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Structure and chemical bonding in *cis*- and *trans*- $M(NO)_2(O_2CR)_2$ (M = Cr and Mo) complexes

Ludmiła Szterenberg^a, Szczepan Roszak^b, Renata Matusiak^a, Antoni Keller^{a,*}

^a Faculty of Chemistry, University of Wrocław, Joliot-Curie 14, 50-383 Wrocław, Poland

^b Institute of Physical and Theoretical Chemistry, Wrocław University of Technology, Wyb. Wyspiańskiego 27, 50-370 Wrocław, Poland

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Abstract

New *cis*- and *trans*-nitrosyl complexes of the formula $M(NO)_2(O_2CR)_2$ (M = Cr and Mo) were synthesized and characterized spectroscopically. The supporting theoretical studies indicate the deviation of molecules from their ideal geometries. The most striking consequence is the deformation of the ON–M–NO fragment from its linear form, in *trans* complexes. This deformation leads to the additional weak $v_s(NO)$ vibration. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

The unique physical and chemical properties of metal nitrosyl complexes [1-9], their importance related to biological and medical aspects [10-15], and their potential application in organic synthesis [16] have led to the constant interest in these compounds observed for more then 100 years [17]. The molecular unit $\{M(NO)_{x}\}^{n}$ (n is the number of d electrons of the metal [2]) is formed, inside which the electron density can move within a wide range. The relation between electronic density distribution in $\{M(NO)_x\}^n$ and the nature of the central atom and other coordinated ligands is still an important issue in structural physicochemistry, biochemistry (because of the biological importance of some complexes ([10-15]) and in catalysis. Complexes of this group are known as catalysts of oxidation [18-23], hydrogenation [24-26], oligomerization and polymerization [27–33], isomerization [34–38], and metathesis [23–34,39,40] reactions. The most active catalysts of the reaction of olefin metathesis are nitrosyl complexes of molybdenum [34,41-43] and tungsten [43,39,44]. These compounds also catalyze oligomerization and polymerization reactions of alkenes and alkynes [30-33,45,46].

The nitrosyl complexes with ligands coordinated via oxygen atoms are especially important. Carbene complexes of the type $[M(NO)_2(=CHR)L_2(AlCl_2)_2]$ (M = Cr, Mo; L = alkoxy or carboxylate ligands), were obtained reactions of dinitrosyl complexes of the in $\{M(NO)_2(OR)_2\}_n$ and $M(NO)_2(O_2CR)_2$ type with RAlCl₂ [32,47,48]. In the case of molybdenum, stable alkylidene complexes are formed. Here, coordinated alkylidene ligands have nucleophilic character in spite of the low oxidation state of the metals. Thus, these compounds are different carbene complexes than the Fischer (low oxidation states, electrophilic carbene ligands) or Schrock (high oxidation state, nucleophilic carbene ligands) compounds. In the synthesis of these compounds, RAlCl₂ plays two roles — as an alkylating agent, but first of all it is a Lewis acid, emptying the coordination sites at the metal due to breaking the bridging (in polymeric complexes) or chelate bonds [32,47,48]. A similar effect is also caused by other Lewis acids, like $M'Cl_4$ (M' = Ti, Sn) [31–33]. Terminal acetylenes, present in such systems, could generate the formation of dinitrosylcarbene (vinylidene) catalysts. These complexes should contain low oxidation state metals. Their stoichiometries, $M(NO)_2(=CRR')L_2(LA)_2$, are similar to those of the dinitrosylcarbene complexes obtained earlier in our laboratory [32,47,48], but the carbene groups are electrophilic in character.

^{*} Corresponding author. Tel.: +48-71-320-4334; fax: +48-71-328-2348.

E-mail address: akeller@wchuwr.chem.uni.wroc.pl (A. Keller).

Synthesis of new trans- and cis-dinitrosylchromium complexes, their spectroscopic characterization and the theoretical study of the structure and chemical bonding of these types of chromium and molybdenum complexes are the subject of this paper.









