Inorg. Chem. **2002**, *41*, 1336–1338

Inorganic Chemistry

Communication

Molecular Metal Sulfide Cluster Model for Substrate Binding to Oil-Refinery Hydrodesulfurization Catalysts

Konrad Herbst,[†] **Magda Monari,**[‡] **and Michael Brorson***[,†]

Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Lyngby, Denmark, and Dipartimento di Chimica "G. Ciamician", University of Bologna, Via Selmi 2, I-40126 Bologna, Italy

Received October 25, 2001

Reaction between $[(\eta^5\text{-Cp}')_3Mo_3S_4]^+$ and $[Ni(1,5\text{-cod})_2]$ (Cp′ = methylcyclopentadienyl; 1,5-cod = 1,5-cyclooctadiene) in THF at ambient temperature yielded a coordinatively unsaturated cubane-like cluster cation, $[(\eta^5\text{-Cp}')_3Mo_3S_4Ni]^+$. The ligand sphere at the Ni atom could be saturated by coordinating dimethyl sulfide, diethyl sulfide, di(*tert*-butyl) sulfide, tetrahydrothiophene, thiochroman-4-ol, 1,4-dithiane, pyridine, quinoline, or 4,4′-bipyridine. The products structurally model a mode of substrate coordination on proposed binding sites of heterogeneous MoNi sulfide hydrotreating catalysts. No stable coordination compounds could be isolated for thiophene derivatives. X-ray crystal structures are reported for the ligand-bridged dicluster compounds $[\{(\eta^5\text{-Cp}')_3Mo_3S_4Ni\}_2(\mu\text{-}C_4H_4S_2)][pts]_2$ ($C_4H_8S_2$ = 1,4-dithiane) and $[\{(\eta^5\text{-Cp}')_3Mo_3S_4Ni\}_2(\mu\text{-bipy})][pts]_2$ (bipy = 4,4′-bipyridine).

The study of metal complexes[1] and clusters[2] that are able to activate and/or break C−S bonds of organosulfur molecules provides insight into possible mechanisms for hydrodesulfurization (HDS),[3] a key oil-refinery process by which sulfur is removed from oil fractions at 300−400 °C and at $p(H_2) = 10-140$ bar. We here report a number of heterobimetallic cubane-like sulfide cluster compounds $[(\eta^5\text{-Cp}')_3Mo_3S_4Ni(L)]^+$ (Cp′ = methylcyclopentadienyl) in which an organosulfur or -nitrogen molecule L is coordinated to the heteroatom site of the cluster. The binding mode may mimic substrate binding to the catalytically active Co−Mo−S and Ni−Mo−S phases of industrial heterogeneous catalysts.[4,5]

With the exception of the $Mo_2Co_2S_x$ (x = 3, 4) cluster cores studied as HDS models by Curtis and co-workers,[6] molecular HDS systems do not, in terms of the elements involved, resemble the industrial catalyst, which contains Mo *and* Co/Ni, all in their sulfidic state. We are here concerned with the heterobimetallic cubane-like cluster core Mo_3S_4Ni. Until recently the chemistry of Mo_3S_4M' clusters was almost completely aqueous,[7] but it has now been extended into the organometallic domain by the discovery of a rational synthesis method for $[(\eta^5\text{-Cp})_3Mo_3S_4]^+$ (Cp = cyclopentadienyl) and the demonstration that group 6 and 8−10 transition metals (M′), in the form of low-valent organometallic compounds, may be incorporated into such cluster cores.[8]

Incorporation of a nickel atom was achieved by reacting $[(\eta^5\text{-Cp}')_3Mo_3S_4][pts]$ (pts = *p*-toluenesulfonate) with $[Ni(cod)_2]$ (cod = 1,5-cyclooctadiene) in tetrahydrofuran and under inert atmosphere conditions; the advance of the reaction was reflected in a color change from green to dark brown within 1 min at room temperature. Subsequent addition of 3−5 times stoichiometric excess of dimethyl sulfide, diethyl sulfide, di(*tert*-butyl) sulfide, tetrahy-

---

* Corresponding author. Tel: +45 45272653. Fax: +45 45272999. E-mail: mib@topsoe.dk.

