

SHORT PAPER

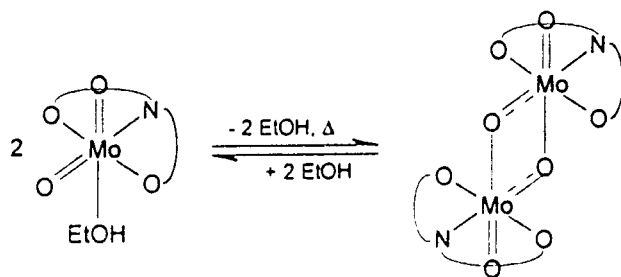
Synthesis, X-ray structure and spectroscopic studies
of $\text{Mo}(\text{O})_2(3,5\text{-di-tert-Busap})(\text{EtOH})^\dagger$ Lucjan B. Jerzykiewicz, Jarosław M. Sobczak* and
Józef J. Ziółkowski

Faculty of Chemistry, University of Wrocław, F.Joliot-Curie 14, Wrocław, Poland

A new six-co-ordinate *cis*-dioxomolybdenum(VI) complex $[\text{Mo}(\text{O})_2(3,5\text{-di-tert-Busap})(\text{EtOH})]$, (where 3,5-di-tert-Busap²⁻ = the Schiff base dianion 3,5-di-tert-butyl-N-salicylidene-2-aminophenolate), has been prepared. The complex is characterised by IR, ¹H and ¹³C NMR and UV/vis spectroscopy and is stable to air, but above 413 K or in non-co-ordinating solvents loses an ethanol molecule, forming an dimeric compound with an unsymmetrical dioxygen bridge as indicated by IR spectroscopy.

Oxomolybdenum compounds are of great interest because of their function in several enzymes¹ and in many catalytic systems.² The presence of the *cis*-dioxomolybdenum(VI) fragment in the oxidative form of certain molybdoenzymes has stimulated search for new structures in which this moiety is co-ordinated to ligands containing nitrogen, oxygen and/or sulfur donors. Molybdenum(VI) Schiff-base complexes represent an important and interesting class of that kind of coordination compound.³ The *cis*-dioxo moiety, *cis*- $\text{Mo}(\text{O})_2^{2+}$, is the most commonly encountered structural form in Mo(VI) co-ordination chemistry.⁴ *cis*- $\text{Mo}(\text{O})_2$ complexes of dianionic tridentate Schiff base ligands can exist as monomers, $\text{Mo}(\text{O})_2(\text{L})(\text{D})$ – where: L = Schiff base, D = monodentate neutral ligand, which is dominant,³ dimers, $[\text{Mo}(\text{O})(\mu\text{-O})(\text{L})]_2$ – with asymmetric double oxygen bridge,⁵ or oligomers with a postulated $\cdots\text{Mo}=\text{O}\cdots\text{Mo}=\text{O}\cdots$ interaction.⁶ This type of complex has a distinct advantage as models for oxo-transfer processes due to the presence of a labile (monomeric form) or easy accessible vacant co-ordination site (dimers and/or oligomers) for potential binding and/or activating of substrates.

In this paper we present the syntheses of a Schiff-base complex, $[\text{Mo}(\text{O})_2(3,5\text{-di-tert-Busap})(\text{EtOH})]$ (1), and its characterisation by spectroscopic and X-ray diffraction analysis. The complex is stable in the solid state (no changes were observed during 10 months storage) whereas the analogue $[\text{Mo}(\text{O})_2(\text{sap})(\text{EtOH})]$ loses the co-ordinated ethanol slowly with simultaneous disappearance of its orange colour. The brown product formed from $[\text{Mo}(\text{O})_2(\text{sap})(\text{EtOH})]$ is probably an oxo-bridged oligomer⁶ or dimer⁵, revertible to its original mononuclear form when treated with ethanol. Thermogravimetric analysis shows that both complexes lose the co-ordinated ethanol in the ranges 413–433 and 363–373 K, respectively for $[\text{Mo}(\text{O})_2(3,5\text{-di-tert-Busap})(\text{EtOH})]$ and $[\text{Mo}(\text{O})_2(\text{sap})(\text{EtOH})]$.