Fig. 1. The cis (a) and trans (b) structures of M(NO)₂(O₂CR)₂ (M = Cr or Mo) complexes. The corresponding geometrical parameters are given in Tables 1 and 2.

Table 1

The relative energies (ΔE) and structural parameters of *cis*- and trans-Cr(NO)₂(O₂CCH₃)₂ complexes from DFT calculations performed in LanL2DZ (L) and LanL2DZ supplemented by the polarization function (L+p) basis sets a

Parameters	cis L	cis L + p	trans L	trans L+p	
ΔE	0	0	25.3	26.6	
Cr–O ₂	2.03	2.016	2.02	2.16	
Cr-O ₃	2.09	2.08	2.17	2.01	
Cr-N ₁	1.70	1.70	1.73	1.73	
N ₁ -O ₁	1.20	1.16	1.20	1.16	
N_1 –Cr– N_{11}	93.9	92.0	132.2	130.1	
$Cr-N_1-O_1$	176.2	174.8	163.0	161.4	
O_2 -Cr- O_3	64.6	64.2	63.0	62.6	
$0_{2} - Cr - 0_{12}$	148.0	147.8	139.2	140.6	
$O_2 - Cr - O_{13}$	91.0	84.5	94.7	94.1	

^a Energy is measured in (kcal mol⁻¹), distance in (Å), angles in (°).

Table 2

The relative energies (ΔE) and structural parameters for the *cis*- and trans-Mo(NO)₂(O₂CCH₃)₂ complexes from calculations performed in LanL2DZ (L) and LanL2DZ supplemented by the single polarization function (L+p) basis sets ^a

Parameters	cis L	cis L + p	trans L	trans L+p	
ΔE	0	0	28.6	29.5	
Mo-O ₂	2.16	2.15	2.14	2.27	
Mo-O ₃	2.23	2.22	2.29	2.14	
Mo-N ₁	1.83	1.83	1.86	1.86	
N ₁ -O ₁	1.21	1.17	1.21	1.18	
N ₁ -Mo-N ₁₁	92.1	91.4	132.4	131.4	
Mo-N ₁ -O ₁	179.9	174.3	164.2	163.6	
O ₂ -Mo-O ₃	60.5	60.2	59.3	59.0	
$O_{2} - M_{0} - O_{12}$	145.9	145.8	141.5	142.3	
O ₂ -Mo-O ₁₃	82.9	83.4	99.8	99.6	

^a Energy is measured in (kcal mol⁻¹), distance in (Å), angles in (°).

2. Experimental

All experiments presented here were performed under an argon atmosphere using standard Schlenk techniques and vacuum-line procedures. Solvents were purified and distilled under argon from appropriate agents. The trans complexes [Cr(NO)₂(CO)₂(MeNO₂)₂]- $(BF_4)_2$, $[Cr(NO)_2(MeNO_2)_4](BF_4)_2$ and $\{Cr(NO)_2 (OR)_2$, (R = Et, Pr) were prepared according to the published procedure [32]. The IR spectra were measured on an Impact 400 (Nicolet) spectrophotometer. The ¹H NMR spectra were recorded using a Bruker 300 spectrometer and referenced to Me₄Si. Molecular weights were determined using a Perkin-Elmer 115 instrument.

2.1. Synthesis of trans- $Cr(NO)_2(O_2CMe)_2$ (1) and $trans-Cr(NO)_2(O_2CCPh_3)_2$ (2)

 NaO_2CR (8.6 mmol, $R = CH_3$, CPh_3) in MeOH was added to $[Cr(NO)_2(CO)_2(MeNO_2)_2](BF_4)_2$ or $[Cr(NO)_2$ - $(MeNO_2)_4](BF_4)_2$ (4.3 mmol) in MeNO₂ (20 ml) at room temperature. The reaction mixtures were stirred for 15 min after which the solutions were filtered and removed under vacuum. The complexes were extracted from the remainder with a small amount of CH₂Cl₂ and precipitated with hexane.

