In situ formation of ligand 2,2'-[(*E*)-diazene-1,2-diyldicarbonothioyl]diphenol and structural characterization of its binuclear rhodium(v) complex containing RhO_2^+ [†]

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Received 19th June 2010, Accepted 10th August 2010 DOI: 10.1039/c0cc01970d

The ligand 2,2'-[(*E*)-diazene-1,2-diyldicarbonothioyl]diphenol has been synthesised *in situ* by aerial oxidation of *o*-hydroxythiobenzhydrazide [H(htbh)] in presence of rhodium(III) in DMSO. Each ligand binds two RhO_2^+ ions through its N and S atoms and the O atom of its deprotonated hydroxy group. Each RhO_2^+ contains two *cis*-Rh=O bonds. The sixth coordination site of each rhodium(v) is occupied by the O of DMSO.

The compounds of rhodium(v) are limited to RhF_5 , $RhF_6^$ and a few less thoroughly characterized oxycations and oxyanions. A single-crystal X-ray structure shows that RhF_5 has a tetrameric structure.¹ Various oxycations and oxyanions of rhodium(v) have been reported to result from the oxidation of rhodium(III) salts by hypochlorite, hypobromite or bismuthate.¹ At pH 2 the hypochlorite oxidation product is a cationic purple species tentatively identified as RhO_2^+ .

The oxyanion of rhodium(v), first prepared by Berzelius¹ as a result of the chemical oxidation of rhodium(III) salts, disproportionates according to the equation

$$3[RhO_3(OH)]^{2-} + 2H^+ \rightarrow 2[RhO_4]^{2-} + Rh(OH)_3 + H_2O^{-}$$

No stable complex of rhodium(v) containing the RhO_2^+ cation has been reported so far.

In a recent communication² we reported the synthesis and structure of a neutral tris(*o*-hydroxythiobenzhydrazido)-cobalt(III)-3DMSO complex where the ligands bind to cobalt(III) through their N and S atoms as donor sites leaving the –OH group to form intra and inter molecular H-bonds.

In an attempt to prepare an analogous rhodium(III) complex from DMSO a new stable complex of rhodium(v) containing RhO_2^+ of an entirely new ligand 2,2'-[(*E*)-diazene-1,2-diyldicarbonothioyl]diphenol has been obtained. A proposed mechanism of the *in situ* formation of the ligand from *o*-hydroxythiobenzhydrazide and the crystal structure of the rhodium(v) complex are reported here.

To synthesize the complex $RhCl_3 \cdot 3H_2O$ (40 mg) was dissolved in 10 ml freshly distilled DMSO and to it *o*-hydroxythiobenzhydrazide [H(htbh)] (115 mg) was added. The solution was kept at room temperature for about a week. Dark needle-shaped crystals were collected by filtration, washed with a 1:10 DMSO-water mixture and dried under vacuum.

The crystalline compound was found to have the formula $C_{18}H_{20}N_2O_8Rh_2S_4$ (33 mg, 60% on the basis of rhodium). Elemental analysis (Found: C, 29.82; H, 2.90; N, 4.02; S, 17.85%. Calc. for $C_{18}H_{20}N_2O_8Rh_2S_4$: C,29.92; H, 2.89; N, 4.08; S, 17.94%).

The compound is insoluble in water and most organic solvents except DMSO and DMF. However, the solubility of the compound at 25 °C in those two solvents is not high enough to prepare even a 10^{-4} M solution. The low solubility of the complex did not permit us to undertake the study on the properties of the compound in solution.

The reaction scheme for the oxidation of H(htbh) by oxygen from air in the presence of rhodium(III) chloride in DMSO as a catalyst is shown in Fig. 1. Rhodium(III) chloride in DMSO may be regarded as $[RhCl_n(DMSO)_{6-n}]^{(3-n)}$ and its ability to act as a catalyst precursor for the oxidation of organic compounds is not a rare phenomenon. It can catalyze the oxidation of thioethers to sulfoxides,³ sulfoxides to sulfones⁴ and the dehydrogenation of triethylamine.⁵ The mechanism of activation of dioxygen by rhodium(III) chloride in DMSO solution is not yet understood. Isolation and characterization of $[(RhO_2)_2(C_6H_4(O)-C(=S)-N=N-C(=S)(O)C_6H_4)(DMSO)_2]$ may provide an insight into the mechanism of such reactions. It may be assumed that $[RhCl_n(DMSO)_{6-n}]^{(3-n)}$ absorbed aerial oxygen to form $[RhO_2Cl_n(DMSO)_{4-n}]^{(1-n)}$ as an unstable intermediate, which oxidized H(htbh) in situ to the new ligand 2,2'-[(*E*)-diazene-1,2-divldicarbonodithiov]]diphenol.

