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Synthesis, structure and spectral properties of dithiocarbamato bridged dirhenium(III,II) complexes: A combined experimental and theoretical study

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ABSTRACT

Sodium salts of dimethyldithiocarbamate, diethyldithiocarbamate and pyrrolidinedithiocarbamate react with the multiply bonded paramagnetic dirhenium(III,II) complex $Re_2(\mu\text{-}O_2CCH_3)Cl_4(\mu\text{-dppm})_2$, **1** (dppm = $Ph_2PCH_2PPh_2$) in refluxing ethanol to afford the paramagnetic substitution products of the type $Re_2(\eta^2\text{-S,S})_2(\mu\text{-S,S})(\mu\text{-Cl})_2(\mu\text{-dppm})$, where S,S represents the dithiocarbamato ligands [S,S = S_2CNMe_2, **4**(L_{Me}); S_2CNEt_2, **4**(L_{Et}) and $S_2CN(CH_2)_4$, **4**(L_{Pyr})]. These are the first examples of dirhenium complexes that contain bridging dithiocarbamato ligand along with the dppm ligand. These complexes have very similar spectral (UV–Vis, IR, EPR) and electrochemical properties which are also reported. The identity of **4**(L_{Et}) has been established by single-crystal X-ray structure determination (Re–Re distance 2.6385 (9) Å) and is shown to have edge-shared bioctahedral structure. The electronic structure and the absorption spectra of the complexes are scrutinized by the density functional theory (DFT) and time-dependent density functional theory (TD-DFT) analyses.

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1. Introduction

The multiply bonded paramagnetic dirhenium(III,II) complex $Re_2(\mu\text{-}O_2CCH_3)Cl_4(\mu\text{-dppm})_2$ **1** (dppm = $Ph_2PCH_2PPh_2$), with the $\sigma^2\pi^4\delta^2\delta^{*1}$ electronic configuration has been prepared almost 25 years ago and its solid state structure was also determined in the year 1988 [1]. Since then efforts have been made to develop the reaction chemistry of this useful synthon **1**. Although there has been a flurry of compounds prepared using the other two multiply bonded dirhenium(II,II) synthons $Re_2Cl_4(\mu\text{-dppm})_2$ **2** [2] and *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dppm})_2$ **3** [1] and an extensive chemistry which has now been developed involving **2** and **3** as the starting materials, there exist few examples of complexes in which **1** has been used as synthon.

The substitutional lability of the $\mu\text{-}O_2CCH_3$ ligand in **1** has been demonstrated by its reaction with carboxylic acids in a fashion similar to that of *cis*-$Re_2(\mu\text{-}O_2CCH_3)_2Cl_2(\mu\text{-dppm})_2$. The reaction of **1** with isonicotinic acid affords the expected dirhenium(III,II) complex $Re_2(\mu\text{-}O_2CC_5H_4N)Cl_4(\mu\text{-dppm})_2$ [3] whereas with terephthalic acid the centrosymmetric “dimer-of-dimers” μ-terephthalate complex $[(\mu\text{-dppm})_2Cl_4Re_2]_2(\mu\text{-}O_2CC_6H_4CO_2)$ [4] is formed. Similar dicarboxylate-bridged complexes are isolated with the use of adipic acid, fumaric acid and 4,4′-biphenyldicarboxylic acid [3]. When *trans*-1,4-cyclohexanedicarboxylic acid is used the reduced Re_2^{4+} complex *cis*-$Re_2(\mu\text{-}O_2CC_6H_{10}CO_2Et)_2Cl_2(\mu\text{-dppm})_2$ was obtained [3]. On the other hand the reactions of **1** with tetrafluoro terephthalic acid and 1,1′-ferrocene dicarboxylic acid afford the known $Re_2Cl_4(\mu\text{-dppm})_3$ complex [3]. When **1** is made to react with acetylene dicarboxylic acid the paramagnetic μ-alkyne complex $Re_2(\mu\text{-Cl})(\mu\text{-}\eta^2\text{-HCCH})Cl_4(\mu\text{-dppm})_2$ [5] is formed whereas when 2-butynoic acid is used the diamagnetic μ-carbyne complex $Re_2(\mu\text{-Cl})(\mu\text{-CCH}_2CH_3)Cl_4(\mu\text{-dppm})_2$ [5] is isolated by decarboxylation method.