[†] Haldor Topsøe A/S.

[‡] University of Bologna.

(1) (a) Vivic, D. A.; Jones, W. D. *J. Am. Chem. Soc*. **1999**, *121*, 7606. (b) Matsubara, K.; Okamura, R.; Tanaka, M.; Suzuki, H. *J. Am. Chem. Soc*. **1998**, *120*, 1108. (c) Angelici, R. J. *Polyhedron* **1997**, *16*, 3073. (d) Bianchini, C.; Frediani, P.; Herrera, V.; Jiménez, M. V.; Meli, A.; Rincón, L.; Sánchez-Delgado, R.; Vizza, F. *J. Am. Chem. Soc.* **1995**, *117*, 4333. (e) Dailey, K. M. K.; Rauchfuss, T. B.; Rheingold, A. L.; Yap, G. P. A. *J. Am. Chem. Soc*. **1995**, *117*, 6396. (f) Arce, A. J.; De Sanctis, Y.; Karam, A.; Deeming, A. J. *Angew. Chem*. **1994**, *116*, 1459. (g) Halbert, T. R.; McGauley, K.; Pan, W.-H.; Czernuszewicz, R. S.; Stiefel, E. I. *J. Am. Chem. Soc.* **1984**, *106*, 1849.

(2) Brorson, M.; King, J. D.; Kiriakidou, K.; Prestopino, F.; Nordlander, E. In *Metal Clusters in Chemistry*; Braunstein, P., Oro, L. A., Raithby, P. R., Eds.; Wiley-VCH: Weinheim, 1999; Vol. 2, Chapter 2.6, pp 741−781.

(3) Topsøe, H.; Clausen, B. S.; Massoth, F. E. In *Catalysis—Science and Technology*; Anderson, J. R., Boudart, M., Eds.; Springer: Berlin, 1996; Vol. 11, pp 1−310.

(4) Stiefel, E. I. In *Transition Metal Sulfur Chemistry, Biological and Industrial Significance*; Stiefel, E. I., Matsumoto, K., Eds.; ACS Symposium Series 653; American Chemical Society: Washington, DC, 1996; pp 2−38.

(5) Chianelli, R. R.; Daage, M.; Ledoux, M. J. *Adv. Catal*. **1994**, *40*, 177.

(6) (a) Curtis, M. D. In *Transition Metal Sulfur Chemistry, Biological and Industrial Significance*; Stiefel, E. I., Matsumoto, K., Eds.; ACS Symposium Series 653; American Chemical Society: Washington, DC, 1996; pp 154−175. (b) Riaz, U.; Curnow, O. J.; Curtis, M. D. *J. Am. Chem. Soc.* **1994**, *116*, 4357. (c) Curtis, M. D.; Druker, S. H. *J. Am. Chem. Soc*. **1997**, *119*, 1027.

(7) Shibahara, T.; Akashi, H.; Kuroya, H. *J. Am. Chem. Soc*. **1986**, *108*, 1342. For recent references, see: Hernandez-Molina, R.; Sokolov, M. N.; Sykes, A. G. *Acc. Chem. Res*. **2001**, *34*, 223.

(8) (a) Rink, B.; Brorson, M.; Scowen, I. J. *Organometallics* **1999**, *18*, 2309. (b) Herbst, K.; Monari, M.; Brorson, M. *Inorg. Chem*. **2001**, *40*, 2979. (c) Herbst, K.; Rink, B.; Dahlenburg, L.; Brorson, M. *Organometallics* **2001**, *20*, 3655.

