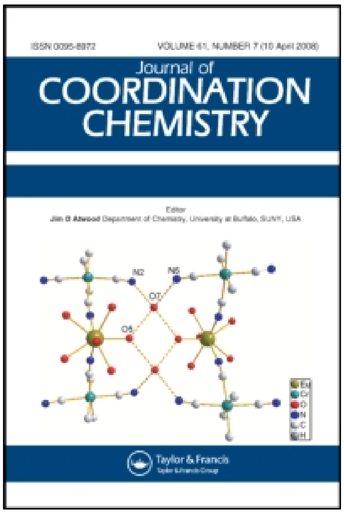

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Trichloro-mono-<i>β</i>-diketonato oxorhenium(V) complexes: synthesis, characterization and crystal structure

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Trichloro-mono-*β*-diketonato oxorhenium(V) complexes: synthesis, characterization and crystal structure

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Oxorhenium(V) complexes of *β*-diketonate systems have been synthesized and isolated in pure form. The red complexes *n*-$Bu_4N[ReO(R_1COCHCOR_2)Cl_3]$ (acac, $R_1{=}R_2{=}CH_3$; bzac, $R_1{=}CH_3$ and $R_2{=}C_6H_5$; bzbz, $R_1{=}R_2{=}C_6H_5$) have been characterized by elemental analyses, spectroscopic and other physico-chemical tools. One complex, *n*-$Bu_4N[ReO(bzbz)Cl_3]$ (**1c**) has been subjected to single-crystal X-ray analysis. In the structure of the anion, the metal has a six-coordinate octahedral environment in which the bidentate *β*-diketone ligand is *cis* and *trans* to the terminal oxygen.

Keywords: Oxorhenium(V) complexes; *β*-diketonate; Crystal structure

1. Introduction

Coordination chemistry of rhenium was initially sparked by the development of ^{99m}Tc-containing radionuclide radiopharmaceuticals as diagnostic agents in nuclear medicine [1–9]. Rhenium as third row congener of technetium was a non-radioactive substitute in chemical studies because of its closeness in molecular properties to that of Tc due to the "lanthanide contraction." Recently, the *β*-emitting isotopes ^{186}Re and ^{188}Re have been used in nuclear medicine for systematic radiotherapy of abnormal tissues [1–4] and in the treatment of cancer [10–12]. This research concentrates mainly on oxidation state (V) because most ^{99m}Tc-containing radiopharmaceuticals in clinical use contain a technetium complex with the TcO^{3+} core, and the core of most of the rhenium complexes is Re(V)O [13,14].

Furthermore, *β*-diketones have attracted attention due to their distinct structural properties and high synthetic utility [15–20]. Metal complexes containing *β*-diketonato bidentate ligands have been reported as photosensitizers [21], magneto-optical materials [22], insulin mimetic chelates [23] and antitumor compounds [24]. Metal chelates of different *β*-diketones are also important in analytical chemistry [25–29].

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There are no reports of oxorhenium(V) complexes containing β-diketonate ligands, only rhenium(III) complexes of the β-diketonate system [30]. We have synthesized a series of oxorhenium (V) complexes of acac, bzac and bzbz and characterized them by elemental analyses, spectroscopic and other physico-chemical tools. One of the complexes, *n*-$Bu_4N[ReO(bzbz)Cl_3]$ (**1c**) has been subjected to single-crystal X-ray analysis in order to confirm the detailed structure.

2. Experimental

2.1. *Materials and physical measurements*

All chemicals were of reagent grade and used as received from the suppliers. Solvents were purified and dried. The synthesis of n-$Bu_4N[ReOCl_4]$ was carried out following the reported procedure [31].

Microanalyses were performed on a Perkin Elmer 2400 CHN elemental analyzer. Infrared spectra and ^1H NMR spectra were obtained by a JASCO FT-IR model 420 using KBr discs and by a Bruker AC300 spectrometer, respectively. Electronic spectra were recorded using JASCO UV-Vis/NIR model V-570. Conductivity measurements, molar conductance (Λ_M, in $cm^2\,Ohm^{-1}\,mol^{-1}$), were measured in a Systronics conductivity meter 304 model using $\sim 10^{-3}$ mol dm^{-3} solutions in methanol and magnetic moments (μ, B.M.) were obtained from vibrating sample magnetometer PAR 155 model.

