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Articles

Rhenium(V) and Technetium(V) Complexes of Bidentate (O, O) Monobasic 3-oxy-4-pyronato and -4-pyridinonato Ligands. X-ray Structures of *cis*-Bromobis(3-methyl-2-oxy-4-pyronato)oxorhenium(V), Tetra-*n*-butylammonium Tribromo(3-methyl-2-oxy-4-pyronato)oxorhenate(V), and Tetra-*n*-butylammonium Trichloro(3-methyl-2-oxy-4-pyronato)oxotechnetate(V)

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A series of technetium(V) and rhenium(V) complexes of the form [MOXL$_2$], where L is a bidentate (O, O) monobasic ligand, 2-methyl-3-oxy-4-pyronate (maltolate, ma$^-$) or 1,2-dimethyl-3-oxy-4-pyridinonate (dpp$^-$), and X is a halo ligand, X = Cl (M = Tc) or Br (M = Re), have been synthesized by ligand substitution on [TcOCl$_4$]$^-$ or [ReOBr$_4$]$^-$ anions in nonaqueous solutions. Trihalo(maltolato)oxometalate complexes of technetium(V) and rhenium(V), [MOX$_3$(ma)]$^-$ (M = Tc, X = Cl; M = Re, X = Br), were also prepared as tetra-*n*-butylammonium (M = Tc, Re) or tetraphenylarsonium (M = Re) salts. The complexes have been studied by IR, ^{1}H NMR, and mass spectra. The X-ray structures of [ReOBr(ma)$_2$], [(*n*-Bu)$_4$N][ReOBr$_3$(ma)] and [(*n*-Bu)$_4$N][TcOCl$_3$(ma)] were determined. Crystals of [ReOBr(ma)$_2$] ($C_{12}H_{10}BrO_7Re$) are triclinic, $P\bar{1}$, with a = 20.846(2) Å, b = 8.484(2) Å, c = 8.4809(8) Å, α = 85.89(1)°, β = 89.831(9)°, γ = 89.80(1)°, V = 1496.0(4) Å^3, and Z = 4; those of [(*n*-Bu)$_4$N][ReOBr$_3$(ma)] ($C_{22}H_{41}Br_3NO_4Re$) are monoclinic, $P2_1/n$, with a = 11.074(3) Å, b = 15.713(4) Å, c = 17.370(4) Å, β = 104.77(2)°, V = 2923(2) Å^3, and Z = 4; and those of [(*n*-Bu)$_4$N][TcOCl$_3$(ma)] ($C_{22}H_{41}Cl_3NO_4Tc$) are monoclinic, $P2_1/c$, with a = 10.724(2) Å, b = 11.327(2) Å, c = 23.651(2) Å, β = 101.46(1)°, V = 2815.6(8) Å^3, and Z = 4. The structures were solved by the Patterson method ([(*n*-Bu)$_4$N][ReOBr$_3$(ma)]) or a combination of the Patterson and direct methods ([ReOBr(ma)$_2$] and [(*n*-Bu)$_4$N][TcOCl$_3$(ma)]). They were refined by full-matrix least-squares procedures to R = 0.043, 0.033, and 0.034 and R_w = 0.050, 0.027, and 0.030 for 4524, 3250, and 4338 observed reflections ($I \geq 3\sigma(I)$) for [ReOBr(ma)$_2$], [(*n*-Bu)$_4$N][ReOBr$_3$(ma)], and [(*n*-Bu)$_4$N][TcOCl$_3$(ma)], respectively. For [ReOBr(ma)$_2$], the solution ^{1}H NMR spectrum and the crystal structure both demonstrate cis-geometry, with the Re atom being in the center of a highly distorted octahedron of cis-(bromo, oxo) donors and ketonic oxygen and hydroxy oxygen donors of the two mutually orthogonal maltolato ligands. In [(*n*-Bu)$_4$N][ReOBr$_3$(ma)] and [(*n*-Bu)$_4$N][TcOCl$_3$(ma)], the [MOX$_3$(ma)]$^-$ anions are isostructural; the metal atom is also in a highly distorted octahedral environment in each case, with the maltol hydroxy oxygen trans to the oxo group.

Introduction

A burgeoning interest in technetium coordination chemistry has resulted from the fact that ^{99m}Tc complexes are widely employed in diagnostic radiopharmaceutical studies because of the optimum nuclear properties of ^{99m}Tc ($t_{1/2}$ = 6.02 h, γ = 141 keV).[1] Rhenium chemistry has a related interest as some of its isotopes are suitable candidates in radiotherapeutic applications; in addition, this element possesses similar chemical properties of those of technetium.[2]

Our interest in technetium chemistry is in the preparation of new neutral or cationic complexes with the relatively stable isotope ^{99}Tc ($t_{1/2}$ = 2.12 × 10^5 y, β = 292 keV) for the potential application of corresponding ^{99m}Tc complexes in brain or heart imaging respectively.[3] We have been studying the trisligand complexes of aluminum(III), gallium(III), and indium(III) with the bidentate (O, O) monobasic substituted 3-oxy-4-pyrones and N-substituted 3-oxy-4-pyridinones.[4–8] Unique combinations of biologically significant properties (water solubility, hydrolytic stability, and lipophilicity) have led to the wide use of tris(maltolato)aluminum in the study of Al neurotoxicity[9] and to the potential applications of a ^{67}Ga complex, tris(1-(*p*-methoxyphenyl)-2-methyl-3-oxy-4-pyridinonato)gallium(III), for heart imaging.[10] These ligands are nontoxic and either naturally occurring or easily synthesized, and the properties of their complexes can be altered by changing the substituents on the ligands to optimize the biodistribution. In an effort to extend these properties to technetium complexes, we now present the synthesis and char-

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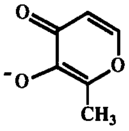
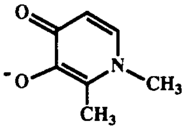
acterization of some neutral and anionic technetium(V) and rhenium(V) complexes of 2-methyl-3-oxy-4-pyronate (maltolate, ma⁻) and 1,2-dimethyl-3-oxy-4-pyridinonate (dpp⁻). These



ma⁻



dpp⁻

complexes are the first oxotechnetium(V) and oxorhenium(V) complexes containing bidentate (O, O) monobasic ligands, to our knowledge. Some stoichiometrically and structurally similar complexes of bidentate (O, N) monobasic ligands have been reported.[11-16]

As this work was in progress, Archer et al.[17] reported the synthesis and crystal structure of a cationic imidorhenium(V) complex of ma⁻, $[Re(ma)_2(NPh)(PPh_3)][BPh_4]$, and Kanvinde et al.[18] presented biodistribution studies on purported cationic ^{99m}Tc complexes of ma⁻ and kojic acid. Preliminary results of Kanvinde's work suggested that Tc derivatives of the 3-oxy-4-pyronate skeleton might be a new class of cationic complexes with potential as heart imaging radiopharmaceuticals.

Experimental Section

Materials. All chemicals were reagent grade and were used as received: $[NH_4][^{99}TcO_4]$ (a gift from the Du Pont Merck Pharmaceutical Co.), $[NH_4][ReO_4]$ (Aldrich), and Hma (Sigma). Hdpp,[19] $[n\text{-}Bu_4N][TcOCl_4]$,[20] $[n\text{-}Bu_4N][ReOBr_4]$,[21] and $[Ph_4As][ReOBr_4]$[21] were prepared according to published procedures.

Caution! ^{99}Tc is a low-energy (0.292 MeV) β^- emitter with a half-life of 2.12×10^5 years. All manipulations of solutions and solids were performed in a laboratory approved for the handling of low-level radioisotopes, and normal safety procedures were followed at all times to prevent contamination.

