
Re(1)—N(5)	2.137(5)	2.118(14)
Re(1)—N(7)	2.079(6)	2.085(14)
Re(1)—X(1)	2.5411(10)	2.7442(15)
Re(2)—O(3)	1.700(5)	1.654(12)
Re(2)—O(1)	1.931(4)	1.896(10)
Re(2)—N(3)	2.124(7)	2.091(15)
Re(2)—N(6)	2.090(6)	2.081(14)
Re(2)—N(8)	2.147(6)	2.103(14)
Re(2)—X(2)	2.5397(10)	2.7302(15)
Angle	ω/deg	
Re(1)—O(1)—Re(2)	122.7(3)	125.6(6)
O(2)—Re(1)—O(1)	169.4(2)	168.7(6)
O(2)—Re(1)—N(7)	97.4(3)	96.6(6)
O(1)—Re(1)—N(7)	80.3(2)	80.1(5)
O(2)—Re(1)—N(1)	99.4(3)	98.8(6)
O(1)—Re(1)—N(1)	83.0(2)	84.2(5)
N(7)—Re(1)—N(1)	163.1(2)	164.3(6)
O(2)—Re(1)—N(5)	89.8(3)	90.8(6)
O(1)—Re(1)—N(5)	80.0(2)	78.5(5)
N(7)—Re(1)—N(5)	90.6(2)	90.4(5)
N(1)—Re(1)—N(5)	88.2(3)	86.6(6)
O(2)—Re(1)—Br(1)	100.9(2)	100.2(5)
O(1)—Re(1)—Br(1)	89.31(14)	90.5(3)
N(7)—Re(1)—Br(1)	87.81(16)	88.8(4)
N(1)—Re(1)—Br(1)	90.3(2)	91.1(4)
N(5)—Re(1)—Br(1)	169.26(16)	169.0(4)
O(3)—Re(2)—O(1)	168.9(3)	168.7(5)
O(3)—Re(2)—N(6)	96.0(3)	96.6(6)
O(1)—Re(2)—N(6)	81.1(2)	79.5(5)
O(3)—Re(2)—N(3)	98.9(3)	97.7(6)
O(1)—Re(2)—N(3)	83.9(2)	86.1(5)
N(6)—Re(2)—N(3)	165.0(2)	165.6(6)
O(3)—Re(2)—N(8)	90.0(3)	91.1(6)
O(1)—Re(2)—N(8)	79.3(2)	78.5(5)
N(6)—Re(2)—N(8)	89.5(2)	91.3(5)
N(3)—Re(2)—N(8)	88.5(2)	86.8(5)
O(3)—Re(2)—Br(2)	102.1(2)	100.9(5)
O(1)—Re(2)—Br(2)	88.59(14)	89.7(3)
N(6)—Re(2)—Br(2)	88.97(18)	88.8(4)
N(3)—Re(2)—Br(2)	89.84(18)	90.2(4)
N(8)—Re(2)—Br(2)	167.92(16)	168.0(4)

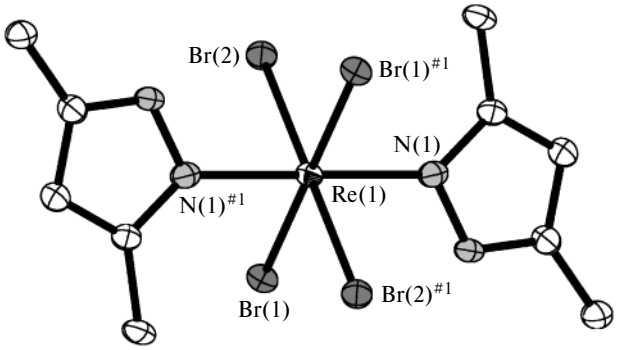

Fig. 3. Molecular structure of the $[ReBr_4(3,5\text{-}Me_2pzH)_2]$ complex in the crystals of **8**. The atoms are represented by anisotropic displacement ellipsoids drawn at the 50% probability level. The hydrogen atoms are omitted.