Scheme 1

* To receive any correspondence. E-mail: js@wchuwr.chem.uni.wroc.pl

† This is a Short Paper, there is therefore no corresponding material in *J. Chem. Research (M)*.

The IR spectral data of the complex are typical for a co-ordinated anionic Schiff base and oxygen donor. The complex does not show a phenolic $\nu(\text{O-H})$ band and the $\delta(\text{C-O})$ band at 1258 and 1284 cm^{-1} has shifted to higher wavenumber compared to the free ligand (1170 and 1202 cm^{-1}), both suggestive of co-ordination of the phenolic C–O groups. The characteristic frequency $\nu(\text{C=N})$ of the free ligand observed at 1616 cm^{-1} displays a shift to lower frequency at 1611 cm^{-1} , indicating co-ordination of the azomethine nitrogen to molybdenum. A broad band at 3269 cm^{-1} and medium one at 1047 cm^{-1} are characteristic of co-ordinated ethanol. An additional $\delta(\text{Mo-O})$ band at 575 cm^{-1} appears after complexation. The complex exhibits strong infrared absorptions at 933 and 916 cm^{-1} (Figure 1), which are characteristic of the *cis*- $\text{Mo}(\text{O})_2^{2+}$ group.³

The complex free of ethanol (bands at 3269 and 1047 cm^{-1} disappear) as well as absorption within the 940–900 cm^{-1} range, shows a very intensive absorptions at 862 and 836 cm^{-1} (Figure 1). The changes in the IR spectrum of both compounds are very similar to those observed for $[\text{Mo}(\text{O})_2(\text{sae})(\text{H}_2\text{O})]$ and $[\text{Mo}(\text{O})(\mu\text{-O})(\text{sae})]_2$ complexes.⁵

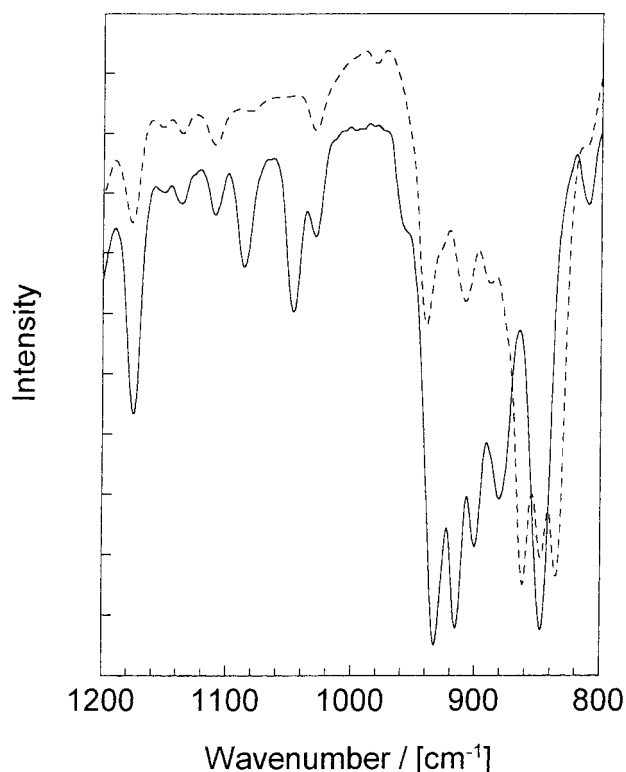


Fig. 1 IR spectrum of $[\text{Mo}(\text{O})_2(3,5\text{-di-tert-Busap})(\text{EtOH})]$ (full line) and $[\text{Mo}(\text{O})(\mu\text{-O})(3,5\text{-di-tert-Busap})]_2$ (dashed line).