Instrumentation. NMR spectra (200, 300, and 400 MHz) were recorded on Bruker AC-200E, Varian XL 300 (VT ^{1}H NMR), or Bruker WH-400 (^{1}H–^{1}H COSY) spectrometers, with δ referenced to TMS and assignments based on those for the unbound ligand. Mass spectra were obtained with either an AEI MS-9 instrument (fast atom bombardment ionization, FAB) or DELSI-NERMAG R10-10c instrument (desorption chemical ionization, DCI). Only the most intense peak is given where consistent isotopic patterns were observed. Infrared spectra were recorded as KBr pellets in the range 4000–400 cm^{-1} on a Perkin-Elmer PE 783 spectrophotometer and were referenced to polystyrene. Melting points were measured on a Mel-Temp apparatus and were uncorrected. Microanalyses were performed by Mr. P. Borda in this department or by Canadian Microanalytical Services Ltd. (Tc complexes).

$[ReOBr(ma)_2]$. To a solution of $[(n\text{-}Bu)_4N][ReOBr_4]$ (152 mg, 0.2 mmol) in 5 mL of ethanol:acetone (1:1) was added Hma (58 mg, 0.46 mmol). The resulting brown green solution was heated for 15 min and was clarified by filtration. Slow evaporation of the solvent at room temperature resulted in green crystals. The supernatant was removed, and the crystals were washed with diethyl ether, collected by centrifugation, and dried in air. The yield was 68 mg (64%) mp 228–231 °C (dec). The product was soluble in acetone, acetonitrile, chloroform, methanol, water, and benzene but insoluble in diethyl ether. Anal. Calcd (found) for $C_{12}H_{10}BrO_7Re$: C, 27.08 (27.31); H, 1.89 (2.00); Br, 15.01 (14.89). Mass spectrum (FAB): m/e = 532 ($[ReOBr(ma)_2]^+$), 453 ($[ReO(ma)_2]^+$). ^{1}H NMR (acetonitrile-d_3): 8.22 (d, 1H, $^3J_{HH}$ = 5.1 Hz), 7.73 (d, 1H, $^3J_{HH}$ = 5.4 Hz), 7.20 (d, 1H, $^3J_{HH}$ = 5.1 Hz), 7.06 (d, 1H, $^3J_{HH}$ = 5.4 Hz), 2.73 (s, 3H), 2.37 (s, 3H). IR (cm^{-1}, KBr disk): 1615, 1580, 1565, 1540, 1510, 1470 (all vs, mixed $\nu_{C=O}$ and $\nu_{C=C}$); 975 (s, $\nu_{Re=O}$), 350 (m, ν_{Re-Br}).

$[TcOCl(ma)_2]$. A procedure similar to that for $[ReOBr(ma_2]$ was followed using 61 mg of $[(n\text{-}Bu)_4N][TcOCl_4]$ (0.12 mmol) and 28 mg of Hma (0.22 mmol), except that the volume of solvent was 10 mL and that five drops of 0.05 M NaOMe in methanol was added before the green solution was heated. The yield of the greenish yellow crystalline product was 21 mg (43%). The product was soluble in acetone and slightly soluble in diethyl ether. Anal. Calcd (found) for $C_{12}H_{10}ClO_7Tc$: C, 36.06 (36.31); H, 2.52 (2.69). Mass spectrum (DCI): m/e = 401 ($[HTcOCl(ma)_2]^+$), 365 ($[TcO(Ma)_2]^+$). ^{1}H NMR (acetonitrile-d_3): 8.30 (d, 1H, $^3J_{HH}$ = 5.2 Hz), 7.99 (d, 1H, $^3J_{HH}$ = 5.0 Hz), 7.10 (d, 1H, $^3J_{HH}$ = 5.1 Hz), 7.08 (d, 1H, $^3J_{HH}$ = 5.1 Hz), 2.71 (s, 3H), 2.20 (s, 3H). IR (cm^{-1}, KBr disk): 1610, 1575, 1560, 1540, 1510, 1470 (all vs, mixed $\nu_{C=O}$ and $\nu_{C=C}$); 965 (s, $\nu_{Tc=O}$); 355, 340 (m, ν_{Tc-X}).

$[ReOBr(dpp)_2)]$. To a solution of $[(n\text{-}Bu)_4N][ReOBr_4]$ (73 mg, 0.096 mmol) in acetonitrile (5 mL) was added Hdpp (28 mg, 0.20 mmol). A blue green solution formed, and it subsequently changed to green upon heating for 10 min. The solution was reduced to ca. 2 mL in volume before it was clarified by filtration. Diethyl ether was added dropwise while shaking until the solution was close to cloudiness. A green solid deposited after storing at –4 °C overnight. The supernatant was removed, and the green solid was washed with acetonitrile and then diethyl ether, collected by centrifugation, and dried in air. The yield was 21 mg (39%), mp 272–275 °C (dec). The product was soluble in acetone, acetonitrile, methylene chloride, methanol, and water but insoluble in diethyl ether. Anal. Calcd (found) for $C_{14}H_{16}BrN_2O_5Re$: C, 30.11 (30.51); H, 2.89 (3.12); N, 5.02 (5.24); Br, 14.14 (14.08). Mass spectrum (FAB): m/e = 496 ($[HReO_2(dpp)_2]^+$), 479 ($[ReO(dpp)_2]^+$). ^{1}H NMR (methanol-d_4): 8.02 (d, 1H, $^3J_{HH}$ = 6.8), 8.01 (d, 1H, $^3J_{HH}$ = 6.8), 7.29 (d, 1H, $^3J_{HH}$ = 6.8), 7.27 (d, 1H, $^3J_{HH}$ = 6.8), 4.10 (two overlapped s, 6H), 2.75 (s, 3H), 2.72 (s, 3H). IR (cm^{-1}, KBr disk): 1615, 1555, 1515, 1495, 1485, 1455 (all vs, mixed $\nu_{C=O}$ and $\nu_{C=C}$); 955 (s, $\nu_{Re=O}$); 375 (m, ν_{Re-Br}).

$[TcOCl(dpp)_2]\cdot 0.5H_2O$. A procedure similar to that for $[ReOBr(dpp)_2]$, using 47 mg of $[(n\text{-}Bu)_4N][TcOCl_4]$ (0.094 mmol) and 30 mg of Hdpp (0.22 mmol), was followed except that the solvent was ethanol acetone (1:1) and that the resulting solution was brown green. Recrystallization from acetonitrile/diethyl ether yielded a red powder (20 mg, 49%). The product was soluble in methanol and water but insoluble in diethyl ether. Anal. Calcd (found) for $C_{14}H_{17}ClN_2O_{5.5}Tc$: C, 38.68 (39.01); H, 3.94 (4.29); N, 6.44 (6.29). Mass spectrum (FAB): m/e = 391 ($[TcO(dpp)_2]^+$). ^{1}H NMR (methano-d_4): 8.08 (d, 2H, $^3J_{HH}$ = 6.8 Hz), 7.20 (d, 1H, $^3J_{HH}$ = 6.8 Hz), 7.18 (d, 1H, $^3J_{HH}$ = 6.8 Hz), 4.10 (two overlapped s, 6H), 2.76 (s, 3H), 2.73 (s, 3H). IR (cm^{-1}, KBr disk): 1615, 1555, 1505, 1485, 1460 (all vs, mixed $\nu_{C=O}$ and $\nu_{C=C}$); 950 (s, $\nu_{Tc=O}$); 375, 335 (m, ν_{Tc-X}).

