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Homo- and hetero-metallic rhenium oxomethoxide complexes with a $M_4(\mu\text{-}O)_2(\mu\text{-}OMe)_4$ planar core—a new family of metal alkoxides displaying a peculiar structural disorder. Preparation and X-ray single crystal study

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The reaction of Re_2O_7 with MeOH at room temperature leads to a fine black powder. A product with the same crystal structure, according to X-ray powder data, was obtained in the form of single crystals on storage of solutions of $Re_2O_3(OMe)_6$, obtained by anodic oxidation of Re metal. It was identified as $Re_4O_6(OMe)_{12}$ (**1**) by an X-ray single crystal study. A mixed-valence complex of analogous composition and structure, $Re_4O_{6-y}(OMe)_{12+y}$ (**2**), earlier erroneously described as $Re_4O_2(OMe)_{16}$, can be obtained *via* anodic dissolution of Re in MeOH using high current densities. The heterometallic members of this family, $Re_{4-x}M_xO_{6-y}(OMe)_{12+y}$ [M = Mo (**3**), W (**4**); $x \le 0.55$, $y < 1.0$], were obtained by interaction of Re_2O_7 with $MO(OMe)_4$ or $M(OMe)_6$ in toluene at reflux. Mo-poor samples of **3** ($x \le 0.25$) could also be obtained on storage of solutions prepared by anodic oxidation of Re in the presence of $MoO(OMe)_4$. The reaction of Re_2O_7 with $Nb(OMe)_5$ or $Ta(OMe)_5$ in refluxing toluene gave $M_4(\mu\text{-}O)_2(\mu\text{-}OMe)_4(OMe)_{14}(ReO_4)_2$ [M = Nb (**5**), Ta (**6**)] as the only crystalline products. The compounds **1**–**6** are insoluble in organic solvents and display a remarkable resistance to ambient atmosphere, making them attractive precursors for soft chemical preparation of rhenium metal and alloy powders.

Introduction

The homo- and hetero-metallic oxide derivatives of rhenium are of current interest, both as components of catalysts[1] and as intermediate products in the preparation of fine rhenium metal and alloy powders.[2,3] Of special interest in this case is the possibility of obtaining single-source precursors for Mo–Re and W–Re alloys with small contents of one of the metals, which find application, in particular, as construction materials for the combustion cameras of spaceships and also as materials for wires in electric lamps.[2,3] The low thermal stability of alkoxide complexes of rhenium makes them attractive as precursors for the preparation of the corresponding oxides.[4]

The synthetic approaches to the high-valent alkoxide complexes of rhenium reported in the literature include the metathesis of $ReOCl_4$, which provides $Re_2O_3(OMe)_6$, $Li_2Re_2O_2(O^iPr)_{10}$, and $ReO(O^tBu)_4$,[5] co-condensation of ReF_6 with $Si(OMe)_4$, which leads to fluoroalkoxides of Re(VI)[6] [initially erroneously reported as $Re(OMe)_6$[7]] which can be converted into $Re_2(OMe)_{10}$ by subsequent reaction with $Mg(OMe)_2$,[6] and also the interaction of ReO_3Cl with ethers and diols, which provides $ReO_3(OR)$[8] [R = Me, $SiMe_3$, and $ReO(O_2R')_2$;[4] R′ = C_6H_{12}, $C_{12}H_{20}$]. In a series of short communications, we have also reported the application of anodic oxidation of rhenium for this purpose. This reaction in pure MeOH led to a derivative formulated as "$Re_4O_2(OMe)_{16}$"[9] and, when the electrolysis was carried out in the presence of $MoO(OMe)_4$, to $ReMoO_2(OMe)_7$[10] (isolable from freshly prepared electrolytes of composition Re : Mo = 1 : 1) and $(Re_{0.9}Mo_{0.1})_4O_{5.86}(OMe)_{12.14}$[11] (which precipitated from the electrolytes of composition Re : Mo = 9 : 1 on storage). Here, we report the isolation and X-ray single crystal study of the solid and insoluble products obtained both on storage of electrochemically generated Re-based solutions of different compositions, and also by the interaction of Re_2O_7 with molybdenum and tungsten methoxides of the $MO(OR)_4$ and $M(OR)_6$ series, and with $Nb_2(OMe)_{10}$ and $Ta_2(OMe)_{10}$. All these compounds turned out to belong to a single molecular structure family based on a $M_4(\mu\text{-}O)_2(\mu\text{-}OMe)_4$ planar rectangular core.

Experimental

All manipulations were carried out in a dry nitrogen atmosphere using Schlenk techniques or a dry box. Methanol was purified by distillation over $Mg(OMe)_2$ and toluene and hexane over $LiAlH_4$ under argon. IR spectra of Nujol mulls were recorded with a Perkin-Elmer 1700X spectrometer. ^1H NMR solution spectra were obtained with a Varian 400 MHz spectrometer with dry deaerated toluene as solvent (using TMS as an internal standard and a 20 vol% solution of $CDCl_3$ as an external standard). Solid state ^{13}C CP MAS NMR spectra were obtained with a Bruker MSL spectrometer operating with a 7 T magnet. The MAS frequency was 4400 Hz. The powder

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diffractograms were recorded using the Guinier technique by Mr Lars Göthe at Stockholm University. The metal ratios in the samples were determined, exploiting the facilities of the Arrhenius Laboratory, Stockholm University, Sweden, on a JEOL-820 scanning electron microscope (SEM), fitted with a Link AN-10000 energy dispersive spectrometer (EDS). Determination of carbon and hydrogen contents was carried out at the Laboratory of Organic Microanalysis of the Institute of Organoelement Compounds, Moscow, Russia and at Mikrokemi AB, Uppsala, Sweden.

Synthesis and isolation of the products obtained

The starting reagents used in this work [$MoO(OMe)_4$, $W(OMe)_6$, $WO(OMe)_4$,[12] and $Nb_2(OMe)_{10}$[13]] were prepared by anodic oxidation of the metals in alcohols and purified according to conventional techniques. Anodic dissolution of rhenium was carried out in a cell without subdivision of cathodic and anodic space and with water cooling (the temperature in the cell was kept at 15 °C). LiCl (0.025 M) in MeOH was used as the electrolyte. Attempts to obtain heterometallic derivatives were carried out with solutions of 0.8 ± 0.05 g of $MO(OR)_4$ (M = Mo, W) in 70 ml of the electrolyte. A cylindrical metal rod (6.0 mm in diameter, 30 mm long) was used as the anode and a nickel steel plate (8 × 30 × 0.3 mm) as the cathode. The total current through the cell was kept constant with the aid of a KYORITSU potentiostat operating at $I = 0.150$ A; the voltage varying between 28 and 32 V. The duration of the experiments ranged between 8 and 36 h. The metal ratios in the solutions obtained were estimated on the basis of the weight loss of the anode.