10.1021/ic011108y CCC: $22.00

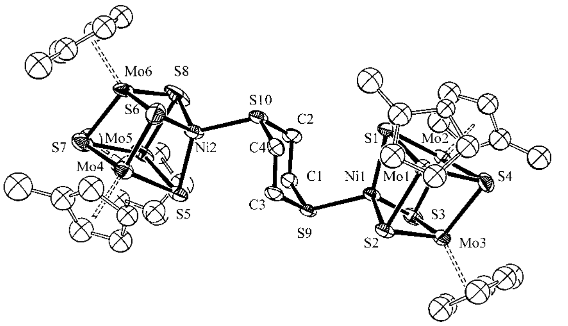


Figure 1. Structure of the cluster cation in $[\{(\eta^5\text{-Cp}')_3\text{Mo}_3\text{S}_4\text{Ni}\}_2(\mu\text{-C}_4\text{H}_8\text{S}_2)][\text{pts}]_2$ ([**2a**][pts]$_2$). Carbon thermal factors of the Cp′ rings are set arbitrarily low for clarity. The remaining thermal ellipsoids are drawn at the 30% probability level.

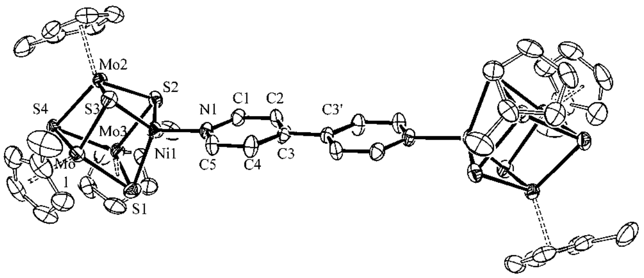
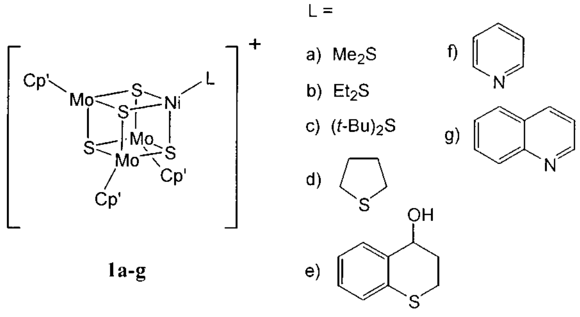


Figure 2. Structure of the cluster cation in $[\{(\eta^5\text{-Cp}')_3\text{Mo}_3\text{S}_4\text{Ni}\}_2\{\mu\text{-(4,4}'\text{-bipy)}\}][\text{pts}]_2$ ([**2b**][pts]$_2$).

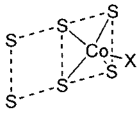
drothiophene, thiochroman-4-ol, pyridine, or quinoline gave after 2 h reaction time at room temperature and precipitation by means of pentane the complexes **1a**−**g** as pts salts. The identity and purity of these compounds were confirmed by ^{1}H NMR, FAB mass spectroscopy, and chemical analyses. No well-defined compounds could be isolated by a similar preparative route with diphenyl sulfide, thiophene, benzothiophene, dibenzothiophene and tetramethylthiophene, most likely due to the lower nucleophilicity of the sulfur atom in the aromatic heterocycles. Carbazole and benzo[*h*]-quinoline did not form complexes either.



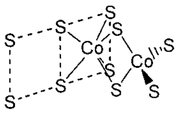
1a-g

Compounds **1a**−**g** did not crystallize well. Single crystals suitable for X-ray crystal structure determinations were obtained with the bis(monodentate) ligands 1,4-dithiane ($\text{C}_4\text{H}_8\text{S}_2$) and 4,4′-bipyridine acting as bridges between two cubane-like clusters. The cluster cations of $[\{(\eta^5\text{-Cp}')_3\text{Mo}_3\text{S}_4\text{Ni}\}_2(\mu\text{-C}_4\text{H}_8\text{S}_2)][\text{pts}]_2$ ([**2a**][pts]$_2$) and $[\{(\eta^5\text{-Cp}')_3\text{Mo}_3\text{S}_4\text{Ni}\}_2\{\mu\text{-(4,4}'\text{-bipy)}\}][\text{pts}]_2$ ([**2b**][pts]$_2$) are shown in Figures 1 and 2.[9]

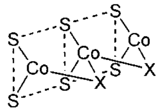
The compounds **1a**−**g** and **2a**,**b** constitute examples of a neutral organosulfur or organonitrogen molecule coordinated to a molecular-based site that resembles the active sites on an industrial HDS/HDN catalyst. The activity of the (usually alumina-supported) heterogeneous catalysts is associated with Co/Ni atoms bound to the MoS_2 crystallite edges, but the exact structure is a pending question. On the basis of XAFS and ^{59}Co NMR the structures **3**[10,11] (X = S) and **4**,[12] respectively, have been proposed. In these structure drawings only the edge sulfur atoms of the MoS_2 structure are displayed.