Raman spectra of these complexes (Figure 2) exhibited peaks at the range 1620–1540 cm^{-1} corresponding to symmetric and asymmetric stretchings of the $-\text{HC}=\text{N}-\text{C}_{\text{Ph}}$ framework. Only medium and weak peaks at 928 and 919 cm^{-1} appeared in the metal-oxo region of monomeric complex. However, the Raman spectrum of the dimeric compound exhibited strong and very strong peaks at 939 and 832 cm^{-1} , respectively.

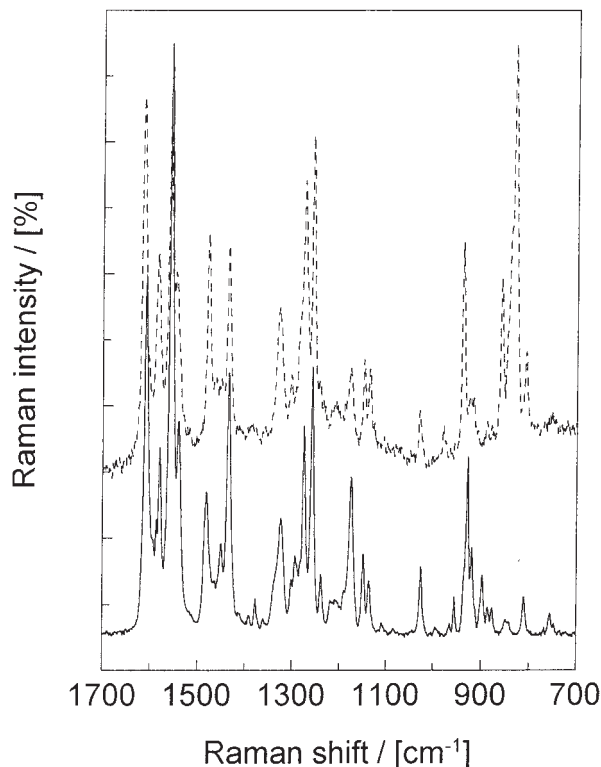


Fig. 2 Raman spectrum of $[\text{Mo}(\text{O})_2(3,5\text{-di-tert-Busap})(\text{EtOH})]$ (full line) and $[\text{Mo}(\text{O})(\mu\text{-O})(3,5\text{-di-tert-Busap})_2]$ (dashed line).

In UV/vis spectrum the $[\text{Mo}(\text{O})_2(3,5\text{-di-tert-Busap})(\text{EtOH})]$ complex exhibits a maximum at 428 nm that is assigned to ligand–metal charge transfer. Additional absorption bands observed at higher energies (356, 313, 244 and 224 nm) are assigned to inter- and intraligand transitions.

The ^1H NMR spectrum of the complex exhibits the CH_3 resonances at 1.18, 1.35 and 1.40 ppm (last two from nonequivalent *tert*-Bu substituents), $-\text{CH}_2-$ protons at 3.69 ppm, the $-\text{O}-\text{H}$ proton at 2.29 ppm (from ethanol), and phenyl and substituted phenyl protons are observed at the range 6.8–7.6 ppm and $-\text{CH}=\text{N}-$ proton at 8.90 ppm. Similarly, the ^{13}C NMR spectra display all the ^{13}C atoms in the ligands coordinated to molybdenum.

A view of the $[\text{Mo}(\text{O})_2(3,5\text{-di-tert-Busap})(\text{EtOH})]$ structure is presented in Figure 3. The co-ordination geometry around the molybdenum atom corresponds to a distorted octahedron. Two oxygen and one nitrogen atoms of the 3,5-di-tert-Busap²⁻ ligand, as well as the oxo group build a basal plane, whereas the other oxo ligand and the oxygen atom of the ethanol molecule are in axial positions. The geometry of the dioxo-Mo(VI) centre is similar to that observed in other molybdenum complexes,^{7–9} in which favourable $p_{\pi}-d_{\pi}$ orbital interactions between the π -base oxo ligands and the π -acid metal centre are optimised when a *cis*-conformation arrangement is adopted. The Mo–O(oxo) bond lengths of 1.699(4) and 1.693(4) Å correspond to those found in other oxo–Mo complexes. The Schiff base ligand displays *mer*-co-ordination

