

Preparation of Heterobimetallic Cuboidal Clusters $[M_3NiS_4(H_2O)_{10}]^{4+}$ ($M = Mo, W$) and Their Reactivity Towards CO

I. Schmidt,^{a,b} J. Hyldtoft,^a J. Hjortkjær^b and Claus J. H. Jacobsen^{a,c,*}

^aHaldor Topsøe Research Laboratories, Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Lyngby, Denmark,

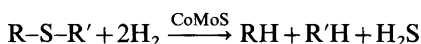
^bTechnical University of Denmark, Department of Chemical Engineering, Building 229, DK-2800 Lyngby, Denmark

and ^cHaldor Topsøe Catalyst Plant, Haldor Topsøe A/S, Linderupvej 2, DK-3600 Frederikssund, Denmark

Schmidt, I., Hyldtoft, J., Hjortkjær, J. and Jacobsen, C. J. H., 1996. Preparation of Heterobimetallic Cuboidal Clusters $[M_3NiS_4(H_2O)_{10}]^{4+}$ ($M = Mo, W$) and Their Reactivity Towards CO. – Acta Chem. Scand. 50: 871–874 © Acta Chemica Scandinavica 1996.

A new substantially improved synthesis of $[W_3NiS_4(H_2O)_9]_2(pts)_8 \cdot 20H_2O$ ($pts = p$ -toluenesulfonate) based on reaction of $[W_3S_4]^{4+}$ with nickel in 2 M HCl is reported. The reaction proceeded within 2 h and an isolated yield of >95% based on $[W_3S_4]^{4+}$ was obtained. Similarly, $[Mo_3NiS_4(H_2O)_{10}](pts)_4 \cdot 7H_2O$ was prepared by a novel procedure based on the reduction of MoS_4^{2-} with excess Ni at 70 °C, followed by oxidation with air to obtain $[Mo_3S_4]^{4+}$ and subsequently reflux under N_2 to yield $[Mo_3NiS_4]^{4+}$. This procedure allowed a one-pot synthesis of $[Mo_3S_4]^{4+}$ and/or $[Mo_3NiS_4]^{4+}$ from tetrathiomolybdate(VI). Furthermore, a new method was developed for the quantitative isolation of $[Mo_3NiS_4(H_2O)_{10}](pts)_4 \cdot 7H_2O$ and $[W_3NiS_4(H_2O)_9]_2(pts)_8 \cdot 20H_2O$. This is based on chromatographic separation by elution with 3.5 M trifluoroacetic acid (CF_3COOH), and successive dilutions and evaporations. The $[M_3NiS_4(H_2O)_{10}]^{4+}$ ($M = Mo, W$) clusters are potential candidates for homogeneous hydrodesulfurisation catalysts and, for comparison with heterogeneous catalysts, their reactivity towards carbon monoxide was studied. UV–VIS absorption, IR and ^{13}C NMR spectroscopy revealed that CO was reversibly coordinated to Ni in the very air-sensitive $[M_3NiS_4]^{4+}$ clusters. Upon coordination of CO the clusters could be handled in air for long periods without oxidation.

Hydrodesulfurisation (HDS) used for the removal of organic sulfur compounds from various crude oil fractions according to the generalized scheme



is one of the most important catalytic reactions in operation world-wide. In a recent review¹ the details of this process are discussed. Despite the more than 2000 publications on HDS catalysis, the mechanism of this reaction remains elusive. From the work of Topsøe and coworkers the structure of the active so-called Co–Mo–S phase^{2,3} was determined (Fig. 1). It can be described as very small crystallites of MoS_2 (<20 Å) decorated with Ni (or Co) at the edges. Various transition metal compounds have been used as structural models to simulate the interaction between the active site(s) and relevant organic sulfur-containing molecules as discussed in several reviews.^{4–8} Since the classical paper by Muetterties⁹ there has been a considerable interest in the so-called

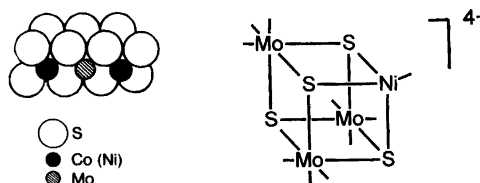


Fig. 1. Co–Mo–S phase compared with $[Mo_3NiS_4(H_2O)_{10}]^{4+}$.

cluster-surface analogy. The basic idea is that small clusters can act as structural and functional models for surface structures and give new information about their reactivity and intermediates in surface reactions, e.g. heterogeneous catalytic reactions. Recently, Curtis *et al.*^{10–12} presented a structural model for the Co–Mo–S phase based on a bimetallic Co–Mo cluster and investigated its applicability as a functional homogenous model by reaction with various organic sulfur-containing compounds.

