Oxovanadium(IV) and Dioxomolybdenum(VI) Complexes: Synthesis from the Corresponding Acetylacetonato Complexes and *X*-Ray Structures†

Seunghee Lee and Carlo Floriani *
Chemistry Department, Columbia University, New York, N.Y. 10027, U.S.A.
Angiola Chiesi-Villa and Carlo Guastini
Istituto di Strutturistica Chimica, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Università di Parma, I-43100 Parma, Italy

Displacement of acetylacetonate (acac) from oxometal complexes of this ligand in the reaction with the acidic form of 7,16-dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetra-azacyclotetradecine (H_2L) is a stepwise process. The reaction of [MoO_2(acac)$_2$] with H_2L in tetrahydronaphthalene gave a partial displacement of the acetylacetonato ligand and formation of [MoO_2(acac)(HL)] (**1**). Two nitrogen atoms only from the macrocycle bind molybdenum, which is six-co-ordinate with the two oxo groups in a *cis* arrangement [ν(Mo–O) 895 and 927 cm^{-1}]. A complete displacement of the acetylacetone occurs in [VO(acac)$_2$] leading to the formation of [VO(L)] (**2**). Vanadium has a pseudo-square-pyramidal co-ordination geometry in (**2**), with the L ligand assuming the usual 'saddle' shape conformation [ν(V–O) 978 cm^{-1}]. The structures of (**1**) and (**2**) have been determined by *X*-ray analysis.

The chemistry of the M=O inorganic functionality has attracted a lot of attention for its role in oxidation catalysed by metals,[1,2] for its relationship with the organic ketonic functionality,[3] and as a group allowing the introduction of other functionalities at the metal.[3,4] Such a study is profitably carried out when the M=O functionality is trapped with a macrocyclic ligand, avoiding the complication of other ligands around the metal, and controlling the stereochemistry. Among the transition metal cations, the oxovanadium, VO^{2+},[5] and the dioxomolybdenum species $MoO_2{}^{2+}$,[6] are the most studied.

An interesting ligand for trapping the M=O functionality is 7,16-dihydro-6,8,15,17-tetramethyldibenzo[*b*,*i*][1,4,8,11]tetra-azacyclotetradecine (H_2L) which provides a suitable cavity for the M=O group. An early report on the synthesis and some interesting chemical aspects of [VO(L)] have appeared,[7] but its structure has never been determined.

We found that the synthetic methods used previously for oxo-cation complexes, though very diversified, are not very good, particularly when using non-aqueous solvents.[5,6] Displacement of Hacac (acetylacetone) from [MO_n(acac)$_m$] complexes can be carried out in hydrocarbon solvents with the acidic form of the macrocyclic ligand distilling out Hacac.[8] We report here the reaction of [VO(acac)$_2$] and [MoO_2(acac)$_2$] with H_2L and the structure of the resulting products.

Experimental

All syntheses were carried out under an atmosphere of purified nitrogen. Solvents were purified and dried by standard methods. Infrared spectra were recorded with a Perkin-Elmer 983 spectrophotometer. ^1H N.m.r. spectra of molybdenum complexes were taken with a 300-MHz Bruker spectrometer. The ligand H_2L[9] and [VO(O_2CMe)$_2$][10] were prepared by published procedures; [MoO_2(acac)$_2$] and [VO(acac)$_2$] were commercial products.

Synthesis of [MoO_2(acac)(HL)] (**1**).—To a suspension of H_2L (7.8 g, 22.7 mmol) in distilled tetrahydronaphthalene (thnp) (180 cm^3) was added bis(acetylacetonato)dioxomolybdenum, [MoO_2(acac)$_2$] (7.4 g, 22.7 mmol). The reaction mixture was heated to 130 °C for 1 h. All the reagents dissolved completely to give a dark brick-red solution at about 120 °C. It was cooled slowly and gave amber coloured crystals and powder (yield 70%). The product was recrystallized from hot toluene (Found: C, 56.60; H, 5.60; Mo, 16.90; N, 9.70. $C_{22}H_{23}MoN_4O_2{\cdot}C_5H_7O_2$ requires C, 56.85; H, 5.30; Mo, 16.80; N, 9.80%). The i.r. spectrum shows two strong bands at 895 and 927 cm^{-1} (Mo–O). In the ^1H n.m.r. (20 °C in $CDCl_3$) a singlet (1 H) at δ 12.65 p.p.m. was assigned as the amine proton in HL, a multiplet (8 H) at 7.38—6.65 p.p.m. as aromatic hydrogens, singlets (3 H) at 5.72—4.65 p.p.m. as methine protons in HL and acac, and singlets (18 H) at 1.98—1.40 p.p.m. as methyl protons.