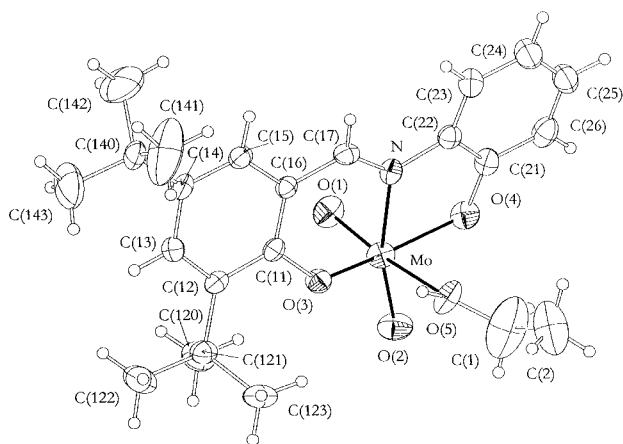


Fig. 3 Structure of $[\text{Mo}(\text{O})_2(3,5\text{-di-tert-Busap})(\text{EtOH})]$ showing 30% probability ellipsoids and the atom-labelling scheme.

as found in $\text{X}[\text{MoOCl}_2(\text{sap})]$ ⁷ and $[\text{Mo}(\text{O})_2(5\text{-tert-Busap})(\text{MeOH})]\cdot\text{MeOH}$ ⁸. In contrast, the *fac*-arrangement is found in $[\text{MoO}(\text{sap})(\text{cat})]$ ¹⁰. The Schiff base ligand acts as a tridentate ligand through its nitrogen and oxygen atoms, respectively, leading to the formation of five-membered and six-membered chelating rings around the Mo atom. The five-membered ring is quite planar. The C–O–Mo angle of the six-membered ring ($134.9(3)^\circ$) is larger than that of the corresponding atoms of the five-membered ring ($122.1(4)^\circ$). The Mo–O distance of the five-membered ring is shorter (1.918(4) Å) than that of the six-membered ring (1.955(4) Å). The Mo–N and Mo–O(5) bond distances: 2.261(5) and 2.340(4) Å, respectively, are considerably elongated due to the *trans* influence of the two terminal oxo ligands. The Schiff base system is slightly twisted, as is indicated by angle of $14.8(3)^\circ$, between two planes passing through the carbon atoms of the phenyl rings.

In conclusion, we report herein the synthesis and the characterization of the new molybdenum complexes with Schiff base: 3,5-di-tert-butyl-N-salicylidene-2-aminophenol. The stability of the $[\text{Mo}(\text{O})_2(3,5\text{-di-tert-Busap})(\text{EtOH})]$, compared to $[\text{Mo}(\text{O})_2(\text{sap})(\text{EtOH})]$, is determined rather by the basicity of the N atom than steric hindrances of the tridentate ligand. On basis of spectral results, removal of EtOH from the coordination sphere gives a dimeric molybdenum(VI) complex with an asymmetric double oxygen bridge.

Experimental

Standard pure grade commercial reagents and solvents have been used. $\text{Mo}(\text{O})_2(\text{acac})_2$ was prepared according to a literature procedure.¹¹

The crystal data were collected on a KUMA KM-4 four-circle diffractometer. IR and Raman spectra were measured using Impact 400 (Nicolet) and Nicolet 860 instruments with Raman Accessory spectrophotometers, respectively. UV-visible electronic spectra were obtained by using a Hewlett Packard Model 8452A Diode Array spectrophotometer and ^1H and ^{13}C NMR spectra were recorded on Bruker 300 spectrometer. A MOM Derivatograf 1500Q was used for thermal analysis. A Hewlett Packard 5890 II series gas chromatograph coupled with Hewlett Packard model mass selective detector was used for the GC/MS analyses. Elemental analyses were performed in the Microanalytical Laboratory of the Faculty of Chemistry, University of Wrocław. Melting points were obtained on a Boëtius apparatus and are uncorrected.