Isolation of $Re_2O_3(OMe)_6$. The dark green solution (70 ml) obtained by dissolution of rhenium in MeOH in the absence of other metal alkoxides (duration of the process 18 h; 1.831 g Re dissolved) was evaporated to dryness *in vacuo*, leaving a violet residue. The latter was layered with 40 ml hexane producing a reddish violet very viscous lower phase and a mobile orange–red upper phase. The upper phase was separated, reduced to half its original volume (≈ 20 ml) by evaporation *in vacuo*, and left to crystallize overnight at −30 °C. The orange diamond-shaped crystals formed were separated by decantation, washed with 2 ml cold hexane, and dried *in vacuo*. Yield 2.74 g, 46% relative to Re metal dissolved. The IR and ^1H NMR spectroscopic data were identical to those reported in the literature.[5] The product was very sensitive to ambient atmosphere and unstable on storage, which precluded elemental analysis, however, its nature was confirmed by the unit cell determinations for 4 randomly chosen single crystals that all showed the same parameters: monoclinic, space group $P2_1/n$, $a = 12.1443(16)$, $b = 15.3579(21)$, $c = 7.3097(10)$ Å, $\beta = 90.164(2)°$, compared with $a = 12.142(1)$, $b = 15.369(1)$, $c = 7.311(1)$ Å, $\beta = 90.22(1)°$ reported earlier for this compound.[5]

$Re_4O_6(OMe)_{12}$ (1). *Method (a).* $Re_2O_3(OMe)_6$ (1.217 g, 2.00 mmol) was dissolved in 25 ml MeOH, giving a brownish green solution which was left at room temperature in thorough isolation from ambient atmosphere. The precipitation of reddish black flaky crystals occurred in practically quantitative yield over 4 days; the color of the residual solution turning very light greenish yellow. Found (%): C 11.76, H 3.06, Re 64. Calculated for $Re_4O_6(OMe)_{12}$ (%): C 11.88, H 3.00, Re 61.5. IR, ν/cm^{-1}: 1160 m, 1057 s, 1034 s, 1005 s, 982 m, 961 s, 952 sh, 784 w, 577 s, 550 s, 526 s, 499 s, 456 s.

Method (b). $Re_2O_3(OMe)_6$ (0.147 g, 0.24 mmol) was dissolved in 1 ml toluene and sealed in an NMR tube. Precipitation of reddish black single crystals occurred at room temperature within a month. The solution turned practically colorless, indicating the completeness of the reaction. The microanalytical and spectral data for this sample were similar to those in (a).

Method (c). Re_2O_7 (0.216 g, 0.45 mmol) was added to 20 ml MeOH. The mixture became dark red and precipitation of a black powder commenced overnight. The precipitation was complete in a week, with a practically quantitative yield, leaving a very light brownish solution. The microanalytical and spectral data for this sample were similar to those in (a).

$Re_4O_{6-y}(OMe)_{12+y}$ (2). Anodic dissolution of rhenium at $U = 110$ V dc and $I \approx 1$ A in the same kind of cell as described above gave a dark red solution and a greenish black crystalline sediment. The amount of the latter varied in different experiments (70–90% yield relative to dissolved Re). Found (%): C 12.29, H 3.49, Re 61. Calculated for $Re_4O_6(OMe)_{12}$ [$Re_4O_2(OMe)_{16}$] (%): C 11.88 [15.09], H 3.00 [3.77], Re 61.5 [58.5]. Calculated for $Re_4O_{5.45}(OMe)_{12.55}$ (%): C 12.29, H 3.07, Re 60.7 ($y = 0.55$). IR, ν/cm^{-1}: 1166 m, 1123 m, 1069 m, 1038 s, 1021 s, 966 s br, 870 sh, 783 w, 597 m, 564 s, 544 m, 431 m.

$(Re_{0.76}Mo_{0.24})_4O_6(OMe)_{12}$ (3a). An electrochemically prepared solution in MeOH with Re : Mo = 3 : 1 was left to crystallize for a week at room temperature. The precipitation of black crystals was observed, with typical yields of 50–60% relative to the amount of dissolved Re. Found (%):† C 12.15, H 3.04. Calculated for $(Re_{0.76}Mo_{0.24})_4O_6(OMe)_{12}$ (%): C 13.11, H 3.28. IR, ν/cm^{-1}: 1166 m, 1070 s, 1035 s, 984 s, 967 s, 950 s, 920 m, 870 m, 820 m, 750 w, 627 s, 570 s br.

$(Re_{0.4}Mo_{0.6})_4O_6(OMe)_{12}$ (3b). Re_2O_7 (0.267 g, 0.55 mmol) was added to a bright yellow solution of $MoO(OMe)_4$ (0.318 g, 1.35 mmol) in 5 ml toluene. The mixture immediately turned dark red. It was subjected to reflux for 30 min and left to crystallize for 3 days at room temperature. Yield 0.203 g, 92% with respect to Re_2O_7. Found (%): C 13.60, H 3.24, Re : Mo = 0.45 : 0.55. Calculated for $(Re_{0.45}Mo_{0.55})_4O_6(OMe)_{12}$ (%): C 14.29, H 3.57. [Found (%):† C 12.64, H 3.26, Re : Mo = 0.45 : 0.55.] IR, ν/cm^{-1}: 1155 s, 1128 m, 1097 m, 1083 m, 1069 m, 1060 m, 1027 s, 1015 vs, 1000 s, 984 w, 973 w, 943 vs, 923 vvs, 909 s, 880 m, 853 m, 837 m, 648 m, 574 s, 549 s, 540 m, 528 vvs, 483 m, 461 m, 432 m.