Pyrolysis of [MoO_2(acac)(HL)].—In order to remove another acetylacetone from the complex, (**1**) was heated to 180 °C *in vacuo* for 20 h. The pyrolysed product was recrystallised from toluene. The i.r. spectrum shows the same bands as that of compound (**1**) at 895 and 927 cm^{-1}(Mo–O). The n.m.r. spectrum shows the same spectrum as that of compound (**1**).

Synthesis of [VO(L)] (**2**).—Bis(acetato)oxovanadium, [VO(O_2CMe)$_2$] (10 g, 54.1 mmol), was added to suspension of H_2L (19 g, 55.2 mmol) in toluene (500 cm^3). The reaction mixture was refluxed with stirring for 20 h and cooled slowly. The deep green crystalline product (yield 77%), was filtered off and dried *in vacuo* (Found: C, 67.40; H, 5.90; N, 12.60; V, 11.55. $C_{22}H_{22}N_4OV{\cdot}0.33C_7H_8$ requires C, 66.40; H, 5.65; N, 12.75; V, 11.60%). The i.r. spectrum shows a strong band at 978 cm^{-1} (V–O). Synthesis of (**2**), having comparable yields, was equally well performed in toluene using [VO(acac)$_2$]. The *X*-ray analysis was performed on the deep purple crystals obtained from thf.

X-*Ray Structure Determination of* [MoO_2(acac)(HL)] (**1**) *and* [VO(L)] (**2**).—*Crystal data for* (**1**). $C_{27}H_{30}MoN_4O_4$, M = 570.5, monoclinic, a = 9.480(2), b = 15.865(4), c = 18.133(4) Å, β = 104.95(2)°, U = 2 635(1) Å^3, Z = 4, D_c = 1.438 g cm^{-3}, $F(000)$ = 1 176, Mo-K_α radiation, λ = 0.710 69 Å, μ(Mo-K_α) = 5.22 cm^{-1}, space group $P2_1/c$.

Crystal data for (**2**). $C_{22}H_{22}N_4OV{\cdot}C_4H_8O$, M = 481.5,

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Fractional atomic co-ordinates ($\times 10^4$) for complex (**1**)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Mo	237(1)	1 407(1)	1 561(1)	C(12)	6 019(12)	311(8)	2 130(7)
O(1)	−572(7)	1 666(5)	2 244(3)	C(13)	5 069(13)	38(7)	2 562(8)
O(2)	620(8)	312(4)	1 723(4)	C(14)	3 853(11)	506(7)	2 568(6)
N(1)	196(8)	2 756(5)	1 195(4)	C(15)	3 614(9)	1 279(6)	2 169(5)
N(2)	2 142(9)	3 134(5)	342(5)	C(16)	2 531(11)	2 497(7)	2 605(5)
N(3)	4 195(9)	2 284(5)	1 326(5)	C(17)	1 598(10)	3 175(7)	2 435(6)
N(4)	2 334(8)	1 774(5)	2 173(4)	C(18)	659(11)	3 352(6)	1 705(5)
C(1)	−346(10)	3 035(6)	404(5)	C(19)	2 827(13)	4 548(8)	−69(9)
C(2)	−1 839(11)	3 056(7)	76(6)	C(20)	6 610(11)	2 977(8)	1 835(7)
C(3)	−2 342(13)	3 299(8)	−698(7)	C(21)	3 879(13)	2 575(8)	3 275(6)
C(4)	−1 396(13)	3 436(7)	−1 133(5)	C(22)	289(14)	4 267(7)	1 547(7)
C(5)	67(12)	3 395(7)	−804(6)	O(3)	1 241(7)	1 300(4)	617(3)
C(6)	643(11)	3 215(7)	−21(6)	O(4)	−1 579(6)	1 271(4)	758(3)
C(7)	3 159(12)	3 717(7)	351(6)	C(23)	−3 514(17)	950(12)	−316(10)
C(8)	4 596(11)	3 606(7)	798(6)	C(24)	−1 878(16)	1 064(9)	71(9)
C(9)	5 088(11)	2 916(7)	1 293(6)	C(25)	−887(17)	967(10)	−380(8)
C(10)	4 545(10)	1 546(6)	1 750(5)	C(26)	653(17)	1 118(8)	−52(8)
C(11)	5 754(12)	1 071(7)	1 728(6)	C(27)	1 776(24)	1 088(10)	−540(10)