Since the first report on the heterobimetallic cubane-type cluster $[Mo_3FeS_4(H_2O)_{12}]^{4+}$ (Ref. 13) a range of other metals have been incorporated in the incomplete

* To whom correspondence should be addressed.

cubane-type cluster $[\text{Mo}_3\text{S}_4]^{4+}$ (Cr,¹⁴ Mo,¹⁵ Fe,¹³ Co,¹⁶ Ni,¹⁷ Pd,¹⁸ Cu,¹⁹ Hg,²⁰ In,²¹ Sn²² and Sb²³). So far, only Ni,²⁴ Cu,²⁵ Ge²⁶ and Sn²⁶ are incorporated in $[\text{W}_3\text{S}_4]^{4+}$, probably due to the difficulty of reducing W^{IV} . Usually these heterobimetallic and incomplete cubane-type clusters are crystallized from highly concentrated solutions in 4 M *p*-toluenesulfonic acid. It is a difficult and time-consuming method which only allows a 30–60% yield after several days. We report an improved synthesis for both $[\text{Mo}_3\text{NiS}_4]^{4+}$ and $[\text{W}_3\text{NiS}_4]^{4+}$ and also a faster and quantitative method for the isolation of $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}](\text{pts})_4 \cdot 7\text{H}_2\text{O}$ and $\{[\text{W}_3\text{NiS}_4(\text{H}_2\text{O})_9\}_2](\text{pts})_8 \cdot 20\text{H}_2\text{O}$. {By dissolution in non-complexing acids the compound dissociates and a water molecule is coordinated to the nickel atom giving $[\text{W}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$.} The method might be adaptable to other $[\text{M}_3\text{S}_4]^{4+}$ and $[\text{M}_3\text{M}'\text{S}_4]^{4+}$ clusters ($\text{M}=\text{Mo}, \text{W}$) as well. The reactivity of the $[\text{M}_3\text{NiS}_4]^{4+}$ clusters towards CO and the use of these clusters as structural models for the Co–Mo–S phase, with which they are compared in Fig. 1, was studied. In several respects the heterobimetallic clusters $[\text{M}_3\text{NiS}_4]^{4+}$ are found to have attracting features as structural and possibly functional models for the Co–Mo–S phase.

Experimental

All reactions and manipulations were performed under an atmosphere of dinitrogen using standard Schlenk techniques unless otherwise stated. All reagents and chemicals were of reagent grade or better and used without further purification. $(\text{NH}_4)_2\text{MoS}_4$ ²⁷ and $[\text{W}_3\text{S}_4]^{4+}$ (Ref. 28) were synthesized according to the literature methods.

Synthesis of $[\text{Mo}_3\text{NiS}_4]^{4+}$. $[\text{Mo}_3\text{NiS}_4]^{4+}$ was synthesized by reacting 10 g (38 mmol) of $(\text{NH}_4)_2[\text{MoS}_4]$ in 250 ml of 2 M HCl with 10 g (170 mmol) of nickel powder ($<1 \mu\text{m}$) at 70 °C for 16 h. During reaction a black suspension formed. This suspension was heated to 90 °C and bubbled with air for 20 h and after purging with N_2 , refluxed for 2 h under N_2 . After cooling, the suspension was filtered and the components separated by cation-exchange chromatography as described in the literature.¹⁷ Yield: 24 % based on Mo.

Synthesis of $[\text{W}_3\text{NiS}_4]^{4+}$. $[\text{W}_3\text{NiS}_4]^{4+}$ was synthesized by refluxing 20 mmol of $[\text{W}_3\text{S}_4]^{4+}$ in 300 ml of 1 M HCl with 11.7 g (200 mmol) of nickel powder ($<1 \mu\text{m}$) for 2 h. During reaction the violet suspension gradually turned dark green. The remaining nickel powder was removed by filtering of the cooled suspension. The clear dark-green solution was diluted with water to $[\text{H}^+]=0.5 \text{ M}$ and absorbed on a Dowex 50W-X2 cation-exchange resin (2.5 cm \times 15 cm). A light green band containing Ni^{2+} was eluted with 0.5 M HCl. Then a second green band containing $[\text{W}_3\text{NiS}_4]^{4+}$ was eluted with 1 M HCl. Occasionally a violet band containing

$[\text{W}_3\text{S}_4]^{4+}$ was eluted with 1 M HCl. The yield of $[\text{W}_3\text{NiS}_4]^{4+}$ based on $[\text{W}_3\text{S}_4]^{4+}$ was always higher than 95%.

