Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1022). Services for accessing these data are described at the back of the journal.

References

Buang, N. A., Hughes, D. L., Kashef, N., Richards, R. L. & Pombeiro, A. J. L. (1987). *J. Organomet. Chem.* **323**, C47–C50.

Christensen, M. T., Eaton, D. R., Green, B. A. & Thompson, H. W. (1956). *Proc. R. Soc. London*, **A238**, 15–30.

Demarne, H. & Cadiot, P. (1968). *Bull. Soc. Chim. Fr.* pp. 211–216.

Eisch, J. J. & Biedermann, J.-M. (1971). *J. Organomet. Chem.* **30**, 167–176.

Imoto, H. (1996). *ANYBLK*. Version 2.6j. *Program for Least-Squares Refinement*. Department of Chemistry, The University of Tokyo, Hongo, Tokyo, Japan.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Johnston, D. H., Gaswick, D. C., Lonergan, M. C., Stern, C. L. & Shriver, D. F. (1992). *Inorg. Chem.* **31**, 1869–1873.

Johnston, D. H., Stern, C. L. & Shriver, D. F. (1992). *Inorg. Chem.* **31**, 1869–1873.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.

Pombeiro, A. J. L., Hills, A., Hughes, D. L. & Richards, R. L. (1990). *J. Organomet. Chem.* **398**, C15–C18.

Rigaku Corporation (1985). *AFD. Diffractometer Control Program System*. Rigaku Corporation, Tokyo, Japan.

Saito, T., Nishida, M., Yamagata, T., Yamagata, Y. & Yamaguchi, Y. (1986). *Inorg. Chem.* **25**, 1111–1117.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1997). C**53**, 862–864

A Dioxomolybdenum(VI) Complex with a New Enantiomerically Pure Tetrahydrosalen Ligand

HORST ELIAS,[a] FRANK STOCK[a] AND CAROLINE RÖHR[b]

[a]*Institut für Anorganische Chemie, Technische Hochschule Darmstadt, Petersenstrasse 18, D-64287 Darmstadt, Germany, and* [b]*Institut für Anorganische und Analytische Chemie, Universität Freiburg, Albertstrasse 21, D-79104 Freiburg, Germany. E-mail: caroline@ruby.chemie.uni-freiburg.de*

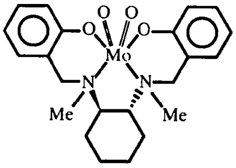
(*Received 14 October 1996; accepted 26 February 1997*)

Abstract

The enantiomerically pure tetradentate ligand H_2L {2,2′-[*trans*-(*R*,*R*)-1,2-cyclohexanediylbis(*N*-methylaminomethyl)]diphenol} forms a neutral dioxomolybdenum(VI) complex, which was isolated as {2,2′-[*trans*-(*R*,*R*)-1,2-cyclohexanediylbis(*N*-methylaminomethyl)]diphenolato-*O*,*N*,*N*′,*O*′}dioxomolybdenum(VI) trichloromethane solvate, $[MoO_2(C_{22}H_{28}N_2O_2)].CHCl_3$, and characterized by a single-crystal X-ray analysis. The coordination geometry around the metal is distorted octahedral. The two oxo O atoms are *cis* and the two phenolate O atoms are in (distorted) *trans* positions. The two N atoms are located approximately *trans* to the oxo O atoms and the Mo—N bonds are remarkably long.

Comment

Molybdenum is an essential element in many enzymes (Spiro, 1985) and plays an important role in industrial oxidation processes (Ullmann's Encyclopedia of Industrial Chemistry, 1993). Numerous Schiff-base complexes containing the MoO_2^{2+} unit have been prepared and studied (Morris, 1995, 1996). However, little is known about the corresponding tetrahydrosalen complexes (Rajan *et al.*, 1983). As part of our studies on the synthesis, characterization and catalytic potential of neutral six-coordinate salen-type Mo complexes, we report here the structure determination of the new chiral *cis*-dioxo–Mo^{VI} complex, (I).