2.2. $Cr(NO)_2(O_2CMe)_2$

IR (Nujol mulls):v(NO) 1778 sh, 1698 vs; $v_{as}(CO_2)$ 1580 vs, v_s(CO₂) 1421 s. ¹H NMR (in CD₃CN at 20°C): δ 2.10 (s, 6H, CH₃) ppm. Anal. Calc. for C₄H₆CrN₂O₆: C, 20.88; H, 2.63; N, 12.17. Found: C, 20.96; H 2.70; 12.01%.

2.3. $Cr(NO)_2(O_2CCPh_3)_2$

IR (Nujol mulls): v(NO) 1777 sh, w, 1696 vs; $v_{as}(CO_2)$ 1559 vs, $v_s(CO_2)$ 1447 m. ¹H NMR (in acetone-d₆ at 20°C): δ 7.26 (m, 30H, Ph) ppm. *Anal.* Calc. for C₄₀H₃₀CrN₂O₆: C, 69.97; H, 4.40; N, 4.08. Found: C, 70.08; H, 4.51; N, 4.00%.

2.4. Synthesis of $cis \{ Cr(NO)_2(OR)_2 \}_n$ (R = Et (3a), ^{*i*}Pr (4a))

A solution of trans-{Cr(NO)₂(OEt)₂}_n in toluene was stirred for 30 min at 60°C. The green precipitate of the *cis*-isomer was filtered off, washed with CH₂Cl₂ and dried in vacuo.

Table 3

Calculated and experimental frequencies v(NO) (cm⁻¹) and intensities I (km mol⁻¹) for *cis*- and *trans*-M(NO)₂(O₂CCH₃)₂ (M = Cr, Mo)^a

	Calculated					Experimental				
	v		Ι	Ι			v	$Iv_{\rm s}/Iv_{\rm as}$	$v_{\rm calc}/v_{\rm exp}$	
	L	L + p	L	L + p	L	L + p	_		L	L+p
v_{as}	1727	1857	1117	1348	0.44	0.50	1699 ^ь	0.43		
V _s	1829	1977	498	676			1849 ^ь			
Δv^{c}	102	102					150 ^b			
v_{as}	1697	1840	1431	1708	0.14	0.18	1698	0.14	1.00	1.08
vs	1778	1926	203	314			1778		1.00	1.08
Δv^{c}	81	86					80			
V _{as}	1670	1811	1098	1294	0.43	0.44	1650 ^d	0.42	1.01	1.09
v _s	1759	1903	472	570			1770 ^d		0.99	1.07
Δv °	89	92					120 ^d			
Vas	1625	1772	1675	1733	0.12	0.17	1665 °			
v.	1710	1857	201	293						
Δv^{c}	85	85								
	v_{as} v_{s} $\Delta v c$	$\begin{array}{c c} & Calculat\\ & & \\ \hline \nu \\ & \\ \hline \nu \\ \\ L \\ \hline \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\ \\$	$\begin{tabular}{ c c c c c } \hline Calculated \\ \hline \hline v \\ \hline v \\ \hline L $L+p$ \\ \hline v_{as} 1727 1857 \\ v_s 1829 1977 \\ $\Delta v \ ^c$ 102 102 \\ v_{as} 1697 1840 \\ v_s 1778 1926 \\ $\Delta v \ ^c$ 81 86 \\ \hline v_{as} 1670 1811 \\ v_s 1759 1903 \\ $\Delta v \ ^c$ 89 92 \\ v_{as} 1625 1772 \\ v_s 1710 1857 \\ $\Delta v \ ^c$ 85 85 \\ \hline \end{tabular}$	$\begin{tabular}{ c c c c } \hline Calculated & \hline v & I \\ \hline v & v & I \\ \hline v & L & $L+p$ & I \\ \hline v & I & 129 & 1977 & 498 \\ \hline Δv c & 102 & 102 & 102 \\ \hline v & as & 1697 & 1840 & 1431 \\ \hline v & 1778 & 1926 & 203 \\ \hline Δv c & 81 & 86 \\ \hline v & as & 1670 & 1811 & 1098 \\ \hline v & s & 1759 & 1903 & 472 \\ \hline Δv c & 89 & 92 \\ \hline v & as & 1625 & 1772 & 1675 \\ \hline v & 1710 & 1857 & 201 \\ \hline Δv c & 85 & 85 \\ \hline \end{tabular}$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