Table 2. Fractional atomic co-ordinates ($\times 10^4$) for complex (**2**)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
V	2 110(1)	1 381(1)	783(1)	C(12)	2 823(7)	−1 880(7)	3 805(9)
O(1)	1 154(4)	2 135(4)	1 944(5)	C(13)	1 877(7)	−2 027(6)	2 683(10)
N(1)	1 520(4)	1 897(5)	−1 400(6)	C(14)	1 508(6)	−1 475(6)	1 316(9)
N(2)	3 214(5)	2 251(5)	766(6)	C(15)	2 118(5)	−793(5)	1 090(7)
N(3)	3 509(4)	198(4)	1 967(6)	C(16)	1 477(5)	−506(6)	−1 693(8)
N(4)	1 806(4)	−125(4)	−185(6)	C(17)	1 230(5)	150(6)	−2 920(8)
C(1)	1 553(6)	3 049(6)	−1 206(8)	C(18)	1 251(5)	1 278(6)	−2 804(8)
C(2)	693(7)	3 983(7)	−1 919(9)	C(19)	5 085(7)	2 634(7)	968(9)
C(3)	755(8)	5 080(7)	−1 545(11)	C(20)	5 621(6)	−945(6)	2 965(8)
C(4)	1 674(9)	5 275(7)	−380(11)	C(21)	1 445(6)	−1 735(6)	−2 226(9)
C(5)	2 529(8)	4 367(7)	409(9)	C(22)	1 034(7)	1 745(7)	−4 360(8)
C(6)	2 492(6)	3 239(6)	−19(8)	O(1S)	2 352(13)	5 491(9)	4 913(14)
C(7)	4 379(6)	1 950(6)	1 263(7)	C(1S)	3 485(14)	5 370(13)	5 851(25)
C(8)	5 045(6)	956(6)	2 006(8)	C(2S)	3 954(33)	4 357(41)	6 615(59)
C(9)	4 658(5)	125(6)	2 307(7)	C(2′S)	4 044(23)	3 950(39)	5 427(121)
C(10)	3 071(5)	−626(5)	2 246(8)	C(3S)	3 174(16)	3 609(11)	5 442(24)
C(11)	3 408(6)	−1 166(6)	3 626(8)	C(4S)	2 137(15)	4 405(14)	4 638(17)

triclinic, $a = 12.266(4)$, $b = 12.501(4)$, $c = 8.700(2)$ Å, $\alpha = 102.24(2)$, $\beta = 102.77(2)$, $\gamma = 67.54(2)°$, $U = 1\,190.3(6)$ Å^3, $Z = 2$, $D_c = 1.344$ g cm^{-3}, $F(000) = 506$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 4.31 cm^{-1}, space group $P\bar{1}$.

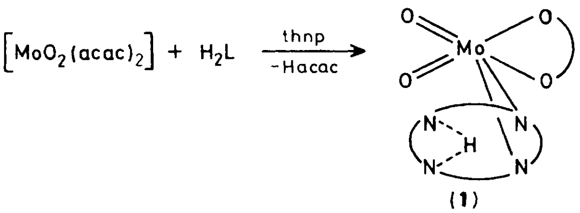
Structure solution and refinement. [The values in square brackets refer to complex (**2**)]. The intensities of 4 311 [3 511] unique intensity data lying in the quadrants $\pm h, k, l$ with $6 < 2\theta \leqslant 48°$ [$\pm h, k, l$ with $6 < 2\theta \leqslant 45°$] were measured on a Philips PW 1100 four-circle automatic diffractometer using graphite-monochromatized Mo-K_α radiation. All dimensions were derived from the angular measurements of 20 strong reflections with $2\theta > 32°$. The peaks were scanned through $\omega/2\theta$. For intensities and background the 'three-point' technique was used: one standard reflection was measured after every 50 intensity data. The structure amplitudes were obtained after the usual Lorentz and polarization corrections. No correction for absorption was applied. Data reduction, structure solution and refinement were carried out on a Gould 32/77 computer using SHELX 76.[11]