Preparation of 3,5-di-tert-butyl-N-salicylidene-2-aminophenol ($\text{H}_23,5\text{-di-tert-Busap}$): The Schiff base, $\text{H}_23,5\text{-di-tert-Busap}$, was obtained *via* condensation of 3,5-di-tert-butyl-2-hydroxybenzaldehyde (1.53 g, 6.5 mmol) and 2-aminophenol (0.71 g, 6.5 mmol) in toluene (40 ml). Progress of the condensation reaction was monitored by GC/MS. After the reaction was complete (3 days), the solvent was evaporated under vacuum and the dark-red crystals were washed with

hexane and dried *in vacuo* to afford 2g (94%) of product; m.p. 138–139°C. IR (KBr disk): $\nu(\text{O-H})$ 3546 m, 3488 m; $\nu(\text{C-H})$ 3073 w, 3042 w, 2956 vs, 2910 m, 2871 m; $\nu(\text{C=N})$ 1616 vs; $\nu(\text{C-C})$ 1584 vs; $\delta(\text{C-C})$ 1490 vs, 1464 m, 1437 s; $\delta(\text{C-O}_{\text{Ph}})$ 1202 s; 1170 vs; $\delta(\text{C-C}_{\text{Ph}})$ 756 s; UV/VIS (MeOH) $-\lambda_{\text{max}}$, nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 454 (444), 356 (11330), 346 (11100), 276 (11520), 230 (17500) 216 (22610); ^1H NMR (CDCl_3 , at 25°C): δ 1.35 (s, 9H, $-\text{C}(\text{CH}_3)_3$), 1.40 (s, 9H, $-\text{C}(\text{CH}_3)_3$), 6.8 (d, 1H, Ph), 6.9 (t, 1H, Ph), 7.2 (t, 1H, Ph), 7.3 (d, 1H, Ph), 7.5 (d, 1H, Ph), 7.6 (d, 1H, Ph), 8.9 (s, 1H, $-\text{HC=N-}$) ppm. (Found: C 77.1, H 8.7, N 4.1 %; $\text{C}_{21}\text{H}_{27}\text{NO}_2$ requires C 77.50, H 8.36, N 4.30 %).

Preparation of $[\text{Mo}(\text{O})_2(3,5\text{-di-tert-Busap})(\text{EtOH})]$: To a solution of $\text{Mo}(\text{O})_2(\text{acac})_2$ (0.656 g, 2 mmol) in EtOH (30 ml) solid $\text{H}_23,5\text{-di-tert-Busap}$ (0.655 g, 2 mmol) was added. Next, the reaction mixture was heated under reflux. After 2 h the red solution was cooled down to room temperature and left for crystallisation. After a few days, orange crystals were collected by filtration, washed with ethanol and dried *in vacuo*; yield 0.7g (70%). IR (KBr disk) and Raman (in parentheses): $\nu(\text{O-H})$ 3269 m,br; $\nu(\text{C-H})$ 3068 w (3063 vw), 2958 s (2960 w), 2905 m (2902 w), 2869 m (2872 w); $\nu(\text{C=N})$ 1611 vs (1609 s); $\nu(\text{C-C})$ 1587 m, 1557 s (1556 vs, 1540 m); $\delta(\text{C-C})$ 1481 vs (1481 m, 1435 m); $\delta(\text{C-O}_{\text{Ph}})$ 1258 vs (1275 m, 1258 m); $\delta(\text{C-O}_{\text{EtOH}})$ 1047 m (1175 m); $\nu(\text{Mo-O})$ 933 vs (928 m), 916 vs (919 w); $\gamma(\text{C-H}_{\text{Ar}})$ 848 vs; $\delta(\text{C-C}_{\text{Ph}})$ 749 s; $\delta(\text{Mo-O})$ 574 m (574 w) cm^{-1} ; UV/VIS (EtOH) $-\lambda_{\text{max}}$, nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 428 (5140), 356 (9100), 313 (22550), 244 (22780), 224 (35770); ^1H NMR (CDCl_3 , at 25°C): δ 1.18 (t, 3H, $-\text{CH}_2\text{CH}_3$), 1.35 (s, 9H, $-\text{C}(\text{CH}_3)_3$), 1.40 (s, 9H, $-\text{C}(\text{CH}_3)_3$), 2.29 (s, 1H EtOH), 3.69 (m, 2H, $-\text{CH}_2-$), 6.8 (d, 1H, Ph), 6.9 (t, 1H, Ph), 7.2 (t, 1H, Ph), 7.3 (d, 1H, Ph), 7.5 (d, 1H, Ph), 7.6 (d, 1H, Ph), 8.9 (s, 1H, $-\text{HC=N-}$) ppm; ^{13}C NMR (CDCl_3 , at 25°C): δ 18.05 ($-\text{CH}_2\text{CH}_3$), 29.76 ($-\text{C}(\text{CH}_3)_3$), 31.30 ($-\text{C}(\text{CH}_3)_3$), 34.41 ($-\text{C}(\text{CH}_3)_3$), 35.31 ($-\text{C}(\text{CH}_3)_3$), 59.03 ($-\text{CH}_2\text{CH}_3$), 114.61, 117.96, 120.87, 120.97, 128.72, 130.18 (all $\text{C}_{\text{Ar}}-\text{H}$), 131.78, 135.70, 139.55, 144.06, 157.19, 159.25 (all $\text{C}_{\text{Ar}}-\text{t-Bu}$), 160.53 ($-\text{HC=N-}$) ppm. (Found: C 54.4, H 6.2, N 3.0, Mo 20.0, EtOH 9.4 % (thermogravimetrically); $\text{C}_{23}\text{H}_{31}\text{NMoO}_5$ requires C 55.53, H 6.28, N 2.82, Mo 19.29, EtOH 9.26 %).