All the reactions cited above show that **1** contains labile $\mu\text{-}O_2CCH_3$ group in combination with substitutionally inert dppm and Cl ligands, but none has yet been reported in which the dppm and the Cl ligands have been replaced by other suitable chelating or bridging ligands. Of the diverse array of dirhenium complexes that are known [6], few have been isolated that contain dithiocarbamate ligand in the coordination sphere. The only compounds that we are aware of are the Re(IV)–Re(IV) dimer, $Re_2(\mu\text{-S})_2(S_2CNR_2)_4$ and the Re(III)–Re(III) dimer $[Re_2(\mu\text{-}SS_2CNR_2)_2(S_2CNR_2)_3]^+$ where R = Me and ^{i}Bu [7]. No other dithiocarbamato complexes of dirhenium are known where there is at least one Re–Re bond

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present. This has prompted us to examine the reactions of $Re_2(\mu\text{-}O_2CCH_3)Cl_4(\mu\text{-dppm})_2$ **1** towards various dithiocarbamato ligands in order to assess the stability of the Re_2^{5+} core to ligands of this type. In the course of this work we have discovered that under refluxing condition in ethanol, **1** reacts with the sodium salts of L_{Me}, L_{Et} and L_{Pyr} ligands (Chart 1) to afford the paramagnetic Re_2^{5+} complexes $Re_2(\mu\text{-}Cl)_2(\mu\text{-dppm})(\mu\text{-}L_R)(\eta^2\text{-}L_R)_2$ **4** [R = Me, Et, Pyr], where substitution of two chloride ligands, one dppm ligand and the acetate ligand occurs and the dithiocarbamato ligands are involved in both the bridging and chelating coordination modes to the dirhenium core. This is, to our knowledge, the first example of bridging dithiocarbamato ligand occurring in a dimetal unit containing dppm ligand. The synthetic procedures, structures and properties of the resulting complexes are reported.

To get better insight into the geometry, electronic structure and optical properties of these complexes, density functional theory (DFT) and time-dependent density functional theory (TD-DFT) studies have also been presented. These combined experimental and theoretical studies provide the first detailed investigation of the electronic structure of the complexes of type **4**.

2. Experimental

2.1. Materials and methods

The compound $Re_2(\mu\text{-}O_2CCH_3)Cl_4(\mu\text{-dppm})_2$ **1** was prepared by the literature method [1]. The ligands sodium dimethyldithiocarbamate hydrate, sodium diethyldithiocarbamate trihydrate and sodium pyrrolidinedithiocarbamate were purchased from Sigma Aldrich, India. All other reagents were obtained from commercial sources and were used as received, except for drying of solvents by routine techniques. All manipulations were carried out under an inert atmosphere using Schlenk techniques. Infrared spectra were recorded on a Perkin-Elmer L120-00A FT-IR spectrometer as a KBr pellet. Electronic spectra were recorded on a Shimadzu UV-1800 PC spectrophotometer. Microanalyses were performed using a Perkin-Elmer 2400 series-II elemental analyser. EPR spectra were recorded on a Bruker EMX series (EMM1843) spectrometer. All electrochemical measurements were performed under a nitrogen atmosphere using CHI 600D electrochemistry system. The supporting electrolyte was tetrabutylammonium perchlorate and potentials are referenced to Ag/AgCl electrode.

2.2. Synthesis of $Re_2(\mu\text{-}Cl)_2(\mu\text{-dppm})(\mu\text{-}S_2CNEt_2)(\eta^2\text{-}S_2CNEt_2)_2$, **4**($L_{Et}$)

A mixture of $Re_2(\mu\text{-}O_2CCH_3)Cl_4(\mu\text{-dppm})_2$ (100 mg, 0.0745 mmol) and sodium diethyldithiocarbamate trihydrate (75.4 mg, 0.3352 mmol) in 30 mL of ethanol was refluxed overnight and then cooled to room temperature. The brown crystalline solid thus obtained was filtered off and washed with ethanol (3 × 5 mL) followed by diethyl ether (2 × 5 mL) and dried in vacuo; yield 70 mg (71%). *Anal.* Calc. for $C_{40}H_{52}N_3P_2S_6Cl_2Re_2\cdot C_2H_5OH$: C, 38.26; H, 4.43; N, 3.19. Found: C, 38.45; H, 4.40; N, 3.26%. IR (KBr, cm^{-1}): 1432 ($\nu_{C\text{–}N}$), 737 (ν_{CS}), 1089 ($\nu_{as(SCS)}$) and 690 ($\nu_{s(SCS)}$); UV–Vis [λ_{max}, nm (ε, $dm^3\ mol^{-1}\ cm^{-1}$)]: 725 (2400), 470 (8180), 430 (8200); $E_{1/2}$ (versus Ag/AgCl, CH_2Cl_2, scan rate 100 mV s^{-1}): −0.29 V (ΔE_p = 170 mV).

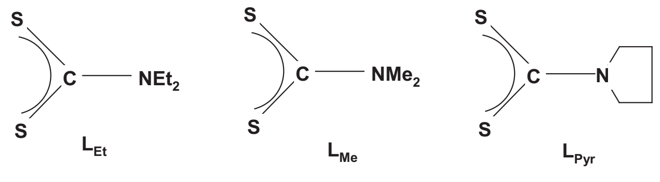

Chart 1.

