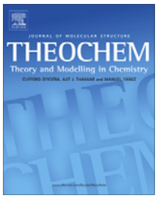
Journal of Molecular Structure: THEOCHEM 865 (2008) 28–35

Contents lists available at ScienceDirect

Journal of Molecular Structure: THEOCHEM

journal homepage: www.elsevier.com/locate/theochem



The nature of the metal–nitric oxide bond in the $[M(CN)_5(NO)]^q$ (M = Cr, Mn, Fe, Ru, Os, and Co) and *trans*-$[Ru(NH_3)_4L(NO)]^q$ (L = pyrazine, pyridine, N_2, H_2O, Cl^-, CN^-, NO_2^-) complexes: A bond-energy decomposition analysis

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A R T I C L E I N F O

Article history:
Received 1 February 2008
Received in revised form 16 June 2008
Accepted 16 June 2008
Available online 24 June 2008

Keywords:
Transition metal complexes
Nitrosyl
Energy decomposition analysis
Bonding energy
Density functional theory

A B S T R A C T

A bond-energy decomposition analysis (EDA) has been carried out to investigate the nature of the M—NO bonding in the pentacyanonitrosyl $[Cr(CN)_5(NO)]^{4-}$, $[Mn(CN)_5(NO)]^{3-}$, $[M(CN)_5(NO)]^{2-}$ (M = Fe, Ru, Os), $[Co(CN)_5(NO)]^{3-}$ complexes and in the *trans*-nitrosyltetraammineruthenium $[Ru(NH_3)_4L(NO)]^q$ (L = pyrazine, pyridine, N_2, H_2O ($q = 3$); and L = Cl^-, CN^-, NO_2^- ($q = 2$)) complexes. For the pentacyanonitrosyl complexes of Fe, Ru, and Os three fragmentation models have been considered: $\{M(CN)_5\}^{3-}\cdots\{NO\}^+$, $\{M(CN)_5\}^{2-}\cdots\{NO\}^0$, and $\{M(CN)_5\}^-\cdots\{NO\}^-$. The results of the EDA show that the linear M—NO bonds are predominantly covalent with a significant (~70%) contribution of π orbital interaction between unpaired electrons on the d_π and $\pi^*(NO^0)$ orbitals. EDA results point to the correlation between M—NO and M—L binding interactions in the *trans*-$[Ru(NH_3)_4L(NO)]^q$ complexes.

1. Introduction

The investigation of transition metal nitrosyl complexes holds much favour now due to the role of nitric oxide (NO) in various physiological processes [1–5]. The other reason of the attention to these species is the discovery of the photoinduced metastable linkage isomers, which have potential technological importance as high capacity storage devices [6–10]. The nitric oxide is a stable free radical, which forms numerous stable complexes with a metal center, however the assignment of oxidation states to the resulting M—NO species is subject to considerable ambiguity. Jørgensen described nitric oxide as a “non-innocent” ligand, i.e. such a ligand that does not allow the oxidation states of the central atoms to be defined [11]. Nitric oxide in the linear M—NO unit is often considered as a bound three electron donor (i.e. formally NO^+), which is isoelectronic with CO [12]. Enemark and Feltham suggested to treat the M—N—O fragment as a covalently bound inorganic $\{MNO\}^n$ functional group, where n is the total number of electrons associated with the metal d and $\pi^*(NO)$ orbitals [13]. Nevertheless, it is sometimes useful to describe the charge distribution between metal and NO as $\{M^{q-1}—NO^+\}$, $\{M^q—NO\}$, or $\{M^{q+1}—NO^-\}$ [14]. For example, the six-coordinate $\{MNO\}^6$ linear complexes have been regarded historically as complexes of M^{II} and NO^+, as this viewpoint has considerable power in predicting synthetic routes [15]. The electronic distribution in the {MNO} unit was elucidated by EPR, UV–vis, ESCA, Mössbauer, and IR spectroscopy as well as reactivity studies. However, experimental investigations resulted in contradictory conclusions, whether nitric oxide coordinated to a metal center should be described as NO^+, NO^0, or NO^- [15–22]. As early as 1971 Brown on the basis of Mössbauer and IR spectroscopy data made a proposal that nitroprusside-ion contains iron with an effective charge of +3 and that its description as a $Fe^{2+}—NO^+$ complex is misleading [16]. Nefedov et al. [17] on the basis of ESCA results concluded that nitric oxide has a negative charge in all nitrosyl complexes regardless of linear or bent structure of the {MNO} group. According to ref. [18] the measured Mössbauer parameters for iron carbonyl and nitrosyl complexes of a tetrapodal pentadentate amine ligand predicted that the iron formal oxidation state lies between IV and V, however, the $\{Fe^{II}NO^+\}$ description is also acceptable. The *trans*-$[(cyclam)Fe(NO)Cl]^{2+,1+,0}$ complexes ($\{Fe—NO\}^{6,7,8}$ series) were interpreted by Mössbauer spectroscopy as $Fe^{IV} \leftarrow NO^-$, $Fe^{III} \leftarrow NO^-$, and $Fe^{III} \leftarrow NO_2^-$, respectively [19]. According to ref. [20] the picture of the bonding in the low-spin non-heme iron nitrosyl series $\{FeNO\}^n$ developed on the basis of IR, Mössbauer, EPR, and DFT data corresponds to NO^+, NO^0 and NO^- for $n = 6$, 7, and $n = 8$, respectively.