(I)

Complex (I) has a distorted octahedral geometry with approximate C_2 symmetry. The two oxo O atoms are *cis* with respect to one another and to the phenolate O atoms

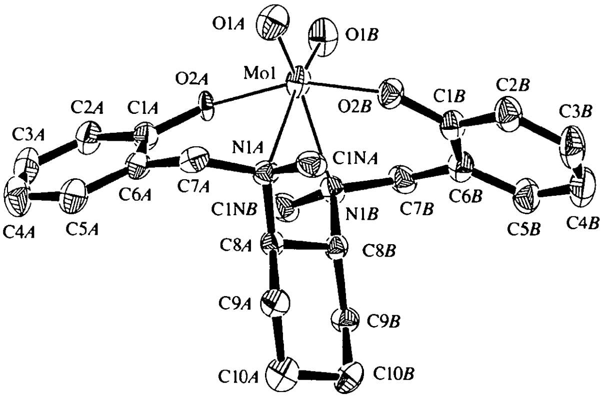


Fig. 1. *ORTEP* (Johnson, 1965) view of the title compound showing the labelling scheme for the non-H atoms. Displacement ellipsoids are drawn at the 50% probability level and H atoms have been omitted.

Acta Crystallographica Section C
ISSN 0108-2701 © 1997

of the ligand. The Mo—O(oxo) bond distances are 1.703 (4) and 1.714 (3) Å, and the Mo—O(phenolate) distances are 1.946 (3) and 1.945 (3) Å. The extreme length of the Mo—N bonds [2.400 (4) and 2.413 (4) Å] is attributed to the *trans* influence of the oxo groups. The two tertiary amine N atoms are located nearly *trans* to the oxo O atoms. Other bond lengths and angles are close to those reported earlier for dioxomolybdenum(VI) complexes with tetradentate ligands (Hinshaw *et al.*, 1989; Subramanian, Spence, Ortega & Enemark, 1984). The crystal packing shows layers (in the *ab* plane) of isolated complex molecules without any specific intermolecular interaction, separated by layers of disordered chloroform molecules.

Experimental

Commercially available chemicals were used as received. The synthesis of the Schiff base bis(salicylidene)cyclohexanediamine and its hydrogenation to the corresponding tetrahydrosalen compound has been described previously (Böttcher *et al.*, 1994). The *N*,*N*′-dimethylation was carried out (Borch, Bernstein & Durst, 1971) as follows. A solution of 2.6 g (8 mmol) of 2,2′-[*trans*-(*R*,*R*)-1,2-cyclohexanediylbis(aminomethyl)]diphenol and 6 ml (75 mmol) of 37% aqueous formaldehyde in 110 ml of acetonitrile and 16 ml of glacial acetic acid was stirred for 20 min at room temperature. Then 2.0 g of $Na[(CN)BH_3]$ (32 mmol) were added in one portion. Stirring was continued for 12 h. The acetonitrile solvent was evaporated *in vacuo* and 50 ml of 4 *N* NaOH were added to the residue. The resulting mixture was extracted with three 20 ml portions of CH_2Cl_2. The combined organic extracts were neutralized with 20 ml of saturated aqueous $NaHCO_3$, dried (Na_2SO_4) and evaporated *in vacuo* to give 2.7 g of H_2L as a colourless glassy oil.

Complex (I) was prepared by ligand exchange with $MoO_2(acac)_2$ in the following way. A stirred solution of 2 mmol of H_2L in 10 ml of MeOH was heated and a solution of 2 mmol of $MoO_2(acac)_2$ in 60 ml of MeOH was added. The mixture initially turned light yellow and gradually changed to brown. The deep-brown solution was stirred for 20 min and a dark precipitate was separated by filtration. Refluxing of the filtrate was continued for 4 h, then the volume was reduced to about 10 ml. Upon cooling, a brown solid precipitated. The solid residue was separated by filtration and treated twice with 30 ml of $CHCl_3$, which was evaporated to dryness to give yellow (I); yield 40%. Analysis calculated for $MoC_{23}H_{29}N_2O_4Cl_3$: C 46.06, H 4.87, N 4.67%; found: C 46.42, H 4.89, N 4.72%. ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.88–1.88 (*m*, 8H, CH_2), 2.62 (*s*, 6H, NCH_3), 2.62–2.69 (*m*, 2H, CH), 4.40 (*dd*, 4H, CH_2), 6.80–7.28 (*m*, 8H, aryl-H); MS(FD) [*m*/*z* (%)]: 482 [$M^+ - CHCl_3$] (100). Crystals suitable for X-ray analysis were obtained by slow evaporation of a solution of MoO_2L in chloroform–petroleum ether (ratio 4:1) at room temperature.