Synthesis of $[\text{M}_3\text{NiS}_4]\text{-pts}$ ($\text{M}=\text{Mo}, \text{W}$). An amount of 0.4 mmol of $[\text{M}_3\text{NiS}_4]^{4+}$ in 100 ml of 1 M HCl was diluted and absorbed on a Dowex 50W-X2 cation-exchanger (2.5 cm \times 20 cm). To remove chloride (checked with Ag^+) the cation-exchanger was washed with 0.1 M CF_3COOH and the cluster eluted with 3.5 M CF_3COOH . Based on the UV–VIS spectrum $\{[\text{Mo}_3\text{NiS}_4]^{4+}: (\lambda, \epsilon)=(677 \text{ nm}, 610 \text{ l mol}^{-1}\text{cm}^{-1}), [\text{W}_3\text{NiS}_4]^{4+}: (\lambda, \epsilon)=(700 \text{ nm}, 620 \text{ l mol}^{-1}\text{cm}^{-1})\}$ the stoichiometric amount of Hpts was added, the solution diluted three times and evaporated to dryness. To remove traces of CF_3COOH , the resulting solid was redissolved in 100 ml of H_2O and evaporated to dryness. Yield: $>95\%$ based on $[\text{M}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$.

Reaction of $[\text{M}_3\text{NiS}_4]^{4+}$ ($\text{M}=\text{Mo}, \text{W}$) with CO. An amount of 4×10^{-5} mol of $[\text{M}_3\text{NiS}_4]^{4+}$ (0.06 g $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}](\text{pts})_4 \cdot 7\text{H}_2\text{O}$ (1465.72 g mol^{-1}) or 0.07 g of $\{[\text{W}_3\text{NiS}_4(\text{H}_2\text{O})_9\}_2](\text{pts})_8 \cdot 20\text{H}_2\text{O}$ (3530.95 g mol^{-1})) was dissolved in 25 ml of methanol, and the clear solution was treated with gaseous CO for 30 min to ensure complete reaction. During the reaction a color change was observed: green to rose for $[\text{Mo}_3\text{NiS}_4]^{4+}$ and green to orange for $[\text{W}_3\text{NiS}_4]^{4+}$. Upon coordination of CO, the heterobimetallic clusters could be handled in air without oxidation for periods of >1 week ($<5\%$ change in UV–VIS spectrum). The CO-containing clusters were isolated by slow evaporation of the methanol.

UV–VIS, ^{13}C NMR and IR spectra. The UV–VIS spectrometer setup was a Perkin-Elmer Lambda 16 interfaced with a PC. Spectra of air-sensitive solutions were recorded under an atmosphere of dinitrogen. The ^{13}C NMR spectra were recorded with a Bruker AM 500 MHz NMR instrument. IR spectra were recorded with a Perkin-Elmer 1710 FTIR spectrometer using KBr pellets.

Results and discussion

Synthesis. The heterobimetallic cubane-type cluster $[\text{Mo}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$ was prepared from ammonium tetrathiomolybdate(VI) in a one-pot synthesis with an overall yield of 24% based on Mo. The use of a one-pot synthesis saved much time compared to the traditional method based on NaBH_4 reduction²⁸ and resulted in a similar yield. The cation exchange of the incomplete cluster before reaction with the heterometal (nickel) and the dropwise addition of NaBH_4 solution could thus be avoided. Since MoS_4^{2-} can be prepared in a simple way from MoO_4^{2-} , a one-pot synthesis of $[\text{Mo}_3\text{M}'\text{S}_4]^{4+}$ from MoO_4^{2-} is in principle possible using other metals as reductants. This synthesis might similarly be used for preparing other heterobimetallic cubane-type clusters.