$(Re_{0.5}W_{0.5})_4O_{6-y}(OMe)_{12+y}$ (4). Re_2O_7 (0.328 g, 0.68 mmol) was added to a transparent colorless solution of $WO(OMe)_4$ (0.622 g, 1.92 mmol) in 5 ml toluene. The mixture immediately turned dark red. It was subjected to reflux for 30 min and left to crystallize for 3 days at room temperature. Yield 0.394 g, 96% with respect to Re_2O_7. Found (%): C 13.39, H 3.59, Re : W = 0.5 : 0.5. Calculated for $(Re_{0.50}W_{0.50})_4O_{3.74}(OMe)_{14.26}$ (%): C 13.39, H 3.34 ($y = 2.26$). IR, ν/cm^{-1}: 1166 s, 1155 s, 1074 m, 1036 s, 1018 s, 1009 m, 997 m, 955 s, 943 m, 930 m, 914 w, 907 w, 880 w, 864 m, 855 w, 817 m, 806 s, 785 w, 643 s, 571 s, 553 s, 535 s, 528 m, 517 s, 461 s, 432 s.

$Nb_4O_2(OMe)_{14}(ReO_4)_2$ (5). Re_2O_7 (0.209 g, 0.43 mmol) was added to a transparent colorless solution of $Nb_2(OMe)_{10}$ (0.369 g, 1.49 mmol) in 5 ml toluene. No immediate dissolution occurred, but a red coloration on the surfaces of the light yellow particles of oxide was noticeable. The mixture was subjected to reflux for 30 min. After cooling the mixture again, comparatively big (0.4–1.2 mm), light pink-colored transparent crystals, a dark grey powder, and a nearly colorless liquid that did not contain metal alkoxides in detectable quantities, remained. The liquid was removed, together with the powder, by decantation and the crystals were washed with two 5 ml portions of hexane and dried *in vacuo*. Yield 0.322 g, 56% with

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† The low carbon and hydrogen contents for the samples indicated can be explained by the fact that they are not completely insensitive to ambient conditions (the samples were sent to Moscow without sealing, packed in ambient atmosphere. It took approximately 10 days before the samples were analyzed).

Table 1 Crystal data and details of diffraction experiments for compounds **1**, **3a**, **3b**, **5**, and **6**

	1	**3a**	**3b**	**5**	**6**
Chemical formula	$C_{12}H_{36}O_{18}Re_4$	$C_{12}H_{36}O_{18}Re_{3.0}Mo_{1.0}$	$C_{12}H_{36}O_{18}Re_{2.0}Mo_{2.0}$	$C_{14}H_{42}O_{24}Nb_4Re_2$	$C_{14}H_{42}O_{24}Ta_4Re_2$
Formula weight	1213.21	1122.96	996.57	1338.52	1690.68
Crystal system	Triclinic	Triclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P2(1)/c$	$P2(1)/c$
μ/mm^{-1}	17.799	4.606	2.771	7.846	18.500
$R1$	0.0348	0.0683	0.0534	0.0556	0.0677
$wR2$	0.0664	0.1456	0.1214	0.1431	0.1698
a/Å	7.8993(8)	7.9141(4)	7.905(2)	9.716(4)	9.826(2)
b/Å	15.994(2)	16.0535(8)	15.997(4)	15.888(7)	15.938(3)
c/Å	17.501(1)	17.5938(9)	17.519(6)	12.128(6)	12.265(3)
α/°	113.434(2)	113.322(1)	113.41(2)	90	90
β/°	93.048(2)	93.355(1)	92.92(2)	101.059(9)	101.34(3)
γ/°	92.736(2)	92.754(1)	92.71(3)	90	90
V/Å^3	2020.1(6)	2042.95(30)	2024.9(10)	1837.5(14)	1883.3(9)
T/K	295(2)	295(2)	295(2)	295(2)	252(2)
Z	3	3	3	2	2
Independent reflections [R(int)]	8746 [0.0255]	7021 [0.0620]	8733 [0.0394]	3307 [0.0575]	2450 [0.1093]
Observed reflections [$I > 2\sigma(I)$]	5990	3766	5036	2021	1458

respect to Re_2O_7. Found (%): C 12.50, H 3.00, Nb : Re = 2 : 1. Calculated for $Nb_4O_2(OMe)_{14}(ReO_4)_2$ (%): C 12.56, H 3.14. [Found † (%): C 11.77, H 2.78, Nb : Re = 2 : 1.] IR, ν/cm^{-1}: 1139 s, 1102 s, 1081 s, 1042 m, 997 m, 934 s, 893 w, 816 s br, 571 s, 526 s.

$Ta_4O_2(OMe)_{14}(ReO_4)_2$ (6). Re_2O_7 (0.514 g, 1.06 mmol) was added to a transparent colorless solution of $Ta_2(OMe)_{10}$ (0.976 g, 1.26 mmol) in 5 ml toluene. No immediate dissolution occurred, but a red coloration on the surfaces of the light yellow particles of oxide was noticeable. The mixture was subjected to reflux for 30 min. During the reflux, the rhenium oxide turned into a black-colored melt and the solution turned light pink. The solution was removed by decantation and left to crystallize for 2 h at −30 °C. The light pink-colored crystals obtained were isolated by decantation and dried *in vacuo*. Yield 0.781 g (46% with respect to Re_2O_7). Found (%): C 9.28, H 2.27, Ta : Re = 2 : 1. Calculated for $Ta_4O_2(OMe)_{14}(ReO_4)_2$ (%): C 9.89, H 2.47. IR, ν/cm^{-1}: 117 m, 1068 s, 1048 s, 983 s, 882 m, 655 w, 586 m, 558 m, 525 m, 428 s br.

$Mo(OMe)_6$ (7). The electrolyte (70 ml) obtained by anodic dissolution of molybdenum metal in MeOH under the conditions described above (2.514 g, 26.2 mmol) was reduced to half its original volume *in vacuo* and left to crystallize overnight at −30 °C. The precipitated orange crystals were separated by decantation, washed with 1 ml cold MeOH, and dried *in vacuo*. Yield 2.143 g, 29%. IR, ν/cm^{-1}: 1377 m, 1148 s, 1060 vs, 1019 sh, 942 s, 555 s, 525 sh, 448 m. The composition was confirmed by the unit cell determination for 6 randomly chosen single crystals: monoclinic, space group $P2/n$, $a = 7.0976(13)$, $b = 6.6103(12)$, $c = 12.286(2)$ Å, $\beta = 90.068(3)$°.