Crystal data

$[MoO_2(C_{22}H_{28}N_2O_2)].CHCl_3$
$M_r = 599.79$
Monoclinic
$P2_1$
$a = 9.673\ (8)$ Å
$b = 11.935\ (9)$ Å
$c = 11.478\ (8)$ Å
$\beta = 105.22°$
$V = 1278.6\ (9)$ Å^3
$Z = 2$
$D_x = 1.555$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 21 reflections
$\theta = 7.0–17.2°$
$\mu = 0.858$ mm^{-1}
$T = 293\ (2)$ K
Plate
0.50 × 0.40 × 0.15 mm
Yellow

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
3328 measured reflections
3074 independent reflections
3047 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$

$\theta_{max} = 27.5°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 16$
$l = -16 \rightarrow 15$
3 standard reflections every 100 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.101$
$S = 1.066$
3074 reflections
323 parameters
H atoms riding ($CHCl_3$ H atoms not included)
$w = 1/[\sigma^2(F_o^2) + (0.0717P)^2 + 0.4911P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.198$

$\Delta\rho_{max} = 1.03$ e Å^{-3}
$\Delta\rho_{min} = -1.27$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.044 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = −0.07 (5)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Mo1	0.28875 (3)	0.39155 (3)	0.46409 (3)	0.04556 (14)
O1*A*	0.2175 (4)	0.5229 (4)	0.4452 (4)	0.0649 (10)
O1*B*	0.4065 (4)	0.3811 (5)	0.3761 (3)	0.0664 (11)
O2*A*	0.1344 (3)	0.3148 (4)	0.3487 (3)	0.0550 (8)
O2*B*	0.4297 (3)	0.4270 (3)	0.6147 (3)	0.0524 (7)
C1*A*	−0.0042 (5)	0.2892 (4)	0.3313 (4)	0.0481 (9)
C2*A*	−0.0741 (6)	0.2347 (5)	0.2245 (5)	0.0587 (13)
C3*A*	−0.2176 (7)	0.2077 (6)	0.2021 (7)	0.073 (2)
C4*A*	−0.2928 (7)	0.2309 (6)	0.2850 (7)	0.071 (2)
C5*A*	−0.2225 (5)	0.2836 (5)	0.3917 (6)	0.0605 (13)
C6*A*	−0.0798 (5)	0.3144 (4)	0.4160 (4)	0.0466 (9)
C7*A*	−0.0143 (4)	0.3815 (5)	0.5275 (4)	0.0507 (10)
N1*A*	0.1355 (4)	0.3506 (3)	0.5926 (3)	0.0411 (7)
C1N*A*	0.1763 (6)	0.4272 (4)	0.6963 (4)	0.0545 (10)
C8*A*	0.1430 (4)	0.2289 (3)	0.6288 (3)	0.0376 (7)
C9*A*	0.0837 (5)	0.2065 (4)	0.7390 (4)	0.0506 (10)
C10*A*	0.0959 (6)	0.0848 (5)	0.7757 (6)	0.0578 (13)
C10*B*	0.2514 (6)	0.0464 (5)	0.8050 (5)	0.0567 (12)
C9*B*	0.3091 (6)	0.0634 (4)	0.6932 (5)	0.0498 (11)
C8*B*	0.2968 (4)	0.1859 (3)	0.6521 (3)	0.0383 (7)
N1*B*	0.3520 (3)	0.2059 (3)	0.5436 (3)	0.0411 (7)
C1N*B*	0.2971 (5)	0.1222 (5)	0.4453 (4)	0.0536 (11)
C7*B*	0.5117 (4)	0.1971 (5)	0.5754 (4)	0.0526 (10)
C6*B*	0.5882 (4)	0.2706 (5)	0.6781 (4)	0.0499 (10)
C5*B*	0.7061 (6)	0.2282 (7)	0.7647 (5)	0.0656 (15)
C4*B*	0.7793 (6)	0.2921 (8)	0.8601 (6)	0.080 (2)