Although the species $[RhO_2Cl_n(DMSO)_{4-n}]^{(1-n)}$ could not be isolated, the following indirect evidence may support the proposed mechanism.

On keeping H(htbh) in DMSO for two weeks the new ligand 2,2'-[(*E*)-diazene-1,2-diyldicarbonodithioyl]diphenol was not generated. H(htbh) has been characterized by a combination of spectroscopic methods² and by X-ray crystallography‡ in order to ascertain that nothing other than the compound was added to rhodium(III)chloride in DMSO solution. Moreover,



o-hydroxythiobenzyhydrazide

2,2'-[(E)-diazene-1,2-diyldicarbonodithioyl]diphenol

Fig. 1 Reaction scheme depicting oxidation of *o*-hydroxythiobenzhydrazide to 2,2'-[(*E*)-diazene-1,2-diyldicarbonodithioyl]diphenol.

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[†] CCDC 766983–766984. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc01970d

an attempt to prepare the rhodium(v) complex using the described method in a nitrogen atmosphere failed while bubbling oxygen through rhodium(III)chloride in DMSO in the presence of H(htbh) produced the complex in two days in powder form (agitation inhibited crystal growth). In addition, tris(*o*-hydroxythiobenzhydrazido)rhodium(III) could be prepared by the reaction between an aqueous solution of rhodium(III) chloride and H(htbh) at pH 6.5–7.0; the compound is soluble in most organic solvents.

The newly formed ligand 2,2'-[(*E*)-diazene-1,2-diyldicarbonodithioyl]diphenol has two N, S, and O donor sites. All chloride ions and (3 - n)DMSO molecules from one molecule of the compound [RhO₂Cl_n(DMSO)_{4-n}]⁽¹⁻ⁿ⁾ were substituted by N, S, O atoms from each donor site leading to the formation of a binuclear rhodium(v) complex. The oxygen atom of one DMSO molecule still remained coordinated to each rhodium(v) creating an octahedral environment.

That the newly synthesized rhodium(v) complex is a low-spin t_{2g}^4 system is evident from its magnetic moment value (magnetic susceptibility was measured with a MAGWAY MFG Mk 1, Sherwood Scientific Ltd, UK) of 2.80 BM per rhodium at 300 K. From the magnetic moment value it may be concluded that there is no significant Rh–Rh interaction in the complex. In view of the large distance between two rhodium centers (6.310 Å) no such interaction is expected. The infrared (IR) spectrum of the complex (KBr disk, using a Unicam SP3-300S) shows a sharp band at 855 cm⁻¹ and the IR spectrum of H(htbh) showed a band at 840 cm⁻¹ which is absent in that of the complex. The sharpness and high intensity of the band at 855 cm⁻¹ suggests it is due to the Rh=O stretching frequency.

The structure of $C_{18}H_{20}N_2Rh_2O_8S_4$ was solved using X-ray crystallography§ and direct methods using the SHELXS97.⁶ The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bonded to carbon and nitrogen were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. An absorption correction was carried out using the ABSPACK program.⁶ The structure was refined on F^2 using SHELXL97⁶ to R_1 0.0659, wR_2 0.1844 for 2777 reflections with $I > 2\sigma(I)$.

The structure of the binuclear rhodium(v) complex together with the atomic numbering scheme is given in Fig. 2.

The structure of the binuclear complex has a crystallographic centre of symmetry with formula

$[(RhO_2)_2(C_6H_4(O)-C(=S)-N=N-C(=S)(O)C_6H_4)(DMSO)_2].$

Each rhodium(v) ion is six-coordinate with a distorted octahedral environment, being bonded to two mutually *cis* terminal oxygens, nitrogen, sulphur and oxygen from ligand 2,2'-[(*E*)-diazene-1,2-diyldicarbonodithioyl]diphenol together with one oxygen atom of a DMSO molecule. The ligand thus has two tridentate donor sites, each site coordinating in a mer configuration to a RhO_2^+ , forming six and five-membered rings respectively with bite angles of $81.9(2)^\circ$ for O(11)-Rh(1)-N(19) and $78.6(2)^\circ$ for N(19)-Rh(1)-S(18)\$1, \$1 = symmetry element 2 - x, 2 - y, 1 - z. The ligand is significantly distorted from planarity, no doubt because of the



