



A joint computational and experimental study of a novel dioxomolybdenum(VI) complex bearing chiral *N,N*-dimethyl lactamide ligand

Fabricio Ronil Sensato^{a,*}, Quezia Bezerra Cass^b, Bianca Rebelo Lopes^b, Tiago Campos Lourenço^b, Julio Zukerman-Schpector^b, Edward R.T. Tiekink^c, Elson Longo^d, Juan Andrés^e

^a Instituto de Ciências Ambientais, Químicas e Farmacêuticas, Universidade Federal de São Paulo (UNIFESP), No. 275, 09972-270 Diadema, Brazil

^b Departamento de Química, Universidade Federal de São Carlos, CP 676, 13565-905 São Carlos, Brazil

^c Department of Chemistry, University of Malaya, 50603 Kuala Lumpur, Malaysia

^d Instituto de Química, Universidade Estadual Paulista, 14800-900 Araraquara, SP, Brazil

^e Departament de Química Física, Universitat Jaume I, Castelló 12080, Spain

ARTICLE INFO

Article history:

Received 24 January 2011

Received in revised form 14 April 2011

Accepted 14 April 2011

Available online 23 April 2011

Keywords:

Dioxomolybdenum(VI) complexes

Crystal-structure

Chiral ligand

Synthesis

Density functional theory

Computational chemistry

ABSTRACT

A new *cis*-dioxomolybdenum complex MoO₂(DMLA)₂ (DMLA = *N,N*-dimethyl lactamide) has been synthesized and characterized by X-ray crystallography, H NMR and IR spectroscopies and electronic structure calculations at DFT/B3LYP level. This compound (chemical formula C₁₀H₂₀MoO₆N₂) crystallizes in the orthorhombic space group *P*2₁2₁ with *Z* = 4, *a* = 6.9357(2) Å, *b* = 11.8761(4) Å, *c* = 17.7251(5) Å, *V* = 1460.00(8) Å³ and renders a slightly distorted octahedral structure with two long Mo–O bonds (2.253(3) Å and 2.257(3) Å) *trans* to each of the Mo=O groups and with two short Mo–O bonds of 1.942(3) Å *cis* to them. The Mo=O bond lengths are 1.715(3) and 1.704(3) Å. Each lactamide ligand is bidentate; they are coordinated in their deprotonated form with the carbonyl oxygen occupying a position *trans* to the Mo=O moiety while the deprotonated hydroxyl oxygen is located *cis* to them. Structural characterization is complemented by DFT/B3LYP calculations.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

The chemistry of transition metal-oxo compounds has become an important area of prime interest. In particular, *cis*-dioxomolybdenum complexes with a *cis*-[MoO₂]²⁺ core are well known catalysts or catalyst precursor for oxygen-atom transfer (OAT) in chemical and biological systems. Many *cis*-dioxomolybdenum complexes of the general formula MoO₂X₂(N–N') (X = Cl, Br, Me or THF) [1–5] or MoO₂X₂(O–O') [6,7] or MoO₂(N–N')₂ [8,9] or MoO₂(N–O')₂ [2,10–12] or MoO₂(O–O')₂ [13–22] (N–N', N–O' and O–O' are bidentate chelate ligands) are usually employed in conjunction with external oxidants such as alkyl hydroperoxide [1–7,11,13,15], H₂O₂ [6,16] or O₂ [12] to oxidize a variety of organic substrates via homogeneous as well as heterogeneous routes such as alkenes [1–3,5–7,10–12,15,16] and sulfides [7,13]. Some dioxomolybdenum complexes have also been found to exhibit biological relevance, for instance, Westcott and co-workers demonstrated that *cis*-MoO₂(ma)₂ (Hma = maltol = 3-hydroxy-2-methyl-4-pyrone) is effective in lowering blood glucose and free fatty acid levels [17]. A number of dioxomolybdenum complexes with

various supporting ligands have also been used as models for the active site of molybdenum-containing oxotransferases (e.g. [9,23]).

Chiral nonracemic epoxides and sulfoxides are useful precursors in synthetic chemistry; therefore, metal catalyzed asymmetric oxidation of these substrates has garnered extensive attention from the synthetic community. Indeed, there is significant interest in the synthesis of chiral oxometallate complexes and their use as catalysts for asymmetric OAT reactions. In particular, some attempts have been made to transform the MoO₂²⁺ moiety into chiral epoxidation or sulfoxidation catalysts by adding chiral Lewis base ligands (e.g. [13,15,24,25]); thus the effect of chelating ligands in metal complexes is very important. A suitable ligand should meet three critical requirements: (i) stability to oxidation, (ii) straightforward to synthesize and (iii) functionalizable to allow fine and easy tuning of its electronic and steric characteristics [12,24]. In particular, the bidentate ligand (*S*)-*N,N*-dimethyl lactamide (2-hydroxy-*N,N*-dimethylpropanamide), hereafter denoted by HDMLA (see Fig. 1), has been found to introduce chirality in Mo(VI)-oxodiperoxo complexes which were efficiently employed in the enantioselective epoxidation of prochiral alkenes to give optically active oxiranes [26–29]. In view of this feature and as part of our ongoing work on the structure [30,31] and reactivity [32–35] of metal-oxo-peroxo molybdenum compounds, we hereby report the synthesis of the novel complex MoO₂(DMLA)₂ and its

* Corresponding author.

E-mail address: fabricao.sensato@unifesp.br (F.R. Sensato).

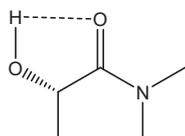


Fig. 1. Free HDMLA ligand.

characterization by X-ray crystallography, ^1H NMR and Infrared spectroscopies. The structural characterizations are assisted by density functional calculations.

2. Experimental

2.1. Physical measurements and X-ray crystallography

IR spectra were recorded as KBr pellets on a BOMEN MB IR spectrophotometer, and the electronic spectra were recorded on a Hitachi U-2001 spectrophotometer. ^1H NMR data were recorded on a Bruker DRX-400 NMR spectrometer referenced to tetramethylsilane (TMS). Elemental analyses were performed using a Fisons EA-1108 CHNS-O elemental analyzer. Crystal data were obtained at 98 K on a Rigaku AFC12 κ /SATURN724 diffractometer fitted with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). Data processing and absorption corrections were accomplished with CrystalClear [36] and ABCOR [37] programs, respectively. The structures were solved by direct methods [38]. Full-matrix least squares refinement on F^2 with anisotropic thermal parameters for all non-hydrogen atoms was performed [39]. H atoms were placed on stereochemical grounds and refined with fixed geometry (each riding on a carrier atom) with an isotropic displacement parameter amounting to 1.2 times (1.5 for methyl-H) the value of the equivalent isotropic displacement parameter of the respective carrier atom. A weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$ was introduced. The absolute structure was determined on the basis of differences in 1400 Friedel pairs included in the data set. PLATON [40], WinGX [41], ORTEPII [42] and DIAMOND [43] were used in this work.