C3*B*	0.7345 (6)	0.3999 (10)	0.8736 (5)	0.080 (2)
C2*B*	0.6162 (5)	0.4455 (6)	0.7907 (4)	0.0611 (12)
C1*B*	0.5443 (4)	0.3799 (5)	0.6922 (3)	0.0471 (10)
Cl1	0.3029 (10)	0.3680 (9)	0.0956 (5)	0.101 (3)
Cl1*A*†	0.2617 (11)	0.2225 (7)	0.0948 (9)	0.090 (2)
Cl1*B*†	0.2736 (18)	0.2336 (14)	0.0806 (12)	0.171 (6)
Cl2*A*†	0.4236 (17)	0.411 (3)	0.0359 (10)	0.225 (12)
Cl2*B*†	0.4335 (18)	0.379 (2)	0.0047 (8)	0.146 (5)
Cl3	0.1442 (4)	0.4410 (3)	0.0357 (3)	0.1446 (12)

† Site occupancy = 0.50.

Table 2. *Selected geometric parameters (Å, °)*

Mo1—O1*A*	1.703 (4)	C7*A*—N1*A*	1.492 (6)
Mo1—O1*B*	1.714 (3)	N1*A*—C1N*A*	1.470 (6)
Mo1—O2*B*	1.946 (3)	N1*A*—C8*A*	1.508 (5)
Mo1—O2*A*	1.945 (3)	C8*A*—C8*B*	1.529 (5)
Mo1—N1*A*	2.400 (4)	C8*B*—N1*B*	1.498 (5)
Mo1—N1*B*	2.413 (4)	N1*B*—C7*B*	1.496 (5)
O2*A*—C1*A*	1.338 (5)	N1*B*—C1N*B*	1.496 (5)
O2*B*—C1*B*	1.349 (6)		
O1*A*—Mo1—O1*B*	107.5 (2)	C1N*A*—N1*A*—C8*A*	113.2 (3)
O1*A*—Mo1—O2*B*	94.5 (2)	C7*A*—N1*A*—C8*A*	110.3 (4)
O1*B*—Mo1—O2*B*	96.9 (2)	C1N*A*—N1*A*—Mo1	107.1 (3)
O1*A*—Mo1—O2*A*	97.7 (2)	C7*A*—N1*A*—Mo1	108.5 (3)
O1*B*—Mo1—O2*A*	94.3 (2)	C8*A*—N1*A*—Mo1	111.9 (2)
O2*B*—Mo1—O2*A*	160.11 (15)	N1*A*—C8*A*—C8*B*	110.2 (3)
O1*A*—Mo1—N1*A*	88.3 (2)	N1*A*—C8*A*—C9*A*	113.0 (3)
O1*B*—Mo1—N1*A*	163.9 (2)	C8*B*—C8*A*—C9*A*	110.6 (3)
O2*B*—Mo1—N1*A*	84.25 (13)	N1*B*—C8*B*—C8*A*	110.1 (3)
O2*A*—Mo1—N1*A*	80.50 (13)	N1*B*—C8*B*—C9*B*	113.1 (4)
O1*A*—Mo1—N1*B*	161.3 (2)	C8*A*—C8*B*—C9*B*	111.6 (4)
O1*B*—Mo1—N1*B*	90.8 (2)	C7*B*—N1*B*—C1N*B*	106.1 (3)
O2*B*—Mo1—N1*B*	79.32 (13)	C7*B*—N1*B*—C8*B*	110.9 (3)
O2*A*—Mo1—N1*B*	84.15 (15)	C1N*B*—N1*B*—C8*B*	112.8 (3)
N1*A*—Mo1—N1*B*	73.55 (12)	C7*B*—N1*B*—Mo1	107.5 (3)
C1*A*—O2*A*—Mo1	140.3 (3)	C1N*B*—N1*B*—Mo1	108.9 (3)
C1*B*—O2*B*—Mo1	139.3 (3)	C8*B*—N1*B*—Mo1	110.5 (2)
N1*A*—C7*A*—C6*A*	115.6 (4)	N1*B*—C7*B*—C6*B*	114.5 (4)
C1N*A*—N1*A*—C7*A*	105.7 (4)		