Crystallography

The crystal data and experimental conditions are shown in Table 1. The data were collected using a SMART CCD 1K diffractometer at 22 °C. All calculations were performed on an IBM PC using the SHELXTL-NT[14] program package. All structures were solved by direct methods. The positions of metal atoms were obtained from the initial solution and refined first in isotropic and then anisotropic approximations. The occupancy factors for all the metal atom positions in the structures of compounds **3a** and **3b** were refined with the supposition that they can be occupied with equal opportunity by both molybdenum and rhenium atoms; the total occupancy for each position being 1.0. The values obtained are, within experimental errors, in agreement with those obtained by EDS analysis. The positions of all other non-hydrogen atoms were obtained from difference Fourier syntheses and refined first in isotropic and then anisotropic approximations. The positions of hydrogen atoms were calculated geometrically and included in the final refinement in isotropic approximations; the thermal parameters for H atoms were taken as $U_{\mathrm{iso}} = 1.50U_{\mathrm{eq}}(\mathrm{C})$, where $U_{\mathrm{eq}}(\mathrm{C})$ is the equivalent parameter for the carbon atom to which the hydrogen atom is attached.

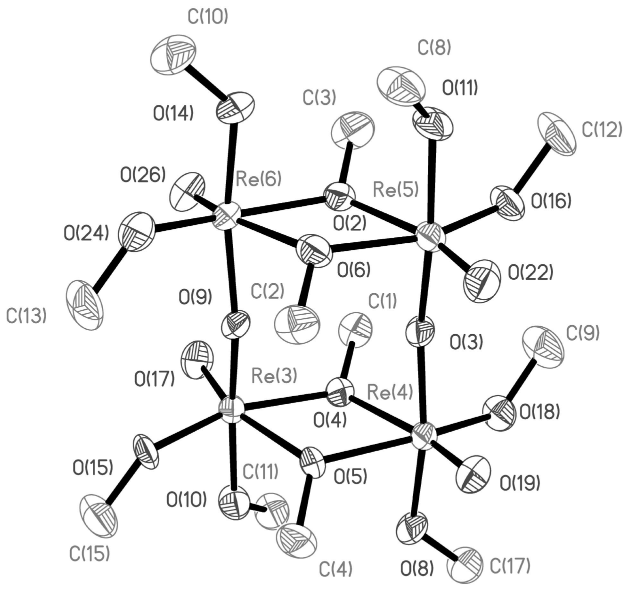


Fig. 1 Molecular structure of $(Re_{1-x}Mo_x)_4O_6(OMe)_{12}$ (**1**, **3a**, **3b**), the metal atom positions being designated as Re to simplify the view (only one symmetrically independent molecule is shown).

The results of the X-ray single crystal study of compound **7** will be published elsewhere.[15]

CCDC reference numbers 152226–152230.

See http://www.rsc.org/suppdata/dt/b1/b103287a/ for crystallographic data in CIF or other electronic format.

Results and discussion

Molecular and crystal structures

The crystal structures of the compounds **1**, **3a**, and **3b** are analogous (see Fig. 1, Tables 1 and 2). They are built up of planar rectangular tetranuclear $M_4(\mu\text{-}O)_2(\mu\text{-}OMe)_4O_4(OMe)_8$ molecules that are packed in helical columns in a direction perpendicular to the crystallographic a-axis. Each centrosymmetric unit cell contains three such molecules and, thus, only one of them possesses a crystallographic center of symmetry, the

Table 2 Selected bond lengths (Å) and angles (°) in the structure of **1**[a]

Re(1)–O(25)	1.682(7)	Re(4)–O(19)	1.674(7)
Re(1)–O(21)	1.886(6)	Re(4)–O(18)	1.894(6)
Re(1)–O(1)	1.891(6)	Re(4)–O(3)	1.901(6)
Re(1)–O(20)	1.936(7)	Re(4)–O(8)	1.911(6)
Re(1)–O(7)	2.074(6)	Re(4)–O(5)	2.062(6)
Re(1)–O(12)#1	2.140(6)	Re(4)–O(4)	2.179(6)
Re(2)–O(23)	1.675(7)	Re(5)–O(22)	1.674(7)
Re(2)–O(1)	1.876(6)	Re(5)–O(3)	1.886(6)
Re(2)–O(27)	1.892(6)	Re(5)–O(16)	1.893(6)
Re(2)–O(13)	1.901(7)	Re(5)–O(11)	1.917(6)
Re(2)–O(12)	2.062(6)	Re(5)–O(6)	2.069(6)
Re(2)–O(7)#1	2.180(6)	Re(5)–O(2)	2.155(6)
Re(3)–O(17)	1.669(7)	Re(6)–O(26)	1.665(8)
Re(3)–O(9)	1.881(6)	Re(6)–O(24)	1.883(7)
Re(3)–O(15)	1.907(6)	Re(6)–O(9)	1.905(5)
Re(3)–O(10)	1.923(6)	Re(6)–O(14)	1.919(6)
Re(3)–O(4)	2.074(6)	Re(6)–O(2)	2.046(6)
Re(3)–O(5)	2.148(6)	Re(6)–O(6)	2.189(7)
O(25)–Re(1)–O(21)	107.7(3)	O(23)–Re(2)–O(1)	93.9(3)
O(25)–Re(1)–O(1)	95.1(3)	(23)–Re(2)–O(27)	104.7(3)
O(21)–Re(1)–O(1)	88.4(3)	O(1)–Re(2)–O(27)	94.8(3)
O(25)–Re(1)–O(20)	95.6(3)	O(23)–Re(2)–O(13)	99.3(3)
O(21)–Re(1)–O(20)	86.7(3)	O(1)–Re(2)–O(13)	166.2(3)
O(1)–Re(1)–O(20)	169.2(3)	O(27)–Re(2)–O(13)	85.8(3)
O(25)–Re(1)–O(7)	92.0(3)	O(23)–Re(2)–O(12)	95.1(3)
O(21)–Re(1)–O(7)	160.0(3)	O(1)–Re(2)–O(12)	90.1(2)
O(1)–Re(1)–O(7)	93.2(2)	O(27)–Re(2)–O(12)	159.2(3)
O(20)–Re(1)–O(7)	88.2(3)	O(13)–Re(2)–O(12)	84.6(3)
O(25)–Re(1)–O(12)#1	162.4(3)	O(23)–Re(2)–O(7)#1	164.5(3)
O(21)–Re(1)–O(12)#1	89.8(3)	O(1)–Re(2)–O(7)#1	82.1(2)
O(1)–Re(1)–O(12)#1	84.0(2)	O(27)–Re(2)–O(7)#1	90.6(3)
O(20)–Re(1)–O(12)#1	86.3(3)	O(13)–Re(2)–O(7)#1	84.2(3)
O(7)–Re(1)–O(12)#1	70.6(2)	O(12)–Re(2)–O(7)#1	70.0(2)
O(17)–Re(3)–O(9)	94.7(3)	O(19)–Re(4)–O(18)	105.2(3)
O(17)–Re(3)–O(15)	107.5(3)	O(19)–Re(4)–O(3)	94.9(3)
O(9)–Re(3)–O(15)	89.0(3)	O(18)–Re(4)–O(3)	93.4(3)
O(17)–Re(3)–O(10)	97.3(3)	O(19)–Re(4)–O(8)	97.6(3)
O(9)–Re(3)–O(10)	168.0(3)	O(18)–Re(4)–O(8)	85.7(3)
O(15)–Re(3)–O(10)	86.1(3)	O(3)–Re(4)–O(8)	167.2(3)
O(17)–Re(3)–O(4)	92.7(3)	O(19)–Re(4)–O(5)	95.0(3)
O(9)–Re(3)–O(4)	93.1(2)	O(18)–Re(4)–O(5)	158.2(3)
O(15)–Re(3)–O(4)	159.5(3)	O(3)–Re(4)–O(5)	93.0(2)
O(10)–Re(3)–O(4)	87.7(2)	O(8)–Re(4)–O(5)	83.5(3)
O(17)–Re(3)–O(5)	162.9(3)	O(19)–Re(4)–O(4)	164.6(3)
O(9)–Re(3)–O(5)	83.3(2)	O(18)–Re(4)–O(4)	90.2(3)
O(15)–Re(3)–O(5)	89.5(3)	O(3)–Re(4)–O(4)	82.0(3)
O(10)–Re(3)–O(5)	85.7(3)	O(8)–Re(4)–O(4)	85.2(3)
O(4)–Re(3)–O(5)	70.5(2)	O(5)–Re(4)–O(4)	70.1(2)