However, the $[W_3S_4(H_2O)_9]^{4+}/[W_3NiS_4(H_2O)_{10}]^{4+}$ clusters could not be obtained from tetrathiotungstate-(VI) and nickel. We found the use of nickel powder instead of nickel plates improved the synthesis of $[W_3NiS_4(H_2O)_{10}]^{4+}$ from $[W_3S_4(H_2O)_9]^{4+}$ substantially. Thus, refluxing a suspension of $[W_3S_4]^{4+}$ with excess nickel powder in 2 M HCl for 2 h gave $[W_3NiS_4(H_2O)_{10}]^{4+}$ in almost quantitative yield. This was a significant improvement compared to the previously reported method²⁹ based on the reaction of $[W_3S_4]^{4+}$ with nickel plates, where the reaction proceeds at 90 °C within 17 h and an overall yield of 86%.

Crystalline $[M_3NiS_4(H_2O)_9]$ -pts (M = Mo, W) was prepared by a new faster and more efficient method. It included elution with 3.5 M CF_3COOH , addition of the stoichiometric amount of Hpts and successive dilutions with water and evaporation as described in the Experimental section. The traditional method requires concentrated solutions and precipitation for several days or weeks, and only yields around 50%. The method described here was fast and gave an almost quantitative yield.

Our experiments showed that CO reacts more readily with $[W_3NiS_4(H_2O)_{10}]^{4+}$ than with $[Mo_3NiS_4(H_2O)_{10}]^{4+}$, and that $[M_3S_4]^{4+}$ (M = Mo, W) did not react with CO under similar conditions. The X-ray structural analysis of the $[Mo_3NiS_4(H_2O)_9(CO)]$ -pts $_4 \cdot 7H_2O$ by Shibahara *et al.*³⁰ verifies that the carbon monoxide is coordinated to the nickel atom in the $[Mo_3NiS_4]^{4+}$ cluster. Upon coordination of CO to the clusters, a colour change is observed: green to rose for $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ and green to orange for $[W_3NiS_4(H_2O)_{10}]^{4+}$. Coordination of carbon monoxide to $[M_3NiS_4(H_2O)_{10}]^{4+}$ (M = Mo, W) in non-coordinating solvents (e.g. methanol or 2 M CF_3SO_3H) was quantitative as judged from the UV-VIS spectra shown in Figs. 2 and 3. Carbon monoxide can be substituted by Cl^- , e.g. by addition of conc. HCl to the clusters. The clusters with coordinated CO are far more stable in air and can be evaporated to dryness and

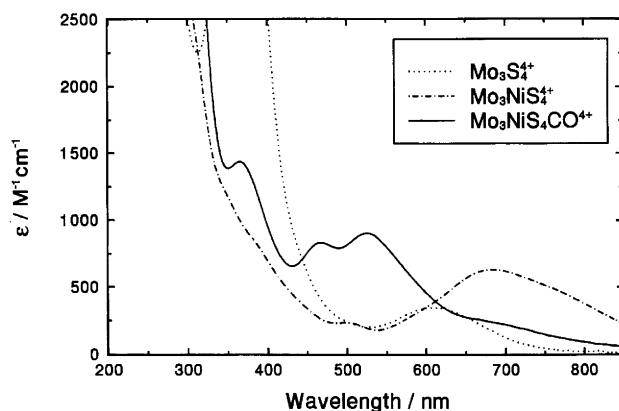


Fig. 2. UV-VIS spectra of $[Mo_3S_4(H_2O)_9]^{4+}$, $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ and $[Mo_3NiS_4(H_2O)_9CO]^{4+}$ in 1 mol l⁻¹ CF_3SO_3H .

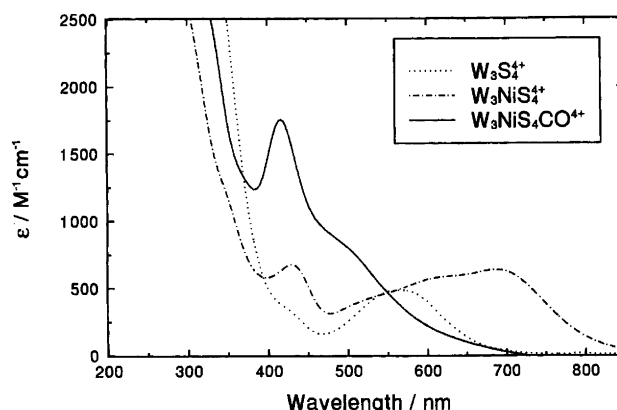


Fig. 3. UV-VIS spectra of $[W_3S_4(H_2O)_9]^{4+}$, $[W_3NiS_4(H_2O)_{10}]^{4+}$ and $[W_3NiS_4(H_2O)_9CO]^{4+}$ in 1 mol l⁻¹ CF_3SO_3H .

redissolved in non-coordinating solvents without a protective atmosphere of N_2 and without any changes in the UV-VIS spectra. The hypothesis by Dimmock *et al.*³¹ that the oxidation of these clusters in air initially involves coordination of O_2 to the hetero-metal, is in accordance with CO occupying the relevant site on Ni and thereby preventing the oxidation.

