

One-pot synthesis of sulphur-bridged rhenium containing molecular cubanes: Spectroscopic and structural characterisation



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ABSTRACT

Sulphur-bridged rhenium(I) based molecular cubanes $[\text{Re}_4(\text{CO})_{12}(\mu_3\text{-SR})_4]$ (**1**, R = C₄H₉; **2**, R = C₆H₅; **3**, R = C₆H₄CH₃; **4**, R = CH₂C₆H₅) have been synthesised in one-pot reaction via oxidative addition of dialkyl/diaryl disulphide, RSSR to low valent transition metal carbonyl, $\text{Re}_2(\text{CO})_{10}$ with catalytic amount of dimethyl formamide. The molecular cubanes **1–4** have been characterised by elemental analysis, NMR, IR and UV–Vis absorption spectroscopic techniques. The molecular structures of **2** and **4** were determined by single crystal X-ray diffraction analysis and the structural studies ascertain the presence of Re_4S_4 distorted cube. The synthetic strategy offers a simple route for preparation of the class of sulphur-bridged Re(I) based molecular cubanes.

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Introduction

Transition metal-sulphido compounds containing cubane-type M_4S_4 core have drawn much attention in recent literature due to their significant relevance to biological systems such as ferredoxins [1–5], hydrogenases [6,7] and nitrogenases [8]. Several transition metal-sulphido compounds of homo- and heterometallic cubanes have been synthesised and characterised for their pertinence to metalloenzymes [9–21]. Apart from nature, this type of transition metal-sulphido cubanes have also been utilised in industrial processes as metal sulphide catalysts [22–28]. Mostly, transition metal containing molecular cubanes were prepared by stepwise synthesis from pre-assembled smaller building blocks of di- and trinuclear sulphide complexes [29–37]. Rauchfuss et al. prepared ruthenium based sulphido cubane $[(\text{MeC}_5\text{H}_4)_4\text{Ru}_4\text{S}_4]$ by thermolysis of $(\text{MeC}_5\text{H}_4)\text{Ru}(\text{PPh}_3)_2\text{SH}$ in toluene medium [38]. Kanatzidis and co-workers prepared the platinum based cubanes $\text{K}_4[\text{Pt}_4\text{S}_{22}]$ by treating K_2PtCl_4 with K_2S_4 in methanol under heating condition [39]. Earlier, Abel and co-workers reported the synthesis of methyl thiolate-bridged rhenium cubane $[\text{Re}(\text{CO})_3(\text{SMe})]_4$ and analogous manganese cubane $[\text{Mn}(\text{CO})_3(\text{SMe})]_4$ by the reaction of $\text{M}(\text{CO})_5\text{Br}$ (M = Mn, Re) and $\text{Me}_2\text{Sn}(\text{SMe})_2$ [40–43]. Later, Villarreal et al. isolated alkyl/aryl thiolate-bridged manganese cubane $[\text{MnSR}(\text{CO})_3]_4$ by treating $[\text{Mn}(\eta^5\text{-C}_5\text{H}_7)(\text{CO})_3]$ with alkyl/aryl mercaptane at room temperature [44,45]. In addition, they have