$[(n\text{-}Bu_4)N][ReOBr_3(ma)]$. To $[(n\text{-}Bu)_4N][ReOBr_4]$ (300 mg, 0.39 mmol) in acetonitrile (5 mL) was added Hma (69 mg, 0.55 mmol). A brown solution resulted, and this was heated for 10 min. The solution was reduced to ca. 3 mL in volume, and then it was clarified by filtration. Diethyl ether was added dropwise while shaking until the solution was close to cloudiness. Brown crystals deposited after storing at –4 °C overnight. The crystals were collected by filtration, washed with diethyl ether, and dried in air. The yield was 214 mg (68%). The product was soluble in acetone, acetonitrile, chloroform, methanol, and water but insoluble in diethyl ether. Anal. Calcd (found) for $C_{22}H_{41}Br_3NO_4Re$: C, 32.64 (32.58); H, 5.11 (5.19); N, 1.73 (1.75); Br, 29.61 (29.63). Mass spectrum, FAB cation detection: m/e = 564 ($[ReOBr_3(ma) - 3H]^+$), 453 ($[ReO(ma)_2]^+$), 344 ($[ReO_2(ma)]^+$), 242 ($[(n\text{-}Bu)_4N]^+$). Mass spectrum, FAB anion detection: m/e = 567 ($[ReOBr_3(ma)]^-$), 487 ($[ReOBr_2(ma) - H]^-$), 79 (Br⁻). ^{1}H NMR (acetonitrile-d_3): 7.67 (d, 1H, $^3J_{HH}$ = 5.4 Hz), 7.07 (d, 1H, $^3J_{HH}$ = 5.4 Hz), 3.08 (t, 8H), 2.41 (s, 3H), 1.59 (q, 8H), 1.35 (h, 8H), 0.96 (t, 12H). Infrared spectrum (cm^{-1}, KBr disk): 1615, 1585, 1520, 1475 (all vs, mixed $\nu_{C=O}$ and $\nu_{C=C}$); 970 (s, $\nu_{Re=O}$); 355 (m, ν_{Re-Br}).

$[Ph_4As][ReOBr_3(ma)]$. To $[Ph_4As][ReOBr_4]$ (93 mg, 0.10 mmol) in ethanol:acetone (1:1, 5 mL) was added Hma (27 mg, 0.21 mmol). A brown green solution resulted; it was clarified by filtration. Diethyl ether was added dropwise to the solution, which was being shaken until it was

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Table I. Selected Crystallographic Data for [ReOBr(ma)$_2$], [(n-Bu)$_4$N][ReOBr$_3$(ma)], and [(n-Bu)$_4$N][TcOCl$_3$(ma)]

	complex		
	[ReOBr(ma)$_2$]	[(n-Bu)$_4$N]-[ReOBr$_3$(ma)]	[(n-Bu)$_4$N]-[TcOCl$_3$(ma)]
formula	$C_{12}H_{10}BrO_7Re$	$C_{22}H_{41}Br_3NO_4Re$	$C_{22}H_{41}Cl_3NO_4Tc$
fw	532.32	809.49	586.93
cryst syst	triclinic	monoclinic	monoclinic
space group	$P\bar{1}$	$P2_1/n$	$P2_1/c$
a, Å	20.846(2)	11.074(3)	10.724(2)
b, Å	8.484(2)	15.713(4)	11.327(2)
c, Å	8.4809(8)	17.370(4)	23.651(2)
α, deg	85.89(1)	90	90
β, deg	89.831(9)	104.77(2)	101.46(1)
γ, deg	89.80(1)	90	90
V, Å^3	1496.0(4)	2923(2)	2815.6(8)
Z	4	4	4
ρ_c, g/cm^3	2.363	1.839	1.384
T, °C	21 ± 1	21 ± 1	21 ± 1
radiation (λ, Å)	Cu Kα (1.541 78)	Mo Kα (0.710 69)	Mo Kα (0.710 69)
μ, cm^{-1}	187.63	83.01	8.02
transm factors	0.47–1.00	0.48–1.00	0.84–1.00
R	0.043	0.033	0.034
R_w	0.050	0.027	0.030

close to cloudiness. Brown crystals deposited after storing at –4 °C overnight. The crystals were washed with diethyl ether, collected by filtration, and dried in air. The yield was 36 mg (37%). The product was soluble in chloroform, acetonitrile, and acetone but insoluble in diethyl ether. Anal. Calcd (found) for $C_{30}H_{25}AsBr_3O_4Re$: C, 37.91 (37.57); H, 2.65 (2.55); Br, 25.22 (24.95). Mass spectrum (FAB): m/e = 453 ([ReO(Ma)$_2$]$^+$), 383 ([Ph$_4$As]$^+$), 344 ([ReO$_2$(ma)]$^+$). ^{1}H NMR (acetonitrile-d_3): 7.90–7.62 (m, 21H), 7.07 (d, 1H, $^3J_{HH}$ = 5.3 Hz), 2.40 (s, 3H). Infrared spectrum (cm^{-1}, KBr disk): 1610, 1580, 1565, 1520, 1480, 1435 (all vs, mixed $\nu_{C=O}$ and $\nu_{C=C}$); 965 (s, $\nu_{Re=O}$); 350 (m, ν_{Re-Br}).

[(n-Bu$_4$)N][TcOCl$_3$(ma)]. A procedure similar to that for [(n-Bu)$_4$N]-[ReOBr$_3$(ma)] was followed using 50 mg of [(n-Bu$_4$)N][TcOCl$_4$] (0.10 mmol) and Hma (41 mg, 0.33 mmol), except that 7 drops of 0.2 M NaOH in methanol were added. The product was collected by centrifugation and dried in vacuo overnight. The yield was 46 mg (78%). The product was soluble in methanol, water, and acetonitrile but insoluble in diethyl ether. Anal. Calcd (found) for $C_{22}H_{41}Cl_3NO_4Tc$: C, 44.94 (44.56); H, 7.03 (6.90); N, 2.38 (2.37). Mass spectrum (FAB): m/e = 365 ([TcO(ma)$_2$]$^+$), 275 ([TcOCl(ma)]$^+$), 242 ([(n-Bu)$_4$N]$^+$). ^{1}H NMR (acetonitrile-d_3): 7.92 (d, 1H, $^3J_{HH}$ = 5.3 Hz), 7.06 (d, 1H, $^3J_{HH}$ = 5.2 Hz), 3.07 (t, 8H), 2.21 (s, 3H), 1.59 (q, 8H), 1.33 (h, 8H), 0.95 (t, 12H). Infrared spectrum (cm^{-1}, KBr disk): 1610, 1580, 1510, 1470 (all vs, mixed $\nu_{C=O}$ and $\nu_{C=C}$); 965 (s, $\nu_{Tc=O}$); 360, 315 (m, ν_{Tc-X}).

X-ray Crystallographic Analyses. Selected crystallographic data for [ReOBr(ma)$_2$], [(n-Bu)$_4$N][ReOBr$_3$(ma)], and [(n-Bu)$_4$N][TcOCl$_3$-(ma)] appear in Table I. The final unit-cell parameters were obtained by least-squares on the setting angles for 25 reflections with 2θ = 37.9–64.4, 24.5–28.3, and 20.5–32.9°, respectively, for the three compounds. The intensities of three standard reflections, measured every 200 reflections throughout the data collections, showed only small random fluctuations for each data set. The data were processed[22] and corrected for Lorentz and polarization effects and absorption (empirical, based on azimuthal scans for three reflections).