The structures were solved by the heavy atom method and refined first isotropically, then anisotropically for all non-hydrogen atoms by blocked full-matrix least-squares. The function minimized during the least-squares refinement was $\Sigma w|\Delta F|^2$. Weights were applied according to the scheme $w = k/[\sigma^2(F_o) + |g|(F_o)^2]$. Solution and refinement were based on 2 209 [1 968] observed reflections having $I > 3\sigma(I)$. The hydrogen atoms were located in difference maps and introduced as fixed-atom contributions ($U_{iso} = 0.10$ Å^2) in the subsequent refinement. In complex (**2**) the thf molecule was found to be affected by disorder that was solved considering the C(2S) carbon atom to be distributed over two positions. The refinement of the occupancy factors gave 0.51 and 0.49 for C(2S) and C(2S′) respectively. The hydrogen atoms of this molecule were ignored. The refinement converged with $R = 0.063$, $R' = 0.067$ and goodness of fit (g.o.f.) = 1.51 ($R = 0.053$, unit weights) $\{R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = \Sigma w^{\frac{1}{2}}||F_o| - |F_c||/\Sigma w^{\frac{1}{2}}|F_o|$, g.o.f. = $[\Sigma|(|F_o| - |F_c|)^2/(N_O - N_V)]^{\frac{1}{2}}\}$. At the end of refinement the values for k and g were 1.2612 and 0.002 063 respectively. Anomalous scattering corrections were included in all structure factor calculations.[12a] Scattering factors for neutral atoms were taken from ref. 12*b* for non-hydrogen atoms and from ref. 13 for H. Among the low-angle reflections no correction for secondary extinction was deemed necessary. In the last difference maps there were no peaks above the general background. Final atomic co-ordinates are listed in Tables 1 and 2.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

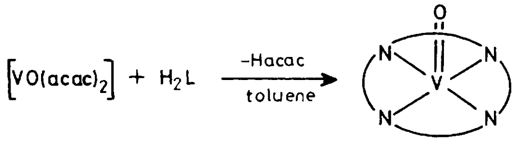
Results and Discussion

The introduction of an oxocation into a macrocyclic ligand can be easily achieved by a displacement reaction of acetylacetone from $[MO_n(acac)_m]$ compounds. Such a method has been employed, reacting $[VO(acac)_2]$ and $[MoO_2(acac)_2]$ with H_2L. The reactions were carried out in hydrocarbons, thus allowing, eventually, to distill out the Hacac formed: equations (1) and (2).



(1)

(1)



(2)

(2)

The synthesis of the vanadyl complex can be equally well carried out using vanadyl acetate. In spite of the rather drastic conditions applied, reaction (1) afforded complex (**1**) only, with a partial retention of the acetylacetonato ligand. This result shows that the replacement of acetylacetonate is a stepwise process. Pyrolysis of (**1**) at 180 °C *in vacuo* for 20 h was unsuccessful for removing the second acac ligand in the form of Hacac. The structure of (**1**) (*X*-ray analysis) showed the *cis* arrangement of the two oxygen atoms [ν(Mo–O) 895 and 927 cm^{-1}] and the partial co-ordination of the HL^- ligand occurring through two nitrogen atoms only. The vanadyl complex has the expected structural features. The paramagnetism ($\mu_{eff.}$ = 1.79 at 293 K) and the ν(V–O) vibration at 978 cm^{-1} are as found for other vanadyl complexes.[5]