^a Calculations were done in LanL2DZ (L) and LanL2DZ supplemented by the polarization function (L+p) basis sets.

^b For cis-{Cr(NO)₂(OEt)₂}_n.

^c $\Delta v = v_{\rm s} - v_{\rm as}$.

^d Ref. [62].

^e For trans-[Mo(NO)₂(Hsal-INH)₂] [59].

Table 4

Frequencies of v(NO) and relative intensities Iv_s/Iv_{as} of other known *cis*- and *trans*-dinitrosyl complexes of chromium and molybdenum

Complex	$v_{\rm s}({\rm NO})~({\rm cm}^{-1})$	$v_{\rm as}(\rm NO)~(\rm cm^{-1})$	$\Delta v(\text{NO})^{\text{a}} (\text{cm}^{-1})$	$Iv_{\rm s}/Iv_{\rm as}$	Ref.
trans-Cr(NO) ₂ (O ₂ CCPh ₃) ₂	1777	1696	81	0.12	b
trans-{ $Cr(NO)_2(OEt)_2$ } _{2n}		1720			[32]
trans-{ $Cr(NO)_2(O^iPr)_2$ } _n		1718			[32]
trans- $[Cr(NO)_2(MeCN)_4]^{2+}$		1793			[32,50]
$trans - [Cr(NO)_2(MeNO_2)_4]^{2+}$		1798			[32]
$trans - [Cr(NO)_2(CO)_2(MeNO_2)_2]^{2+}$		1791			[32]
$trans - [Cr(NO)_2(bipy)_2]^{2+}$		1702			[32]
$cis-{Cr(NO)_2(O'Pr)_2}_n$	1854	1698	156	0.41	ь
cis-[Cr(NO) ₂ (OEt) ₂ (SnCl ₄)]	1887	1766	121	0.45	ь
cis-[Cr(NO) ₂ (O ₂ CCPh ₃) ₂ (SnCl ₄) ₂]	1885	1763	122	0.48	ь
trans-[Mo(NO) ₂ (Hsal-BZH) ₂]		1678			[49]
trans-[Mo(NO) ₂ (Hvan-BZH) ₂]		1671			[49]
trans-[Mo(NO) ₂ (Hvan-INH) ₂]		1678			[49]
cis -{Mo(NO) ₂ (OEt) ₂ EtOH} _n	1740	1616	124	0.45	[66]
$cis-{Mo(NO)_2(O'Pr)_2}_n$	1772	1630	142	0.44	[66]
$cis-Mo(NO)_2(O_2CPh)_2$	1790	1682	118	0.43	[62]

^a $\Delta v(NO) = v_s(NO) - v_{as}(NO).$

^b This work.



Fig. 2. The HOMO for the cis-Cr(NO)₂(O₂CR)₂ molecule plotted in the N–Cr–N plane. The contour lines from 1–12 are positive (increasing order), from 13–17 are negative (decreasing order). The contour 1 denotes zero. The spacing between lines is 0.0125 units. Note the π character of the Cr–N bond in the orbital.

2.5. $\{Cr(NO)_2(OEt)_2\}_n$

IR (Nujol mulls): v_s (NO) 1849 s, v_{as} (NO) 1699 vs, v(OR) 1093 m, 1050 m, 1025 sh. ¹H NMR (acetone-d₆): δ 3.62, 3.35 (s, br, 6H, CH₃CH₂), 1.35, 1.06 (s, 9H, CH₃CH₂) ppm. *Anal.* Calc. for C₄H₁₀CrN₂O₄: C, 23.77; H, 4.99; N, 13.86. Found: C, 23.89; H, 5.04; N, 13.73%.