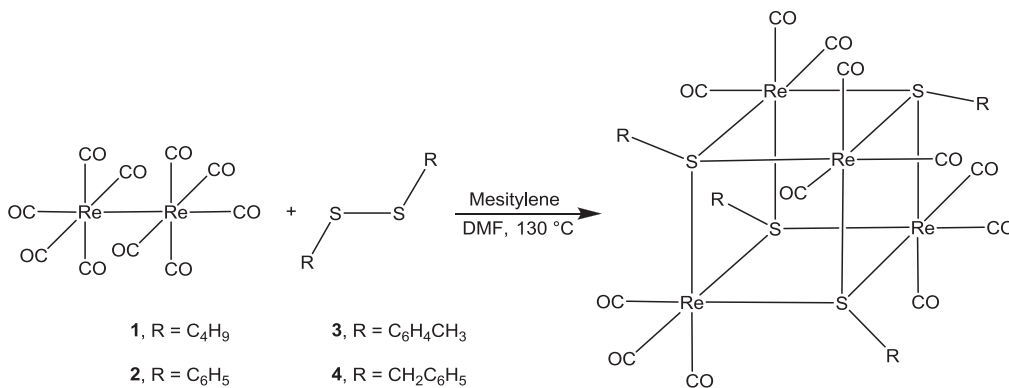
also reported the selenato-bridged manganese cubane by reacting $[\text{Mn}(\eta^5\text{-C}_5\text{H}_7)(\text{CO})_3]$ with selenol at room temperature to yield $[\text{MnSeR}(\text{CO})_3]_4$ [46]. Rhenium based anionic cubane $(\text{PPh}_4)_4\text{Re}_4\text{S}_4(\text{SCN})_{12}$ was synthesised by the heating reaction of $\text{Re}_4\text{S}_4\text{Te}_4\text{Cl}_{16}$ with KSCN [47]. Mizobe et al. prepared rhenium containing heterometallic cubane $[\text{M}_2(\text{ReL})_2(\mu_3\text{-S})_4]$ (M = Ru($\eta^5\text{-C}_5\text{Me}_5$), PtMe₃, Cu(PPh₃); L = S₂C₂(SiMe₃)₂) by treating dirhenium tetra sulphido complex with a series of group 8–11 metal complexes [48]. Saito and co-workers reported the synthesis of rhenium and copper containing cubane $[(\text{Ph}_3\text{P})_2\text{N}][\text{Re}_3(\text{CuX})\text{S}_4\text{Cl}_6(\text{PMe}_2\text{Ph})_3]$ by the reaction of $\text{Re}_3\text{S}_7\text{Cl}_7$, dimethylphenylphosphine and CuX_2 (X = Cl, Br) [49]. In literature, very few reports are available for the spontaneous formation of molecular cubanes via self-assembly process to give thermodynamically favoured product [50,51]. Herein, we report on the spontaneous formation of $[\text{Re}_4(\text{CO})_{12}(\mu_3\text{-SR})_4]$ (**1–4**) via oxidative addition of S–S bond across Re–Re bond. The self-assembly of molecular cubanes **1–4** was achieved in a facile one-pot reaction of rhenium carbonyl with dialkyl/diaryl disulphide in presence of catalytic amount of dimethyl formamide.

Results and discussion

Synthesis of sulphur-bridged rhenium based molecular cubanes **1–4** from rhenium carbonyl and dialkyl/diaryl disulphides

Synthesis of sulphur-bridged rhenium containing molecular cubanes $[\text{Re}_4(\text{CO})_{12}(\mu_3\text{-SR})_4]$ (**1–4**) was accomplished in a one-pot

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Scheme 1. Synthesis of sulphur-bridged molecular cubanes **1–4**.

reaction via oxidative addition of dialkyl/diaryl disulphide (RSSR) to the rhenium carbonyl (Re₂(CO)₁₀) with dimethyl formamide as catalyst in mesitylene medium (Scheme 1). Dimethyl formamide facilitated the removal of terminal carbonyl groups of rhenium carbonyl via coordination through carbonyl oxygen of dimethyl formamide [52]. Due to the labile nature of dimethyl formamide coordination to rhenium metal centre, it further aided the formation of molecular cubane [53]. Reaction of rhenium carbonyl with dialkyl/diaryl disulphide for the formation of molecular cubane was tuned by using different catalysts like triethyl amine, trimethyl amine oxide and dimethyl formamide. The reaction in which dimethyl formamide was used as a catalyst afforded better yield of the product in comparison with other catalysts. Moreover, the preparative method involving dimethyl formamide as catalyst is a single step one-pot process. Compounds **1–4** were isolated as air stable solids and soluble in common organic solvents. Molecular cubanes **1–4** were characterised by spectroscopic techniques and the structural details of **2** and **4** were determined by single crystal X-ray diffraction analysis.

