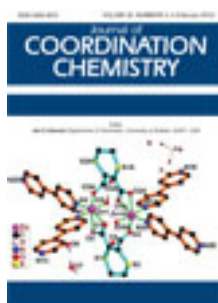


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Polyoxomolybdate(VI) anion stabilized by ammonium cation via CS₂ elimination from *N*-benzyl-*N*-methylferrocenyl dithiocarbamate

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A new polyoxomolybdate [(FcCH₂)NH₂(CH₂C₆H₅)₄][Mo₈O₂₆] has been obtained by the reaction of ammonium molybdate and potassium *N*-benzyl-*N*-methylferrocenyl dithiocarbamate in mild acidic condition. The resulting cluster has been characterized by microanalyses, electronic absorption, photoluminescence, IR, and ¹H NMR spectroscopy, and its electrochemical properties. Quantum chemical calculations have been performed in order to explain the CS₂ elimination from the dithiocarbamate moiety. Single-crystal X-ray analysis of this compound reveals that the ammonium cation generates an intricate 2-D supramolecular architecture.

Keywords: Polyoxomolybdate; Ferrocenyl dithiocarbamate; Supramolecular architecture

1. Introduction

Polyoxometalates (POMs) are discrete metal oxide clusters that are of interest as soluble metal oxides and for applications in catalysis, medicine, and materials science [1–5]. Preparation of POM-based materials is therefore an active field of research. Combination of POMs with cluster cations or macrocations has resulted in the formation of various interesting intercluster compounds for ionic crystals, crystal growth, crystal engineering, structures, and sorption properties [6–9]. Charge transfer complexes based on ferrocene-type donor and POM acceptors have been synthesized and structurally characterized [10–15]. Very recently some organic–inorganic hybrid polyoxomolybdate frameworks have been synthesized and characterized [16, 17]. Considering the above interesting aspects of these systems we herein report the synthesis, structure, photoluminescent, and electrochemical properties of a new

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polyoxomolybdate compound $[(\text{FcCH}_2)\text{NH}_2(\text{CH}_2\text{C}_6\text{H}_5)]_4[\text{Mo}_8\text{O}_{26}]$ obtained by the reaction of ammonium molybdate and potassium *N*-benzyl-*N*-methylferrocenyl dithiocarbamate.

2. Experimental

2.1. Materials and physical measurements

All synthetic manipulations were performed under ambient conditions. The solvents were dried and distilled before use following standard procedures. Potassium *N*-benzyl-*N*-methylferrocenyl dithiocarbamate was prepared by slight modification of the literature method [18, 19]. IR as KBr pellets and ^1H NMR (DMSO-d_6) spectra were recorded on Varian 3100 FTIR and JEOL AL300 FTNMR spectrophotometers, respectively. Chemical shifts were reported in parts per million using TMS as internal standard. Elemental analysis was performed on an Exeter Analytical Inc. "Model CE-440 CHN analyser." Electronic absorption and fluorescence spectra in DMSO were recorded on Shimadzu UV-1700 PharmaSpecUV-Vis. and Perkin Elmer LS-45 fluorescence spectrophotometers, respectively. Electrochemistry of the compound was investigated by cyclic voltammetry, obtained from a bipotentiostat (Model No. AFRDE 4E, Pine Instrument Company, USA) and e-Corder 201 Australia in $10^{-3}\text{ mol L}^{-1}$ DMSO solution using $10^{-1}\text{ mol L}^{-1}$ tetrabutylammonium perchlorate as supporting electrolyte. Ag/Ag+ (in acetonitrile) as a reference electrode and platinum as working electrode were utilized.

2.2. X-ray crystallography

The data for the yellow crystal of this cluster was collected at 298(2)K on a Sapphire2-CCD OXFORD diffractometer system equipped with graphite monochromated Mo-K α radiation $\lambda = 0.71073\text{ \AA}$ and corrected empirically for absorption effects. The final unit cell determination, scaling of data, and corrections for Lorentz and polarization effects were performed with CrysAlis RED [20]. The structures were solved by direct methods (SHELXS-97) [21] and refined by a full-matrix least-squares procedure based on F^2 [22]. Structure solution, followed by full-matrix least-squares refinement was performed using the WINGX-1.70 suite [23]. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were located at calculated positions and refined using a riding model with isotropic thermal parameters fixed at 1.2 times the U_{eq} value of the appropriate carrier atom.