2.2. *Synthesis of the oxorhenium(V)complexes(1)*

To the methanol/ethanol solution (10–15 mL) of the corresponding chelating reagents (0.5 mmol; 50 mg acac for **1a**, 81 mg for **1b**, and 112 mg for **1c**), the MeOH or EtOH solution (25 mL) of *n*-$Bu_4NReOCl_4$ (0.5 mmol, 294 mg) was added dropwise. The reaction mixture was then stirred at 60°C for 1.5 h. The reddish solid oxorhenium(V) complexes were isolated upon cooling and reducing the solvent by rotary evaporator. The products were collected by filtration. Pure products were obtained through recrystallization from CH_2Cl_2-MeOH. Yield: 75%–80%.

n-$Bu_4N[ReO(acac)Cl_3]$ (**1a**): $C_{21}H_{43}Cl_3NO_3Re$; Yield: 79%: Anal. Calcd.: C, 38.79; H, 6.62; N, 2.15. Found: C, 38.08; H, 6.69; N, 2.01. IR: $\nu_{(Re=O)}$ 982(s); $\nu_{(C–O)}$ 1576(s); $\nu_{(C=C)}$ 1535(s); $\nu_{(Re–Cl)}$ 335(m), 320(m); ^1H NMR (δ, in DMSO-d_6) ppm: 5.61(s, 1H), 0.95(t, $J = 7.2$ Hz, 12H), 1.30(m, 8H), 1.58(m, 8H), 1.88(s, 6H) and 3.20(br m, 8H). Conductivity (Λo, $Ohm^{-1}\,cm^2\,mol^{-1}$): 105.

n-$Bu_4N[ReO(bzac)Cl_3]$ (**1b**): $C_{26}H_{45}Cl_3NO_3Re$; Yield: 75%: Anal. Calcd.: C, 43.85; H, 6.32; N, 1.97. Found: C, 44.06; H, 6.25; N, 1.99. IR: $\nu_{(Re=O)}$ 976 (s); $\nu_{(C–O)}$ 1576(s); $\nu_{(Re–Cl)}$ 336(m), 318(m); ^1H NMR (δ, in DMSO-d_6) ppm: 6.86(d, $J = 7.6$ Hz, 2H), 6.75(m, 1H), 6.55(m, 2H), 5.67(s, 1H), 0.98(t, $J = 7.2$ Hz, 12H), 1.32(m, 8H), 1.65(m, 8H), 1.97(s, 3H) and 3.05(br m, 8H). Conductivity (Λo, $Ohm^{-1}\,cm^2\,mol^{-1}$): 94.

n-$Bu_4N[ReO(bzbz)Cl_3]$ (**1c**): $C_{31}H_{47}Cl_3NO_3Re$; Yield: 80%: Anal. Calcd.: C, 48.09; H, 6.21; N, 1.88. Found: C, 48.22; H, 6.08; N, 1.81. IR: $\nu_{(Re=O)}$ 979 (s); $\nu_{(C–O)}$ 1575(s);

$\nu_{(\text{Re–Cl})}$ 327(m); ^{1}H NMR (δ, in DMSO-d_6) ppm: 6.90(d, $J = 7.5$ Hz, 4H), 6.82(m, 2H), 6.65(m, 4H), 5.72(s, 1H), 0.92(t, $J = 7.3$ Hz, 12H), 1.25(m, 8H), 1.60(m, 8H) and 3.14(br m, 8H). Conductivity (Λo, $\text{Ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1}$): 92.

2.3. *X-ray crystal structure analysis*

Single crystals suitable for X-ray analysis of $\text{Bu}_4\text{N[ReO(bzbz)Cl}_3]$ (**1c**) were grown by slow diffusion of hexane into a benzene solution of the complex at 293K. Data of **1c** were measured with MoKα radiation using the Oxford Diffraction X-Calibur CCD System. The crystal was positioned at 50 mm from the Image Plate and 321 frames were measured with a counting time of 2 s. Data analysis was carried out with the Crysalis program [31] to provide 8622 independent reflections. The structure was solved using direct methods with the SHELXS97 program [32]. Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. An empirical absorption correction was carried out using the ABSPACK program. [33] The structure was refined on F^2 using SHELXL97 [32] with $I > 2\sigma(I)$.

3. Results and Discussion

3.1. *Synthesis*

The reaction of n-$\text{Bu}_4\text{N[ReOCl4]}$ with β-diketones (LH) at 1 : 1 mole ratio in boiling ethanol (or methanol) gave the anions $[\text{ReOL)Cl}_3]^-$ which were precipitated as n-Bu_4N^+ salts (scheme 1). The β-diketones are bidentate monobasic ligands. The complexes are soluble in common organic solvents, except for ether and hexane, and are sparingly soluble in CHCl_3 and CH_2Cl_2. The complexes are stable to air and moisture in the solid state. The solid state structure of **1c** has been characterized by X-ray crystallography. Microanalytical data confirm the composition of the complexes. Conductivity measurements of the complexes in MeOH solution shows the conductance to be in the 92–105 Λo $\text{Ohm}^{-1}\,\text{cm}^2\,\text{mol}^{-1}$ range, confirming 1 : 1 electrolyte nature of the complexes in solution. The diamagnetic nature of the oxorhenium(V) complexes corresponding to $5d^2$ configuration has been confirmed by magnetic moment measurement.