Delaunay reduction of the triclinic unit cell of [ReOBr(ma)$_2$] indicated possible orthorhombic and monoclinic C-centered lattices. A careful check of the diffraction symmetry before data collection indicated that the crystal had true $\bar{1}$ Laue symmetry and approximate $2/m$ Laue symmetry. The data were collected by assuming triclinic symmetry. The structure is very close to being monoclinic (space group $C2/c$, a = 12.417(2) Å, b = 11.558(2) Å, c = 20.846(2) Å, β = 90.25 (1)°, Z = 8), but the fact that the R_{merge} of 0.161 for the monoclinic model is substantially higher than the corresponding value of 0.039 for the 180 Friedel pairs in the triclinic data set prompted us to retain the triclinic model with two molecules in the asymmetric unit. A refinement of the structure in $C2/c$ converged at R = 0.063 and R_w = 0.077.

Table II. Selected Final Atomic Coordinates (Fractional) and Equivalent Isotropic Thermal Parameters B_{eq} (Å^2)[a] for [ReOBr(ma)$_2$],[b] [n-Bu$_4$N][ReOBr$_3$(ma)], and [n-Bu$_4$N][TcOCl$_3$(ma)]

atom	x	y	z	B_{eq}
		[ReOBr(ma)$_2$]		
Re(1)	0.86545(2)	0.25710(6)	0.39283(6)	3.03(2)
Br(1)	0.94249(6)	0.4323(2)	0.2350(2)	4.84(7)
O(1)	0.8890(4)	0.303(1)	0.572(1)	4.4(4)
O(3)	0.8474(3)	0.1542(8)	0.1890(9)	3.4(3)
O(4)	0.9354(3)	0.076(1)	0.389(1)	3.9(4)
O(6)	0.7910(3)	0.391(1)	0.3359(9)	4.0(4)
O(7)	0.7935(3)	0.1095(9)	0.4807(9)	3.8(4)
		[n-Bu$_4$N][ReOBr$_3$(ma)]		
Re(1)	0.35701(1)	0.20849(20	0.15185(2)	3.30(1)
O(1)	0.2851(5)	0.1781(3)	0.0598(3)	5.0(3)
O(3)	0.3164(4)	0.0898(3)	0.1952(3)	4.0(2)
O(4)	0.4375(4)	0.2158(3)	0.2708(3)	4.0(2)
Br(1)	0.56647(9)	0.14743(6)	0.14407(6)	5.90(5)
Br(2)	0.16227(9)	0.26506(6)	0.18490(6)	5.64(5)
Br(3)	0.42468(9)	0.35516(6)	0.13237(5)	5.14(4)
		[n-Bu$_4$N][TcOCl$_3$(ma)]		
Tc(1)	0.28086(3)	0.09103(2)	0.15172(1)	3.50(1)
O(1)	0.3664(2)	0.1656(2)	0.20554(9)	4.8(1)
O(3)	0.2149(2)	0.0221(2)	0.07274(9)	4.2(1)
O(4)	0.4087(2)	0.1592(2)	0.1001(1)	4.7(1)
Cl(1)	0.41344(8)	–0.08075(8)	0.16973(4)	5.46(4)
Cl(2)	0.12549(8)	–0.00110(8)	0.19103(4)	5.16(4)
Cl(3)	0.1389(1)	0.24987(8)	0.12044(4)	5.43(4)

[a] $B_{eq} = (8/3)\pi^2\sum\sum U_{ij}a_i^*a_j^*(\mathbf{a}_i \cdot \mathbf{a}_j)$. [b] For one of the two independent molecules. See text.

All three structures were solved by conventional heavy-atom methods, the coordinates of the heavy atoms being determined from the Patterson functions and those of the remaining non-hydrogen atoms from subsequent difference Fourier syntheses. The structure analysis of [ReOBr(ma)$_2$] was initiated in the centrosymmetric space group $P\bar{1}$ based on E-statistics and the Patterson function, this choice being confirmed by the subsequent successful solution and refinement of the structure. The asymmetric unit of [ReOBr(ma)$_2$] contains two independent molecules. The terminal carbon atom of one of the n-butyl groups in [(n-Bu)$_4$N][ReOBr$_3$(ma)] was found to be disordered over two sites. A split-atom model was refined. Site occupancy factors for the component atoms could not be refined at the same time as the thermal parameters but were adjusted as the refinement progressed to result in approximately equal thermal parameters. There is a relatively high degree of thermal motion associated with two of the n-butyl groups, suggesting the possibility of some additional minor disordering of the cation, but no attempt was made to model this possible disorder.

All non-hydrogen atoms with the exception of the low-occupancy C(18A) atom in [(n-Bu)$_4$N][ReOBr$_3$(ma)] were refined with anisotropic thermal parameters. The hydrogen atoms were fixed in idealized positions (based on difference map positions where appropriate, d_{C-H} = 0.98 Å, $B_H = 1.2B_{\text{bonded atom}}$). Secondary extinction corrections were applied in all three cases, the final values of the extinction coefficient being 3.2(3) × 10^{-7}, 7.1(5) × 10^{-8}, and 0.47(11) × 10^{-7}, for [ReOBr(ma)$_2$], [(n-Bu)$_4$N][ReOBr$_3$(ma)], and [(n-Bu)$_4$N][TcOCl$_3$(ma)], respectively. Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the ref 23. Selected final atomic coordinates and equivalent isotropic thermal parameters, selected bond lengths, and selected bond angles appear in Tables II–IV respectively; appropriate ORTEP diagrams appear in Figures 1 and 2. Complete tables of crystallographic data, atomic coordinates, and bond distances and bond angles, as well as tables of hydrogen atom parameters, anisotropic thermal parameters, torsion angles, intermolecular contacts, and least-squares planes, are included as supplementary material (see paragraph at the end of the paper).

Results and Discussion

The [TcOCl$_4$]$^-$ or [ReOBr$_4$]$^-$ anions react with 2-methyl-3-hydroxy-4-pyrone (Hma) to give both mono- and bisligand

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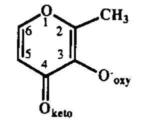
(22) TEXSAN/TEXRAY structure analysis package which includes versions of the following: DIRDIF, direct methods for difference structures, by P. T. Beurskens, ORFLS, full-matrix least-squares, and ORFFE, function and errors, by W. R. Busing, K. O. Martin, and H. A. Levy; ORTEP II, illustrations, by C. K. Johnson.

(23) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K. (present distributor Kluwer Academic Publishers: Dordrecht, The Netherlands), 1974; Vol. IV, pp 99–102 and 149.

Table III. Selected Bond Lengths (Å) for One of the Two Independent Molecules in $[ReOBr(ma)_2]$, and for the Anions in $[(n\text{-}Bu)_4N][ReOBr_3(ma)]$ and $[(n\text{-}Bu)_4N][TcOCl_3(ma)]$

	$[ReOBr(ma)_2]$ (M = Re, X = Br)	$[(n\text{-}Bu)_4N]$-$[ReOBr_3(ma)]$ (M = Re, X = Br)	$[(n\text{-}Bu)_4N]$-$[TcOCl_3(ma)]$ (M = Tc, X = Cl)
M–X and M–O			
M–X(1)	2.510(1)	2.545(1)	2.398(1)
M–X(2)		2.530(1)	2.3121(9)
M–X(3)		2.473(1)	2.378(1)
M–O(1)	1.673(8)	1.664(5)	1.647(2)
M–O(3)	2.028(7)	2.103(5)	2.019(2)
M–O(4)	2.114(7)	2.034(5)	2.152(2)
M–O(6)	1.961(7)		
M–O(7)	2.060(7)		
Coordinated Ligand[a]			
O_{keto}–C(4)	1.27(1),[b] 1.29(1)[c]	1.264(8)[b]	1.269(4)[b]
O_{oxy}–C(3)	1.35(1),[b] 1.36(1)[c]	1.349(8)[b]	1.327(4)[b]
O(1)–C(2)	1.37(1),[b] 1.36(2)[c]	1.366(9)[b]	1.363(4)[b]
O(1)–C(6)	1.35(2),[b] 1.34(2)[c]	1.34(1)[b]	1.331(5)[b]
C(2)–C(3)	1.36(2),[b] 1.38(1)[c]	1.37(1)[b]	1.360(4)[b]
C(3)–C(4)	1.42(1),[b] 1.40(2)[c]	1.41(1)[b]	1.416(4)[b]
C(4)–C(5)	1.39(1),[b] 1.42(2)[c]	1.42(1)[b]	1.432(5)[b]
C(5)–C(6)	1.32(2),[b] 1.32(2)[c]	1.35(1)[b]	1.338(5)[b]