2.3. Synthesis of $Re_2(\mu\text{-}Cl)_2(\mu\text{-dppm})(\mu\text{-}S_2CNMe_2)(\eta^2\text{-}S_2CNMe_2)_2$, **4**($L_{Me}$)

This complex was prepared by the same procedure as above using $Re_2(\mu\text{-}O_2CCH_3)Cl_4(\mu\text{-dppm})_2$ (100 mg, 0.0745 mmol) and sodium dimethyldithiocarbamate hydrate (48 mg, 0.3352 mmol); yield 72 mg (81%). *Anal.* Calc. for $C_{34}H_{40}N_3P_2S_6Cl_2Re_2$: C, 34.36; H, 3.39; N, 3.54. Found: C, 34.25; H, 3.46; N, 3.62%. IR (KBr, cm^{-1}): 1434 ($\nu_{C\text{–}N}$), 739 (ν_{CS}), 1092 ($\nu_{as(SCS)}$) and 689 ($\nu_{s(SCS)}$); UV–Vis [λ_{max}, nm (ε, $dm^3\ mol^{-1}\ cm^{-1}$)]: 710 (1660), 470 (6340), 430 (6240); $E_{1/2}$ (versus Ag/AgCl, CH_2Cl_2, scan rate 100 mV s^{-1}): −0.23 V (ΔE_p = 150 mV).

2.4. Synthesis of $Re_2(\mu\text{-}Cl)_2(\mu\text{-dppm})(\mu\text{-}S_2CN(CH_2)_4)(\eta^2\text{-}S_2CN(CH_2)_4)_2$, **4**($L_{Pyr}$)

The procedure was the same as for compound **4**(L_{Et}) but by using sodium pyrrolidinedithiocarbamate (56.7 mg, 0.3352 mmol); yield 75 mg (79%). *Anal.* Calc. for $C_{40}H_{46}N_3P_2S_6Cl_2Re_2$: C, 37.93; H, 3.66; N, 3.32. Found: C, 37.83; H, 3.58; N, 3.38%. IR (KBr, cm^{-1}): 1446 ($\nu_{C\text{–}N}$), 738 (ν_{CS}), 1091 ($\nu_{as(SCS)}$) and 690 ($\nu_{s(SCS)}$); UV–Vis [λ_{max}, nm (ε, $dm^3\ mol^{-1}\ cm^{-1}$)]: 660 (2060), 460 (6300); $E_{1/2}$ (versus Ag/AgCl, CH_2Cl_2, scan rate 100 mV s^{-1}): −0.26 V (ΔE_p = 150 mV).

2.5. X-ray crystallography

Single crystals of composition $Re_2(\mu\text{-}Cl)_2(\mu\text{-dppm})(\mu\text{-}S_2CNEt_2)(\eta^2\text{-}S_2CNEt_2)_2\cdot C_2H_5OH$, **4**($L_{Et}$) $\cdot C_2H_5OH$ were harvested directly from the reaction medium. The crystal was mounted on a Bruker AXS SMART APEX CCD diffractometer (Mo Kα, λ = 0.71073 Å). The data were reduced in SAINTPLUS [8] and empirical absorption corrections were applied using the SADABS [8] package. The metal atoms were located by Patterson method and the rest of the non-hydrogen atoms were emerged from successive Fourier synthesis. The isotropic refinement of all the atoms revealed high thermal parameters for the ethyl groups attached to N1 atom. Careful inspection indicated that the ethyl groups are disordered in two different orientations and they were modeled accordingly. Refinement with two different orientations of ethyl groups resulted in better *R*-factor and gave a ratio of 65:35 for the occupancies of the two orientations. Hydrogen atoms were placed in idealized positions. The structures were refined by a full matrix least-squares procedure on F^2. All non-hydrogen atoms were refined anisotropically. All calculations were performed using the SHELXTL V6.14 program package [9]. Molecular structure plots were drawn using the Oak Ridge thermal ellipsoid plot ORTEP-32 [10]. The key crystallographic data for **4**(L_{Et})$\cdot C_2H_5OH$ is given in Table 1.

2.6. Computational study

The *ORCA* 2.9.1 software package was used for all DFT computations [11]. The geometry of the complexes was fully optimized in the gas phase without imposing any symmetry constraints. The single crystal X-ray coordinates have been used as the initial input in the calculation. Geometry optimizations for the complexes were converged to the $S = 1/2$ spin and employed the Becke–Perdew (BP86) functional [12] and the SV(P) (Ahlrichs split valence polarized) basis with the SV/C auxiliary basis for all atoms except for sulfur, nitrogen, phosphorus and chlorine, where the larger TZVP (Ahlrichs triple-valence polarized) basis in conjunction with the TZV/J auxiliary basis were used [13]. For rhenium atoms the scaled-ZORA (zeroth-order regular approximation) Hamiltonian was used to take account of the relativistic effect in the calculations [14]. These calculations employed the resolution of identity (RI) approximation developed by Neese [15]. The coordinates of all DFT energy minimized model of the complexes presented in

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