2.2. Synthesis and characterization of $\text{MoO}_2(\text{DMLA})_2$

The chiral ligand (*S*)-*N,N*-dimethylactamide, [MeCH(OH)CONMe $_2$], HDMLA, was obtained according to the procedure proposed by Seebach [44]. The synthesis of $\text{MoO}_2(\text{DMLA})_2$ was based on a well established experimental procedure [16]. Hydrated sodium molybdate, Na $_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ (0.625 g, 2.5 mmol), was dissolved in a minimum volume of water (5 mL), and an ethanolic solution of HDMLA (5 mmol) was added dropwise to the aqueous solution under stirring. The addition of two drops of hydrochloric acid (6 M) precipitated the desired complex as a white solid. The solid was filtered off, washed thoroughly with distilled water and ethanol and recrystallized from a dichloromethane/*n*-hexane mixture. Yield: 72%. *Anal.* Calc. C $_{10}\text{H}_{20}\text{MoO}_6\text{N}_2$: C, 33.15; N, 7.70; H, 6.08. Found: C, 35.15; N, 8.78; H, 6.85%. δ_{H} (400 MHz): 1.47 (d, 6H, $J = 6.6 \text{ Hz}$), 3.13 (s, 6H), 3.29 (s, 6H), 5.46 (q, 2H, $J = 6.6 \text{ Hz}$). IR: 2978 (w, $\nu_{\text{as}}(\text{C-H})$), 2935 (w, $\nu_{\text{as}}(\text{C-H})$), 1615 (s, $\nu(\text{C=O})$), 1508 (m, $\nu(\text{C-N})$), 1448 (w, $\delta_{\text{as}}(\text{CH}_3)$), 1361 (w, $\delta_{\text{s}}(\text{CH}_3)$), 1257 $\nu_{\text{as}}(\text{w, N-CH}_3)$), 1115 (s, $\omega(\text{CH}_3) + \nu(\text{C-O})$), (m, 1054 ($\omega(\text{CH}_3) + \nu(\text{C-O}) + \nu(\text{C-CH}_3)$), 926 (s, $\nu_{\text{s}}(\text{Mo=O})$), 905 (s, $\nu_{\text{as}}(\text{Mo=O})$), 642 (w, $\delta(\text{O=C-N})$), 584 (m, $\nu_{\text{as}}(\text{Mo-O}_h)$). UV-Vis (λ (nm)): 252.

3. Computational details

In order to provide a detailed description of the $\text{MoO}_2(\text{DMLA})_2$ complex, we have also carried out DFT calculations at the B3LYP level, a well known hybrid density functional method, which com-

bins three contributions for the exchange energy due to Becke (B88, a nonlocal functional) [45], Slater [46] and Hartree-Fock [47] with local and nonlocal correlation functional by Vosko, Wilk and Nusair (VWN) [48] and by Lee, Yang and Parr (LYP) [49], respectively, as implemented in the GAUSSIAN03 program [50]. This highly popular functional (B3LYP) was chosen as it is known to produce reliable geometries involving oxo-diperoxo molybdenum complexes (e.g. [30,31,33,34,51,52]). The standard 6-311+G-(2fd,2p) basis set was employed to represent the H, C, O and N atoms. To represent the Mo center, a valence basis set (8s6p7d2f) [31] tailored with the application of the generator coordinate method (GCM) [53,54] was used in conjunction with the RECP (quasi-relativistic effective core potential) of Hay and Wadt [55]. A natural population analysis (NPA) [56] and the resulting Wiberg indices (WI) [57] were used to analyze the electronic structure and bonding in the complex. The geometric optimization was performed by imposing a twofold axis which bisects the O=Mo=O angle in the *cis*- MoO_2^{2+} core. The corresponding stationary point was checked via a vibrational frequency calculation.

4. Results and discussion

4.1. Structural characterization

The $\text{MoO}_2(\text{DMLA})_2$ complex is found to be a mononuclear and neutral compound which crystallizes in the orthorhombic space group $P2_12_12_1$ with $Z = 4$. The molecule has approximate C_2 symmetry, and the coordination sphere around the molybdenum atom consists of six oxygen atoms arranged in a distorted octahedral geometry. Indeed, the molybdenum atom is coordinated in a pseudo-octahedral fashion by two oxo functions and two chelating dimethylactamide ligands in their nonprotonated form, [MeCH(OH)CONMe $_2$] $^-$, exhibiting an *S* configuration at C10 and C11. The molecular structure was determined by X-ray diffraction and the corresponding atom numbering scheme for the complex $\text{MoO}_2(\text{DMLA})_2$ is depicted in Fig. 2.

It should be noted that due to the unsymmetric nature of the DMLA ligand, the formation of three pairs of diastereomers and their corresponding enantiomers is in principle possible for this type of *cis*-dioxo complex (see Fig. 3): (i) the two hydroxylic oxygen (O_h) atoms *cis* to both oxo groups (stereoisomer **A**), (ii) each O_h atom *trans* to one oxo group (stereoisomer **B**) and (iii) one O_h atom *cis* to the two oxo groups and another O_h atom *trans* to one oxo group (stereoisomer **C**). However, X-ray diffraction analysis revealed only diastereomer **A**.

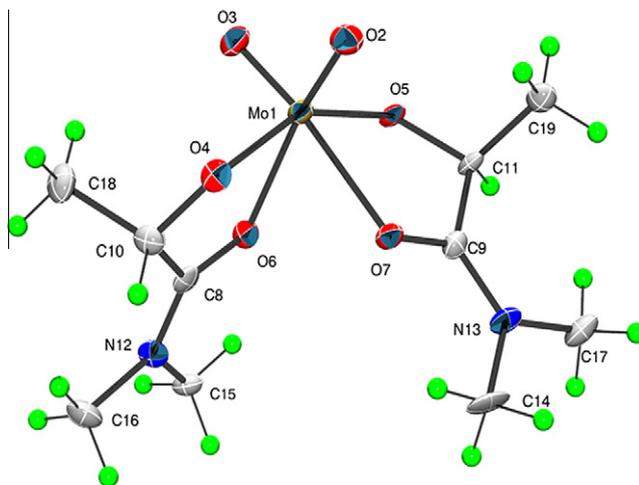


Fig. 2. Molecular structure of $\text{MoO}_2(\text{DMLA})_2$ complex. Displacement ellipsoids are drawn at 50% probability level, except for H-atoms that are at an arbitrary radii.