The structure of complex (**1**) comprises discrete monomeric units of formula $[MoO_2(acac)(HL)]$. A view of the molecule is shown in Figure 1, and selected bond distances and angles are summarized in Table 3. The co-ordination polyhedron around the metal can be described as a distorted octahedron and involves two terminal oxygen atoms, two nitrogen atoms from a bidentate monoprotonated HL ligand, and two oxygen atoms from an acac molecule. The terminal oxygens are *cis* to each other, the O(1)–Mo–O(2) angle being 103.3(4)°, comparable to related angles in the literature.[14,15] The Mo–O(1) and Mo–O(2) distances, respectively 1.668(7) and 1.784(7) Å, are significantly different; the former agrees well with those generally found,[14] while the latter is longer. This lengthening could be hardly justified by intraligand steric hindrance or crystal packing effects because there is no dramatic difference in the environments of the terminal oxygens, intra- or inter-molecular contacts being consistent with van der Waals interactions. It could be most reasonably ascribed to the influence of the unsaturated system *trans* to O(2). It is interesting to note that a significant lengthening, even though to a lesser extent, was found in $[MoO_2(ttp)]$ (ttp = 5,10,15,20-tetra-*p*-tolylporphyrinate) [1.709(9) and 1.744(9) Å],[15] where the two *cis* oxygen atoms are *trans* to the ttp system which is very similar to L. The Mo–O(3) distance is longer than the Mo–O(4) distance [2.169(7) *vs.* 1.959(7) Å] as a consequence of the *trans* effect exerted by the O(1) oxygen atom; in addition the Mo–N(1) distance, *trans* to O(2), is longer than the Mo–N(4) distance [2.238(8) *vs.* 2.094(7) Å]. All these values are within the ranges usually observed.[14–16]

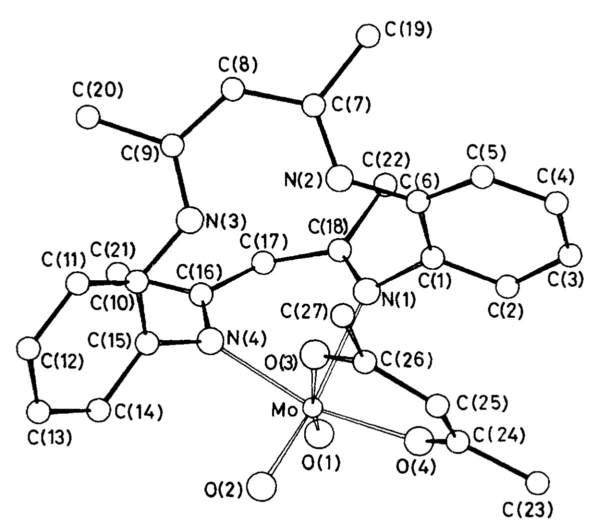


Figure 1. Molecular structure of complex (**1**)

The N(2) and N(3) atoms not involved in co-ordination are at a distance of 2.65(1) Å, which is the shortest one in the N_4 core, the others ranging from 2.74(1) to 2.80(1) Å. This is suggestive of an intramolecular hydrogen bond, although the proton could not be directly located. The four nitrogen atoms are nearly coplanar, showing small tetrahedral distortions ranging from −0.045(8) to 0.045(8) Å. The HL ligand exhibits a saddle-shape conformation, the groups of atoms N_2C_2 and N_2C_3 being alternatively tilted up and down with respect to the N_4 core. However, as a consequence of protonation there is a strong asymmetry in the two halves of the ligand, as indicated by the dihedral angles the N(4)–C(16)–C(17)–C(18)–N(1) and N(2)–C(7)–C(8)–C(9)–N(3) planes form with respect to the N_4 core: 81.6(4) *vs.* 41.3(4)°. The dihedral angle between the two N_2C_3 groups is 57.1(4)°. The six-membered chelate ring is strongly folded along line N(1) ··· N(4), molybdenum being displaced by 1.162(2) Å from the plane through the other atoms. The N_2C_2 groups, N(1)–C(1)–C(6)–N(2) and N(3)–C(10)–C(15)–N(4), form a dihedral angle of 43.9(4)° to each other and angles of 20.4(4) and 23.5(4)° respectively with the N_4 plane. Bond distances and angles within HL compare well to those reported:[17] the N–C(aromatic) distances have single-bond character, the N–C(aliphatic) distances have double-bond character. It should be noted that the N–C(aromatic) distances involving the co-ordinated nitrogens [N(1)–C(1) 1.46(1), N(4)–C(15) 1.45(1) Å] are significantly longer than those involving the unco-ordinated ones [N(2)–C(6) 1.41(1), N(3)–C(10) 1.39(1) Å]. The six-membered chelate ring involving acac is nearly planar molybdenum being 0.198(2) Å out of the plane through the acac ligand [excluding the C(23) and C(27) methyl carbons which deviate by −0.040(19) and −0.137(16) Å respectively]. Bond distances and angles within this ligand are as usually found.[17] All the intermolecular contacts are consistent with van der Waals interactions. There is only one contact suggestive of hydrogen bonding: C(11) ··· O(4′) = 3.45(1) Å, H(11) ··· O(4′) = 2.39 Å, C(11)–H(11) ··· O(4) = 160° (prime denotes atom at 1 + *x*, *y*, *z*).