[a] Numbers corresponding to the scheme shown as follows:



[b] Axial ligand (with respect to M═O). [c] Equatorial ligand (with respect to M═O).

complexes $[MOX_3(ma)]^-$ and $[MOX(ma)_2]$ (M = Tc, X = Cl; M = Re, X = Br), depending on the reaction conditions (solvents, countercations of the starting materials, etc.). For instance, acetone:ethanol (1:1) as the reaction solvent (with subsequent slow evaporation of the solvent) was effective in depositing either $[TcOCl(ma)_2]$ or $[ReOBr(ma)_2]$ in crystalline form, but addition of diethyl ether as a precipitant to these systems produced ($[(n\text{-}Bu)_4N][TcOCl_3(ma)]$ or $[Ph_4As][ReOBr_3(ma)]$. Substitution in acetonitrile yielded $[(n\text{-}Bu)_4N][TcOCl_3(ma)]$ or $[(n\text{-}Bu)_4N]$-$[ReOBr_3(ma)]$. Reaction of $[(n\text{-}Bu)_4N][ReOBr_3(ma)]$ with Hma in acetone:ethanol (1:1) produced $[ReOBr(ma)_2]$. Using tetraphenylarsonium tetrabromooxorhenate as the starting material tended to produce monoligand complexes with Hma. With Hdpp, however, only bisligand products, $[MOX(dpp)_2]$, were obtained with different solvents (e.g. acetonitrile, methanol, or 1:1 acetone:ethanol) and countercations.

All products were air stable in the solid state and in solution. It was observed, however, that, upon standing, $[(n\text{-}Bu)_4N]$-$[ReOBr_3(ma)]$ converted to $[ReOBr(ma)_2]$ in acetonitrile or water (*vide infra*), indicating that the bisligand product is thermodynamically favored. All complexes were characterized by elemental analyses plus infrared, mass, and ^1H NMR spectra, as well as X-ray crystallography in some cases. Analytical data established the formulations of all the complexes, while IR measurements confirmed that the ligands are coordinated as evidenced by the disappearance of the O–H stretch and the shifting of the mixed $\nu_{C═O}$ and $\nu_{C═C}$ bands to lower wavenumbers.

Bisligand Complexes. The mass spectra were diagnostic of the complex formulations. In all cases, loss of one halo ligand from a $[MOXL_2]$ unit to give $[MOL_2]^+$ was observed as the base peak, indicating that the bidentate ligands were more strongly bound than the monodentate halo ligands. The IR spectra of the technetium complexes were almost superimposable on those of the rhenium complexes. The Tc═O bond stretching vibrations were found at 965 cm^{-1} in $[TcOCl(ma)_2]$ and 950 cm^{-1} in $[TcOCl(dpp)_2]$, much lower values than 1020 cm^{-1} for the starting material $[(n\text{-}Bu)_4N][TcOCl_4]$.[20] Similarly, the Re═O bond stretching vibrations at 975 cm^{-1} for $[ReOBr(ma)_2]$ and 955

Table IV. Selected Bond Angles (deg) for One of the Two Independent Molecules in $[ReOBr(ma)_2]$ and for the Anions in $[(n\text{-}Bu)_4N][ReOBr_3(ma)]$ and $[(n\text{-}Bu)_4N][TcOCl_3(ma)]$

	$[ReOBr(ma)_2]$ (M = Re, X = Br)	$[(n\text{-}Bu)_4N]$-$[ReOBr_3(ma)]$ (M = Re, X = Br)	$[(n\text{-}Bu)_4N]$-$[TcOCl_3(ma)]$ (M = Tc, X = Cl)
O–M–X and O–M–O			
O(1)–M–X(1)	97.4(3)	93.5(2)	93.38(8)
O(1)–M–X(2)		95.3(2)	104.84(8)
O(1)–M–X(3)		102.9(2)	94.40(8)
O(1)–M–O(3)	166.8(3)	89.8(2)	162.3(1)
O(1)–M–O(4)	91.5(3)	166.1(2)	86.2(1)
O(1)–M–O(6)	106.9(4)		
O(1)–M–O(7)	93.5(4)		
X(1)–M–O(3)	86.7(2)		
X(1)–M–O(4)	87.3(2)		
X(1)–M–O(6)	93.7(2)		
X(1)–M–O(7)	168.8(2)		
O(3)–M–O(4)	76.1(3)	76.4(2)	76.08(8)
O(3)–M–O(6)	85.2(3)		
O(3)–M–O(7)	83.2(3)		
O(6)–M–O(7)	80.7(3)		
O_{oxy}[a]–M–X(1)	86.7(2)	84.6(1)	86.37(7)
O_{oxy}[a]–M–X(2)		85.9(1)	92.84(7)
O_{oxy}[a]–M–X(3)		91.0(1)	85.41(7)
Coordinated Ligand[a]			
O_{keto}–C(4)–C(3)	117.2(9),[b] 116(1)[c]	117.4(7)[b]	117.7(3)[b]
O_{oxy}–C(3)–C(4)	114(1),[b] 117.8(8)[c]	114.9(7)[b]	115.2(3)[b]
O(1)–C(2)–C(3)	118(1),[b] 118(1)[c]	118.0(8)[b]	119.3(4)[b]
C(2)–C(3)–C(4)	121(1),[b] 120(1)[c]	122.4(8)[b]	120.7(3)[b]
C(3)–C(4)–C(5)	119(1),[b] 120(1)[c]	117.3(8)[b]	117.8(3)[b]
C(4)–C(5)–C(6)	118(1),[b] 116(1)[c]	117.7(8)[b]	117.3(4)[b]
C(5)–C(6)–O(1)	124(1),[b] 125(1)[c]	123.9(8)[b]	124.3(4)[b]
C(6)–O(1)–C(2)	121(1),[b] 121(1)[c]	120.6(7)[b]	120.6(3)[b]

[a–c] Letters and numbers correspond to those indicated in footnotes *a–c* of Table III.

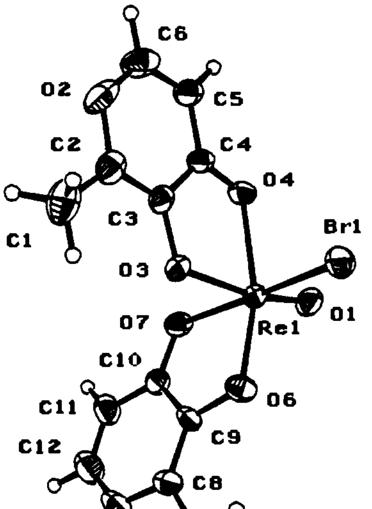


Figure 1. ORTEP drawing of one of the two independent molecules in the asymmetric unit of $[ReOBr(ma)_2]$.

cm^{-1} for $[ReOBr(dpp)_2]$ were lower than 1010 cm^{-1} for $[(n\text{-}Bu)_4N][ReOBr_4]$ or 1000 cm^{-1} for $[Ph_4As][ReOBr_4]$.[21] These observations suggested that a sixth bond was formed trans to the M═O group.[16] The four-band infrared spectral pattern (mixed $\nu_{C═O}$ and ring $\nu_{C═C}$ between 1660 and 1450 cm^{-1}, which is characteristic of 4-pyrones and 4-pyridinones,[24] was preserved in all the complexes although the energy ordering was changed upon coordination.[5,8] In the bisligand complexes, there were one or

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(24) Katritzky, A. R.; Jones, R. A. *J. Chem. Soc.* **1960**, 2947; *Spectrochim. Acta* **1961**, *17*, 64.