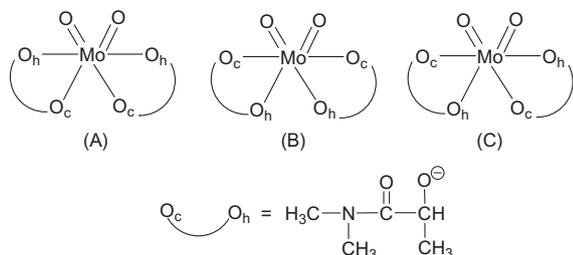


Fig. 3. Possible geometrical isomers for $\text{MoO}_2(\text{DMLA})_2$.

We have also rationalized the stereoisomeric preference in the $\text{MoO}_2(\text{DMLA})_2$ complex on the basis of relative energies. Our DFT calculations show that diastereomer **A** is the most stable stereoisomer. In fact, our efforts to optimize stereoisomer **B** under a C_2 symmetry constraint yielded a structure in which each hydroxylic oxygen is located *trans* to one carbonyl oxygen. Such an isomer was calculated to be higher in energy by $10.1 \text{ kcal mol}^{-1}$. Furthermore, stereoisomer **C** was found to be $5.5 \text{ kcal mol}^{-1}$ less stable than isomer **A**. It should be mentioned that **A**, **B** and **C** stereoisomer exhibited no imaginary frequencies, which confirms them to be true minima. Therefore we have confined the ensuing discussion to the more stable stereoisomer **A**.

The multiply bonded terminal oxygen atoms (O2 and O3) in the dioxomolybdenum group MoO_2^{2+} are *cis* to each other. The *cis* feature of oxo ligands in $[\text{MoO}_2]^{2+}$ moiety has been rationalized in terms of the increased π donation into the empty t_{2g} orbitals of the d^0 metal center [58]. Yet, it was showed that only the *cis* arrangement of two oxo ligands in the d^0 complexes ensures the maximal involvement of all three t_{2g} orbitals as oxygen π -electron acceptors [59]. In particular, we have very recently investigated the electronic features of the Mo-oxo bond in a parent complex and therefore a very detailed topological characterization of this chemical bonding is given elsewhere [35].

The oxo oxygen atoms (O2 and O3) define the equatorial plane together with the molybdenum atom and the two carbonyl oxygen atoms (O6 and O7) from the DMLA ligands. Thus, the carbonyl oxygen atoms O6 and O7 are positioned *trans* to the oxo oxygen atoms O2 and O3, respectively. The hydroxylic oxygen atoms (O4 and O5) occupy the axial positions. However, the molybdenum is off-center and shifted away from the carbonyl oxygen atoms towards the midpoint of the two oxo oxygen atoms. The DMLA ligands are so arranged that the two hydroxylic oxygen atoms (O4 and O5 at the anionic moieties) are approximately *trans* to each other which compels the carbonyl oxygen atoms (O6 and O7) to occupy approximate *cis* positions. Such an arrangement closely resemble the usual *cis*-oxo, *trans*-X, *cis*-L configuration (to the detriment of *all-cis* configuration) found in six-coordinated d^0 complexes of $\text{MO}_2\text{X}_2\text{L}_2$ type (M = Mo, W; X and L are anionic and neutral ligands, respectively) [60] with the unprotonated hydroxylic oxygen (anionic moiety) corresponding to the anionic ligands (X) and the carbonyl oxygen atoms to the neutral ligands (L); i.e., by using the same designation, it could be denoted by *cis*-oxo, *trans*- O_h , *cis*- O_c . Indeed, it has been reputed that the *trans* position to the oxo moiety is preferably occupied by the least polarizable σ -donor ligand (or functional group) (see [61] and references therein). To ascertain this feature we have calculated (via conceptual DFT [62]) the local softness index for an electrophilic attack (s^-) [63] on both hydroxylic and carbonylic oxygen atoms in the free unprotonated DMLA molecule inasmuch as the softness is recognized as a direct measure of polarizability. Within a finite difference approximation and by using the condensed form [64] of the Fukui function obtained from the Hirshfeld's stockholder partitioning technique of the electron density [65,66] we found the O_c softness index to

be 10 times smaller than the softness index of O_h which is in line with the premise mentioned above.

Notably, in the parent molybdenum oxodiperoxo complex $\text{MoO}(\text{O}_2)_2$ (HDMLA) reported by Schurig [29], the ligand binds to the metal in its protonated form with the hydroxylic oxygen (O_h) positioned *trans* to the oxo group. Interestingly, for the protonated form, the s^- index of O_h (0.36) is slightly smaller than that of O_c (0.39).

Details of cell data, X-ray data collection, and structure refinement are given in Table 1 (numbers in parentheses after the numerical results are the standard uncertainties). Relevant bond distances and angles from X-ray diffraction are collected in Tables 2 and 3, respectively.

An analysis of X-ray data reveals that the bond length at the $\text{Mo}=\text{O}$ moieties are found to be $1.704(3)$ and $1.715(3) \text{ \AA}$ for $\text{Mo}=\text{O}2$ and $\text{Mo}=\text{O}3$, respectively, and are comparable to those found in other dioxomolybdenum(VI) complexes (e.g. [1,6,12,17–20,22]). The main structural characteristics around the metal center include two long Mo–O bonds (Mo–O6: $2.257(3) \text{ \AA}$; Mo–O7: $2.253(3) \text{ \AA}$) *trans* to each of the $\text{Mo}=\text{O}$ groups and two shorter Mo–O bonds (Mo–O4: $1.942(3) \text{ \AA}$; Mo–O5: $1.942(3) \text{ \AA}$) *cis* to them. These results indicate that the bonding of molybdenum to the hydroxylic oxygen O4 (or O5) is much stronger (avg = 1.942 \AA) than that the bonding to the carbonyl oxygen O6 (or O7) (avg = 2.2550 \AA). This inference is further corroborated by our DFT calculations (as discussed below). The lengthening of the Mo–O6 (or Mo–O7) has been in some extension related to the *trans* influence of the $\text{Mo}=\text{O}2$ (or $\text{Mo}=\text{O}3$) bond. These main molecular features are very similar to the features reported for the framework of analogous dioxomolybdenum complexes bearing a bidentate O–O' ligand such as hydroxypyronato, hydroxypyridinonato [17,19,22], tropolonato [20] or hydroxamates [16,21].