[a] Symmetry transformation used: #1 $x + 1, -y, -z$.

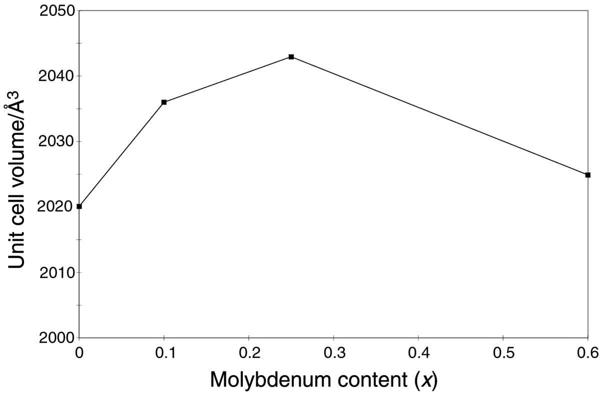


Fig. 2 The dependence of the unit cell volume (Å^3) on the molybdenum content (x) in $(Re_{1-x}Mo_x)_4O_6(OMe)_{12}$.

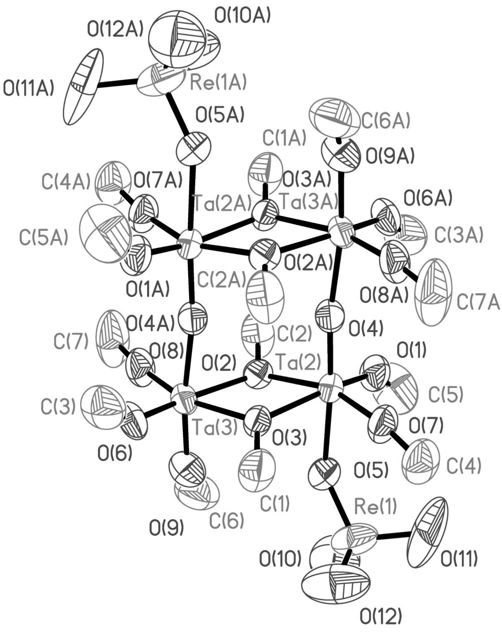


Fig. 3 Molecular structure of $Ta_4O_2(OMe)_{14}(ReO_4)_2$ (6).

other two being transformed one into the other by it and not possessing their own centers of symmetry. The coordination of the metal atoms is nearly the same, within experimental errors, for all these structures, as well as within each structure. The distribution of rhenium and molybdenum atoms in the metal atom positions is statistical but not uniform (slightly different Mo content in different positions), which presumably reflects the small effects of the different M=O bond polarities on the lattice energy, producing some changes in the packing of different molecules. The major difference between these structures lies in the fact that the compound with lower molybdenum content—**3a**—displays lower crystallinity and lower order (much broader reflections), which results in higher standard deviations for the bond lengths and angles. This is also reflected by a noticeably higher unit cell volume in this case [2042.95(30) Å^3] compared with those for **1** and **3b** [2020.1(6) and 2024.9(10) Å^3, respectively; see Fig. 2]. The strong disorder in the Re(Mo)–O distances has already been reported earlier by us for the first representative of this family, $(Re_{0.9}Mo_{0.1})_4O_{5.86}(OMe)_{12.14}$,[11] which has an even lower molybdenum content and also an increased unit cell volume [2036(1) Å^3]. The size of Re(VI) and Mo(VI) atoms being essentially the same, it is not surprising that the M–O distances in the structures of the derivatives fall into the ranges usually observed for both Re and Mo. For example, for **1**, the Re=O distances (see Table 2) are 1.669(7)–1.682(7) Å, as compared with 1.690(11) Å in $Re_2O_3(OMe)_6$[5] or 1.699(10) Å in $ReO(O_2C_6H_{12})_2$,[4] and 1.672(5) Å for Mo=O in $[MoO(OMe)_4]_2$.[15] Re–O(Me)-terminal and Re–μ-O(Me) distances are 1.893(6)–1.936(7) and 2.046(6)–2.189(7) Å, respectively, compared with 1.867(12)–1.903(11) and 1.917(11)–2.139(10) Å, respectively, in $Re_2O_3(OMe)_6$[5] and 1.873(5)–1.886(6) and 2.050(5)–2.226(5) Å for Mo–O(Me)-terminal and Mo–μ-O(Me), respectively, in $[MoO(OMe)_4]_2$.[16] The most interesting and unusual feature of these structures, and also that of $(Re_{0.9}Mo_{0.1})_4O_{5.86}(OMe)_{12.14}$,[11] is the presence of nearly symmetric 1.876(6)–1.905(6) Å, <157.5–161.9° Re–O–Re bridges. Such pronounced linearity is usually associated with asymmetric bridges and is known for the alkoxide complexes of quinquevalent metals, especially Re(V) and Ta(V) (see below in the description of the structures of compounds **5** and **6**).