Fig. 2 ORTEP views (30% probability thermal ellipsoids) of the molecular structure of the complex ($C_{18}H_{20}N_2O_8Rh_2S_4$) together with the atomic numbering scheme. Selected bond lengths (Å): Rh(1)–S(18)\$1 = 2.340(3), Rh(1)–N(19) = 2.261(5), Rh(1)–O(11) = 1.953(4), Rh(1)–O(31) = 2.305(5), Rh(1)–O(1) = 1.700(5), Rh(1)–O(2) = 1.712(5), C(18)–S(18) = 1.661(7), C(18)–N(19) = 1.323(9), C(12)–O(11) = 1.365(7), N(19)–N(19)\$1 = 1.393(10).

effect of the terminal oxygen atoms O(1) and O(2) in the coordination sphere. Thus the four atoms in the equatorial plane, O(2), O(11), N(19) and S(18)\$1 show a r.m.s. deviation of 0.349 Å with the metal 0.083 Å from the plane in the direction of O(1).

The C–S, C–N and N–N bond lengths in H(htbh) are 1.6853(15) Å, 1.3289(19) and 1.4187(18) Ň respectively compared to 1.661(7), 1.323(9) and 1.393(10) Å in the complex. Both sets of distances are intermediate between formal single-bond and double-bond lengths and they indicate extensive electron delocalization.

The N=N covalent bond distance in azenes is 1.252(1) Å.⁷ In the complex it changes to 1.393(2) Å indicating extensive delocalization of double bond on complex formation.

Comparison of the bond lengths in the coordinated ligand with those in the H(htbh) shows that both the C–S and C–N bonds suffer contraction. These changes in bond length are attributable to stabilization of the ligand. The phenolic C–O length increases a little, signifying the removal of phenolic hydrogen upon coordination.

The Rh(1)–O(1) and Rh(1)–O(2), metal-to-terminal-oxygen bond lengths are 1.700(5), 1.712(5) Å respectively. These bond lengths are shorter than that [1.953(4) Å] of Rh(1)–O(11) by more than 0.2 Å. The fact signifies the double-bond character of Rh(1)–O(1) and Rh(1)–O(2) bonds. The most significant feature in the structure of the complex is the involvement of the methyl hydrogen of C(33)\$1–H in H-bonding with O(1). It explains the small difference between Rh(1)–O(1) and Rh(1)–O(2) bond lengths.

We thank the EPSRC (U.K.) and the University of Reading for funds for the diffractometer. Financial assistance received from the Higher Education Department, Government of West Bengal is gratefully acknowledged.

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‡ The compound H(htbh) (C₁₄H₂₀N₄O₄S₂) crystallizes in the monoclinic, space group $P_{2_1/n}$ with a = 9.2078(4) Å, b = 7.9309(4) Å, c = 11.4536(4) Å, $\alpha = 90.00^{\circ}$, $\beta = 91.796(4)^{\circ}$, $\gamma = 90.00^{\circ}$, V = 836.00(6) Å³, M = 372.46, Z = 2, $D_c = 1.480$ g cm⁻³. A Oxford Diffraction X-Calibur CCD system with graphite monochromatized Mo K α radiation ($\lambda = 0.71073$ Å) was used to collect 5426 reflections (2337 unique) in the range 2.88 < $\theta < 29.99$ at 150(2) K giving a final residual value of $R_1 = 0.0522$ (all data) and $wR_2 = 0.0939$ ([$I > 2\sigma(I)$]). Full diffraction data collection, refinement, and structural details are given in the ESI.†

§ The compound C₁₈H₂₀N₂Rh₂O₈S₄ crystallizes in the triclinic space group $P\bar{1}$ with M = 726.42, Z = 1, a = 7.2911(6), b = 8.9330(8), c = 10.6189(9) Å, $\alpha = 68.437(8)^{\circ}$, $\beta = 87.346(7)^{\circ}$, $\gamma = 71.086(8)^{\circ}$, V = 606.40 Å³, $D_c = 1.752$ g cm⁻³. 4289 independent reflections were collected with Mo K α ($\lambda = 0.71073$ Å) radiation at 150(2) K using the Oxford Diffraction X-Calibur CCD system. The crystal was positioned at 50 mm from the CCD. 321 frames were measured with a counting time of 10 s. Data analysis was carried out using the CrysAlis program.⁶

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