Within each coordinated DMLA ligand the two C–O distances are notably different: 1.406 \AA (avg) for the C– O_h bond and 1.256 \AA (avg) for the C– O_c bond in accordance with the short and the long adjacent Mo–O distances, respectively. The $\text{O}=\text{Mo}=\text{O}$ angle value is $106.11(14)^\circ$, and the opposite angle formed by the carbonyl oxygen atoms (O6–Mo–O7) is $75.17(10)^\circ$. The two axial ligands are bent away from the oxo groups such as the corresponding angle between the hydroxylic oxygen atoms (O4–Mo–O5) is

Table 1
Summary of crystallographic data and parameters for $\text{MoO}_2(\text{DMLA})_2$.

Molecular formula	$\text{C}_{10}\text{H}_{20}\text{MoO}_6\text{N}_2$
Formula weight	360.22
T (K)	100(2)
Wavelength (\AA)	0.71073
Crystal system	orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	
a (\AA)	6.9357(2)
b (\AA)	11.8761(4)
c (\AA)	17.7251(5)
V (\AA^3)	1460.00(8)
Z	4
Absorption coefficient (mm^{-1})	0.921
Calculated density (mg m^{-3})	1.639
Crystal size (mm)	$0.40 \times 0.20 \times 0.15$
θ range for data collection	$2.1\text{--}27.5^\circ$
Reflections collected	3325 [2885 $I > 2\sigma(I)$]
No. of parameters	178
Flack parameter	–0.03(5)
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.038$, $wR_2 = 0.085$
Final R indices (all data)	$R_1 = 0.049$, $wR_2 = 0.091$
Goodness-of-fit (GOF) on F^2	1.127
Largest difference in peak and hole ($e \text{ \AA}^{-3}$)	1.59^a , –0.82

^a This peak is located at 0.80 \AA from the Mo atom.

Table 2
Selected bond distances (Å) for MoO₂(DMLA)₂ obtained by X-ray and DFT/B3LYP calculations.

Bonding	Exp.	Bonding	Exp.	Mean (Exp.)	Calc. ^a
Mo–O2	1.715(3)	Mo–O3	1.704(3)	1.710	1.695
Mo–O4	1.942(3)	Mo–O5	1.942(3)	1.942	1.957
Mo–O6	2.257(3)	Mo–O7	2.253(3)	2.255	2.405
O4–C10	1.402(5)	O5–C11	1.411(5)	1.406	1.389
O6–C8	1.249(5)	O7–C9	1.263(5)	1.256	1.238
C8–C10	1.528(6)	C9–C11	1.518(6)	1.523	1.535
C8–N12	1.322(5)	C9–N13	1.320(6)	1.321	1.347
N12–C15	1.452(5)	N13–C14	1.445(6)	1.449	1.458
N12–C16	1.466(5)	N13–C17	1.469(5)	1.468	1.454
C10–C18	1.541(6)	C11–C19	1.528(6)	1.535	1.537

^a Geometry optimization was performed imposing a twofold axis which bisects the O=Mo=O angle in the cis-MoO₂²⁺ core.

Table 3
Selected bond angles (°) for MoO₂(DMLA)₂ obtained by X-ray and DFT/B3LYP calculations.

Bond angle	Exp.	Bond angle	Exp.	Mean	Calc. ^a
O2–Mo–O3	106.11(14)				106.7
O4–Mo–O5	151.62(12)				144.7
O5–Mo–O7	74.21(11)				76.2
O2–Mo–O4	92.93(13)	O3–Mo–O5	94.72(13)	93.8	97.9
O2–Mo–O5	102.65(13)	O3–Mo–O4	103.63(13)	103.2	102.9
O4–Mo–O6	73.60(10)	O5–Mo–O7	74.21(11)	73.9	70.9
O2–Mo–O6	162.01(12)	O3–Mo–O7	161.11(12)	161.6	162.6
O2–Mo–O7	91.43(13)	O3–Mo–O6	88.95(12)	90.6	89.2
Mo–O4–C10	123.3(2)	Mo–O5–C11	122.4(2)	122.8	125.3
Mo–O6–C8	115.0(2)	Mo–O7–C9	114.2(3)	114.6	112.8

^a Geometry optimization was performed imposing a twofold axis which bisects the O=Mo=O angle in the cis-MoO₂²⁺ core.

151.62(12)° which deviates markedly from an ideal octahedron and indicates distortion in the coordination geometry. X-ray analysis also reveals that atoms Mo, O5, O7, C9 and C11 which form a five-membered ring do not lie strictly in the same plane: e.g., the dihedral angle Mo–O7–O5–C11 is found to be of 163.1(2). The same holds for the ring constituted by atoms Mo, O4, O6, C8 and C10.

It should be mentioned that for a related free compound, namely, *N,N*-dimethylacetamide (DMA, (CH₃)₂NC(O)CH₃), the planarity or non-planarity of the bonds around nitrogen atom has

been an issue of prime interest (e.g. [67]). In the complex MoO₂(DMLA)₂, a slightly non-planar structure for the bonds around the nitrogen atom is found with the dihedral angles C10–C8–N12–C16 and O6–C8–N12–C15 being –5.0° and 2.1°, respectively (C15 and C16 are *anti* and *syn* to carbonylic oxygen atom, respectively). The sum of the N12 bond angles is 359.84°. For another DMLA ligand, the dihedral angles C11–C9–N13–C17 and O7–C9–N13–C14 are 1.6° and 2.4°, respectively; the sum of N13 bond angles equals 359.99°. These findings reveal that the acetyl group deviates very little from planarity.

A packing diagram of MoO₂(DMLA)₂ molecules in the crystal is presented in Fig. 4. Complex molecules are connected into a three-dimensional architecture by a number of C–H...O interactions as summarized in Table 4. All oxygen atoms but O7 participate in these interactions with both the oxo-O3 and acetamido-O4 atoms forming two such contacts; each of the O6 and O7 atoms forms an intramolecular C–H...O contact.