2.6. $\{Cr(NO)_2(O^{1}Pr)_2\}_n$

IR (Nujol mulls): $v_s(NO)$ 1854 s, $v_{as}(NO)$ 1698 vs.

2.7. Synthesis of $cis - \{Cr(NO)_2(OEt)_2(SnCl_4)\}_n$ (5) and $cis - \{Cr(NO)_2(O_2CCPh_3)_2(SnCl_4)_2\}_n$ (6)

 $SnCl_2$ in CH_2Cl_2 was added to a stirred solution of the appropriate $\{Cr(NO)_2L_2\}_n$ complex $(L = OEt, O_2CCPh_3)$ in CH_2Cl_2 in a 1:2 molar ratio. The yellowbrown adduct precipitates were filtered off, washed with CH_2Cl_2 and dried in vacuo.

2.8. $[Cr(NO)_2(OEt)_2(SnCl_4)]$

IR (Nujol mulls): v_{s} (NO) 1887 s, v_{as} (NO) 1766 vs, v(OR) 1088 m, 1008 m, 993 sh. ¹H NMR (in CD₃CN at 20°C): δ 4.54, 3.64 (s, br, 4H, CH₂CH₃), 1.26, 0.91 (s, br, 6H, CH₂CH₃) ppm. *Anal.* Calc. for C₄H₁₀Cl₄CrN₂O₄ Sn: C, 10.38; H, 2.18; Cl, 30.65; N, 6.05. Found: C, 10.44; H, 2.27; Cl, 35.71; N, 5.97%.

2.9. $[Cr(NO)_2(O_2CCPh_3)_2(SnCl_4)_2]$

IR (Nujol mulls): v_s (NO) 1885 s, v_{as} (NO) 1763 vs, v_{as} (CO) 1550 vs, v_s (CO) 1421 s. ¹H NMR (in CD₃CN at 20°C): δ 7.26 (m, 30H, Ph) ppm. *Anal.* Calc. for

 $C_{40}H_{30}Cl_8CrN_2O_6Sn_2$: C, 39.78; H, 2.50; Cl, 23.48; N, 2.32. Found: C, 39.87; H, 2.54; Cl, 23.55; N, 2.27%.

3. Details of theoretical studies

The studies presented here were performed applying density functional theory (DFT) [49]. The DFT approach utilized Becke's three parameters hybrid functional (B3LYP) [50], based on earlier works [51,52]. Calculations were performed within the LanL2DZ [53,54] basis set. Additional calculations were performed with the LanL2DZ basis supplemented by the single five-component d function on heavy atoms. The exponents of polarization functions for chromium and molybdenum are 0.058317 and 0.1270, respectively. Exponents for other atoms were adopted from Huzinaga et al. [55]. The computations presented were made using the program GAUSSIAN-94 [56].

4. Results and discussion

The structure and the nature of bonding in nitrosyl complexes were discussed in 1974 by Enemark and Feltham [2]. In the case of dinitrosyl complexes possessing the $\{M(NO)_2\}^n$ fragment the important problem concerns the N-M-N angle. The number of d electrons, *n*, determines the linearity $(D_{\infty h})$ or nonlinearity (C_{2v}) of the N-M-N angle. The six-coordinated dinitrosyl complexes of Group 6 metals should contain the nonlinear $M(NO)_2$ fragment. All the structurally characterized compounds, including Mo(NO)₂TTP, possess nitrosyl ligands in the *cis* position [6,57]. However, the dinitrosylchromium complex $[Cr(NO)_2(MeCN)_4](PF_6)_2$, synthesized 30 years ago by Connolly et al. [58], is trans with regard of the nitrosyl groups. Only a single band in the region of the v(NO) frequency was observed in the IR spectrum of this compound. The replacement of acetonitrile ligands by sulfur chelating ones (S₂CNEt₂⁻



Fig. 3. The HOMO-1 for the *cis*-Cr(NO)₂(O₂CR)₂ molecule plotted in the N–Cr–N plane. The contour lines from 1–12 are positive (increasing order), from 13–17 are negative (decreasing order). The contour 1 denotes zero. The spacing between lines is 0.0125 units. Note the σ character of the Cr–N bond in the orbital.