Spectroscopic characterisation of **1–4**

The IR spectra of compounds **1–4** in CH₂Cl₂ exhibited two carbonyl stretches in the region of ν(CO) 2030–1938 cm⁻¹, characteristic of the *fac*-Re(CO)₃ core [45], indicating higher symmetrical nature of molecular cubanes in solution state. ¹H NMR spectrum of compound **1** showed three multiplets and one triplet for butyl group protons at around δ 1.02–2.92 ppm. The ¹H NMR spectra of compounds **2–4** displayed signals for aryl group protons at around δ 7.35–7.87 ppm. Compound **3** showed a singlet at δ 2.43 ppm for methyl group protons of *p*-tolyl group and compound **4** displayed a singlet at δ 3.98 ppm for methylene group protons present in benzyl moiety. The alkyl/aryl group protons attached to sulphur moiety in **1–4** were shifted to down field when compared to free dialkyl/diaryl disulphides. The ¹³C NMR spectra of compounds **1–4** displayed a signal at around δ 195.0–195.8 ppm for terminal carbonyl groups. ¹³C NMR spectrum of **1** exhibited signals at δ 41.0–12.6 ppm for butyl group carbons. Compounds **2–4** showed signals for aryl group carbons at around δ 129.3–139.7 ppm. Compound **3** displayed a signal at δ 21.1 ppm for methyl carbon of *p*-tolyl group and compound **4** showed a signal at δ 46.1 ppm for methylene carbon present in benzyl moiety (Table S1). UV–Vis absorption spectra of **1–4** in CH₂Cl₂ showed intense bands in UV region at around λ_{max} 226–290 nm, and were attributed to ligand based π–π* transitions [54–56].

Structural characterisation of **2** and **4**

Single crystals of compound **2** and **4** were obtained by slow diffusion of hexane into concentrated solution of compound in dichloromethane at 25 °C. Good quality single crystals of **2** and **4** were subjected to X-ray diffraction studies. Details about data collection, solution and refinement were summarised in Table 1 for **2** and **4**. The ORTEP diagram of **2** and **4** were depicted in Fig. 1 and Fig. 2 respectively.

Crystal structure of [Re₄(CO)₁₂(μ₃-SCoH₅)₄] (**2**) adopted a distorted cubic structure, where rhenium and sulphur occupy alternative corners of the cube. Each rhenium by *fac*-Re(CO)₃ core is bonded to three phenyl sulphido groups and thereby rhenium

Table 1
Crystallographic data and structure refinement of **2** and **4**.

Compound	2	4
Empirical formula	C ₃₆ H ₂₀ O ₁₂ Re ₄ S ₄	C ₄₀ H ₂₈ O ₁₂ Re ₄ S ₄
Formula weight	1517.56	1573.74
T (K)	293(2) K	150(2) K
Crystal system	monoclinic	Tetragonal
Space group	P 21/c	I 41/a
<i>a</i> (Å)	11.56	18.98
<i>b</i> (Å)	22.16	18.98
<i>c</i> (Å)	16.57	24.42
α (°)	90	90
β (°)	107.96	90
γ (°)	90	90
<i>V</i> (Å ³)	4039.8(2)	8805.7(2)
<i>Z</i>	4	8
<i>D</i> _{calc} (mg m ⁻³)	2.495	2.374
μ (mm ⁻¹)	12.213	11.210
<i>h</i> , <i>k</i> , <i>l</i> collected	–13, 13; –23, 26; –19, 19	–22, 21; –22, 22; –29, 26
F(000)	2784	5822
Crystal size (mm)	0.25 × 0.20 × 0.20	0.29 × 0.21 × 0.17
Theta range for data collection (°)	2.61 to 25.00	3.03 to 25.00
Reflections collected	18697	20158
<i>R</i> _{int}	0.0459	0.0260
Completeness to theta = 25.00°	99.8%	99.8%
Max. and min. transmission	0.087 and 0.067	0.2516 and 0.1394
Data/restraints/parameters	7113/216/488	3879/0/271
Goodness-of-fit on F ²	1.139	1.054
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0453, <i>wR</i> ₂ = 0.0950	<i>R</i> ₁ = 0.0250, <i>wR</i> ₂ = 0.0608
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0568, <i>wR</i> ₂ = 0.1009	<i>R</i> ₁ = 0.0349, <i>wR</i> ₂ = 0.0626
Largest difference in peak and hole (e.Å ⁻³)	2.167 and –2.135	1.197 and –0.979

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