Data collection: *XSCANS* (Siemens, 1994). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965).

The authors thank Professor Dr R. Kniep for providing access to the X-ray equipment in his laboratory. The enantiomer *trans*-(*R*,*R*)-1,2-cyclohexane diammonium-di[hydrogen $(-)_L$-tartrate] was kindly provided by Professor J. Springborg, Royal Veterinary and Agricultural University, Department of Inorganic Chemistry, Copenhagen. The authors thank the 'Deutsche Forschungsgemeinschaft', the 'Verband der chemischen Industrie e. V.' and the 'Otto-Röhm-Stiftung'.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MU1300). Services for accessing these data are described at the back of the journal.

References

Borch, R. F., Bernstein, M. D. & Durst, H. D. (1971). *J. Am. Chem. Soc.* **93**, 2897–2904.

Böttcher, A., Elias, H., Glerup, J., Neuburger, M., Olsen, C. E., Paulus, H., Springborg, J. & Zehnder, M. (1994). *Acta Chem. Scand. Ser. A*, **48**, 967–980.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Hinshaw, C. J., Peng, G., Singh, R., Spence, J. T., Enemark, J. H., Bruck, M., Kristofzski, J., Merbs, S. L., Ortega, R. B. & Wexler, P. A. (1989). *Inorg. Chem.* **28**, 4483–4491.

Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.

Morris, M. J. (1995). *Coord. Chem. Rev.* **146**, 43–87.

Morris, M. J. (1996). *Coord. Chem. Rev.* **152**, 310–348.

Rajan, O. A., Spence, J. T., Leman, C., Minelli, M., Sato, M., Enemark, J. H., Kroneck, P. M. H. & Sulger, K. (1983). *Inorg. Chem.* **22**, 3065–3072.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Siemens (1994). *XSCANS. X-ray Single Crystal Analysis System*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Spiro, T. G. (1985). Editor. *Molybdenum Biochemistry*. New York: Wiley.

Subramanian, P., Spence, J. T., Ortega, R. & Enemark, J. H. (1984). *Inorg. Chem.* **23**, 2564–2572.

Ullmann's Encyclopedia of Industrial Chemistry (1993). Vol. A22, 5th ed, pp. 239–260. Weinheim: Verlag Chemie.

Acta Cryst. (1997). C**53**, 864–866

Dichloro(η^6-hexamethylbenzene)(pyridine-*N*)ruthenium

Andrew J. Steedman and Anthony K. Burrell

Department of Chemistry, Massey University, Private Bag 11222, Palmerston North, New Zealand. E-mail: a.k.burrell@massey.ac.nz

(*Received 5 November 1996; accepted 19 February 1997*)

Abstract

The title compound, $[RuCl_2(C_{12}H_{18})(C_5H_5N)]$, crystallizes with two discrete independent molecules per asymmetric unit. In each molecule, the Ru atom displays a 'piano-stool' configuration.

Comment

The title compound was prepared during investigations into the synthesis of terminal imido complexes of ruthenium (Burrell & Steedman, 1995). The ruthenium starting materials for the synthesis of imido complexes are the arene–ruthenium chloride dimers, $[RuCl_2(\eta^6\text{-arene})]_2$, which are poorly soluble in the solvents necessary for the preparation of imido complexes. The pyridine adducts, $[RuCl_2(py)(\eta^6\text{-arene})]$, have been employed in reactions where the dimeric complex gives poor results (Müller, Qiao, Siewing & Westphal,