Spectroscopy. The IR spectra of $[M_3NiS_4(H_2O)_9(CO)]^{4+}$ showed CO stretching bands at 2077 cm^{-1} for $[Mo_3NiS_4(H_2O)_9CO]^{4+}$ and at 2045 cm^{-1} for $[W_3NiS_4(H_2O)_9CO]^{4+}$, which demonstrates the end-on bonding³² to the nickel atom. A ¹³C NMR analysis of $[M_3NiS_4(H_2O)_9CO]^{4+}$ in 0.1 M HCl showed a ¹³C peak at a chemical shift of 189.0 ppm for $[Mo_3NiS_4(H_2O)_9CO]^{4+}$ and 186.8 ppm for $[W_3NiS_4(H_2O)_9CO]^{4+}$ relative to TMS. These results showed that the $[W_3NiS_4(H_2O)_9CO]^{4+}$ is analogous to the $[Mo_3NiS_4(H_2O)_9CO]^{4+}$ cluster.

On comparison of $[Mo_3NiS_4(H_2O)_9]^{4+}$ with the CoMoS phase there are some structural similarities. The CoMoS phase typically consists of single-layer structures of MoS_2 containing 10–20 Mo atoms with Co or Ni decorating the edge sites.¹ This is similar to the $[Mo_3NiS_4(H_2O)_9]^{4+}$ in which the nickel atom also decorates an edge site (Fig. 1). It is believed that these edge sites are the active sites of the CoMoS phase and this also compares well with the fact that the nickel is far more reactive than the molybdenum in the $[Mo_3NiS_4(H_2O)_9]^{4+}$ cluster. Exactly, the same pattern was seen by comparison of the NiWS phase with the $[W_3NiS_4(H_2O)_{10}]^{4+}$ cluster.

The uptake of CO is often used as a measure of the HDS activity of the heterogeneous catalysts. Because of the uptake of CO directly on the active CoMoS sites there is a linearity between CO uptake and HDS activity.³³ The CO uptake on the active site (the nickel site) of the $[M_3NiS_4(H_2O)_{10}]^{4+}$ clusters was 1:1 even at a partial pressure of 1 atm of CO and 25 °C. IR spectra of heterogeneous NiWS HDS catalysts after CO

uptake exhibited a CO peak at 2090 cm^{-1} ,³⁴ which was displaced 45 cm^{-1} from the CO band in $[\text{W}_3\text{NiS}_4(\text{H}_2\text{O})_9\text{CO}]^{4+}$. This demonstrates that despite the apparent similarity, there are differences in the chemical environment of the nickel atoms in NiMoS (NiWS) and $[\text{Mo}_3\text{NiS}_4]^{4+}$ ($[\text{W}_3\text{NiS}_4]^{4+}$). The similar behavior mentioned above supports the idea that the $[\text{M}_3\text{NiS}_4(\text{H}_2\text{O})_{10}]^{4+}$ clusters (M=Mo, W) might be functionally models in, e.g., homogeneous HDS catalysis.

Work is in progress on the isolation of compounds in which organic sulfur molecules are coordinated to the nickel site in the cubane-type clusters. The aim is to use these cubane-type clusters under realistic conditions as functional models for HDS catalysts.