The molecular structure of MoO₂(DMLA)₂ was also fully optimized using quantum chemical calculation at DFT/B3LYP level; the corresponding calculated geometric parameters are also included in Tables 2 and 3. An analysis of the corresponding values reveals that the agreement between experimental and theoretical sets of values is rather satisfactory. The bond length deviation with respect to the experimental mean values are, in general, at most ~0.03 Å. The only exception refers to the bond distance between the molybdenum center and the carbonyl oxygen atom, Mo–O6 or Mo–O7, whose experimental mean value is 2.255 Å, whereas the predicted theoretical result is found to be 2.405 Å. The difficulty in reconciling the experimental and theoretical results related to the bond distance *trans* to the oxo group in oxo-metal complexes has already been addressed by us [30] and others [51,68], and it has been partially attributed to the negligence of crystal packing effects in the computational chemistry model. For the theoretical set of data in Table 2, the overall root mean square error (RMS_{tot}) is 0.049 Å, which drops to 0.015 Å when the bond distance Mo–O6 (and the corresponding Mo–O7) is excluded from the computation. The agreement between calculated and experimental bond angles appears worse but they are still satisfactorily predicted. The RMS_{tot} for the set of bond angles as presented in Table 3 is about 3.0°.

We have also calculated Wiberg indices (WI) [57] obtained from the natural population analysis (NPA) [56]. This index is proved to reflect the bond strengths and to be more reliable than distances. A typical value of WI is about 2 for the C–C double bond in the

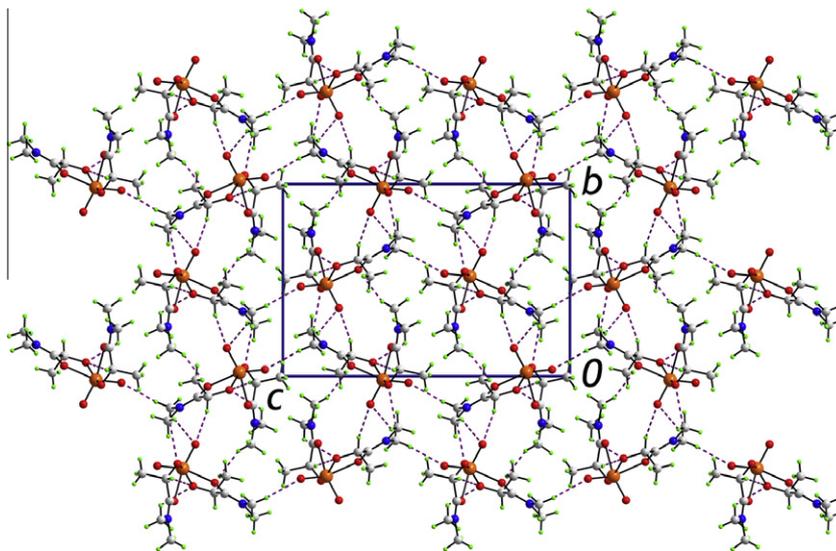


Fig. 4. Packing diagram of MoO₂(DMLA)₂. Dotted lines represent the hydrogen bonds.

Table 4
Summary of C–H...O interactions (Å, °) in **1**.

A	H	B	A–H	H...B	AB	A–H...B	Symmetry operation
C10	H20	O3	1.00	2.51	3.479(5)	164	2 – x, –½ + y, ½ – z
C11	H21	O4	1.00	2.29	3.250(5)	161	–1 + x, y, z
C16	H30	O3	0.98	2.49	3.240(5)	133	2 – x, –½ + y, ½ – z
C17	H33	O4	0.98	2.49	3.143(6)	124	–1 + x, y, z
C14	H36	O6	0.98	2.47	3.342(6)	148	1 – x, –½ + y, ½ – z
C15	H38	O2	0.98	2.54	3.491(5)	163	3/2 – x, 2 – y, ½ + z
C15	H39	O5	0.98	2.59	3.491(5)	153	1 – x, –½ + y, ½ – z
C15	H37	O6	0.98	2.30	2.731(5)	106	x, y, z
C14	H34	O7	0.98	2.30	2.734(6)	106	x, y, z

ethylene molecule and about 1 for the C–C single bond in ethane. The calculated Mo–O2 (and Mo–O3) bond distance is 1.695 Å (exp. avg. 1.710 Å) and the corresponding WI is 1.77. The strongest bonding chemical between the metal center and the hydroxylic oxygen when compared to the bond with the carbonyl oxygen is also reflected by the calculated bond length and the respective WI indices: 1.957 Å and 0.662 for the bonding with the hydroxylic oxygen and 2.405 Å and 0.166 for the carbonyl oxygen. Thus each deprotonated DMLA can be described as a chelating, anionic, bidentate ligand, which complexes the molybdenum atom with a coordinative bond by the carbonyl oxygen and a nearly covalent simple bond by the hydroxylic oxygen which forms a five-membered ring.

The geometry of the lactamide ligand is somewhat altered as a result of deprotonation and coordination. The calculated lengthening of the C8–O6 (and C9–O7) bond distance in the keto group to 1.238 Å as well as the shortening of the C8–N12 (or C9–N13) amide bond to 1.347 Å indicates that the zwitterionic resonance form $\text{MoO}_2[\text{OCHCH}_3\text{O}^- - \text{C} = \overset{+}{\text{N}}(\text{CH}_3)_2]_2$ renders an increased contribution in comparison to the free HDMLA inasmuch as the corresponding distances in the free HDMLA are calculated to be 1.228 and 1.358 Å, respectively. This finding is also corroborated by the WI. For the free HDMLA molecule, the WI related to the keto group C–O is 1.697 whereas for the C–N amide bond it is 1.206. Upon coordination, the WI of C–O decreases to 1.509 while the WI of the C–N amide increases to 1.248. The same conclusion can be derived from the NPA charge analysis. On passing from the free HDMLA to the coordinated DMLA, the NPA charge on the nitrogen atom changes from –0.50 to –0.48 whereas the charge on the carboxylic oxygen changes from –0.66 to –0.68.

