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Heterobimetallic cuboidal $[Mo_3NiS_4]$ and $[W_3NiS_4]$ cluster diphosphane complexes as molecular models in hydrodesulfurization catalysis

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Abstract

Treatment of the cationic, incomplete cubane-type sulfido clusters $[M_3S_4X_3(diphos)_3]^+$ (M = Mo, W; X = Cl, Br; diphos = dmpe (1,2-bis(dimethylphosphanyl)ethane), dppe (1,2-bis(diphenylphosphanyl)ethane)) with an excess of $[Ni(cod)_2]$ (cod = 1,5-cyclooctadiene) afforded the heterobimetallic single cube clusters $[M_3NiS_4X_3(diphos)_3(CH_3CN)]^+$ as PF_6^- salts. The acetonitrile ligand could be substituted by pyridine, tetrahydrothiophene and carbon monoxide in CH_2Cl_2 at room temperature, modelling the catalytic sites of heterogeneous Ni–MoS_2 hydrodesulfurization catalysts. X-ray crystal structure analyses of $[Mo_3NiS_4Cl_3(dmpe)_3(CH_3CN)]BPh_4$ and $[W_3NiS_4Br_3(dmpe)_3(CO)]PF_6$ are reported. Electrochemical studies by cyclic voltammetry reported for all heterobimetallic $[M_3NiS_4]$ clusters show two quasireversible oxidation processes, the molybdenum complexes being ca. 0.2 V more difficult to oxidize than the tungsten analogues.

Keywords: Heterobimetallic; Cubane cluster; Nickel; Catalysis; Cyclic voltammetry; Sulphur

1. Introduction

The chemistry of transition metal cubane-type sulfido clusters continues to attract widespread attention mostly due to their potential applications as models for biological and industrial catalysts [1]. In particular heterobimetallic molybdenum clusters with $[Mo_3NiS_4]$ and $[Mo_3CoS_4]$ cores are taken as molecular models for substrate binding in the hydrodesulfurization (HDS) process due to the fact that cobalt and nickel are known to act as promoters for the catalytic activity of industrial heterogeneous molybdenum sulfide catalysts [2,3].

The aqua cluster complex $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ has been incorporated into zeolites and acted there as a precursor for a sulfide phase that catalyzed benzothiophene HDS at 300 °C [4–6]. Also, in homogeneous phase, it was shown that $[Mo_2Co_2S_x]$ ($x = 3$, 4) cluster compounds may act as HDS catalysts for a variety of organosulfur molecules [2]. In contrast, structural data on the $[Mo_3NiS_4Cp_3'L]^+$ complex, with L = 1,4-dithiane or 4,4′-bipyridine, do not indicate any activation of the C–S and C–N bonds [3]. In a different catalytic domain, a high catalytic activity of the cluster $[\{Mo_3NiS_4Cp_3^*\}_2$-(cod)]$[PF_6]_2$ (cod = 1,5-cyclooctadiene) has recently

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been described for the intramolecular addition of carboxylic acid to alkynes to afford enol lactones, by activation of the alkyne [7].

Theoretical studies on these cuboidal heterobimetallic systems suggest a crucial dependence of the reactivity at the heterometal site from the coordination environment around the molybdenum atoms [8]. It is well known that phosphanes occupy a unique role in the design and development of transition metal catalysts. These facts have prompted us to investigate the synthesis, structure, redox properties and reactivity of phosphane substituted [M_3NiS_4] (M = Mo, W) cluster complexes.

2. Experimental

2.1. General remarks

All reactions were carried out under nitrogen atmosphere using standard Schlenk techniques. The solids $\{Mo_3S_7Cl_4\}_n$, $\{Mo_3S_7Br_4\}_n$ and $\{W_3S_7Br_4\}_n$, as well as the homometallic clusters [$Mo_3S_4Cl_3$(dmpe)$_3$]PF_6, [$Mo_3S_4Br_3$(dmpe)$_3$]PF_6, [$W_3S_4Br_3$(dmpe)$_3$]PF_6 and [$Mo_3S_4Cl_3$(dppe)$_3$]PF_6 (dmpe = 1,2-bis(dimethylphosphanyl)ethane) were obtained according to literature methods [9]. [Ni(cod)$_2$] (cod = 1,5-cyclooctadiene) was purchased from Strem Chemicals. Solvents for synthesis and electrochemical measurements were dried and degassed by standard methods before use. Chromatographic work was performed on silica gel 60 Å.

Elemental analyses were performed on an EA 1108 CHNS microanalyzer at the Universidad de La Laguna. $^{31}P\{^1H\}$ NMR spectra were recorded with a reference of 85% H_3PO_4 on a Varian 300 MHz. IR spectra were recorded on a Perkin–Elmer System 2000 FT-IR using KBr pellets. Electronic absorption spectra were obtained on a Perkin–Elmer Lambda-19 spectrophotometer. Electrospray mass spectra (ESI-MS) were recorded with a Micromass Quattro LC instrument. Nitrogen was employed as a drying and nebulizing gas. Cone voltage was typically varied from 20 to 100 V in order to investigate the effect of higher voltages on the fragmentation pathways of the parent ions. Isotope experimental patterns were compared with theoretical patterns obtained using the MassLynx 3.5 program. Cyclic voltammetry experiments were performed with an Echochemie Pgstat 20 electrochemical analyzer. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and an Ag/AgCl reference electrode containing aqueous 3 M KCl. Dichloromethane was used in all experiments and dried and degassed by standard methods. The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate. $E_{1/2}$ values were determined as 1/2 ($E_a + E_c$), where E_a and E_c are the anodic and cathodic peak potentials, respectively. All potentials reported are not corrected for the junction potential.