(1)

and/or $S_2C_2(CN)_2^{2-}$ leads to the formation of respective *cis*-dinitrosylchromium complexes. Recently, the trans-dinitrosylmolybdenum complexes with Schiff bases were also synthesized [59]. A number of diatomic trans-dinitrosylchromium complexes were obtained in our laboratory [32]. The reaction of complexes containing the trans-[Cr(NO)]²⁺ core with M^IOR (M^I = Na, Li) leads to the formation of respective trans complexes. A similar reaction Eq. (1) yields dicarboxylatochromium complexes, i.e. $Cr(NO)_2(O_2CR)_2$ (where $R = CH_3$ or CPh_3).

[Cr(NO)2(CO)2(MeNO2)2](BF4)2 or $[Cr(NO)_{2}L_{4}](BF_{4})_{2}$ (L = MeCN or MeNO₂) + 2NaO₂CR \rightarrow Cr(NO)₂(O₂CR)₂ + 2NaBF₄ (R = Me (1) or CPh₃ (2)) The brown complex 1, soluble in donor solvents

(MeCN, MeNO₂, MeOH) is polymeric ({Cr(NO)₂- $(O_2CMe)_2\}_n$). The $\Delta v(CO_2) = v_{as} - v_s$ splitting equals 151 cm⁻¹ confirms the above [60,61]. Very low $\Delta v(CO_2)$ values (<105) generally indicate chelation [61]. For example, in [Mo(NO)₂(O₂CMe)₂]·MeOH, $\Delta v(CO_2)$ is 97 cm⁻¹ [62]. The ¹H NMR spectrum of 1 in CD₃NO₂ contains one methyl proton signal at 2.10 ppm.

Complex 2 (soluble in CH_2Cl_2 , benzene, toluene, CCl_{4}) exists in the monomeric form as indicated by its weight (Found: 683.91. Calc. molecular for $Cr(NO)_2(O_2CCPh_3)_2$: 686.68). The $\Delta v(CO_2)$ value for chelate triphenylacetate ligands is 112 cm⁻¹. The ¹H NMR spectrum (in CD₂Cl₂ at 20°C) exhibits a multiplet at 7.26 ppm due to phenyl protons. The IR spectra of 1 and 2 are similar to all the *trans*-dinitrosylchromium complexes [32,58] and are characterized by a single strong band at 1700 cm⁻¹ related to the v(NO)vibration. However weak shoulders at 1778 and 1777 cm^{-1} may also be observed.

Dinitrosylchromium complexes with alkoxy ligands (i.e. *trans*-{ $Cr(NO)_2(OR)_2$ }, R = Et (3), ^{*i*}Pr (4)), when heated (60°C) in noncoordinating solvents, undergo isomerization to *cis* complexes (3a, 4a). However, only the cis-{Cr(NO)₂(OEt)₂}_n (3a) complex was obtained in pure form, as a brown powder soluble only in polar solvents. Complex 4 partially disintegrates during such treatment, while complex 2 does not isomerize at all and at higher temperatures decomposes. Complex 1 is not soluble in noncoordinating solvents.

