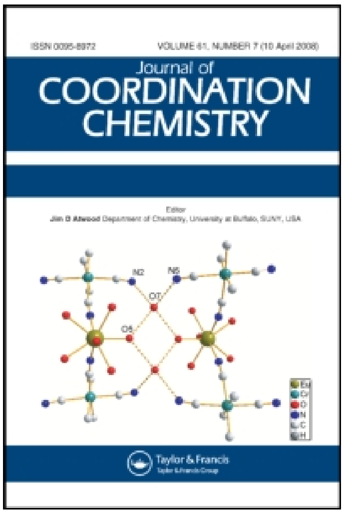

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ISOLATION AND CHARACTERIZATION OF A COMPLEX FORMED BY THE REDUCTION OF YLETHANETHIOL FIVE-COORDINATE CATIONIC RHENIUM (V) PERRHENATE WITH 2-BENZIMIDAZOLE-2'-

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NOTE

ISOLATION AND CHARACTERIZATION OF A FIVE-COORDINATE CATIONIC RHENIUM(V) COMPLEX FORMED BY THE REDUCTION OF PERRHENATE WITH 2-BENZIMIDAZOLE-2′-YLETHANETHIOL

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Keywords: Reduction, perrhenate, benzimidazolylthiols, oxorhenium(V)

Recently[1] we reported the synthesis of the cationic complex $[TcO(bls)_2]^+$, which was formed by the direct reaction of NH_4TcO_4 with the ligand Hbls (Hbls = 2-benzimidazole-2′-ylethanethiol; Figure 1) in methanol at room temperature. This reaction is unusual in that the ligand Hbls simultaneously acts as an acid, to protonate the oxo oxygens of pertechnetate, as a reducing agent for Tc(VII) and as a chelating agent for Tc(V).

Since five-coordinate cationic complexes of rhenium(V) are extremely rare, and since perrhenate is a weaker oxidizing agent than pertechnetate, we have repeated this reaction with perrhenate. The product of this reaction is the cationic five-coordinate rhenium(V) complex $[ReO(bls)_2]^+$, which was isolated as perrhenate and tetraphenylborate salts.

EXPERIMENTAL

Ammonium perrhenate was obtained commercially. The ligands Hbls and benzimidazole-2-ylemethanethiol (Hbms) were prepared according to literature procedures.[2] Scientific instrumentation used in the study is the same as was reported elsewhere.[3]

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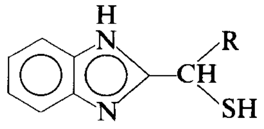

R	
CH_3	Hbls
H	Hbms

FIGURE 1 Benzimidazolylthiols (Hbls = 2-benzimidazole-2′-ylethanethiol; Hbms = 2-benzimidazole-2′-ylmethanethiol).

Preparation of the Complexes

[ReO(bls)$_2$](ReO$_4$)

To a solution of 0.4012 g of the ligand Hbls (2250 μmol) in 10 cm^3 methanol was added a solution of 0.200 g of NH_4ReO_4 in 5 cm^3 methanol. After stirring for 30 min at room temperature, no reaction was detected, and the reaction mixture was heated under reflux. After 30 min of heating the light yellow solution changed colour to pink, and it became darker (dark magenta after 1 h of heating). Heating was continued for another hour and the clear solution was cooled to room temperature and filtered. After standing overnight, a magenta coloured crystalline precipitate formed from the solution. After its removal from solution it was washed with ethanol and dried under vacuum. On partial evaporation of the filtrate a further crop of crystalline material was recovered. The yield was 0.1973 g; 66% based on Re; m.p. > 300°C. The compound is soluble in DMF, slightly soluble in methanol and insoluble in acetone, acetonitrile, benzene, ethanol, THF, *n*-pentane, chloroform and dichloromethane. Anal.: Calcd. for $C_{18}H_{18}N_4O_5S_2Re_2$: C, 26.97; H, 2.25; N, 6.94%. Found: C, 26.49; H, 2.33; N, 6.88%. Electronic spectrum (DMF, nm ($\varepsilon/M^{-1}\,cm^{-1}$)): 553(530), 352(5750), 268(2020), 260sh. IR spectrum (KBr): $\nu(Re^{V}{=}O)$, 993; $\nu(Re^{VII}{=}0)$, 909, 885; ν(N–H), 3165; ν(Re–S), 365; ν(Re–N), 409 cm^{-1}. Conductivity: Λ_M(DMF, 10^{-3} M) = 63 cm^2 mol^{-1} ohm^{-1}.