4.2. Spectroscopic characterization

The main experimental and theoretical IR spectroscopic data for $\text{MoO}_2(\text{DMLA})_2$ are collected in Table 5. Certainly the designation of these modes as pure bond-stretching or deformation is only approximate. For the sake of comparison, corresponding data for the free HDMLA is also included. In particular, we anticipate that the main assignments made for the free HDMLA are in line with assignments reported for the DMA (*N,N*-dimethylacetamide) molecule [69,70]. In general, calculated vibrational frequencies are overestimated (avg 3.3%) as compared with experimental values. The most relevant characteristics are summarized below.

The band centered at 3411 cm^{-1} (calc. 3661 cm^{-1}) corresponding to the O–H stretch $\nu(\text{O–H})$ in the free HDMLA ligand is, of course, absent in the complex in accordance with the non-protonated form of the ligand when chelated to the $[\text{MoO}_2]^{2+}$ core.

The peaks at 2978 cm^{-1} (calc. 3110 cm^{-1}) and 2935 cm^{-1} (calc. 3067 cm^{-1}) are assigned to the $\nu_{\text{as}}(\text{C–H})$ related to the $(\text{CH}_3)\text{–C}$ and $(\text{CH}_3)_2\text{–N}$ moieties, respectively. The band at 1615 cm^{-1} (calc. 1654 and 1669 cm^{-1}) in $\text{MoO}_2(\text{DMLA})_2$ is due to the C=O stretching vibration and some relevant contribution of a symmetrical bending

Table 5
Selected IR bands (cm^{-1}) with tentative assignments of dioxomolybdenum(VI) complex and the free HDMLA molecule.

Predominant mode	$\text{MoO}_2(\text{DMLA})_2$ (exp.)	$\text{MoO}_2(\text{DMLA})_2$ (calc.)	HDMLA (exp.)	HDMLA (calc.)
$\nu(\text{O–H})$			3411	3661
$\nu_{\text{as}}(\text{C–H})$	2978	3110	2984	3107
$\nu_{\text{as}}(\text{C–H})$	2935	3067	2936	3057
$\nu(\text{C=O})$	1615	1654; 1669	1643	1697
$\nu(\text{C–N})$	1508	1550	1507	1548
$\delta_{\text{as}}(\text{CH}_3)$	1448	1510	1454	1510
$\delta_{\text{s}}(\text{CH}_3)$	1361	1407	1378	1414
$\nu_{\text{as}}(\text{N–CH}_3)$	1257	1270	1261	1269
$w(\text{CH}_3) + \nu(\text{C–O})$	1115	1141	1104	1129
$w(\text{CH}_3) + \nu(\text{C–O}) + \nu(\text{C–CH}_3)$	1054	1066	1032	1045
$\nu_{\text{s}}(\text{Mo=O})$	926	992		
$\nu_{\text{as}}(\text{Mo=O})$	905	964		
$\delta(\text{O=C–N})$	642	633	645	611
$\nu_{\text{as}}(\text{Mo–O}_h)$	584	577		

vibration, $\delta_{\text{s}}(\text{CH}_3)$. For the free HDMLA ligand, this vibrational mode appears at 1643 cm^{-1} (calc. 1697 cm^{-1}). On passing from free HDMLA ligand to $\text{MoO}_2(\text{DMLA})_2$, the shift towards a lower frequency of $\nu(\text{C=O})$ is related to the coordination of the carbonyl oxygen. It should be noted that in the free HDMLA ligand, the $\nu(\text{C=O})$ stretching (exp. 1643 cm^{-1} ; calc. 1697 cm^{-1}) is also influenced by intramolecular bonding hydrogen between the hydroxyl and carbonyl groups (see Fig. 2) which is not present in $\text{MoO}_2(\text{DMLA})_2$ complex. Since the $\text{MoO}_2(\text{DMLA})_2$ complex bears two DMLA ligands, the two C=O moieties can vibrate in-phase or out-of-phase. Our theoretical treatment allowed us to characterize both of them. In-phase $\nu(\text{C=O})$ stretching is calculated to appear at 1654 cm^{-1} whereas out-of-phase vibration occurs at 1669 cm^{-1} .

The frequency at 1508 cm^{-1} is assigned to the C–N stretching vibration, although there is a considerable contribution of $\delta_{\text{a}}(\text{CH})$ to this band. The peaks at 1448 cm^{-1} (calc. 1510 cm^{-1}) and the peaks at 1361 cm^{-1} (calc. 1407 cm^{-1}) are due to the asymmetrical bending vibration $\delta_{\text{as}}(\text{CH}_3)$ and symmetrical bending vibration $\delta_{\text{s}}(\text{CH}_3)$, respectively. The band around 1256 cm^{-1} is predominantly related to the asymmetric stretching of the $\text{N–}(\text{CH}_3)_2$ moiety.

The peak appearing at 1115 cm^{-1} is due to two major contributions: an out-of-plane bending (wagging) mode, $w(\text{CH}_3)\text{–C}$ and $w(\text{CH}_3)\text{–N}$, and C–O stretching, $\nu(\text{C–O})$. The corresponding vibrational mode for the free HDMLA is found at 1104 cm^{-1} . A similar pattern is predicted by our calculated frequencies (1141 and 1129 cm^{-1} , respectively). The corresponding shift towards higher frequencies upon coordination is somewhat related to the shortening of the C–O_h bond length as a result of chelation; calculated C–O_h bond distances in $\text{MoO}_2(\text{DMLA})_2$ complex and in free HDMLA are 1.389 and 1.409 Å, respectively. Three major vibrational modes correspond to the peak at 1054 cm^{-1} , namely, $w(\text{CH}_3)\text{–C}$, $\nu(\text{C–CH}_3)$ and $\nu(\text{C–O})$.

The IR spectra of $\text{MoO}_2(\text{DMLA})_2$ show two strong bands around 905 cm^{-1} (calc. 964 cm^{-1}) and 926 cm^{-1} (calc. 992 cm^{-1}) which are assigned to the asymmetric and symmetric Mo=O stretches, in *cis*- $[\text{MoO}_2]^{2+}$ moiety, respectively. The strong/strong feature of these bands is very characteristic for *cis*-dioxo complexes. Interestingly, an analysis of the intensity ratio of these two bands can be explored in the diagnostic if a particular complex is an oxo-peroxo (strong/medium) or a dioxo (strong/strong) complex [16]. Other frequencies related to the molybdenum center include: $\nu_{\text{as}}(\text{Mo–O}_h)$ (exp. 584 cm^{-1} ; calc. 577 cm^{-1}); $\nu_{\text{s}}(\text{Mo–O}_h)$ (calc. 569 cm^{-1}); $\rho(\text{O}_h\text{–Mo–O}_h)$ (calc. 517 cm^{-1}); $\delta_{\text{s}}(\text{O}_h\text{–Mo–O}_h)$ (calc. 510 cm^{-1}); $\delta_{\text{s}}(\text{O=Mo=O})$ (calc. 364 cm^{-1}); $w(\text{O=Mo=O})$ (calc. 309 cm^{-1}); $\tau(\text{O=Mo=O})$ (calc. 226 cm^{-1}).