2.2. Syntheses

2.2.1. [$Mo_3NiS_4Cl_3$(dmpe)$_3$(CH_3CN)]PF_6 ([**1**]PF_6)

To a green solution of [$Mo_3S_4Cl_3$(dmpe)$_3$]PF_6 (0.4 g, 0.36 mmol) in CH_3CN (40 mL) was added an excess of [Ni(cod)$_2$] (0.153 g, 0.56 mmol) under nitrogen without any apparent colour change. After stirring for 48 h, the resulting solution was taken to dryness and the solid was redissolved in CH_2Cl_2 and adsorbed in a silica gel column. After washing the column with CH_2Cl_2, elution with acetone/CH_2Cl_2 (1/3) afforded a very concentrated green solution. Finally, the resulting solution was taken to dryness to give an air stable green solid characterized as [$Mo_3NiS_4Cl_3$(dmpe)$_3$(CH_3CN)]PF_6 [**1**]PF_6 (0.346 g, 79%). *Anal.* Calc. for $C_{20}H_{51}Cl_3F_6Mo_3NNiP_7S_4$: requires C, 19.73; H, 4.22; N, 1.15; S, 10.53. Found: C, 19.79; H, 4.17; N, 0.76; S, 11.03%; λ_{max}/nm (CH_2Cl_2) 650, 463, 330 (sh), 260 (sh) and 237; δ_P(CH_2Cl_2): −145.00 (1P, sept, ^1J(P–F) 704.0 Hz), 17.74 (3P, dd) and 25.26 (3P, dd); *m*/*z* (CH_2Cl_2): 1074 (M^+), 1033 ($M^+ - CH_3CN$) and 882 ($M^+ - CH_3CN$ − dmpe).

2.2.2. [$Mo_3NiS_4Br_3$(dmpe)$_3$(CH_3CN)]PF_6 ([**2**]PF_6)

This compound was prepared following the general procedure described for [**1**]PF_6, except that [$Mo_3S_4Br_3$(dmpe)$_3$]PF_6 (0.300 g, 0.24 mmol) was used instead of [$Mo_3S_4Cl_3$(dmpe)$_3$]PF_6. This compound was reacted with an excess of [Ni(cod)$_2$] (0.101 g, 0.37 mmol). The air stable green product obtained was characterized as [$Mo_3NiS_4Br_3$(dmpe)$_3$(CH_3CN)]PF_6 [**2**]PF_6 (0.120 g, 31%). *Anal.* Calc. for $C_{20}H_{51}Br_3F_6Mo_3NNiP_7S_4$: requires C, 17.78; H, 3.81; N, 1.04; S, 9.49. Found: C, 17.89; H, 3.72; N, 0.75; S, 9.06%; λ_{max}/nm (CH_2Cl_2): 656, 470 (sh), 270 (sh) and 240; δ_P (CH_2Cl_2): −145.00 (1P, sept, ^1J(P–F) 704.0 Hz), 10.95 (3P, dd) and 22.90 (3P, dd); *m*/*z* (CH_2Cl_2): 1207 (M^+), 1166 ($M^+ - CH_3CN$) and 1016 ($M^+ - CH_3CN$ − dmpe).

2.2.3. [$Mo_3NiS_4Cl_3$(dppe)$_3$(CH_3CN)]PF_6 ([**3**]PF_6)

This compound was prepared following the general procedure described for [**1**]PF_6 except that [$Mo_3S_4Cl_3$(dppe)$_3$]PF_6 (0.500 g, 0.27 mmol) was used instead of [$Mo_3S_4Cl_3$(dmpe)$_3$]PF_6. This compound was reacted with an excess of [Ni(cod)$_2$] (0.110 g, 0.40 mmol) during 4 h. The air stable green product obtained was characterized as [$Mo_3NiS_4Cl_3$(dppe)$_3$(CH_3CN)]PF_6 [**3**]PF_6 (0.078 g, 15%). *Anal.* Calc. for $C_{80}H_{75}Cl_3F_6Mo_3NNiP_7S_4$ requires C, 48.96; H, 3.85; N, 0.71; S, 6.54. Found: C, 49.09; H, 4.10; N, 1.20; S, 6.07%; λ_{max}/nm (CH_2Cl_2): 646, 500 (sh) and 240; δ_P (CH_2Cl_2): −145.00 (1P, sept, ^1J(P–F) 704.0 Hz), 26.59 (3P, t, ^3J(P–P_{trans}) 9.1 Hz) and 33.74 (3P, t, ^3J(P–P_{trans}) 10.0 Hz); *m*/*z* (CH_2Cl_2): 1818 (M^+), 1777 ($M^+ - CH_3CN$) and 1379 ($M^+ - CH_3CN$ − dppe).