Crystal data for $(\text{C}_{36}\text{H}_{40}\text{Fe}_2\text{Mo}_4\text{N}_2\text{O}_{13})_2$: formula mass 2408.35, monoclinic space group $P2_1/c$, $a = 18.917(3)\text{ \AA}$, $b = 10.6603(9)\text{ \AA}$, $c = 21.266(3)\text{ \AA}$, $\beta = 111.435(18)^\circ$, $V = 3991.7(9)\text{ \AA}^3$, $Z = 4$, $d_{\text{Calcd}} = 2.004\text{ Mg m}^{-3}$, linear absorption coefficient 1.992 mm^{-1} , $F(000) = 2376$, crystal size $= 0.40 \times 0.38 \times 0.37\text{ mm}^3$, reflections collected $= 17,136$, independent reflections $= 9072$ [$R_{\text{int}} = 0.0282$], final R indices [$I > 2\sigma(I)$], $R_1 = 0.0286$, $wR_2 = 0.0597$, R indices (all data) $R_1 = 0.0511$, $wR_2 = 0.0642$, goodness-of-fit on $F^2 = 0.927$, largest difference peak and hole is 0.953 and -0.687 e \AA^{-3} .

2.3. Computational details

In order to explain the elimination of CS₂ from the *N*-benzyl-*N*-methylferrocenyl dithiocarbamate, density functional theory calculations were performed on the dithiocarbamate. Optimized molecular geometries were calculated using the B3LYP exchange-correlation functional [24]. The LANL2DZ basis set for Fe, while 6-31G** for C, H, N, and S were used. The optimized structures of the dithiocarbamate was used for the calculations of atomic charges using natural population analyses (NPA) [25] as implemented in Gaussian 03 [26].

2.4. Synthesis of [(FcCH₂)NH₂(CH₂C₆H₅)₄][Mo₈O₂₆]

Potassium *N*-benzyl-*N*-methyl ferrocenyl dithiocarbamate (1.258 g, 3 mmol) was dissolved in 25 mL THF : methanol (1 : 1, v/v) mixture and solid ammonium molybdate (0.176 g, 0.14 mmol) was added in portions and acidifying the reaction with dilute hydrochloric acid. The reaction mixture was stirred for 48 h and the solvent was removed under vacuum. The residue was washed with water which afforded yellow crystals in dichloromethane layered with hexane (yield 60%).

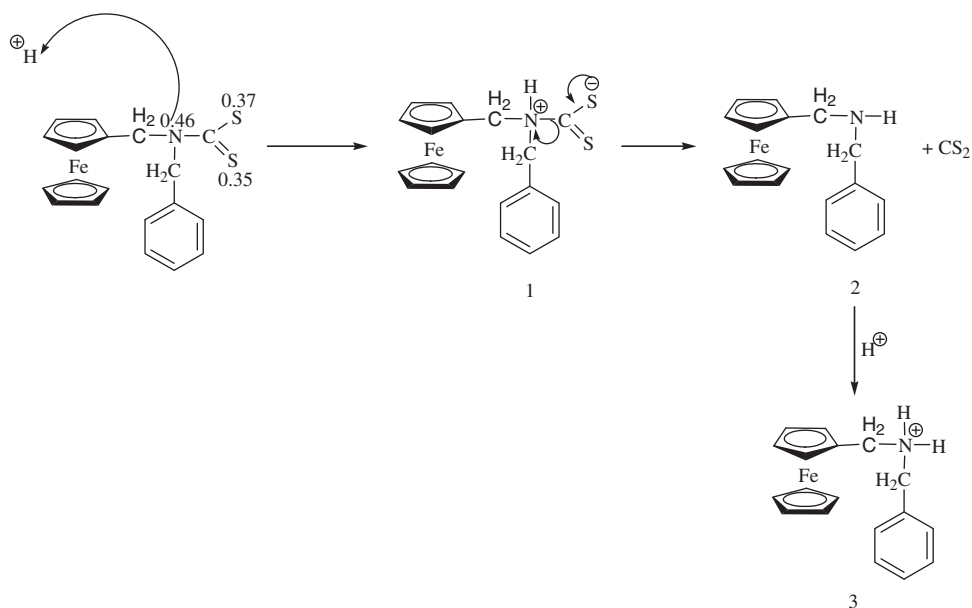
M.p. > 300°C. Anal. Calcd for (C₃₆H₄₀Fe₂Mo₄N₂O₁₃)₂: C, 35.91; H, 3.35; N, 3.33. Found (%): C, 35.75; H, 3.34; N, 3.18. IR (KBr), (cm⁻¹): 3448 ν(NH₂), 2811 ν(C-H, CH₂), δ 1650 (N-H), 1600 ν(C=C), 780 ν(C-H, C₆H₅), 840–940 ν(Mo–O_t). ¹H NMR (300.40 MHz, DMSO-*d*₆) δ/ppm 3.94 (s, 2H, –CH₂–), 4.05 (s, 2H, –CH₂–), 4.21 (s, 5H, Cp), 4.27 (s, 2H, Cp), 4.39 (s, 2H, Cp), 7.43 (m, 5H, –C₆H₅).