5. Conclusion

A novel neutral *cis*-dioxomolybdenum complex bearing a bidentate chiral ligand ((*S*)-*N,N*-dimethylactamide), MoO₂(DM-LA)₂, has been synthesized and structurally characterized through experimental and theoretical approaches. The use of this compound in the catalytic (a)symmetric oxidation of organic substrates is a special issue which is being currently investigated in our laboratory.

Acknowledgements

F.R.S. acknowledges the FAPESP (2009/01628-8) and CNPQ funding agencies. Q.B.C., J.Z.-S. thank the Brazilian foundation CNPq for research grants. Excellent computational facilities were provided by the computer center of CENAPAD – Centro Nacional de Processamento de Alto Desempenho em São Paulo. This study was also supported by the “Programa de Cooperación Internacional” maintained by CAPES (Brazil) and by the Ministerio de Educación y Cultura del Gobierno Español. Spanish –Brazilian (PHB2009-0065-PC).

Appendix A. Supplementary material

CCDC contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (CSD 794655). Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.ica.2011.04.022](https://doi.org/10.1016/j.ica.2011.04.022).

References

- [1] F.E. Kühn, M. Groarke, E. Bencze, E. Herdtweck, A. Prazeres, A.M. Santos, M.J. Calhorda, C.C. Romão, I.S. Gonçalves, A.D. Lopes, M. Pillinger, *Chem. Eur. J.* 8 (2002) 2370.
- [2] F.E. Kühn, A.M. Santos, A.D. Lopes, I.S. Gonçalves, J.E. Rodríguez-Borges, M. Pillinger, C.C. Romão, *J. Organomet. Chem.* 621 (2001) 207.
- [3] C.D. Nunes, M. Pillinger, A.A. Valente, A.D. Lopes, I.S. Gonçalves, *Inorg. Chem. Commun.* 6 (2003) 1228.
- [4] M. Groarke, I.S. Gonçalves, W.A. Herrmann, F.E. Kühn, *J. Organomet. Chem.* 649 (2002) 108.
- [5] A. Gunyar, M.D. Zhou, M. Drees, P.N.W. Baxter, G. Bassioni, E. Herdtweck, F.E. Kühn, *Dalton Trans.* (2009) 8746.
- [6] A. Jimtaisong, R.L. Luck, *Inorg. Chem.* 45 (2006) 10391.
- [7] A.P. Costa, P.M. Reis, C. Gamelas, C.C. Romão, B. Royo, *Inorg. Chim. Acta* 361 (2008) 1915.
- [8] H.K. Lee, Y.-L. Wong, Z.-Y. Zhou, Z.-Y. Zhan, D.K.P. Ng, T.C.W. Mak, *J. Chem. Soc., Dalton Trans.* (2000) 539.
- [9] G. Lyashenko, G. Saischek, M.E. Judmaier, M. Volpe, J. Baumgartner, F. Belaj, V. Jancik, R. Herbst-Irmer, N.C. Mösch-Zanetti, *Dalton Trans.* (2009) 5655.
- [10] Z. Dawoodi, R.L. Kelly, *Polyhedron* 5 (1986) 271.
- [11] M. Bagherzadeh, L. Tahsini, R. Latifi, L. Keith Woo, *Inorg. Chim. Acta* 362 (2009) 3698.
- [12] W.A. Herrmann, G.M. Lobmaier, T. Priermeier, M.R. Mattner, B. Scharbert, *J. Mol. Catal. A* 117 (1997) 455.
- [13] A. Basak, A.U. Barlan, H. Yamamoto, *Tetrahedron: Asymmetry* 17 (2006) 508.
- [14] W.P. Griffith, C.A. Pumphrey, T.-A. Rainey, *J. Chem. Soc., Dalton Trans.* (1986) 1125.
- [15] A.U. Barlan, A. Basak, H. Yamamoto, *Angew. Chem., Int. Ed.* 45 (2006) 5849.
- [16] S.K. Maiti, K.M.A. Malik, S. Gupta, S. Chakraborty, A.K. Ganguli, A.K. Mukherjee, R. Bhattacharyya, *Inorg. Chem.* 45 (2006) 9843.
- [17] S.J. Lord, N.A. Epstein, R.L. Paddock, C.M. Vogels, T.L. Hennigar, M.J. Zaworotko, N.J. Taylor, W.R. Driedzic, T.L. Broderick, S.A. Westcoot, *Can. J. Chem.* 77 (1999) 1249.
- [18] W.P. Griffith, H.I.S. Nogueira, A.J.P. White, D.J. Williams, *Polyhedron* 16 (1997) 1323.
- [19] N.C. Tam, S.P. Fletcher, C.M. Vogels, S.A. Westcoot, *Transition Met. Chem.* 28 (2003) 103.
- [20] W.P. Griffith, C.A. Pumphrey, A.C. Skapski, *Polyhedron* 6 (1987) 891.
- [21] V.I. Dzyuba, L.I. Koval, V.V. Bon, V.I. Pekhnyo, *Polyhedron* (2010) 2900.
- [22] E.J. Brown, A.C. Whitwood, P.H. Walton, A.K. Duhme-Klair, *Dalton Trans.* (2004) 2458.
- [23] R. Dinda, P. Sengupta, S. Ghosh, W.S. Sheldrick, *Eur. J. Inorg. Chem.* (2003) 363.
- [24] F.E. Kühn, J. Zhao, W.A. Herrmann, *Tetrahedron: Asymmetry* 16 (2005) 3469.
- [25] R.D.R.S. Manian, R. Leino, O. Wichmann, A. Lehtonen, *Inorg. Chem. Commun.* 12 (2009) 1004.
- [26] A.J. Burke, *Coord. Chem. Rev.* 252 (2008) 170.
- [27] H.B. Kagan, H. Mimoun, C. Mark, V. Schurig, *Angew. Chem., Int. Ed.* 18 (1979) 485.
- [28] V. Schurig, K. Hintzer, U. Leyrer, C. Mark, P. Pitchen, H.B. Kagan, *J. Organomet. Chem.* 370 (1989) 81.
- [29] W. Winter, C. Mark, V. Schurig, *Inorg. Chem.* 19 (1980) 2045.