The structure of complex (**2**) comprises discrete molecules of formula [VO(L)], where the vanadium atom co-ordinates four nitrogen atoms from a L ligand and a terminal oxygen atom. A view of the molecule is shown in Figure 2, and selected bond distances and angles are given in Table 4. The co-ordination polyhedron is a flattened square pyramid, the metal being displaced by 0.680(2) Å from the N_4 basal plane toward the oxygen atom. The V–O bond is perpendicular to that plane, the

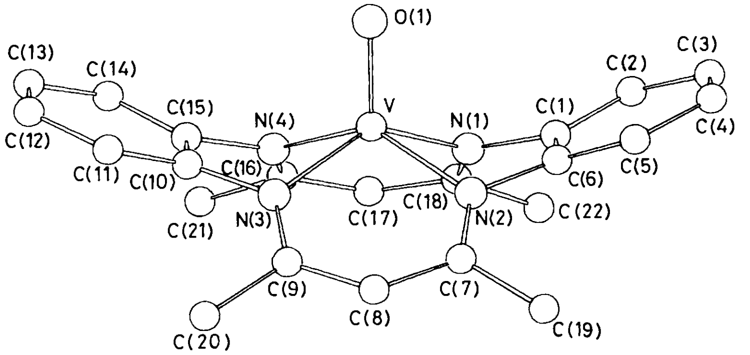


Figure 2. Molecular structure of complex (**2**)

Table 3. Selected bond distances (Å) and angles (°) for complex (**1**)

Mo–O(1)	1.668(7)	N(3)–C(9)	1.32(1)
Mo–O(2)	1.784(7)	N(3)–C(10)	1.39(1)
Mo–O(3)	2.169(7)	N(4)–C(15)	1.45(1)
Mo–O(4)	1.959(7)	N(4)–C(16)	1.37(1)
Mo–N(1)	2.238(8)	C(1)–C(6)	1.39(2)
Mo–N(4)	2.094(7)	C(7)–C(8)	1.41(1)
O(3)–C(26)	1.23(1)	C(8)–C(9)	1.42(2)
O(4)–C(24)	1.25(2)	C(10)–C(15)	1.37(1)
N(1)–C(1)	1.46(1)	C(16)–C(17)	1.38(1)
N(1)–C(18)	1.32(1)	C(17)–C(18)	1.42(1)
N(2)–C(6)	1.41(1)	C(24)–C(25)	1.40(2)
N(2)–C(7)	1.33(1)	C(25)–C(26)	1.45(2)
N(1)–Mo–N(4)	80.4(3)	O(1)–Mo–O(3)	170.0(3)
O(4)–Mo–N(4)	163.1(3)	O(1)–Mo–O(2)	103.3(4)
O(4)–Mo–N(1)	86.6(3)	Mo–O(3)–C(26)	128.1(9)
O(3)–Mo–O(4)	83.7(3)	Mo–O(4)–C(24)	134.5(8)
O(3)–Mo–N(1)	79.5(3)	Mo–N(1)–C(18)	120.1(6)
O(3)–Mo–O(4)	83.4(2)	Mo–N(1)–C(1)	123.7(6)
O(2)–Mo–O(4)	93.4(3)	C(1)–N(1)–C(18)	116.2(8)
O(2)–Mo–N(1)	165.4(3)	C(6)–N(2)–C(7)	125.5(9)
O(2)–Mo–O(4)	96.8(3)	C(9)–N(3)–C(10)	126.7(9)
O(2)–Mo–O(3)	86.7(3)	Mo–N(4)–C(16)	120.3(7)
O(1)–Mo–N(4)	95.4(3)	Mo–N(4)–C(15)	122.0(6)
O(1)–Mo–N(1)	90.5(3)	C(15)–N(4)–C(16)	117.7(8)
O(1)–Mo–O(4)	95.4(3)		