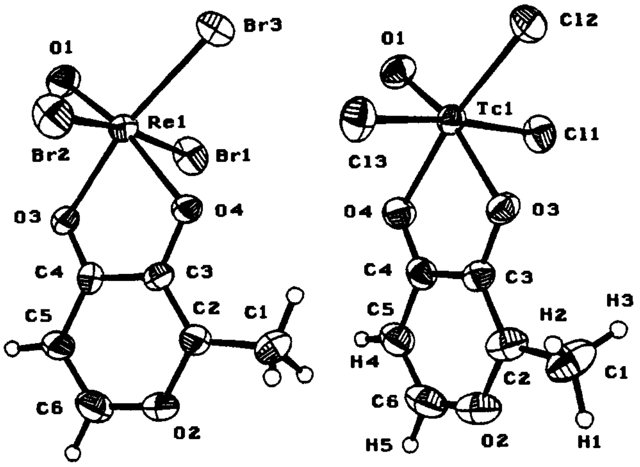

Figure 2. ORTEP drawing of the anions in $[(n\text{-Bu})_4N][ReOBr_3(ma)]$ (left) and $[(n\text{-Bu})_4N][TcOCl_3(ma)]$ (right).

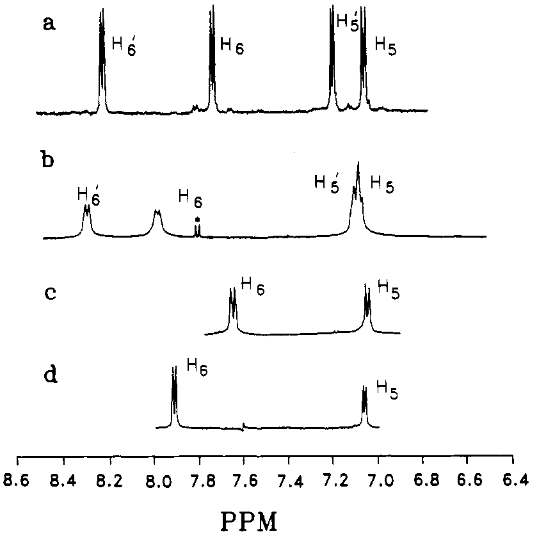

Figure 3. ^1H NMR spectra of the characteristic pair of ring hydrogens of the bis(maltolato) and mono(maltolato) complexes in CD_3CN (H_5, H_6 from the axial ligand; $H_{5'}$, $H_{6'}$ from the equatorial ligand): (a) $[ReOBr(ma)_2]$; (b) $[TcOCl(ma)_2]$; (c) $[(n\text{-Bu})_4N][ReOBr_3(ma)]$; (d) $[(n\text{-Bu})_4N][TcOCl_3(ma)]$; (*) free maltol.

two additional absorptions in that region, as might be expected for the two inequivalent environments of the two ligands (axial and equatorial relative to the M=O linkage). A cis-(halo, oxo) structure was proposed for these complexes, as ^1H NMR and ^1H–^1H COSY spectra revealed two sets of ligand hydrogen signals in a 1:1 ratio, corresponding to two nonequivalent deprotonated ligands in each complex. This structure is consistent with other reported oxometal(V) complexes of bidentate monobasic ligands[11-16] and was confirmed by the X-ray structure of $[ReOBr(ma)_2]$ (*vide infra*).

A characteristic pair of ring hydrogen doublets (H_5–H_6) was observed in the ^1H NMR spectra of all the complexes (those for the four maltolate complexes are shown in Figure 3). The values of the vicinal coupling constants (5.0–5.4 for ma^- complexes, 6.8 for dpp^- complexes) were consistent with those of the Al(III), Ga(III),[5] and Zn(II)[25] complexes of ma^-, and those of the Al(III), Ga(III),[26] and Si(IV)[27] complexes for dpp^-. For $[ReOBr(ma)_2]$, the set of hydrogen signals less shifted from those of Hma, and with chemical shifts similar and J_{HH} coupling constants identical to those of $[ReOBr_3(ma)]^-$, where the ligand was known to chelate axially (*vide infra*), was assigned to the ligand in the axial position. Further credence was lent to this assignment by the fact that this ma^- ligand was structurally very similar to the axial ma^- of $[ReOBr_3(ma)]^-$ in the solid state. The spectrum of $[TcOCl(ma)_2]$ was similarly assigned by comparison with that of $[TcOCl_3(ma)]^-$ (Figure 3). In the assignment of the spectra for $[ReOBr(dpp)_2]$ or $[TcOCl(dpp)_2]$, it was also assumed that the ^1H NMR signals of the axial ligand would shift less than those of the equatorial ligand. The two doublets of H_5 and $H_{5'}$ in $[TcOCl(ma)_2]$, which partially overlapped at room temperature (Figure 3), were observed to split completely upon cooling to −30 °C and to collapse fully to one doublet at 65 °C in acetonitrile-d_3. Such a collapse occurred at 58 °C in $[TcOCl(dpp)_2]$ (methanol-d_4), but for $[ReOBr(ma)_2]$ there was no collapse to 120 °C (DMF-d_7). The Tc complexes were more fluxional than their Re analogs.

Monoligand Complexes. Substitution of bidentate monobasic ligands onto $[TcOCl_4]^-$ or $[ReOBr_4]^-$ anion is thought to proceed in steps,[16] in which a monoligand intermediate complex is involved. The isolated intermediates in the above substitutions were trihalo(maltolato)-oxometalate(V) anions $[MOX_3(ma)]^-$ (M = Tc, X = Cl; M = Re, X = Br) as tetra-*n*-butylammonium (M = Tc, Re) and tetraphenylarsonium salts (M = Re). Intense peaks for the $[(n\text{-Bu})_4N]^+$ and $[Ph_4As]^+$ cations were present in the positive ion detection mass spectra, while the cationization of the anionic moiety was very weak and the pattern was different for different compounds. For instance, the spectrum of $[(n\text{-Bu}_4)N][ReOBr_3(ma)]$ contained a peak corresponding to $[ReOBr_3(ma) - 3H]^+$, while $[Ph_4As][ReOBr_3(ma)]$ showed a $[ReO_2(ma)]^+$ peak, and $[(n\text{-Bu})_4N][TcOCl_3(ma)]$ showed a $[TcOCl(ma)]^+$ peak. All of them had $[MO(ma)_2]^+$ peaks, also seen in the bisligand analogs, indicating that under ionizing conditions the monoligand intermediate molecules reacted with themselves to form the more stable bisligand complexes. The negative ion detection FAB mass spectrum of $[(n\text{-Bu})_4N][ReOBr_3(ma)]$ showed an intense $[ReOBr_3(ma)]^-$ peak.

