Synthesis and structure of $[(DMSO)_2H][OsNO(DMSO)Cl_4]$

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A new complex of dimethyl sulfoxide nitrosoosmium $[(DMSO)_2H][OsNO(DMSO)Cl_4]$ has been prepared by reacting $H_2[OsNOCl_5]$ with DMSO in acetone. Its structure has been established by IR spectroscopy and X-ray structural analysis.

Key words: coordination compounds; osmium; dimethyl sulfoxide; IR spectra; structure.

Despite the fact that coordination compounds with DMSO have come to the attention of many researchers in recent years, data on osmium complexes with dimethyl sulfoxide are scarce.

A number of osmium complexes with DMSO have been synthesized: $[Os(DMSO)_3Cl_3]$,[1] $[Os(DMSO)_4Cl_2]$,[2] $\{Os(DMSO)_4\sigma\text{-}CH_2S(O)CH_3]_2\} \cdot 2DMSO$,[3] $K_3[Os(CN)_5(DMSO)]$,[4] and $Bu_4N[OsCO(DMSO)X_4]$ (X = Cl and Br).[5]

We found no literature data on the synthesis of (chloro)dimethyl sulfoxide complexes of nitrosoosmium. In this work, we report the synthesis and the structure of a new coordination compound of nitrosoosmium with DMSO.

Results and Discussion

The $[(DMSO)_2H][Os(NO)(DMSO)Cl_4]$ complex was synthesized by reacting $H_2[OsNOCl_5]$ with DMSO in an acetone solution.

The IR spectrum of the synthesized compound shows intense ν(NO) and ν(SO) absorption bands at 1820 and 922 cm^{-1}, respectively. The shift of ν(SO) to lower frequency compared to the spectrum of free DMSO indicates that DMSO is coordinated through the oxygen atom. The fact that the $[(DMSO)_2H]^+$ cation enters into the complex is confirmed by a broad intense absorption band in the region 600—900 cm^{-1} with the maximum at 730 cm^{-1} and by smeared absorption in the region 1100—1600 cm^{-1}. Similar IR spectra were obtained for cations in $[(DMSO)_2H][M(DMSO)_2Cl_4]$ complexes (M = Ru, Rh, and Ir).[6—9] In the region of the metal—chlorine stretching vibrations, an intense band at 312 cm^{-1} is observed. The rather low frequency of the ν(NO) stretching (1820 cm^{-1}) is noteworthy. This may result from the presence of an outer-sphere cation.

X-ray structural analysis confirmed the suggested structure of the complex. In the cation of the complex $[(DMSO)_2H]^+$, the DMSO molecules are linked by the proton through the oxygen atoms; in the anion, the DMSO molecule coordinated through the oxygen atom is *trans* to the NO group (Fig. 1).

The structure of the $[(DMSO)_2H]^+$ cation is similar to that in $[(DMSO)_2H][trans\text{-}[M(DMSO)_2Cl_4]$ complexes (M = Ru and Ir) except for the rather long S—O bond in one of the DMSO molecules (1.561 Å), which is longer than in the above-mentioned complexes, in which the S—O distances are in the range of 1.528—1.548 Å.[9] The second S—O distance in the cation of the complex under study (1.530 Å) falls within this range.

The H(1) hydrogen atom is statistically disordered between the two oxygen atoms (O(3) and O(4)). The O—H bonds (1.302 and 1.192 Å) apparently reflect the asymmetric position of the proton.

The coordination polyhedron of the osmium atom is a slightly distorted octahedron. The chlorine atoms are located nearly in the equatorial plane. The osmium atom is displaced from the plane that passes through the

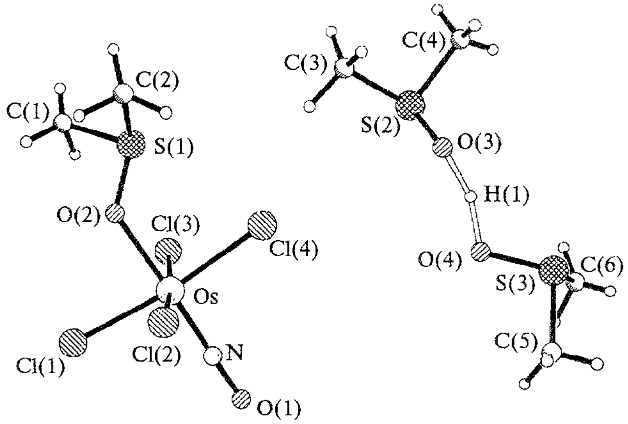

Fig. 1. Structure of the $[(DMSO)_2H][OsNO(DMSO)Cl_4]$ complex.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1333—1334, July, 1994.