Table 4. Selected bond distances (Å) and angles (°) for complex (**2**)

V–O(1)	1.600(5)	N(4)–C(15)	1.427(9)
V–N(1)	2.025(6)	N(4)–C(16)	1.326(8)
V–N(2)	2.039(8)	C(1)–C(6)	1.424(10)
V–N(3)	2.029(4)	C(7)–C(8)	1.400(10)
V–N(4)	2.029(5)	C(7)–C(19)	1.518(14)
N(1)–C(1)	1.429(10)	C(8)–C(9)	1.386(12)
N(1)–C(18)	1.348(8)	C(9)–C(20)	1.527(9)
N(2)–C(6)	1.425(9)	C(10)–C(15)	1.414(8)
N(2)–C(7)	1.325(9)	C(16)–C(17)	1.394(11)
N(3)–C(9)	1.346(8)	C(17)–C(18)	1.402(11)
N(3)–C(10)	1.413(10)		
N(3)–V–N(4)	78.7(2)	V–N(1)–C(1)	105.9(4)
N(2)–V–N(4)	141.3(2)	C(1)–N(1)–C(18)	125.0(6)
N(2)–V–N(3)	88.6(2)	V–N(2)–C(7)	128.8(5)
N(1)–V–N(4)	87.9(2)	V–N(2)–C(6)	105.7(5)
N(1)–V–N(3)	140.5(2)	C(6)–N(2)–C(7)	125.3(6)
N(1)–V–N(2)	79.0(2)	V–N(3)–C(10)	106.4(4)
O(1)–V–N(4)	108.7(3)	V–N(3)–C(9)	128.0(4)
O(1)–V–N(3)	109.6(2)	C(9)–N(3)–C(10)	125.3(5)
O(1)–V–N(2)	110.0(3)	V–N(4)–C(16)	129.7(4)
O(1)–V–N(1)	109.9(2)	V–N(4)–C(15)	106.0(4)
V–N(1)–C(18)	128.9(5)	C(15)–N(4)–C(16)	124.2(5)

dihedral angle it forms with the to-plane-normal being 0.7(2)°. The fourV–N distances ranging from 2.025(6) to 2.039(8) Å are not significantly different and fall in the usual range.[18] The vanadium–oxygen bond distance [1.600(5) Å] is comparable to those found in the literature and it is consistent with a double bond.[5,19]

The L ligand adopts the usual saddle shape conformation.[17] As generally observed, the six-membered chelate rings are not far from planarity, vanadium being 0.103(1) and 0.141(2) Å from the planes through N(2)–C(7)–C(8)–C(9)–N(3) and N(4)–C(16)–C(17)–C(18)–N(1) respectively. These planes form a dihedral angle of 65.2(3)° and angles of 31.9(2) and 33.3(3)° respectively with respect to the N_4 core which is planar within experimental error. The two five-membered chelate rings show an envelope conformation, vanadium being 1.032(2) and 1.015(2) Å out of the plane through N(1)–C(1)–C(6)–N(2) and N(3)–C(10)–C(15)–N(4) respectively. They form a dihedral angle of 30.1(3)° and dihedral angles of 15.5(3) and 14.7(2)° respectively with respect to the N_4 plane. As usually found, bonding patterns describing the 16-π-electron ring system which is not delocalized, are maintained.[17] The N–C(aliphatic) bond distances [av. 1.336(9) Å] show a remarkable double-bond character, while the N–C(aromatic) bond distances [av. 1424(8) Å] aproach a single bond.

Packing is mainly determined by van der Waals contacts. Possible hydrogen bonds are: C(3)···O(1^{i}) 3.413(9), H(3)···O(1^{i}) 2.33 Å, C(3)–H(3)···O(1^{i}) 156°; C(21)···O(1^{ii}) 3.477(10), H(212)···O(1^{ii}) 2.56 Å, C(21)–H(212)···O(1^{ii}) 164° (symmetry codes: i $-x$, $1 - y$, $-z$; ii $-x$, $-y$, $-z$).

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