The IR spectra showed strong ν_{C-H} stretches for $[(n\text{-Bu})_4N]^+$ or medium ν_{C-H} for $[Ph_4As]^+$ in each compound. The spectrum of $[(n\text{-Bu})_4N][TcOCl_3(ma)]$ was almost superimposable on that of $[(n\text{-Bu})_4N][ReOBr_3(ma)]$. The M=O bond stretching vibrations were found to be at the same frequency for these tetra-*n*-butylammonium salts as in each corresponding bisligand complex. The $\nu_{Re=O}$ for the tetraphenylarsonium salt was 10 cm^{-1} lower than that for its tetra-*n*-butylammonium analog (the same difference in $\nu_{Re=O}$ between $[(n\text{-Bu})_4N][ReOBr_4]$ and $[Ph_4As][ReOBr_4]$).[21] The four-band infrared spectral pattern between 1660 and 1450 cm^{-1}, shifted to lower energy upon coordination, was preserved in the two $[(n\text{-Bu})_4N]^+$ salts, while in the $[Ph_4As]^+$ salts this pattern was augmented by aromatic $\nu_{C=C}$ bands. ^1H NMR spectra showed the presence of the cations and only one set of ^1H signals for the one bound ligand in each complex (Figure 3).

Structure of $[ReOBr(ma)_2]$. Single crystals of $[ReOBr(ma)_2]$ and $[TcOCl(ma)_2]$ were obtained from acetone:ethanol (1:1) solvent mixtures by slow evaporation. Crystals of $[ReOBr(dpp)_2]$ were obtained from acetonitrile by slow evaporation. All the spectral data suggested that these bisligand complexes had the same cis-(halo, oxo) structure so only the crystal structure of $[ReOBr(ma)_2]$ was solved. An ORTEP diagram of one of the enantiomers of one of the two independent molecules is shown in Figure 1. The asymetric unit consists of two molecules each of which has two enantiomers which appear side by side without significant interactions; Figure 1 shows a Δ stereoisomer. Bond distances and angles quoted are for the molecule containing Re(1); those for the molecule containing Re(2) are very similar.

The overall geometry around the rhenium atom is best described as highly distorted octahedral with cis-(bromo, oxo) and cis-maltolato ligands. The Re atom is 0.2 Å out of the equatorial BrO_3 plane. The two maltolato moieties, each of which acts as

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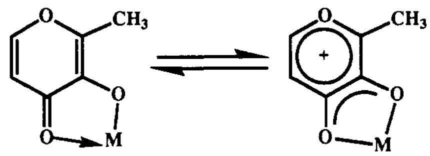
[25] Morita, H.; Shimomura, S.; Kawaguchi, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 2461.
[26] Nelson, W. O.; Karpishin, T. B.; Rettig, S. J.; Orvig, C. *Inorg. Chem.* **1988**, *27*, 1045.
[27] Evans, D. F.; Wong, C. Y. *Polyhedron* **1991**, *10*, 1131.

Scheme I



a bidentate (O, O) donor ligand, are close to mutually orthogonal (dihedral angle 94.6°), with one ligand sitting in an equatorial plane and the other in an axial plane relative to Re═O. The axial ligand chelates with its anionic oxy O-donor trans to the Re═O group, while the equatorial ligand coordinates such that the bromo ligand and an oxy O-donor are each trans to a neutral ketone O-donor, consistent with known examples of this type of complex.[11-16] The distortions from octahedral geometry are mainly caused by the acute bite angles of the two bidentate maltolato ligands (O(3)–Re(1)–O(4) = 76.1(3)° for the axial ligand, and O(6)–Re(1)–O(7) = 80.7(3)° for the equatorial ligand) and by repulsions between the sterically demanding Re═O linkage and the negatively charged cis-donors (either bromo or oxy oxygen of the equatorial maltolato ligand). The O_{oxo}–Re–Br and O_{oxo}–Re–O_{oxy} angles are 97.4(3) and 106.9(4)°, respectively, in contrast with those with the neutral donoros O_{oxo}–Re–$O_{keto,eq}$ and O_{oxo}–Re–$O_{keto,ax}$ at 93.5(4) and 91.5(3)°, respectively. The Re–O_{keto} and Re–O_{oxy} bonds are significantly different in each maltolato moiety; as in maltolato complexes of Al(III),[28] B(III),[29] and Fe(III),[30] the M–O_{oxy} bonds are shorter than M–O_{keto}.

The Re═O bond length of 1.673(8) Å was consistent with the values found in other oxo complexes of rhenium(V), indicating the retention of a multiple bond.[31] As in Tc(V)–O_{oxo} complexes, the oxo group exerts a profound trans effect/influence on the sixth coordination site kinetically/structurally. As a result, the linkage between the central atom and the sixth donor is usually lengthened.[12] However, exceptions with the trans bond not significantly lengthened have been observed in complexes containing six-membered chelate rings.[11,13,32] In [ReOBr(ma)$_2$], the trans Re–O_{oxy} bond (2.028(7) Å) was significantly longer than the cis bond (1.961(7) Å); in [Re(ma)$_2$(NPh)(PPh$_3$)]$^+$ values of 1.996(7) and 1.987(7) Å were found for Re–O_{oxy} bonds trans and cis to the Re═NPh group, respectively.[17] This indicates that the oxo O-donor has a stronger trans influence than the phenyl imido N-donor. The Re–Br distance (2.510(1) Å) is close to the average value in [ReOBr$_4$]$^-$ (2.48 Å).[33]

Each maltolato ligand was found to be quite planar, as in its complexes of Al(III)[28] and Fe(III).[30] Upon coordination, an increase in aromaticity of the ligand skeleton may be expected,[34] since chelating to a Lewis acid like O═Tc(V) or O═Re(V) favors forming a delocalized π system as is shown in Scheme I. In fact, significant bond averaging and planarity in comparison with the free ligand were observed in Al(III) and Ga(III)[26] complexes of dpp$^-$, a congener of ma$^-$. There has been no report on the crystal structure of maltol itself; nevertheless, comparison can still be made with other maltolate complexes[28-30,35] as well as with 4-pyrone.[36] The averaging of bond lengths within the ligand skeleton was observed: the single C–C bonds were shortened to 1.39–1.42 Å from 1.440 Å in 4-pyrone whereas the double C═C bonds were slightly lengthed to 1.36–1.38 Å from the reported value of 1.356 Å, with the exception of C(5)–C(6), where the bonds were shortened instead (Table III). Considering the longer O_{oxy}–C(3) and O_{keto}–C(4) bond lengths as well as the shorter Re–O bond lengths for the equatorial ligand versus the axial ligand, one may conclude that the equatorial ligand donates electron density to the central atom more than the axial ligand.