The IR spectra of complexes 3a and 4a (see Section 2) contain two v(NO) frequencies characteristic for the cis-{Cr(NO)₂}⁶ unit (C_{2v} symmetry), corresponding to symmetric and asymmetric stretching motions of the N–O bond. The v(CO) frequencies of RO⁻ ligands (e.g. for R = Et 1093, 1050 and 1025 cm⁻¹) may indicate the presence of bridging as well as terminal alkoxy ligands in these complexes [32,63]. The ¹H NMR spectrum of the complex 3a (see Section 2) also confirms the above. It contains two resonance signals for the CH₂ and CH₃ protons corresponding to the terminal and bridging ethoxy ligands.

Reactions of complexes 2 and 3 with Lewis acids (e.g. $SnCl_4$) induce similar trans- $[Cr(NO)_2] \rightarrow cis-[Cr(NO)_2]$ transformations, in 1:1 as well as in 1:2 molar ratios of reagents. The adducts cis-[Cr(NO)₂(OEt)₂(SnCl₄)] (5) and cis-[Cr(NO)₂(O₂CCPh₃)₂(SnCl₄)₂] (6) are produced in such reactions. Their IR spectra contain two characteristic v(NO) frequencies. The character of the spectrum of complex 5, in the range of v(OEt) frequencies, indicates the bridging and terminal coordination of ethoxy ligands [32,63]. Examination of the ¹H NMR spectrum (see Section 2) also leads to the same conclusion.

4.1. Theoretical results

Theoretical studies were performed for the M(NO)₂- $(O_2CMe)_2$ (M = Cr and Mo) complexes. The valence orbitals of chromium and molybdenum undergo the $d^{5}s^{1}$ hybridization which leads to a trigonal bipyramid structure. In the molecules studied, however, the metal-acetate rings destroy the perfect D_{4h} symmetry. Two equilibrium structures were located (Fig. 1) with the cis isomers (C_2 symmetry) being more stable then its *trans* partners (C_{2v} symmetry) (Tables 1 and 2). The X-ray structures for the trans-dinitrosyl complexes of Group 6 metals are unknown. The main structural difference between the ideal structures of the cis and trans isomers concerns the N-M-N angle. In the ideal trans structure the ON-M-NO fragment is linear. The studies performed, however, indicated a significant deviation from linearity with the N-M-N angle being 130.1 and 163.6° for Cr and Mo compounds, respectively. In the case of the cis isomers N-M-N angles of 92.0° (Cr) and 91.0° (Mo) are close to the values found for the perfect geometry (90.0°). The M-N-O branch was also found to be nonlinear. It was noted several years ago [64] that slightly bent M–N–O fragments are a common feature of polynitrosyl complexes. The electronic rationalization of this phenomenon was given by Kettle [65]. In an every molecule studied, the O-M-O angles of metal-acetate rings amount to about 60°, again far from the 90° expected for the ideal D_{2h} symmetry. This distortion leads to two different M-O bonds within the same ring.

The vibrational spectra of studied compounds reflects the geometry of the molecules. Two different frequencies for NO vibrations (asymmetrical and symmetrical) were expected and both are observed. The calculated and experimental frequencies are presented in Table 3. The most striking effect comparing this structure to the ideal is that there are two, instead of just one, vibra-

tional motions for NO in the trans case. The frequencies calculated applying the LanL2DZ basis set closely reproduces the available experimental spectra. The extension of the basis set by the polarization functions, however, leads to the systematically higher values of frequencies which have to scaled by 0.9 to reproduce experimental data. This scaling factor reflects the quality of the method and the basis set applied. The excellent agreement of the smaller basis results with experimental values has to be treated with caution. The differences between asymmetric and symmetric modes of N-O vibrations are reproduced satisfactorily. The calculated ratio of Iv_s/Iv_{as} is also close to that observed experimentally. This agreement gives us confidence in the calculations performed for trans isomers where experimental results are scarce. The inflection observed in the wide band of the trans isomer in the Cr based molecule fits the theoretically found symmetric vibration. The much lower ratio of Iv_s/Iv_{as} (0.14) for the *trans* isomer compared to that of the *cis* form (0.43) is consistent with molecular structures. The weak symmetric band would vanish in the case of the perfect D_{4h} structure. Table 4 collects the v(NO) frequencies and relative intensities Iv_s/Iv_{as} of other known cis- and complexes *trans*-dinitrosyl of chromium and molybdenum.