Since the standard theoretical methodologies based on the molecular orbitals analysis do not yield a definite description of

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doi:10.1016/j.theochem.2008.06.014

the oxidation states and the M—NO chemical bond in nitrosyl complexes, attempts to employ new approaches have been undertaken. In ref. [23] the configuration interaction (CI) wave functions of ruthenium complexes $[RuL_5(NO)]^q$ ($L = NH_3$, Cl^-, CN^-) are presented as linear combinations of the valence bond structures, each of them referring to a certain model of bonding in the Ru—XY group. The results of this analysis demonstrated the predominant contribution of the covalently bound Ru^{III}—NO^0 structure.

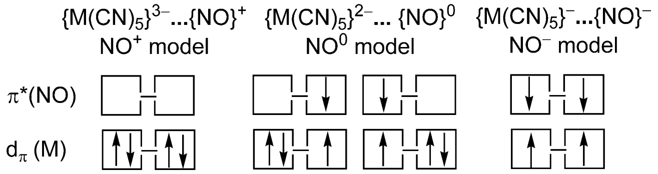
Energy decomposition analysis (EDA) is one of the most promising approaches to the study of chemical bonds in transition metal complexes [24]. Atanasov and Schönherr carried out the EDA for all minima and saddle points of the $[Fe(CN)_5(NO)]^{2-}$ ground state potential surface [25], in this work nitric oxide was considered as NO^+ and NO^0. Lubimova [26,27] performed the EDA for the series of nitrosyl cationic and anionic complexes considering nitric oxide as NO^+, NO^0, and NO^-. Caramori and Frenking [28] analyzed the electrostatic and covalent components of the Ru—NO bonding in the η^1-NO, η^1-ON, and η^2-NO linkage isomers of *trans*-$[Ru(NH_3)_4(L)(NO)]^q$ and *trans*-$[Ru(NH_3)_4(L)(NO)]^{q-1}$ complexes ($L = NH_3$, Cl^-, and H_2O) by means of EDA for NO^+ and NO^0 fragments. For innocent ligands, such as CN^- and CO, the choice of fragments is unambiguous [29], however the coordinated nitric oxide is a more sophisticated case.

In the present work, we make an attempt to use the EDA approach for the assignment of metal and NO ligand oxidation states in transition metal nitrosyl complexes with linear {MNO} group. We report the EDA results for two series of η^1-NO nitrosyl complexes: the pentacyanonitrosyl $[M(CN)_5(NO)]^q$ anions with $\{MNO\}^n = \{CrNO\}^6$ ($q = -4$), $\{MnNO\}^6$ ($q = -3$), $\{FeNO\}^6$, $\{RuNO\}^6$, $\{OsNO\}^6$ ($q = -2$), $\{CoNO\}^8$ ($q = -3$), and the nitrosyltetraammineruthenium *trans*-$[Ru(NH_3)_4L(NO)]^q$ cations with L = pyrazine (pyz), pyridine (py), N_2, H_2O ($q = 3$), and $L = Cl^-$, CN^-, NO_2^- (q = 2).