The structures of the isomorphous compounds **5** and **6** (see Fig. 3 and 4; Tables 3 and 4) are built up of centrosymmetric molecules that also display the planar tetranuclear $M_4(\mu\text{-}O)_2(\mu\text{-}OMe)_4$ core, where M = Nb or Ta (only) in this case, coordinating 10 methoxo and 2 perrhenate ligands. Attempts to introduce into the structural analysis the possibility for Re atoms to occupy the positions inside the core immediately led to a very strong increase in the *R*-factor and such models should therefore be excluded. The Nb–O(Me) distances fall into the

Table 3 Selected bond distances (Å) and angles (°) in the structure of **5**[a]

Re(1)–O(12)	1.637(11)	Nb(2)–O(2)	2.097(6)
Re(1)–O(11)	1.724(13)	Nb(2)–O(5)	2.236(8)
Re(1)–O(5)	1.707(8)	Nb(3)–O(8)	1.804(7)
Re(1)–O(10)	1.512(16)	Nb(3)–O(6)	1.852(8)
Nb(2)–O(4)	1.780(7)	Nb(3)–O(9)	1.848(9)
Nb(2)–O(7)	1.846(7)	Nb(3)–O(4)#1	2.042(7)
Nb(2)–O(1)	1.850(7)	Nb(3)–O(2)	2.093(6)
Nb(2)–O(3)	2.084(6)	Nb(3)–O(3)	2.097(6)
O(12)–Re(1)–O(11)	109.6(8)	O(4)–Nb(2)–O(5)	175.1(3)
O(12)–Re(1)–O(5)	111.2(6)	O(7)–Nb(2)–O(5)	85.0(3)
O(11)–Re(1)–O(5)	109.2(7)	O(1)–Nb(2)–O(5)	83.1(3)
O(12)–Re(1)–O(10)	111.3(7)	O(3)–Nb(2)–O(5)	79.8(3)
O(11)–Re(1)–O(10)	109.8(8)	O(2)–Nb(2)–O(5)	82.0(3)
O(5)–Re(1)–O(10)	105.8(6)	O(8)–Nb(3)–O(6)	105.2(4)
O(4)–Nb(2)–O(7)	99.5(3)	O(8)–Nb(3)–O(9)	95.3(4)
O(4)–Nb(2)–O(1)	97.7(3)	O(6)–Nb(3)–O(9)	97.0(4)
O(7)–Nb(2)–O(1)	103.3(3)	O(8)–Nb(3)–O(4)#1	88.1(3)
O(4)–Nb(2)–O(3)	98.0(3)	O(6)–Nb(3)–O(4)#1	89.1(3)
O(7)–Nb(2)–O(3)	92.0(3)	O(9)–Nb(3)–O(4)#1	172.0(3)
O(1)–Nb(2)–O(3)	155.9(3)	O(8)–Nb(3)–O(2)	92.7(3)
O(4)–Nb(2)–O(2)	93.2(3)	O(6)–Nb(3)–O(2)	159.5(3)
O(7)–Nb(2)–O(2)	159.8(3)	O(9)–Nb(3)–O(2)	91.0(3)
O(1)–Nb(2)–O(2)	90.4(3)	O(4)#1–Nb(3)–O(2)	81.5(3)
O(3)–Nb(2)–O(2)	70.6(2)	O(8)–Nb(3)–O(3)	162.4(3)

[a] Symmetry transformation used: #1 $x + 1, -y, z + 1$.

Table 4 Selected bond distances (Å) and angles (°) in the structure of **6**[a]

Re(1)–O(10)	1.44(4)	Ta(2)–O(2)	2.083(15)
Re(1)–O(5)	1.65(2)	Ta(2)–O(5)	2.24(2)
Re(1)–O(12)	1.68(4)	Ta(3)–O(9)	1.77(3)
Re(1)–O(11)	1.70(3)	Ta(3)–O(6)	1.86(2)
Ta(2)–O(4)	1.77(2)	Ta(3)–O(8)	1.86(2)
Ta(2)–O(7)	1.82(2)	Ta(3)–O(4)#1	2.02(2)
Ta(2)–O(1)	1.85(2)	Ta(3)–O(2)	2.034(18)
Ta(2)–O(3)	2.029(18)	Ta(3)–O(3)	2.108(15)
O(10)–Re(1)–O(5)	106.3(18)	O(4)–Ta(2)–O(5)	176.7(8)
O(10)–Re(1)–O(12)	114(2)	O(7)–Ta(2)–O(5)	83.4(10)
O(5)–Re(1)–O(12)	111.7(17)	O(1)–Ta(2)–O(5)	82.7(9)
O(10)–Re(1)–O(11)	106(2)	O(3)–Ta(2)–O(5)	81.9(8)
O(5)–Re(1)–O(11)	113.2(17)	O(2)–Ta(2)–O(5)	82.8(8)
O(12)–Re(1)–O(11)	106(2)	O(9)–Ta(3)–O(6)	93.8(11)
O(4)–Ta(2)–O(7)	99.7(9)	O(9)–Ta(3)–O(8)	94.8(11)
O(4)–Ta(2)–O(1)	97.6(9)	O(6)–Ta(3)–O(8)	106.2(10)
O(7)–Ta(2)–O(1)	100.2(10)	O(9)–Ta(3)–O(4)#1	174.4(9)
O(4)–Ta(2)–O(3)	96.8(8)	O(6)–Ta(3)–O(4)#1	90.2(9)
O(7)–Ta(2)–O(3)	93.3(9)	O(8)–Ta(3)–O(4)#1	87.7(9)
O(1)–Ta(2)–O(3)	158.2(8)	O(9)–Ta(3)–O(2)	90.6(10)
O(4)–Ta(2)–O(2)	94.0(7)	O(6)–Ta(3)–O(2)	160.7(8)
O(7)–Ta(2)–O(2)	159.3(9)	O(8)–Ta(3)–O(2)	92.1(8)
O(1)–Ta(2)–O(2)	93.2(8)	O(4)#1–Ta(3)–O(2)	84.3(7)
O(3)–Ta(2)–O(2)	69.5(8)	O(9)–Ta(3)–O(3)	90.5(10)
O(8)–Ta(3)–O(3)	160.4(9)	O(6)–Ta(3)–O(3)	92.2(8)

[a] Symmetry transformation used: #1 $x + 1, -y, z + 1$.