Structures of [(*n*-Bu)$_4$N][ReOBr$_3$(ma)] and [(*n*-Bu)$_4$N][TcOCl$_3$(ma)]. Single crystals of [(*n*-Bu)$_4$N][ReOBr$_3$(ma)] suitable for X-ray studies were obtained from acetonitrile with diethyl ether as precipitant. Crystals of [(*n*-Bu)$_4$N][TcOCl$_3$(ma)] were grown by cooling an acetone:ethanol (1:1) solution with diethyl ether as the precipitant. The X-ray structures of the anionic complexes are shown in Figure 2, where the atom-numbering schemes are also defined. The two [MOX$_3$(ma)]$^-$ anions are isostructural; each unit cell contains pairs of [MOX$_3$(ma)]$^-$ anions and [(*n*-Bu)$_4$N]$^+$ cations, with no significant interactions between them. The coordination environments around the metal atom in each complex are both highly distorted octahedral. The oxo oxygen of the M═O bond and the negatively charged oxy oxygen donor of the ma$^-$ ligand occupy apical trans positions subtending an angle at M of 162.3(1)° (M = Tc) or 166.1(2)° (M = Re); the three halo ligands and the ketonic oxygen donor of the ma$^-$ ligand form an equatorial plane out of which M is displaced about 0.2 Å toward the oxo O (Figure 2). The distortions from ideal octahedral geometry are primarily due to the acute bite angle of the bidentate maltolato ligand and also due to repulsions between the sterically demanding M═O linkage and the negatively charged equatorial halo ligands. The bite angles are 76.08(8) and 76.4(2)° for M = Tc and for M = Re, respectively; the O_{oxo}–M–X angles range from 93 to 105° while the O_{oxo}–M–O_{keto} are 86.2(1)° for M = Tc and 89.8(2)° for M = Re. Tc and Re have a similar size due to the lanthanide contraction, the covalent radii being 0.74 and 0.72 Å (ionic radii 0.60, 0.58 Å) for six-coordinated Tc(V) and Re(V), respectively.[37] In these two complexes, however, the Tc–O bonds are significantly different than the Re–O bonds. The Tc–O_{oxo} (1.647(2) Å) and Tc–O_{oxy} (2.019(2) Å) bonds are shorter than the corresponding Re bonds (1.664(5) and 2.034(5) Å, respectively), whereas Tc–O_{keto} (2.152(2) Å) is longer than Re–O_{keto} (2.103(5) Å), indicating that Tc(V) has a greater affinity for the negatively charged donors than does Re(V). The mean M–X distances (2.359 Å for M = Tc and 2.515 Å for M = Re) are longer than those in the corresponding halo complexes (2.305 Å in [TcOCl$_4$]$^-$ [20] and 2.48 Å in [ReOBr$_4$]$^-$ [33]). In comparison to [ReOBr(ma)$_2$], similar bond lengths are found for Re–O_{oxo}, Re–O_{oxy}(axial), and Re–O_{keto}(axial) in [ReOBr$_3$(ma)]$^-$; in addition, the two molecules have very similar O_{oxo}–Re–O_{oxy} angles. The similarity in chemical environments of the axial ma$^-$ ligands in each complex was also supported by the very similar ^{1}H NMR chemical shifts (Figures 3 and 4). The bond lengths and bond angles in the coordinated maltolato of [ReOBr$_3$(ma)]$^-$ and [TcOCl$_3$(ma)]$^-$ parallel, for the most part, those in the axial ligand of [ReOBr(ma)$_2$] (Tables III and IV).

Conversions between the Mono- and Bisligand Complexes. A slow conversion of [ReOBr$_3$(ma)]$^-$ ([(*n*-Bu)$_4$N]$^+$ salt) to [ReOBr(ma)$_2$] was observed by ^{1}H NMR in acetonitrile-*d$_3$* (Figure 4); a proposed scheme for the overall conversion is shown in Scheme II. After prolonged standing (ca. 1 year) the solution was found to be a 3:2 mixture of [ReOBr(ma)$_2$] and [ReOBr$_3$(ma)]$^-$. For the technetium analog, however, no evidence for this conversion was found under the same conditions after standing for over 4 months, indicating that an even slower conversion reaction was involved, if one even takes place at all. The reverse conversion of bisligand to monoligand complexes was not observed.

Reactivity with Water. While stirred in deionized water, [(*n*-Bu)$_4$N][ReOBr$_3$(ma)] slowly dissolved, resulting in a brown

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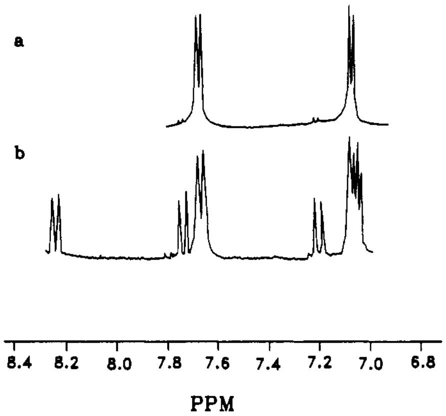
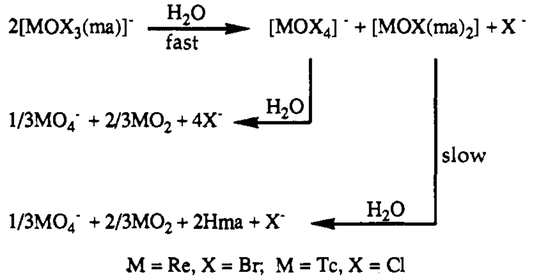


Figure 4. ^{1}H NMR spectra showing the conversion of $[\mathrm{ReOBr_3(ma)}]^-$ to $[\mathrm{ReOBr(ma)_2}]$ in $\mathrm{CD_3CN}$: (a) $[(n\text{-}\mathrm{Bu})_4\mathrm{N}][\mathrm{ReOBr_3(ma)}]$, brown solution after 2 weeks; (b) green solution after 5 months.

Scheme II

$$2[\mathrm{ReOBr_3(ma)}]^- \xrightarrow{\mathrm{CH_3CN}} [\mathrm{ReOBr(ma)_2}] + [\mathrm{ReOBr_4}]^- + \mathrm{Br}^-$$

Scheme III



solution, which then changed to green in about 10 min. The green color became darker but, after stirring overnight, changed to greenish yellow and white crystals deposited; upon evaporating the solvent a black residue was isolated (Scheme III). The former product was identified[38] as $[(n\text{-}\mathrm{Bu})_4\mathrm{N}][\mathrm{ReO_4}]$ and the latter as $\mathrm{ReO_2}$, the known products of the hydrolytic disproportionation reaction of $[\mathrm{ReOBr_4}]^-$.[33]

All four of the rhenium and technetium maltolato complexes in acetonitrile-d_3 were treated with $\mathrm{D_2O}$. Both monoligand and bisligand complexes were found to hydrolyze (Scheme III). As was also observed to occur slowly in $\mathrm{CH_3CN}$ (Scheme II), ^{1}H-NMR showed that after being treated with $\mathrm{D_2O}$, the monoligand complexes converted to bisligand complexes relatively fast; subsequently the concentration of bisligand complexes decreased slowly while that of the free Hma increased. In contrast to the expected lability of Tc > Re,[39,40] $[\mathrm{TcOCl_3(ma)}]^-$ and $[\mathrm{TcOCl(ma)_2}]$ were found to form Hma more slowly than their Re/Br analogs. This may be explained by the fact that the reactions are disproportion reactions and not simple ligand exchange[39] or racemization[40] processes.

Conclusion

Neutral and anionic technetium(V) and rhenium(V) complexes of the forms $[\mathrm{MOXL_2}]$ and $[\mathrm{MOX_3(ma)}]^-$, respectively, where M = Tc, X = Cl or M = Re, X = Br and L is a bidentate (O, O) monobasic ligand, 2-methyl-3-oxy-4-pyronate (maltolato, ma$^-$) or 1,2-dimethyl-3-oxy-4-pyridinonate (dpp$^-$), have been synthesized and characterized. The bidentate (O, O) monobasic ligands form stable oxotechnetium(V) and oxorhenium(V) complexes, which are structurally analogous to those complexes of the bidentate (O, N) monobasic ligands. The monoligand complexes are intermediates in the formation of the bisligand complexes. These compounds are important since they provide fully characterized models for the structures of intermediates in the synthesis of potential radiopharmaceuticals.

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Supplementary Material Available: An ORTEP diagram with the numbering scheme for $[n\text{-}\mathrm{Bu_4N}]^+$ and complete tables of crystallographic data, final atomic coordinates and equivalent isotropic thermal parameters, bond lengths, bond angles, hydrogen atom parameters, anisotropic thermal parameters, torsion angles, intermolecular contacts, and least-squares planes (64 pages). Ordering information is given on any current masthead page.

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(38) FABMS (both + and −) was performed to identify this white crystal: m/e = 242 ($[(n\text{-}\mathrm{Bu})_4\mathrm{N}]^+$), 251 ($[\mathrm{ReO_4}]^-$).

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