$$\underset{1:1}{n\text{-Bu}_4\text{N[ReOCl}_4] + \text{LH}} \xrightarrow[\text{Reflux}]{\text{MeOH / EtOH}} \underset{1}{n\text{-Bu}_4\text{N[ReO(L)Cl}_3]} + \text{HCl}$$

LH	Complex
$\text{MeCOCH}_2\text{COMe}$ (= acacH)	n-$\text{Bu}_4\text{N[ReO(acac)Cl}_3]$ (**1a**)
$\text{PhCOCH}_2\text{COMe}$ (= bzacH)	n-$\text{Bu}_4\text{N[ReO(bzac)Cl}_3]$ (**1b**)
$\text{PhCOCH}_2\text{COPh}$ (= bzbzH)	n-$\text{Bu}_4\text{N[ReO(bzbz)Cl}_3]$ (**1c**)

Scheme 1. Synthetic procedure for n-$\text{Bu}_4\text{N[ReO(L)Cl}_3]$.

3.2. *X-ray structure of* **1c**

The complex contains Bu_4N^+ cations and $ReOLCl_3$ anions. The ORTEP view of **1c** is illustrated in figure 1 together with the numbering scheme. The crystallographic data are tabulated in table 1 with bond lengths and angles in the metal coordination sphere in table 2.

The analysis shows the metal to be octahedral, bonded to one terminal oxygen atom, three chlorides and the bidentate β-diketonato ligand. The length of the bond from the metal to the terminal oxygen atom (Re–O1) is 1.662(3) Å. The equatorial plane is occupied by three chlorides and one oxygen O11 of the β-diketonato ligand.

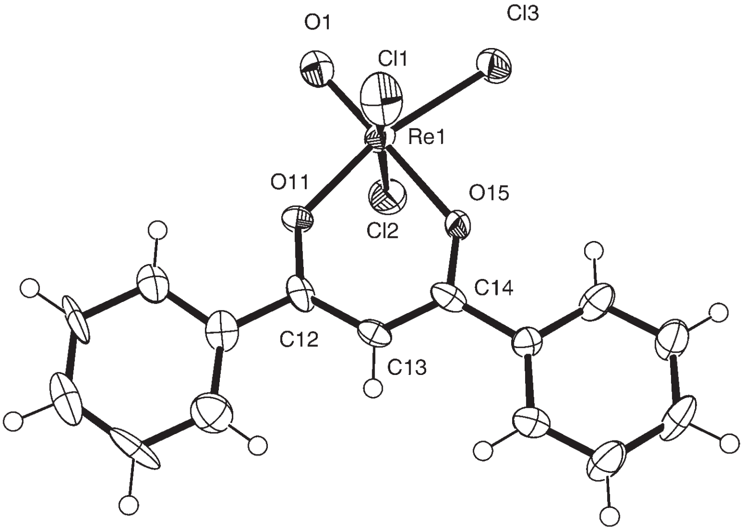

Figure 1. An ORTEP view of [ReO(bzbz)Cl3]$^-$ in **1c** with thermal ellipsoids drawn at the 50% probability level and showing the atom numbering scheme.

Table 1. Crystallographic data for *n*-$Bu_4N[ReO(bzbz)Cl_3]$.

Empirical formula	$C_{31}H_{47}Cl_3NO_3Re$
Formula weight	774.25
Temperature (K)	150(2)
Wavelength (Å)	0.71073
Crystal system, space group	Orthorhombic, *Pc*21*a*
Unit cell dimensions (Å)	
a	18.3511(16)
b	17.5961(15)
c	10.3597(9)
Volume (A^3)	3345.2(5)
Z, Calculated density ($g\,cm^{-3}$)	4, 1.601
Absorption coefficient (mm^{-1})	3.910
F(000)	1624
θ range for data collection (°)	2.54 to 30.10
Total reflections	8622
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0364$, $wR_2 = 0.0523$
Goodness-of-fit on F^2	0.730