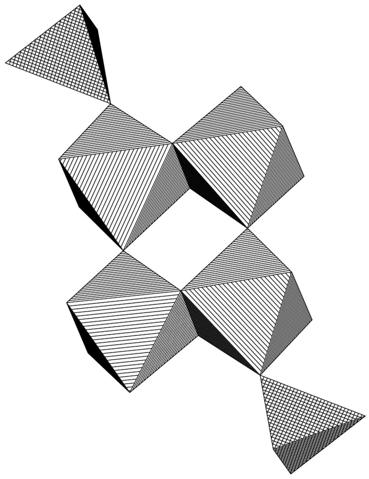


Fig. 4 Polyhedral representation of the molecular structures of $M_4O_2(OMe)_{14}(ReO_4)_2$, M = Nb (**5**), Ta (**6**).

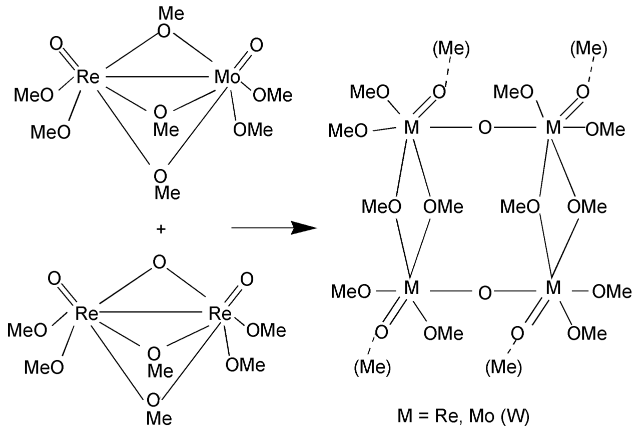
range usually observed and are very close to those observed in, for example, $[Nb(OMe)_5]_2$.[17] The Nb–O–Nb bridges are rather asymmetric; 1.780(7) and 2.042(7) Å, respectively. The angle Nb(2)–O(4)–Nb(3) is 172.1(4)°, probably reflecting that they are situated *trans* to the oxobridge with the perrhenate ligand [Nb(2)–O(5) 2.236(8) Å]. Such nearly linear and asymmetric oxobridges have been observed previously in the structures of $I_2Zn_2Ta_4O_4(O^iPr)_{14}$,[18] $Mo_2Ta_4O_8(OMe)_{16}$[19] and $[ReO(\mu\text{-}O)(P\{CH_2OH\}_3)(\mu,\eta^2\text{-}P\{CH_2OH\}_2CH_2O)]_4$.[20] The geometry of the perrhenate ligand appears to be quite common, comparable to both that of free inorganic perrhenates, such as NH_4ReO_4,[21] or Re(VII) alkoxide complexes.[4]

Synthetic approaches to the homo- and heterometallic rhenium methoxides

One of the most intriguing features of rhenium alkoxides described by Wilkinson *et al.*[5] is their tendency toward "decomposition" on storage or on heating, with the formation of what have been described as "black tars". This is especially pronounced for the Re(VI) methoxide. We have obtained this decomposition product in very high yields on anodic oxidation of Re metal in MeOH at high current densities. On the basis of the incomplete structural model from the single crystal X-ray diffraction experiment, the microanalytical data, and the pronounced diamagnetic properties of this product, we have formulated it as $Re^V_4(\mu\text{-}O)_2(\mu\text{-}OMe)_4(OMe)_{12}$, *i.e.* solely an Re(V) derivative.[9] This formulation appears to be further confirmed by the isolation and structural characterization of the bimetallic complex of Re(V) and Mo(VI), $ReMoO_2(OMe)_7$,[10] obtained in an analogous synthesis carried out in the presence of $MoO(OMe)_4$ in the electrolyte. The isolation of this heteronuclear cluster was achieved from solutions containing Re and Mo in a 1 : 1 ratio. Subsequent experiments show that the storage of electrolytes, possessing considerably higher Re : Mo ratios leads to precipitation (directly from the electrolytes) of a heterometallic derivative possessing a molecular structure analogous to that formulated as $Re^V_4(\mu\text{-}O)_2(\mu\text{-}OMe)_4(OMe)_{12}$, but containing mainly Re(VI). Both the elementary microanalysis and the refinement of the X-ray single crystal structure gave the formula $(Re_{0.9}Mo_{0.1})_4O_{5.86}(OMe)_{12.14}$[11] [only one terminal Re=O bond appeared to be alternated statistically with a Re–O(R) bond]. In the present work, we have tried to isolate the intermediate soluble products of the anodic dissolution of rhenium at low current densities (with a minimal influence from the cathodic reduction on their composition). It turns out that the product isolated on changing the medium to a hydrocarbon after cooling is identical to the previously described $Re_2O_3(OMe)_6$.[5] The latter was found to be stable in the solid state, but in solution, especially on heating, was quantitatively converted into the above-mentioned "black tar". The X-ray single crystal study of the latter showed it to be $Re^{VI}_4O_4(\mu\text{-}O)_2(\mu\text{-}OMe)_4(OMe)_8$; *i.e.* simply a dimer of $Re_2O_3(OMe)_6$ (see Scheme 1). This permits us to formulate the reaction pathway as:

$$Re + MeOH \xrightarrow{\text{anodic oxidation}} Re_2O_3(OMe)_6 \xrightarrow{\text{storage/heating}} Re_4O_6(OMe)_{12} \quad (1)$$

providing the second structurally characterized example for the phenomenon of coordination polymerism for metal alkoxides (see ref. 22), the first being the trimer–tetramer equilibrium for aluminum isopropoxide.[23] It is necessary to mention