3. Results and discussion

3.1. Synthesis

Reaction of a suspension of ammonium molybdate with potassium *N*-benzyl-*N*-methylferrocenyl dithiocarbamate in THF : methanol mixture followed by acidification with dilute hydrochloric acid and subsequent washing with water, afforded yellow crystals of [NH₂(FcCH₂)CH₂C₆H₅]₄[Mo₈O₂₆]. The compound is stable at room temperature (m.p. > 300°C) and can be stored for indefinite periods because the overall anionic entity is held together by covalent Mo–O bonds, thus providing sufficient thermodynamic stability for its existence in the solid state. The formation of this cluster stems from the need to acidify the reaction mixture which leads to protonation of the thioureide *N* which favors elimination of CS₂ to give the amine with subsequent formation of the ammonium salt in the presence of the molybdate anion present in solution. Quantum chemical calculations have been performed in order to explain the elimination of CS₂ from the *N*-benzyl-*N*-methylferrocenyl dithiocarbamate. The natural charges for atoms of interest are displayed in scheme 1.

As apparent from the scheme, the thioureide nitrogen possesses slightly more negative charge than the two sulfurs of the dithiocarbamate. The relatively hard nature of the NCS₂ nitrogen induces attack by H⁺ to form species **1**. The species **1** eliminates CS₂ to generate the neutral secondary amine **2**. The secondary amine **2** accepts another



Scheme 1. Proposed mechanism for formation of $[\text{NH}_2(\text{FcCH}_2)\text{CH}_2\text{C}_6\text{H}_5]_4[\text{Mo}_8\text{O}_{26}]$.

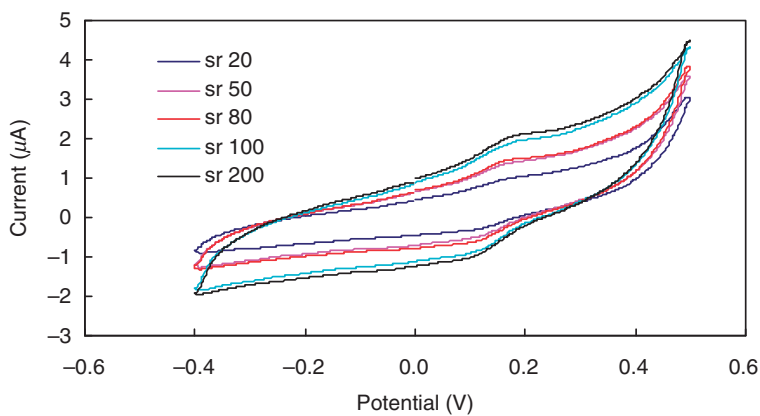


Figure 1. Cyclic voltammogram of the complex recorded in $10^{-3} \text{ mol L}^{-1}$ DMSO solution.

proton to form the quaternary ammonium cation in order to balance the negative charge over the polyoxomolybdate.

3.2. Cyclic voltammetry

As expected the redox active ferrocenyl group of this compound exhibits only one quasi-reversible oxidation wave at $E^{\text{ox}} = 0.18 \text{ V}$ (figure 1). As compared to ferrocene standard ($E^{\text{ox}} = 0.19 \text{ V}$) very small cathodic shift suggests almost no electron-withdrawing effect of

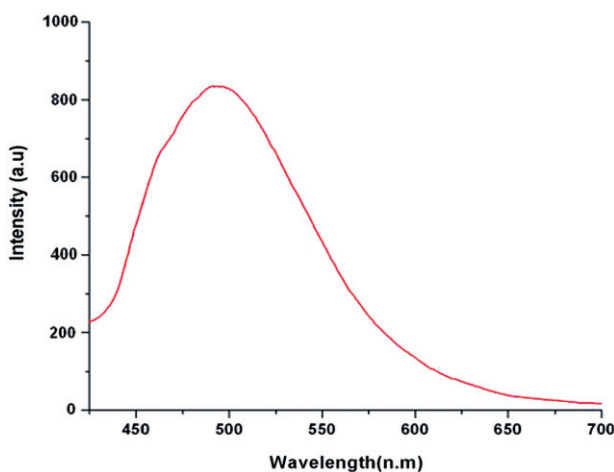


Figure 2. Photoluminescent spectrum of the complex recorded in 10^{-3} mol L $^{-1}$ DMSO solution.

the ammonium cation, which is in sharp contrast to ferrocenyl dithiocarbamate transition metal complexes [18, 19], where considerable anodic shift in potential occurred due to electron-withdrawing effect of the transition metals. The appearance of a single quasi-reversible cyclic voltammogram is indicative that the molybdenum center is in the electrochemically inactive +6 oxidation state and intact.