The nature of bonds formed by the metal are similar in Cr and Mo compounds. The analysis of bonding performed here is based on the Mulliken population analysis. The two highest molecular orbitals (Figs. 2 and 3) describe the Me-NO bonds. These bonds are covalent, and may be described as two three-centered N–Me–N σ and π bonds. The central metal atom donates 0.5 of an electron to the acetate rings, although the total loss of electrons in d orbitals amounts to 1.2 electrons. Due to the rearrangement of the electronic density of metal, its s orbitals gain 0.4 of an electron, while 0.3 of an electron is shifted to the metal p orbitals. The involvement of p orbitals in the formation of bonds indicates the deviation from the d⁵s hybridization and in effect the distortion of the perfect D_{2h} symmetry. The electronic structure of the center of coordination is similar in both the *cis* and *trans* isomers, and is visible as an almost equal occupation of the orbitals on the central atom.

5. Conclusions

The number of d electrons in the $\{M(NO)_2\}^n$ fragment determines its structural properties. The six-coordinated dinitrosyl complexes of Group 6 metals should have the *cis* form. However, *trans* isomers containing Cr or Mo are also known (Tables 3 and 4) and some of them were synthesized in this work. X-ray structures are not known for *trans*-dinitrosyl complexes of Group 6. Based on the previous IR studies [32,50,51], D_{2h} symmetry was expected for *trans* structures with a linear ON-M-NO fragment.

Theoretical studies determined two isomers (Fig. 1): cis (C_2 symmetry) and trans (C_{2v} symmetry), with the cis forms being energetically more stable (Tables 1 and 2). The trans NO groups are divided by a plane defined by the acetate rings. The latter structures are significantly distorted from ideal geometries. The expected D_{2h} symmetry of *trans* complexes, due to the nonlinearity of the ON–M–NO fragment, is lowered to C_{2v} . This distortion is observed as an additional symmetric NO vibration. The weak band corresponding to $v_s(NO)$ may be easily hidden in the strong one associated with the $v_{as}(NO)$ vibrational motion. In the case of compounds 1 and 2, the single bands at about 1700 cm⁻¹ is related to $v_{\rm as}(\rm NO)$, but weak shoulders at 1778 and 1777 cm⁻¹ may correspond to the symmetrical NO vibrations. The reasonable reproduction of the properties of the cis isomers gives confidence for the overall theoretical studies presented. The calculated intensities of observed bands are comparable in the *cis* case, while the second (symmetrical) vibration in the trans molecule is barely seen. The calculations led to the distortion of ON-M-NO structures in every isomer studied. The study of structures of other complexes would help to answer if this is a property of Cr and Mo complexes only or if this is a more general feature of nitrosyl complexes. The M-N-O branches were also distorted from linearity in every structure studied. The geometry optimization also indicated a significant deformation of the acetate rings. Different lengths of M-O bonds within the same rings were observed.

The electronic density rearrangement on the central atom is almost the same in both *cis* and *trans* isomers. The change in the electronic density is due to the transfer of electrons from d orbitals to the acetate rings (0.5 electron) and s and p orbitals (0.7 electron).

The reported results, including the charge distribution picture on the central and ligand atoms confirm the suggested mechanism of the formation of carbene and vinylidene catalysts in cis-M(NO)₂(O₂CR)₂-Lewis acid and {M(NO)₂(OR)₂}_n-Lewis acid systems [31– 33,47,48,54,66]. The favorable conditions for the electrophilic attack of Lewis acid molecules on the carboxylate ligand oxygen atoms are in the equatorial plane (M1O3O14N9N11 plane in Fig. 1). In the same plane, on the side opposite to the NO groups, carbene and vinylidene ligands will coordinate.

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