[ReO(bls)$_2$](BPh$_4$)

A 15 cm^3 methanolic solution containing 0.401 g of Hbls and 0.200 g NH_4ReO_4 was heated under reflux for 2 h. After heating was stopped, 2 cm^3 of a saturated methanolic solution of $NaBPh_4$ was added to the hot magenta coloured solution, and the solution was left to cool to room temperature. A pink crystalline precipitate was collected after an hour, was washed with ethanol and dried under vacuum. The yield was 63%, based on Re; m.p.: decomp. 190°C. The compound is soluble in acetone, DMF and acetonitrile, and insoluble in benzene, chloroform, *n*-pentane and dichloromethane. Anal.: Calcd. for $C_{42}H_{38}N_4BOS_2Re$: C, 57.59; H, 4.37; N, 6.40%. Found: C, 57.37; H, 4.27; N, 6.67%. Electronic spectrum (CH_3CN, nm($\varepsilon/M^{-1}\,cm^{-1}$)): 552(300), 350(1100), 274sh(8500), 266(11600), 243(22500). IR spectrum (KBr): $\nu(Re{=}O)$, 990; ν(N–H), 3168; ν(Re–S), 365; ν(Re–N), 411; $\nu(B\text{–}\phi)$, 857 cm^{-1}. Conductivity: Λ_M(DMF, 10^{-3} M) = 45 cm^2 mol^{-1} ohm^{-1}.

RESULTS AND DISCUSSION

The magenta-coloured complex $ReO(bls)_2^+$ is formed by the reaction of an excess of the ligand Hbls with NH_4ReO_4 in methanol. This reaction occurs extremely slowly at room temperature, and considerable heating was necessary before the product could be formed in reasonable yield. The complex was isolated as $[ReO(bls)_2](ReO_4)$, which precipitated from the reaction solution, and as $[ReO(bls)_2](BPh_4)$ by the addition of $NaBPh_4$. Both salts precipitated from solution analytically pure, and no mixture of products was obtained or could be detected.

The formation of these compounds was supported by elemental analysis. They are indefinitely stable in the solid state and in solution. They are not particularly soluble in common organic solvents, and conductivity measurements in DMF solution confirmed their ionic character.

$[ReO(bls)_2](ReO_4)$ exhibits a single strong absorption band at 993 cm^{-1} in the infrared spectrum, which is ascribed to the $Re^V{=}O$ stretching vibration. This value is at the upper end of the range normally found for square-pyramidal oxorhenium(V) complexes. The corresponding technetium complex[1] shows the Tc=O stretching absorption at 972 cm^{-1}. This difference of about 20 cm^{-1} between analogous Tc(V) and Re(V) complexes has been previously observed.[4] Two strong bands at 909 and 885 cm^{-1} are typical of the $Re^{VII}{=}O$ stretching vibrations of the ReO_4^- anion. In the tetraphenylborate salt, the $\nu(Re^V{=}O)$ mode appears at 990 cm^{-1}, with only ligand and BPh_4^- bands present in the 840–920 cm^{-1} region. There are no peaks which could be ascribed to ν(S–H), and bands around 3160 cm^{-1} [ν(N–H)], 365 cm^{-1} [ν(Re–S)] and 410 cm^{-1} [ν(Re–N)] indicate that the ligand bls^- is coordinated in bidentate fashion through the deprotonated thiolic sulfur and the neutral imidazole imine nitrogen atoms.

Both compounds give pink solutions in DMF and acetonitrile. The electronic spectrum of $[ReO(bls)_2](ReO_4)$ in DMF displays a strong peak at 268 nm, with shoulders tailing into the visible region at 352 and 553 nm. The BPh_4^- analogue exhibits two strong bands at 243 and 266 nm in addition to shoulders at 274, 350 and 552 nm in acetonitrile. The peaks around 267 nm are ascribed to the overlapping of an intraligand $\pi \rightarrow \pi^*$ transition with the oxo oxygen-to-rhenium(V) charge transfer transition. The intensities of all other peaks indicate that they are due to ligand-to-metal charge transfer, although the peak at 552 nm may be the result of a spin-forbidden d–d transition, with possible "stealing" from the adjacent charge transfer bands around 350 nm.

No reaction between NH_4ReO_4 and the ligand benzimidazole-2-ylmethanethiol (Hbms) was observed, even after heating with a six-fold excess of the ligand in methanol for 4 h under reflux. We also found that the reaction of the corresponding benzimidazolylalcoholates with NH_4ReO_4 does not occur.

Examples of ligands that serve simultaneously as an acid, as reducing agent for Re(VII) and as a chelating agent for Re(V) are scarce in the literature, and only one such an example could be found. It was reported[5] that 1-phenyl-thiosemicarbazide reacts with perrhenate, in the absence of a reducing agent to form 1:1 and 1:2 complexes of Re(V). Methods of preparation of oxorhenium(V) complexes from perrhenate usually employ the use of reducing agents such as $SnCl_2$, $NaBH_4$, Zn and H_3PO_2 in the presence of coordinating ligands.[6]

Although five-coordinate anionic oxorhenium(V) complexes are quite common, $ReO(bls)_2^+$ is a rare example of a five-coordinate cationic complex. The reaction of

$ReO_2I(PPh_3)_2$ with dioxygen was reported[7] to produce the five-coordinate complex $ReOCl_2(PPh_3)_2^+$, which was isolated as the perrhenate salt. No other well-characterized examples could be found in the literature.

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