3.3. Electronic absorption and photoluminescent properties

The electronic absorption spectrum of the complex recorded in DMSO displays bands at 440, 300, 260, and 235 nm. The first lower energy band at ~ 440 nm arises due to d–d transition of d_{z^2} orbital of Fe with some admixture of metal-to-ligand charge-transfer (MLCT) transitions involving orbitals of the Cp ring and benzyl [18, 19]. The next band at 300 nm is ascribed to charge-transfer transition from the Cp ring to Fe center of the ferrocenyl. The higher energy bands at 260 and 235 nm arise from intraligand charge-transfer (ILCT) transitions. When excited at 400 nm in DMSO solution at room temperature this compound displays a medium strong photoluminescence emission at 500 nm (figure 2) emanating from MLCT transitions of the ferrocenyl moiety [19]. This clearly shows that $[\text{Mo}_8\text{O}_6]^{4-}$ is not playing any role in the photoluminescent emission behavior of this compound.

3.4. Molecular structure determination

The compound crystallizes in the monoclinic, $P2_1/c$ space group with an asymmetric unit comprising $[\text{Mo}_8\text{O}_{26}]^{4-}$ and two ammonium cations $[(\text{FcCH}_2)(\text{CH}_2\text{C}_6\text{H}_5)\text{NH}_2]^+$ (figure 3). On the basis of this asymmetric unit, the molecular formula of the compound can be formulated as $[(\text{FcCH}_2)(\text{CH}_2\text{C}_6\text{H}_5)\text{NH}_2]_4[\text{Mo}_8\text{O}_{26}]$. The oxygen atoms in the polyoxomolybdate can be classified into four different (O_t , μ_2 , μ_3 , and μ_4) categories, $\text{Mo}-\text{O}_t = 1.687\text{--}1.714$ Å, $\text{Mo}-\text{O}(\mu_2) = 1.737\text{--}2.295$ Å, $\text{Mo}-\text{O}(\mu_3) = 1.952\text{--}2.310$ Å, and $\text{Mo}-\text{O}(\mu_4) = 2.117\text{--}2.412$ Å.

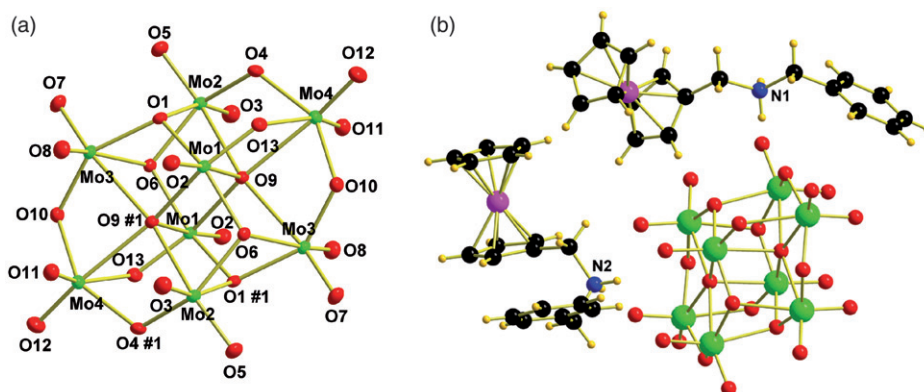


Figure 3. (a) The thermal ellipsoidal plot (50% probability) of the asymmetric unit of $[(\text{FcCH}_2)(\text{CH}_2\text{C}_6\text{H}_5)\text{NH}_2]_4[\text{Mo}_8\text{O}_{26}]$ excluding the cation. (b) The molecular structure of $[(\text{FcCH}_2)(\text{CH}_2\text{C}_6\text{H}_5)\text{NH}_2]_4[\text{Mo}_8\text{O}_{26}]$. Color code: Mo, green; oxygen, red; carbon, black; nitrogen, blue; and hydrogen, yellow. Selected metric data: bond lengths (Å) Mo1–O2 1.707(2), Mo1–O13 1.737(2), Mo1–O1 1.952(2), Mo1–O6 1.964(2), Mo1–O9#1 2.1174(19), Mo1–O9 2.353(2), Mo2–O5 1.700(2), Mo2–O3 1.703(2), Mo2–O4 1.896(2), Mo2–O6 1.989(2), Mo2–O1#1 2.310(2), Mo2–O9#1 2.344(2), Mo3–O7 1.701(2), Mo3–O8 1.702(2), Mo3–O10 1.881(2), Mo3–O1#1 1.9940(19), Mo3–O6 2.316(2), Mo3–O9 2.396(2), Mo4–O11 1.714(2), Mo4–O4#1 1.942(2), Mo4–O13 2.295(2), Mo4–O9 2.4117(19). Symmetry op. #1: $= -x + 1, -y + 1, -z + 1$.