2. Computational methods

The EDA method was developed by Morokuma and Kitaura [30] and Ziegler and Rauk [31]. The bonding analysis according to the EDA scheme for the [AB] complex includes the following steps:

1. Geometry optimization for the complex [AB].
2. Decomposition of [AB] into the fragments A and B; for the metal–nitric oxide bond in $[M(CN)_5(NO)]^q$ anions (M = Fe, Ru, Os) three fragmentation models were considered:



For $[Co(CN)_5(NO)]^{3-}$ with the bent $\{MNO\}^8$ group NO^0 and NO^- models were examined; for $[Cr(CN)_5(NO)]^{4-}$, $[Mn(CN)_5(NO)]^{3-}$ and $[Ru(NH_3)_4(L)(NO)]^q$ only the NO^0 model was used. The *trans*-CN ligand in $[Fe(CN)_5(NO)]^{2-}$ was considered as CN^- anion with closed shells. For the Ru—L bond in $[Ru(NH_3)_4L(NO)]^q$ the $\{L\}^{q-3}\cdots\{Ru(NH_3)_4(NO)\}^{3+}$ fragmentation was examined.

3. Calculations of the free fragments [A] and [B], in which the atoms are placed at the same positions as in the complex. The interaction energy ΔE_{int} between [A] and [B] is calculated as

$$\Delta E_{int} = (E_{AB}-E_A-E_B);$$

A negative ΔE_{int} value corresponds to a stabilizing interaction between the fragments.

4. Calculation of the [AB] complex in which the interaction energy ΔE_{int} is decomposed into three physically meaningful terms [32,33]:

$$\Delta E_{int} = \Delta E_{elstat} + \Delta E_{Pauli} + \Delta E_{orb}.$$

The term ΔE_{elstat} is associated with the electrostatic interaction between the unperturbed charge distributions of the prepared fragments as they are brought together at their final positions, yielding the overall density that is a superposition of fragment densities $\rho_A + \rho_B$. For neutral fragments the electrostatic term is usually attractive, but it changes noticeably from the anions $[M(CN)_5(NO)]^q$ to the cations $[Ru(NH_3)_4L(NO)]^q$, so ΔE_{elstat} does not reveal the intrinsic features of M—NO bonds. The repulsive term ΔE_{Pauli} is caused by going from the product of fragment wave functions Ψ_A and Ψ_B to $\Psi_0 = NA[\Psi_A\Psi_B]$ that properly obeys the Pauli principle (A – antisymmetrization operator, N – renormalization constant). The orbital interaction energy ΔE_{orb} is the energy change due to the relaxation of the wave function to its final form through electron pair bonding, charge transfer and polarization [32]. It should be noted that ΔE_{orb} describes not only the interactions between the two fragments, but also the relaxation of orbitals at one fragment without mixing with orbitals at the other fragment [24]. It is implied that the higher the similarity between the electronic structures of the bonded and separated fragments, the less the $|\Delta E_{orb}|$ value. The ratio $\Delta E_{elstat}/\Delta E_{orb}$ is often used for the description of the nature of the chemical bond, though for the charged complexes and fragments this should be done with caution.

The ΔE_{orb} contribution was decomposed into the components from the irreducible representations of the C_{2v} point group

$$\Delta E_{orb} = \Delta E_{orb}(a_1) + \Delta E_{orb}(a_2) + \Delta E_{orb}(b_1) + \Delta E_{orb}(b_2).$$

This allows to determine the contributions of σ and π bonding to a covalent multiple bond: ΔE_σ value consists of the contributions from orbitals which belong to irreducible representation a_1, the ΔE_π value consists of contributions from b_1 and b_2 orbitals, neither ΔE_σ nor ΔE_π contain the irreducible representation a_2.

The bond dissociation energy $D_e = -\Delta E$ can be determined from ΔE_{int} and the fragment preparation energy ΔE_{prep}, which is the energy necessary to promote fragments from their equilibrium geometry and electronic ground state to the geometry and electronic state of the optimized structure:

$$\Delta E = \Delta E_{prep} + \Delta E_{int}.$$

The small $|\Delta E_{prep}|$ values indicate a reasonable choice of the fragmentation model.

For energy decomposition analysis the geometries of the complexes (except the chromium complex) have been optimized at the non-local DFT level of theory with the exchange functional of Becke [34] and the correlation functional of Perdew [35] (BP86) using the program package ADF [32]. For all complexes except $[Co(CN)_5(NO)]^{3-}$ the C_{2v} molecular symmetry was used. The calculations were carried out using uncontracted Slater type orbitals [36] with triple- quality in the valence region and double- quality in the core region augmented by one set of polarization functions (TZP) (basis I). Relativistic effects were taken into account by the zero order regular approximation (ZORA) [37,38]. The core electrons were treated in the frozen core approximation [39]. The primary argument in favour of the chosen basis set and method is the possibility to preserve the common methodology with the earlier studies, in which Fe^{II} complexes with CO and CN^- ligands have been considered [29]. This allowed us to keep to the same methodology as in the previous studies [25,29] and to facilitate the com-