These four atoms are coplanar with an r.m.s. deviation of 0.01 Å. The metal atom is 0.25Å from this plane in the direction of the terminal oxygen O1. The Re–O11 bond length of 2.022(3) Å is significantly shorter than the Re–O15 bond length of 2.066(3) Å, no doubt because this latter oxygen atom is trans to the terminal oxygen O100 and Re1–O11 is trans to the comparatively weak bond of Re1–Cl3 [2.336(1) Å]. The angle subtended by the two axial atoms at the metal (O15–Re1–O1) is 178.4(2)°. This difference in the Re–O11 and Re–O15 bond lengths is concomitant with other differences in bond lengths in the bidentate ligand, thus C12–O11 [1.295(6) Å] is significantly longer than C14–O15 [1.258(6) Å] and C12–C13 [1.408(6) Å] is also slightly higher than that of C13–C14 [1.374(7) Å]. This effect is still noticeable in the next similar type of bonds as the bond length of C12–C91 [1.461(7) Å] is slightly lower than that of C14–C81 [1.506(7) Å]. The bond lengths of C12–C13 [1.408(6) Å] and C13–C14 [1.374(7) Å] in the chelate ring of the β-diketonato ligand of **1c** are greater than the normal aliphatic C=C bond length [1.337 Å] and less than typical C–C single bonds [1.54 Å] [35]. Again, C12–O11 [1.295(6) Å] or C14–O15 [1.258(6) Å] is also greater than the usual C=O bond length. This observation emphasizes that electron delocalization has occurred in the pseudo aromatic core of the β-diketonato ligand. The chelate ring is planar with an r.m.s deviation of 0.02 Å. The two phenyl rings intersect this ring at angles of 5.7(3) and 7.3(3)°.

The Re=O bond distance [1.662(3) Å] in **1c** is equivalent to the Re=O distance [1.654(11) Å] observed in an oxorhenium(V) complex [34] but longer than the 1.640(3) Å found in [ReOCl$_2$(OPPh$_3$)(biimH$_2$)]Cl [36]. The Re–Cl bond lengths are comparable to the Re–Cl distances [2.34(2)–2.44(2) Å] observed for Re(V) complexes [37].

3.3. *Spectroscopic characterization*

In the infrared spectrum of the complexes, a sharp strong peak in the range of 976-982 cm^{-1} corresponds to the typical asymmetric Re=O stretching frequency [34]. The absence of any band around 1700 cm^{-1} rules out the possibility of a keto group, but a band around ca. 1575 cm^{-1} for $\nu_{(C=O)}$ in all three complexes and particularly a sharp peak at 1535 cm^{-1} in **1a** assignable to $\nu_{(C=C)}$ suggest the presence of the keto-enolate form of the ligand. In addition to those bands, the spectra show bands at ca. 335 and 318 cm^{-1} corresponding to $\nu_{(Re\text{-}Cl)}$ indicating more than one coordinated chloride.

Table 2. Selected bond lengths (Å) and angles (°) for **1c**.

Re1–O11	2.022(3)	Re1–Cl3	2.336(1)
Re1–O15	2.066(3)	C12–C13	1.408(6)
Re1–O1	1.662(3)	C13–C14	1.374(7)
Re1–Cl1	2.388(2)	C12–O11	1.295(6)
Re1–Cl2	2.369(2)	C14–O15	1.258(6)
O11–Re1–Cl1	86.2(1)	Cl3–Re1–Cl2	92.0(1)
O11–Re1–Cl2	87.8(1)	Cl2–Re1–Cl1	167.5(1)
O11–Re1–Cl3	166.5(1)	Cl3–Re1–Cl1	91.2(1)
O11–Re1–O15	82.5(1)	O1–Re1–O11	96.2(1)
O15–Re1–Cl3	84.0(1)	O1–Re1–Cl1	95.8(1)
O15–Re1–Cl1	83.2(1)	O1–Re1–Cl2	95.8(1)
O15–Re1–Cl2	85.1(1)	O1–Re1–Cl3	97.3(1)
O15–Re1–O1	178.4(2)	C12–C13–C14	124.7(6)

The UV-Vis spectra of the complexes in MeOH were recorded at room temperature. A broad weak absorption observed around 511 nm (ca $700\,\mathrm{M^{-1}\,cm^{-1}}$) is the characteristic band of ReO(V) complexes [38].

The well-resolved ^{1}H NMR spectra of the complexes clearly indicate the presence of the n-$\mathrm{Bu_4N^+}$ group. The spectra show a series of signals, triplet (12 protons), multiplet (8 protons), another multiplet (8 protons) and a broad multiplet (8 protons) near δ 0.92, 1.25, 1.60 and 3.15 ppm, respectively. The ratio of the integration of the signals of n-$\mathrm{Bu_4N^+}$ to those of the β-diketonate ligands shows a molar ratio of 1:1 in the complexes which is also supported by conductivity studies.

Supporting material

CCDC 656084 contains the crystallographic data for complex **1c**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; (fax: +44-1223-336-033; www:http://www.ccdc.cam.ac.uk or e-mail: deposit@ccdc.ac.uk).

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