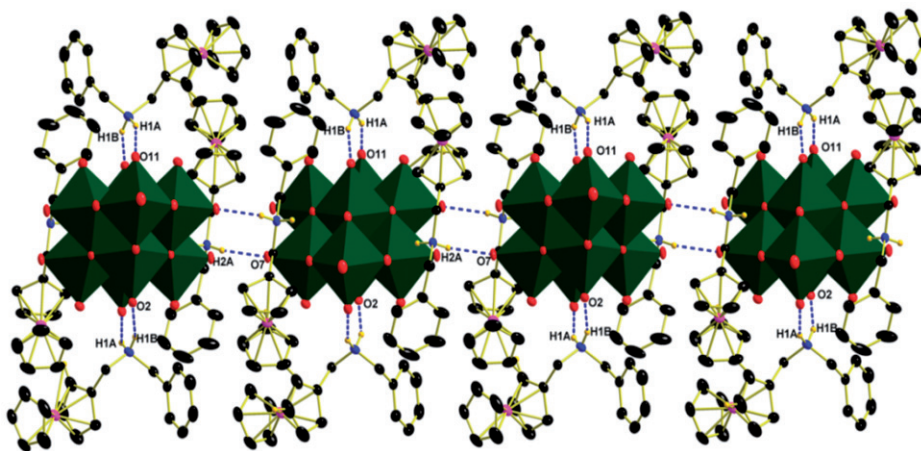


Figure 4. Intricate supramolecular architecture through intermolecular hydrogen bonding.

The crystal structure analysis reveals a supramolecular framework of quaternary ammonium cation containing methylferrocene and benzyl groups as synthons. The term “supramolecular synthon” was coined by Desiraju to describe building blocks that are common to many structures and hence can be used to order specific groups in the solid state [27]. This dimer of ammonium (supramolecular synthon) interacts with the POM cluster through protons on nitrogen, resulting in intricate supramolecular network (figure 4) through $\text{O}2 \cdots \text{H}1\text{B} - \text{N}2$ (symmetry op. $= 1 - x, 1 - y, 1 - z$) and

O11...H1A–N2 (symmetry op. = $1 - x, 1 - y, 1 - z$) interactions having dimensions 2.029 and 2.070 Å, respectively, in the axial position with only one POM cluster. Additionally, protons belonging to N1 also undergo O7...H2A–N1 (symmetry op. = $1 - x, -1/2 + y, 1/2 - z$) and O4...H2B–N1 (symmetry op. = $1 - x, 1 - y, 1 - z$) interactions of 2.188 and 2.048 Å, respectively, with two adjacent POM anions.

4. Conclusions

Quaternary ammonium cations as charge balancing species for anionic polyoxomolybdate act as a supramolecular synthon generating an interesting supramolecular framework. In the solution phase the electrochemical as well as the photoluminescent properties of ammonium possessing a ferrocenyl group remain unaffected in the presence of the POM anion. A comparison of the structural characteristics of this cluster compound $[(\text{FcCH}_2)\text{NH}_2(\text{CH}_2\text{C}_6\text{H}_5)]_4[\text{Mo}_8\text{O}_{26}]$ with those of reported polyoxomolybdate compounds [16, 17] $[\text{Zn}(\text{Hppz})_3]_2(\text{Mo}_8\text{O}_{26})$, $[\text{Ni}(\text{bpy})_2]_2(\text{Mo}_8\text{O}_{26})$, $[\text{Co}(\text{H}_2\text{biim})_2(\text{Hbiim})]_2(\text{H}_2\text{Mo}_8\text{O}_{26})(\text{H}_2\text{O})_4$ clearly reveals that the topology of POMs depends on reaction conditions, stoichiometry, and also on the complex cationic species.

Supplementary material

Supplementary material of the compound contains the IR and ^1H NMR spectra. Further details on the crystal structure investigation of the compound may be obtained from the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (telephone: +44-(0)1223-762-910, fax: +44-(0)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk; <http://www.ccdc.cam.ac.uk/deposit>), on quoting depository number CCDC 801306.

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