Preparation of $[\text{Mo}(\text{O})(\mu\text{-O})(3,5\text{-di-tert-Busap})_2]$: Slow evaporation of the $\text{Mo}(\text{O})_2(3,5\text{-di-tert-Busap})(\text{EtOH})$ complex solution in chloroform gives dark-red microcrystalline compound without the ethanol molecule. IR (KBr disk) and Raman (in parentheses): $\nu(\text{C-H})$ 3074 w (3067) vw), 2959 s (2959 w), 2905 sh (2901 w), 2869 m (2874 w); $\nu(\text{C=N})$ 1613 vs (1614 vs); $\nu(\text{C-C})$ 1588 m, 1559 m, 1548 m (1584 m, 1558 vs, 1546 m); $\delta(\text{C-C})$ 1479 vs (1478 m, 1436 m); $\delta(\text{C-O}_{\text{Ph}})$ 1256 vs (1274 s, 1257 vs); $\nu(\text{Mo-O})$ 940 m (939 m), 909ms, 889 sh, 862 vs, 836 vs (832 vs); $\gamma(\text{C-H}_{\text{Ar}})$ 848 vs (860 m); $\delta(\text{C-C}_{\text{Ph}})$ 751 m; $\delta(\text{Mo-O})$ 575 m (575 w) cm^{-1} ; (Found: C 55.4, H 5.3, N 3.0, Mo 21.0; $\text{C}_{21}\text{H}_{25}\text{NMoO}_4$ requires C 55.88, H 5.58, N 3.10, Mo 21.26 %).

Determination and refinement of the structure: Crystal data: $\text{C}_{23}\text{H}_{31}\text{NMoO}_5$, $M_r = 497.43$, monoclinic, $\text{P}2_1/c$, $a = 13.814(3)$, $b = 10.949(3)$, $c = 17.245(3)$ Å, $\beta = 113.33(3)^\circ$, $V = 2395.0(8)$ Å³, $D_x = 1.380$ g·cm⁻³, $Z = 4$, $T = 298(2)$. An orange crystal was used for data collection with a KUMA KM-4 four-circle diffractometer¹² using graphite-monochromated $\text{Mo-K}\alpha$ radiation (0.71073 Å). Intensities were collected with ω - 2θ scan mode up to $2\theta = 44^\circ$. After each group of 100 reflections three standard intensities were monitored and no evidence of crystal decay was observed. The data were corrected for Lorentz and polarisation factors. From a total of 2008 reflections measured ($0 \leq h \leq 10$, $0 \leq k \leq 11$, $-16 \leq l \leq 16$), 1874 were independent and 1625 reflections were considered observed using the criteria $I > 2\sigma(I)$. The structure was solved by direct methods (SHELXS86)¹³ and refined on F^2 by full-matrix least-squares