Scheme 1

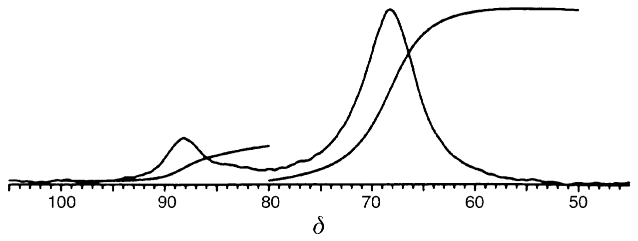


Fig. 5 The CP MAS ^{13}C spectrum of $Re_4O_{6-y}(OMe)_{12+y}$ (**2**).

that the single crystals of compound **1** did not display unit cell parameters differing substantially from those earlier determined for "$Re_4O_2(OMe)_{16}$". However, **1** did not display pronounced diamagnetism (in contrast to the latter), had a different color nuance (reddish black in contrast to greenish black), and possessed a lower, while still quite remarkable, stability in the open air; several hours compared with at least a month for "$Re_4O_2(OMe)_{16}$". A statistically good number of microanalysis tests for the latter compound showed that its carbon and hydrogen contents were noticeably lower than predicted by a formula implying the presence of only Re(v), but still definitely exceeding the values required for **1**. The analogy in their molecular structures appears evident and we propose to formulate it as $Re_4O_{6-y}(OMe)_{12+y}$ **2**. An attempt to compare **1** and **2** using the solid state (CP MAS) ^{13}C NMR technique again shows a considerable difference between them. **2** gives a spectrum containing two distinct signals, apparently corresponding to the bridging and terminal methoxide groups (Fig. 5), while the signal from the sample of **1** is repeatedly destroyed when subjected to a radiofrequency pulse. This might be explained by the supposition that a transition occurs from a non-magnetic spin-compensated state for the ensembles of Re(vi) d^1 atoms into paramagnetic, or even ferromagnetic, states in a strong magnetic field, being associated with uptake and release of very high amounts of energy. The presence of even a small amount of randomly distributed Re(v) d^2 atoms in **2** can act as a hindrance for such a transition, which permits us to observe the expected NMR response.

Simple theoretical calculations predict that a noticeable difference should be observed in the size of the Re(vi) and Re(v) alkoxide aggregates. The average Re–O distance in the model compounds $Re^{VI}O(OMe)_5^{2-}$ and $Re^{V}(OMe)_6^{-}$, not including the Re=O oxygen, is at least 0.05 Å longer in the Re^{VI} compound.‡ It is supposedly this difference that introduces disorder into the crystal structure of **2** (as the unit cell volume does not increase substantially). This explains the difficulties in the refinement of the single crystal diffraction experiments for **2**.

It is important to note that the speed of the described dimerization reaction is apparently solvent dependent: the reaction is complete in MeOH within several days and in hydrocarbon solvents, like hexane or toluene, within 2–4 weeks at room temperature. This effect should be attributed in the first instance to the difference in polarity of the solvents as the product obtained is almost insoluble in any organic solvents, the dimerization reaction thus being irreversible.

Systematic studies of the composition of the solid products precipitating from electrolytes obtained by anodic dissolution of Re in MeOH in the presence of $MoO(OMe)_4$ showed that the maximum Mo content does not exceed 25 mol% (compound **3a**). For syntheses in the presence of $WO(OMe)_4$, a great difference was observed in the compositions of the products obtained at different cathodic current densities: at 0.05–0.08 A cm^{-2} it was possible to isolate only pure compound **1**, and while the incorporation of tungsten did occur at values higher than ~0.3 A cm^{-2}, the W content in the precipitate obtained varied from 0 to ~25 mol% in the same sample. We therefore assume that the presence of reduced complexes of the type we observed previously, *i.e.* $Re^{V}Mo^{VI}O_2(OMe)_7$, might be crucial for the formation of the heterometallic species like **3**, as they could quite logically originate from the dimerization of the dinuclear heterometallic species in analogy to the dimerization of $Re_2O_3(OMe)_6$ producing **1** (see Scheme 1). Since we have recently observed that the reduction of Mo and W alkoxides takes place on thermal treatment in toluene (aldehydes and ketones, and also the corresponding acetals and ketals being the major organic by-products),[19] and since it was shown that Re_2O_7 is reduced under the same conditions by the alkoxide ligands,[4] we investigated the interaction of rhenium heptoxide with $MO(OMe)_4$ and with $M(OMe)_6$. This led to the isolation of the heterometallic complexes with an approximately 1 : 1 metal ratio. The molecular structure is analogous to that of **1** and very moderately sensitive to ambient atmosphere, thus confirming the idea of dimerization of dinuclear heterometallic complexes put forward to explain why no considerable excess of Mo or W could be achieved in the derivatives prepared by this reaction. It is worth mentioning that the dimeric species and the tetramers have distinctly different colors (purple or reddish purple and almost black, respectively). This fact is in good agreement with the transformation of aggregates with isolated binuclear metal–metal bonds into a solid containing ensembles of centers bearing unpaired electrons {compare I_2(g), violet, and $[I_2]_\infty$(s), grey with metallic glitter}.

The application of the same synthetic strategy for niobium and tantalum derivatives showed more complex behavior than for Re_2O_7. Only about half of the rhenium was transformed into a heterometallic product, in this case, in the form of a perrhenate ligand. Again though, the products are very stable to ambient atmosphere, indicating that this stability at least partially results from the properties of the $M_4(\mu\text{-}O)_2(\mu\text{-}OMe)_4$ core (apparently in combination with a rather dense packing of the molecules in the crystal structure). The absence of Re atoms inside the core in this case can be explained by both the considerable difference in the sizes of Re atoms on one hand, and Nb and Ta atoms on the other. Furthermore, the considerable difference in the energies of the d-orbitals for the latter metals makes the formation of dinuclear species like those formed in the Re–Mo(W) systems less likely.

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‡ Test calculations were made using a few different basis sets (ECP-based for Re) of double-zeta quality in GAUSSIAN 98[24] at Hartree–Fock and B3LYP levels.

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