3



4



X = S
or
X=* (sulfur vacancy)

5

Recently, scanning tunneling microscopy has indicated the structure **5**[13] (X = S) for cobalt-promoted MoS_2 crystallites (supported on Au). Some coordinatively unsaturated edge atoms are formed by increasing the ratio $\text{H}_2/\text{H}_2\text{S}$ in the gas that is in contact with the MoS_2 crystallites.[14] For the structures **3** and **5** this corresponds to replacing edge sulfur atoms by vacancies (i.e., X = * rather than S). The sulfur vacancies are envisaged to play a role in the catalytic cycle for HDS by acting as binding sites for S of organosulfur molecules.[15] The coordination site on Ni in the cluster Mo_3NiS_4 is of a type similar to the sulfur vacancy site in the MoS_2-edge structure **3**, and in this way **1a**−**g** and **2a**,**b** may model substrate binding to the catalyst. The Ni coordination geometry in the cluster Mo_3NiS_4 is tetrahedral as is the Co coordination geometry in the edge structure **5**.

Structural data for **2a**,**b** do not indicate any activation of the C−S or C−N bonds. We therefore examined the HDS/

---

(9) Crystal structure of [**2a**][pts]$_2$ ($\text{C}_{54}\text{H}_{64}\text{Mo}_6\text{Ni}_2\text{O}_6\text{S}_{12}$): $M_r = 1886.83$, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.0275(7)$ Å, $b = 17.088(1)$ Å, $c = 18.795(1)$ Å, $\alpha = 99.412(2)°$, $\beta = 90.945(2)°$, $\gamma = 91.768(2)°$, $V = 3174.9(3)$ Å^3, $Z = 2$, $T = 293(2)$ K, $D_{\text{calc}} = 1.974$ Mg/m^3, $\mu = 2.166$ mm^{-1}, Mo Kα with graphite monochromator, Bruker CCD diffractometer, 37018 reflections collected, 18230 independent reflections, GOF = 0.926, R1 = 0.0820, wR2 = 0.2002 ($I > 2\sigma(I)$). Crystal structure of [**2b**][pts]$_2$ ($\text{C}_{60}\text{H}_{64}\text{Mo}_6\text{N}_2\text{Ni}_2\text{O}_6\text{S}_{10}$): $M_r = 1922.79$, monoclinic, space group $P2_1/c$ (No. 14), $a = 14.762(4)$ Å, $b = 13.647(4)$ Å, $c = 17.469(6)$ Å, $\beta = 105.72(1)°$, $V = 3388(2)$ Å^3, $Z = 2$, $T = 293(2)$ K, $D_{\text{calc}} = 1.885$ Mg/m^3, $\mu = 1.973$ mm^{-1}, Mo Kα with graphite monochromator, Bruker CCD diffractometer, 46153 reflections collected, 9866 independent reflections, GOF = 0.846, R1 = 0.0505, wR2 = 0.0957 ($I > 2\sigma(I)$).

(10) Clausen, B. S.; Niemann, W.; Zeuthen, P.; Topsøe, H. *Prepr.—Am. Chem. Soc., Div. Pet. Chem.* **1990**, *35*, 208.

(11) Louwers, S. P. A.; Prins, R. *J. Catal.* **1992**, *133*, 94.

(12) Ledoux, M. J.; Maire, G.; Hantzer, S.; Michaux, O. In *Proc. 9th International Congress on Catalysis*; Phillips, M. J., Ternan, M., Eds.; Calgary: Canada, 1988; Vol. 1, pp 74−81.

(13) Lauritsen, J. V.; Helveg, S.; Lægsgaard, E.; Stensgaard, I.; Clausen, B. S.; Topsøe, H.; Besenbacher, F. *J. Catal.* **2001**, *197*, 1.