References

1. Topsøe, H., Clausen, B. S. and Massoth, F. *Science and Technology Catalysis*, Vol 11. *In press*.
2. Topsøe, H., Clausen, B. S. and Massoth, F. *J. Catal.* **68** (1981) 433.
3. Topsøe, H., Candia, R., Topsøe, N.-Y. and Clausen, B. S. *Bull. Soc. Chim. Belg.* **93** (1984) 783.
4. Angelici, R. J. *Acc. Chem. Res.* **21** (1988) 387.
5. Angelici, R. J. *J. Coord. Chem. Rev.* **105** (1990) 61.
6. Rauchfuss, T. B. *Prog. Inorg. Chem.* **39** (1991) 259.
7. Sanchez-Delgado, R. A. *J. Mol. Cat.* **86** (1994) 287.
8. Angelici, R. J. *Bull. Soc. Chim. Belg.* **104** (1995) 265.
9. Muettterties, E. L., Rhodin, T. N., Band, E., Brucker, C. F. and Pretzer, W. R. *Chem. Rev.* **79** (1979) 91.
10. Riaz, U., Curnow, O. J. and Curtis, M. D. *J. Am. Chem. Soc.* **113** (1991) 1416.
11. Riaz, U., Curnow, O. J. and Curtis, M. D. *J. Am. Chem. Soc.* **116** (1994) 4357.
12. Druker, S. H. and Curtis M. D. *J. Am. Chem. Soc.* **117** (1995) 6366.
13. Shibahara, T., Akashi, H. and Kuroya, H. *J. Am. Chem. Soc.* **108** (1986) 1342.
14. Routledge, C. A., Humanes, M., Li, Y.-J. and Sykes, A. G. *J. Chem. Soc. Dalton Trans.* (1994) 1275.
15. Shibahara, T. and Kuroya, H. *J. Am. Chem. Soc.* **106** (1984) 789; Brorson, M., Hyldtoft, J., Jacobsen, C. J. H. and Olesen, K. G. *Inorg. Chim. Acta* **232** (1995) 171.
16. Shibahara, T., Akashi, H., Yamasaki, M. and Hashimoto, K. *Chem. Lett.* (1991) 689.
17. Shibahara, T., Yamasaki, M., Akashi, H. and Katayama, T. *Inorg. Chem.* **30** (1991) 2693.
18. Murata, T., Gao, H., Mizobe, Y., Nakano, F., Motomura, S., Tanase, T., Yano, S. and Hidai, M. *J. Am. Chem. Soc.* **114** (1992) 8287.
19. Shibahara, T., Akashi, H. and Kuroya, H. *J. Am. Chem. Soc.* **110** (1988) 3313.
20. Shibahara, T., Akashi, H., Yamasaki, M. and Hashimoto, K. *Chem. Lett.* (1991) 689.
21. Sakane, G. and Shibahara, T. *Inorg. Chem.* **32** (1993) 777.
22. Akashi, H. and Shibahara, T. *Inorg. Chem.* **28** (1989) 2906.
23. Shibahara, T., Hashimoto, K. and Sakane, G. *J. Inorg. Biochem.* **43** (1991) 280.
24. Shibahara, T., Yamamoto, T. and Sakane, G. *Chem. Lett.* (1994) 1231.
25. Zhan, H.-Q., Zheng, Y.-F., Wu, X.-T. and Lu, J.-X. *Inorg. Chim. Acta* **156** (1989) 277.
26. Müller, A., Fedin, V. P., Diemann, E., Bögge, H., Krickemeyer, E., Sölter, D., Giuliani, A. M., Barbieri, R. and Adler, P. *Inorg. Chem.* **33** (1994) 2243.
27. McDonald, J. W., Friesen, G. D., Rosenheim, L. D. and Newton, W. E. *Inorg. Chim. Acta* **72** (1983) 205.
28. Shibahara, T., Yamasaki, M., Sakane, G., Minami, K., Yabuki, T. and Ichimura, A. *Inorg. Chem.* **31** (1992) 640.
29. Shibahara, T., Yamamoto, T. and Sakane, G. *Chem. Lett.* (1994) 1231.
30. Shibahara, T., Mochida, S. and Sakane, G. *Chem. Lett.* (1993) 89.
31. Dimmock, P. W. and Sykes, A. G. *J. Chem. Soc. Dalton Trans.* (1990) 3101.
32. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, 4th Edn., Wiley, New York 1986, pp. 291–310.
33. Bachelier, J., Tiliette, M. J., Cornac, M., Duchet, J. C., Lavalley, J. C. and Cornet, D. *Bull. Soc. Chim. Belg.* **93** (1984) 743.
34. Breyse, M., Bachelier, J., Bonnelle, J. P., Cattenot, M., Cornet, D., Decamp, Duchet, J. C., Durand, R., Engelhard, P., Frety, R., Gachet, C., Geneste, P., Grimblot, J., Guegen, C., Kasztelan, S., Lacroix, M., Lavalley, J. C., Leclercq, C., Moreau, de Morgues, L., Olive, J. L., Payen, E., Portefaix, J. L., Toulhoat, H. and Vrinat, M. *Bull. Soc. Chim. Belg.* **93** (1984) 829.

Received November 21, 1995.