- [30] F.R. Sensato, Q.B. Cass, E. Longo, J. Zuckerman-Schpector, R. Custodio, J. Andrés, M. Zaldini-Hernandes, R.L. Longo, *Inorg. Chem.* 40 (2001) 6022.
- [31] F.R. Sensato, R. Custodio, Q.B. Cass, E. Longo, M. Zaldini-Hernandes, R.L. Longo, J. Andres, *J. Mol. Struct. (THEOCHEM)* 589–590 (2002) 251.
- [32] F. Batigaglia, M. Zaldini-Hernandes, A.G. Ferreira, I. Malvestiti, Q.B. Cass, *Tetrahedron* 57 (2001) 9669.
- [33] F.R. Sensato, R. Custódio, E. Longo, V.S. Safont, J. Andres, *J. Org. Chem.* 68 (2003) 5870.
- [34] F.R. Sensato, R. Custodio, E. Longo, V.S. Safont, J. Andres, *Eur. J. Org. Chem.* (2005) 2406.
- [35] S. Berski, F.R. Sensato, V. Polo, J. Andrés, V.S. Safont, *J. Phys. Chem. A* 115 (2011) 514.
- [36] CrystalClear, User Manual, Rigaku/MSI Inc., Rigaku Corporation, The Woodlands, TX, 2005.
- [37] T. Higashi, ABCOR, Rigaku Corporation, Tokyo, Japan, 1995.
- [38] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, *J. Appl. Crystallogr.* 26 (1993) 343.
- [39] G.M. Sheldrick, SHELXL97, Program for Crystal Structure Analysis (Release 97-2), University of Göttingen, Germany, 1997.
- [40] A.L. Spek, PLATON, A Multipurpose Crystallographic Tool, Utrecht University, The Netherlands, 1998.
- [41] L.J. Farrugia, *J. Appl. Crystallogr.* 32 (1999) 837.
- [42] C.K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Tennessee, 1976.
- [43] DIAMOND, Visual Crystal Structure Information System, Version 3.1, CRYSTAL IMPACT, Postfach 1251, D-53002 Bonn, Germany, 2006.
- [44] D. Seebach, H.O. Kalinowski, B. Bastani, G. Crass, H. Daum, H. Dorr, N.P. Dupreez, V. Ehrig, W. Langer, C. Nussler, H.A. Oei, M. Schmidt, *Helv. Chim. Acta* 60 (1977) 301.
- [45] A.D. Becke, *Phys. Rev. A* 38 (1988) 3098.
- [46] J.C. Slater, first ed., *Quantum Theory of Molecules and Solids: The Self-Consistent Field for Molecules and Solids*, vol. 4, McGraw-Hill, New York, 1974.
- [47] A.D. Becke, *J. Chem. Phys.* 98 (1993) 5648.
- [48] S.H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* 58 (1980) 1200.
- [49] C.T. Lee, W.T. Yang, R.G. Parr, *Phys. Rev. B* 37 (1988) 785.
- [50] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, J.J.A. Montgomery, T. Vreven, K.N. Kudin, J.C. Burant, J.M. Millam, S.S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G.A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J.E. Knox, H.P. Hratchian, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, P.Y. Ayala, K. Morokuma, G.A. Voth, P. Salvador, J.J. Dannenberg, V.G. Zakrzewski, S. Dapprich, A.D. Daniels, M.C. Strain, O. Farkas, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J.V. Ortiz, Q. Cui, A.G. Baboul, S. Clifford, J. Cioslowski, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, C. Gonzalez, J.A. Pople, *GAUSSIAN03*, Revision B.04 ed., Gaussian, Inc., Wallingford, CT, 2004.
- [51] C.A. Bayse, A. Jimtaisong, A.K. Kabadalam, R.L. Luck, R. Pandey, M.J. Stevens, *J. Mol. Struct.* 754 (2005) 96.
- [52] D.V. Deubel, J. Sundermeyer, G. Frenking, *Inorg. Chem.* 39 (2000) 2314.
- [53] J.J. Griffin, J.A. Wheeler, *Phys. Rev.* 108 (1957) 311.
- [54] D.L. Hill, J.A. Wheeler, *Phys. Rev.* 89 (1953) 1102.
- [55] P.J. Hay, W.R. Wadt, *J. Chem. Phys.* 82 (1985) 299.
- [56] A.E. Reed, L.A. Curtiss, F. Weinhold, *Chem. Rev.* 88 (1988) 899.
- [57] K. Wiberg, *Tetrahedron* 24 (1968) 1083.
- [58] M.P. Mingos, *J. Organomet. Chem.* 179 (1979) C29.
- [59] K. Tatsumi, R. Hoffmann, *Inorg. Chem.* 19 (1980) 2656.
- [60] G. Barea, A. Lledos, F. Maseras, Y. Jean, *Inorg. Chem.* 37 (1998) 3321.
- [61] V.L. Abramenko, V.S. Sergienko, *Russ. J. Inorg. Chem.* 54 (2009) 2031.
- [62] P. Geerlings, F. De Profit, W. Langenaeker, *Chem. Rev.* 103 (2003) 1793.
- [63] W. Yang, R.G. Parr, *Proc. Natl. Acad. Sci. USA* 82 (1985) 6723.
- [64] W. Yang, W.J. Mortier, *J. Am. Chem. Soc.* 108 (1986) 5708.
- [65] F. De Profit, C.v. Alsenoy, A. Peeters, W. Langenaeker, P. Geerlings, *J. Comp. Chem.* 23 (2002) 1198.
- [66] F.L. Hirshfeld, *Theor. Chim. Acta* 44 (1977) 129.
- [67] H.-G. Mack, H. Oberhammer, *J. Am. Chem. Soc.* 119 (1997) 3567.
- [68] P. Gisdakis, S. Antonczak, S. Köstlmeier, W.A. Herrmann, N. Rösch, *Angew. Chem., Int. Ed.* 37 (1998) 2211.
- [69] V.V. Chalapatih, K.V. Ramiah, *Proc. Math. Sci.* 68 (1968) 109.
- [70] R.L. Jones, *J. Mol. Spectrosc.* 11 (1963) 411.