independent *trans*-$[ReBr_4(3,5\text{-}Me_2pzH)_2]$ molecules (Fig. 3) characterized by very similar geometric parameters (Table 4). The rhenium atoms are in a slightly distorted octahedral environment (angles at the rhenium atoms are 88—92°) formed by four bromine atoms (Re—Br, 2.4826(5)—2.5024(8) Å) and two nitrogen atoms of the pyrazolate ligands in *trans* positions with respect to each other (Re—N, 2.118(3)—2.130(3) Å). The Re—Br distances are similar to those observed[41] in the salt $K_2[ReBr_6]$ (2.49(4) Å). The Re—N—Re angle is 180°, and the rhenium atoms lie on inversion centers. Both pyrazole rings in complex **8** are in a single plane. However, the crystallographically independent molecules differ slightly in the orientation of the heterocyclic rings. The angles between these rings and the $ReBr_2N_2$ plane in two molecules are 44.42(2)° and 48.26(2)°.

Electrochemistry

All dinuclear rhenium complexes synthesized in the present study can undergo oxidation under conditions of cyclic voltammetry experiments. Generally, only one quasireversible peak in the region from 2.0 to −1.0 V is observed. This peak corresponds to oxidation of Re^{V} to Re^{VI}. The potentials $E_{1/2}$ (in $CHCl_3$, relative to Ag/AgCl) are 1.357 V for chloride *cis*-**1** and 1.373 V for bromide *trans*-**2**. For comparison, two one-electron oxidation peaks and two one-electron reduction peaks are observed for the pyridine complexes $[Re_2O_3Cl_4(Rpy)_4]$ (Rpy are different pyridine derivatives).[42] The pyrazolate-bridged complexes are characterized by substantially lower potentials. For complex **4**, $E_{1/2}$ = 1.082 V. For triphenylphosphine complex **7** ($E_{1/2}$ = 1.095 V), an additional irreversible oxidation peak is observed at 1.4 V, which is apparently associated with oxidation of the coordinated PPh_3 ligand to form oxide. The mononuclear oxo methoxo complex **6** has one pronounced reversible reduction peak ($E_{1/2}$ = −0.785 V) in the region from 1.0 to −1.2 V corresponding to the reversible Re^{V}/Re^{IV} pair. It is known[43] that the analogous complexes with pyridine, $[Re(O)(OMe)(Rpy)_4]^{2+}$, can undergo one-electron reduction at similar potentials. Tetrabromo complex **8** can undergo quasireversible reduction at moderately negative potentials (E_c = −0.20 V, E_a = −0.11 V). This indicates that the corresponding rhenium(III) complex $[ReBr_4(3,5\text{-}MepzH)_2]^-$ can be isolated taking into account that the *trans*-$[ReBr_4(py)_2]^-$ complex was synthesized.[44]

Vibrational and electronic spectra

The IR spectra show characteristic ν(Re=O) bands at 970—950 cm^{-1} and ν(Re—O—Re) bands at 600—700 cm^{-1} belonging to the $Re_2O_3^{4+}$ fragments. In the spectra of *cis*-**1** and *trans*-**2**, vibrations involving the bridging oxygen atom are observed at 705 and 680 cm^{-1}, respectively, whereas these bands in the spectra of complexes **3—5** are observed at lower frequencies in the 600—630 cm^{-1} region. The IR spectrum of complex **6**