program (SHELXL93).¹⁴ All non-hydrogen atoms were refined anisotropically. The carbon bonded H-atoms were included in calculating the positions and refined using a riding model with isotropic displacement parameters equal to 1.2 U_{eq} of the attached C atom. Other H atoms were located from the difference Fourier map and refined without any constraints. The final of R and wR_2 are 0.0313 and 0.0784, respectively. A weighting scheme of the form: $w = 1/2(\text{Fo}^2) + (0.0393\text{P})^2 + 5.55\text{P}$ (where P is defined as $(\text{Fo}^2 + 2\text{Fc}^2)/3$) was applied. The final difference map showed a generally featureless background within -0.26 and 0.52 eÅ⁻³.

Full crystallographic details for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no CCDC 138458. Copies of the data are available from the CCDC, 12 Union Road, Cambridge CB2, 1EZ, UK (Fax: +44 (1223) 336-033; e-mail: deposit@ccdc.cam.ac.uk).

Financial support by a grant no. 2 P303 156 04 from the Polish Committee of Scientific Researches (KBN) is gratefully acknowledged.

Received 9 April 2000; accepted 10 June 2000

Paper 00/259

References

- R.H. Holm, P. Kennepohl, E.I. Solomon, *Chem.Rev.*, 1996, **96**, 2239; D. Collison, C.D. Garner, J.A. Joule, *Chem.Soc.Rev.*, 1996, **25**, 25.
- A. Keller, J.M. Sobczak, J.J. Ziólkowski, in "Molybdenum: An Outline of its Chemistry and Uses", E.R. Braithwaite, J. Haber, Eds., Elsevier: Amsterdam, 1994; pp 618–649.
- A. Syamal, M.R. Maurya, *Coord.Chem.Rev.*, 1989, **95**, 183.
- E.I. Stiefel, in "Comprehensive Coordination Chemistry", G. Wilkinson, R.D. Gillard, J.A. McCleverty, Eds., Pergamon Press: Oxford, 1987, **Vol.3**, pp 1375–1420.
- J.M. Sobczak, T. Glowiak, J.J. Ziólkowski, *Transition Met. Chem.*, 1990, **15**, 208.
- O.A. Rajan, A. Chakravorty, *Inorg.Chem.*, 1981, **20**, 660.
- K. Yamanouchi, S. Yamada, J.H. Enemark, *Inorg.Chim.Acta*, 1984, **85**, 129.
- J.A. Craig, E.W. Harlan, B.S. Snyder, M.A. Whitener, R.H. Holm, *Inorg.Chem.*, 1989, **28**, 2082.
- C.J. Hinshaw, G. Peng, R. Singh, J.T. Spence, J.H. Enemark, M. Bruck, J. Kristofzski, S.L. Merbs, R.B. Ortega, P.A. Wexler, *Inorg.Chem.*, 1989, **28**, 4483.
- J.U. Mondal, F.A. Schultz, T.D. Brennan, W.R. Scheidt, *Inorg.Chem.*, 1988, **27**, 3950.
- G.J.J. Chen, J.W. McDonald, W.E. Newton, *Inorg.Chem.*, 1976, **15**, 2612.
- Kuma Diffraction (1996). Kuma KM4 software. *User's Guide*, version 6.1. Kuma Diffraction, Wroclaw, Poland.
- G.M. Sheldrick, *Acta Cryst.*, 1990, **A46**, 467.
- G.M. Sheldrick, *SHELXL93*. Program for the Refinement of Crystal Structures; University of Göttingen, Germany, 1993.