(14) Topsøe, H.; Clausen, B. S.; Topsøe, N.-Y.; Hyldtoft, J.; Nørskov, J. K. *Prepr.—Am. Chem. Soc., Div. Pet. Chem.* **1993**, *38*, 638.

(15) Topsøe, H.; Clausen, B. S.; Topsøe, N.-Y.; Nørskov, J. K.; Ovesen, C. V.; Jacobsen, C. J. H. *Bull. Soc. Chim. Belg.* **1995**, *104*, 283.

HDN ability of the cluster at elevated temperatures and in the presence of H_2. Reactions between $[(\eta^5\text{-Cp}')_3Mo_3S_4Ni]$-[pts] and benzothiophene/quinoline in ethylene glycol solution conducted in a stainless steel pressure vessel (30 bar H_2, 16 h, 130 °C) did not reveal any of the expected desulfurization and denitrogenation products to have formed. At higher temperature (250 °C) and with decaline as solvent/dispersion medium, some reactivity was observed, most likely due to partial thermal decomposition of the cluster that produced catalytically active black solids.

The possibility[16] that the cluster Mo_3S_4Ni may display catalytic activity originates in the observation[17] that CO binds to the heterometal atom in $[(H_2O)_9Mo_3S_4M']^{4+}$ for M′ = Co, Ni,[18] but not for M′ = Cu, Fe. In this respect the molecular clusters closely resemble the heterogeneous MoS_2-based catalyst whose HDS activity is promoted by Co and Ni, but not by Fe and Cu. Furthermore, heterogeneous catalysts absorb CO in amounts correlated with their activities.[19] On the basis of Fenske−Hall molecular orbital calculations it was concluded[20] that the Mo_3S_4Ni cluster is unlikely to be active for HDS catalysis due to low electron density on Ni, which would prevent insertion of Ni into a C−S bond. The alternative route of homolytic C−S bond cleavage as, e.g., seen[21] in the desulfurization of 4-methylbenzenethiol by $[\{(\eta^5\text{-Cp}')Mo\}_2S_3\{Co(CO)_2\}_2]$ was, however, not considered.

In conclusion, the molecular cluster compound $[(\eta^5\text{-Cp}')_3\text{-}Mo_3S_4Ni(L)]^+$ was prepared as a model for heterogeneous Ni−Mo−S hydrodesulfurization catalysts. Catalytically relevant organosulfur and -nitrogen molecules were found to bind to the Ni site of the cluster, but no homogeneous HDS or HDN activity was detected.

Acknowledgment. This work was supported by the European Commission (TMR Network “Metal Clusters in Catalysis and Organic Synthesis”; Contract FMRX-CT96-0091; postdoctoral grant to K.H.). We thank our TMR partner at the University of Lund, Sweden, for access to their Varian UNITY 300 MHz NMR spectrometer. M.M. thanks the CNR, the MURST (COFIN2000), and the University of Bologna (project “Funds for Selected Research Topics”) for financial support.

Supporting Information Available: Syntheses, ^1H NMR, and FAB mass spectrometric data for **1a**−**g** and **2a**,**b**; X-ray crystallographic data for **2a**,**b** in the form of structural parameter listings and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

IC011108Y

---

(16) Schmidt, I.; Hyldtoft, J.; Hjortkjær, J.; Jacobsen, C. J. H. *Acta Chem. Scand*. **1996**, *50*, 871.

(17) Hernandez-Molina, R.; Sykes, A. G. *Coord. Chem. Rev*. **1999**, *187*, 291.

(18) The carbonyl band of $[(\eta^5\text{-Cp}')_3Mo_3S_4Ni(CO)][pts]$ was observed at 2032 cm^{-1} (in KBr).

(19) Bachelier, J.; Duchet, J. C.; Cornet, D. *J. Catal*. **1984**, *87*, 283.

(20) Bahn, C. S.; Tan, A.; Harris, S. *Inorg. Chem*. **1998**, *37*, 2770.

(21) Druker, S. H.; Curtis, M. D. *J. Am. Chem. Soc*. **1995**, *117*, 6366.