Cl(1)···Cl(4) atoms by 0.16 Å toward the nitrosyl group. This displacement is typical of nitroso complexes of osmium and ruthenium.[10] The NO group is linear, the Os—N—O angle is 179.2°, and the Os—N distance (1.717 Å) and the N—O bond (1.16 Å) are typical of a linearly bonded NO group.[11,12] The Os—Cl distances are in the range 2.370—2.376 Å and are close to the mean value of r(Os—Cl$_{eq}$) in $K_2[OsNOCl_5]$, which is equal to 2.380(3) Å.[12] The Os—O and S—O distances in DMSO coordinated to the osmium atom are 2.040 and 1.569 Å, respectively; these bond distances are similar to those observed in the $[OsNOBr_3(Et_2S)(Et_2SO)]$ complex, in which Et_2SO is also *trans* to the NO group (2.074 and 1.576 Å).[13]

A comparison with similar anions of the structures $[Os(NO)(DMSO)Cl_4]^-$ and $[Os(CO)(DMSO)Cl_{2.68}Br_{1.32}]^-$ shows[5] that in the carbonyl complex the Os—O distance (2.130 Å) is longer and the S—O bond (1.517 Å) is shorter than in the nitroso complex.

Experimental

The $H_2[OsNOCl_5]$ complex, which was prepared from metallic osmium according to the following scheme:

$$\mathrm{Os} \xrightarrow[\sim 500\ ^{\circ}\mathrm{C}]{\mathrm{Cl_2,\ NaCl}} \mathrm{Na_2[OsCl_6]} \xrightarrow{\mathrm{NaNO_2}} \mathrm{Na_2[OsNO(NO_2)_4OH]} \xrightarrow{\mathrm{HCl}}$$

$$\longrightarrow \mathrm{Na_2[OsNOCl_5]} \xrightarrow[-\mathrm{NaCl}]{\mathrm{HCl}} \mathrm{H_2[OsNOCl_5]},$$

was used as the starting compound in the synthesis.

Bis(dimethylsulfoxide)protium tetrachloro(dimethyl sulfoxide)nitrosoosmate, $[(DMSO)_2H][Os(NO)(DMSO)Cl_4]$. 0.5 mL of DMSO was added to a solution of 0.3 g of $H_2[OsNOCl_5]$ in 3 mL of acetone, the reaction mixture was heated in a water bath for 1 h, and 5 mL of acetone was added to the cooled solution. The violet precipitate was filtered off, washed with a small amount of acetone, and dried in a desiccator. After two days, additional crystals precipitated from the mother liquor. The yield of the complex was *ca.* 70 %. Found (%): Os, 31.6; S, 16.8; Cl, 24.6. Calculated (%) for $[(C_2H_6OS)_2H][Os(NO)(C_2H_6OS)Cl_4]$: Os, 31.8; S, 16.1; Cl, 23.8. The electronic absorption spectrum (DMSO), λ_{max}/nm: 360 sh (ε 97); 430 (ε 71); 476 (ε 58); 554 (ε 53).

Crystals suitable for **X-ray structural analysis** were obtained by crystallization of the complex from ethanol. For X-ray structural analysis we chose a prismatic single crystal with dimensions 0.25×0.20×0.15 mm. The crystals are orthorhombic with the following unit-cell parameters: a = 18.863(4), b = 10.445(2), c = 19.423(4) Å, V = 3826.8(2.3) Å^3, space group *Pcab*, and Z = 8. The experimental data were obtained on a Syntex automated diffractometer (Mo-Kα radiation, a β filter, θ/2θ scanning technique to sinθ/λ = 0.6). 1627 reflections with $I > 3\sigma$ were measured, and a correction was applied for X-ray absorption (μ = 75.58 cm^{-1}) from the known crystal habitus. The structure was solved by the heavy-atom method. The structure was refined anisotropically to R = 0.024, R_w = 0.028. Hydrogen atoms were refined isotropically. All calculations were carried out using the SHELXTL program package on a NOVA-3 computer.

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Received February 16, 1994;
in revised form May 10, 1994