Table 4. Bond lengths (*d*) and bond angles (ω) in molecule **8***

Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
Re(1)—N(1)	2.119(3)	$N(1)^{\#1}$—Re(1)—N(1)	180	N(3)—Re(2)—$N(3)^{\#2}$	180
Re(1)—$N(1)^{\#1}$	2.119(3)	$N(1)^{\#1}$—Re(1)—Br(2)	89.25(8)	N(3)—Re(2)—Br(3)	88.62(9)
Re(1)—Br(1)	2.4946(6)	N(1)—Re(1)—Br(2)	90.75(8)	$N(3)^{\#2}$—Re(2)—Br(3)	91.38(9)
Re(1)—Br(2)	2.4925(8)	N(1)—Re(1)—$Br(2)^{\#1}$	89.25(8)	N(3)—Re(2)—$Br(3)^{\#2}$	91.38(9)
Re(1)—$Br(1)^{\#1}$	2.4946(6)	Br(2)—Re(1)—$Br(2)^{\#1}$	180	Br(3)—Re(2)—$Br(3)^{\#2}$	180
Re(1)—$Br(2)^{\#1}$	2.4925(8)	N(1)—Re(1)—$Br(1)^{\#1}$	91.75(9)	N(3)—Re(2)—$Br(4)^{\#2}$	91.18(8)
Re(2)—N(3)	2.131(3)	Br(2)—Re(1)—$Br(1)^{\#1}$	91.94(2)	Br(3)—Re(2)—$Br(4)^{\#2}$	88.36(2)
Re(2)—$N(3)^{\#2}$	2.131(3)	$N(1)^{\#1}$—Re(1)—Br(1)	91.75(9)	N(3)—Re(2)—Br(4)	88.82(8)
Re(2)—Br(3)	2.4825(5)	N(1)—Re(1)—Br(1)	88.25(9)	$N(3)^{\#2}$—Re(2)—Br(4)	91.18(8)
Re(2)—$Br(3)^{\#2}$	2.4825(5)	Br(2)—Re(1)—Br(1)	88.06(2)	Br(3)—Re(2)—Br(4)	91.64(2)
Re(2)—$Br(4)^{\#2}$	2.5024(8)	$Br(2)^{\#1}$—Re(1)—Br(1)	91.94(2)	$Br(3)^{\#2}$—Re(2)—Br(4)	88.36(2)
Re(2)—Br(4)	2.5024(8)	$Br(1)^{\#1}$—Re(1)—Br(1)	180	$Br(4)^{\#2}$—Re(2)—Br(4)	180

* The symmetry codes: $^{\#1}$ $-x+1, -y+1, -z+1$; $^{\#2}$ $-x+2, -y+2, -z+1$.

shows ν(Re—OCH_3) (712 cm^{-1}), ν(Re=O) (948 cm^{-1}), and ν(ReO—CH_3) (1120 cm^{-1}) bands. The bands corresponding to the C=C and C=N bonds are shifted to lower frequencies by ~70 cm^{-1} (*cf.* 1663 and 1595 cm^{-1} for free 3,5-dimethylpyrazole). The N—H bonds in the coordinated ligand are responsible for the appearance of intense bands at 3330—3100 cm^{-1}. The electronic absorption spectra of the dinuclear complexes show characteristic absorption maxima at ~700 cm^{-1}, which undergo a weak bathochromic shift on going from the linear to nonlinear central fragment in complexes **3**—**5**. These maxima correspond to the $^1A_1$—$^1T_2$ transition in a Re^V chromophore with the d^2 electronic configuration.[24] Iodide complex **5** also shows a slight bathochromic shift (by ~10 cm^{-1}) compared to chloride complex **3**. The spectrum of complex **6** exhibits one absorption band in the 300—900 nm region (543 nm), which is characteristic of all $[Re(O)(OR)(L)_4]^{2+}$ complexes (R = H or Me; L are pyridines or imidazoles) and corresponds to the *d*—*d* transition.[43]

^{1}H NMR spectra

In the ^{1}H NMR spectra of complexes *cis*-**1** and *trans*-**2**, all four pyrazole ligands are equivalent. The same is evident from the crystal structure established by X-ray diffraction. This indicates that the molecular structure in solution is identical to that in the solid phase and that the complex is stereochemically rigid. These facts are in sharp contradiction with nonrigidity of the $[Re_2O_3Cl_4L_4]$ complexes with the bulky 3,5-lutidine and 1,5,6-trimethylbenzimidazole ligands.[17—19] The signal for the protons at the nitrogen atoms is observed as a sharp peak. The methyl groups in the ligand are nonequivalent and appear as two singlets. The ^{1}H NMR spectra of complexes **3**—**6** contain two different sets of signals due to the presence of four types of Me groups and two types of ring protons of the terminal and bridging pyrazole ligands (in a ratio of 1 : 1), whereas the protons of the NH groups give only one signal because only the terminal pyrazole ligands are neutral, whereas the bridging ligands are deprotonated. The well-resolved narrow signals in the ^{1}H NMR spectra (at room temperature) rule out the occurrence of exchange processes between the bridging and terminal ligands in solution. In the structure of **6**, all four pyrazole ligands are oriented in the same direction so that the NH groups point toward the methoxy groups. In solution, the protons of the methoxy groups give one signal at δ 3.74, which rules out the existence of several rotamers in solution. In the ^{1}H NMR spectrum of paramagnetic complex **8** (configuration d^3-Re^{IV}), no proton signals were observed.

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