ISSN 1070-3632, Russian Journal of General Chemistry, 2012, Vol. 82, No. 10, pp. 1619–1628. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © O.V. Sizova, 2012, published in Zhurnal Obshchei Khimii, 2012, Vol. 82, No. 10, pp. 1585–1599.

Procedure for the Analysis of Interfragment Donor–Acceptor Interactions in Transition Metal Complexes

O. V. Sizova

St. Petersburg State University, Universitetskii pr. 26, St. Petersburg, 198504 Russia
e-mail: ovsizova@mail.ru

Received January 26, 2012

Abstract—The procedure based on the first order density matrix has been suggested for the description of molecular electronic structures. The procedure includes: The calculation of interatomic bond-order indices and their σ-, π-, and δ-components; the construction of multicenter orbitals localized on fragments responsible for the formation of bonds inside fragments and between fragments; the classification of the constructed orbitals according to their population, valence activity, and orientation; the characterization of the realized donor–acceptor abilities of the fragments (ligands and more complicated structural units). The interaction between fragments is described by a rather small number of multicenter orbitals localized on them. The concept of the valence activity of a polyatomic fragment has been introduced and the algorithm of its calculation has been offered. The procedure is illustrated by the analysis of electronic structures of ruthenium(II), platinum(II), and rhodium(I) complexes.

DOI: 10.1134/S1070363212100015

Theoretical concepts of chemical bonds in transition metal complexes are based on the model [1], according to which ligands are coordinated to a metal due to the formation of a σ-donor M←L bond by means of the electronic density transfer from lone pairs (or occupied MOs) of a ligand to metal orbitals and, in those cases when a ligand has vacant π-MOs with a low energy, due to M→L back-bonding with the electronic density transfer from the occupied *d*-AOs of the metal. For more complicated compounds, supramolecular compounds among them, it is convenient to consider more complicated fragments (F) as structural units: one-center metal complexes, clusters, and extended organic molecules built, in turn, from several more simple molecules. Donor and acceptor abilities of a combined system remain its main characteristics required to understand a role and function of each fragment, as is the case with the classical model [1]. Meanwhile, neither experimental methods nor computational quantum-chemistry methods allow us to characterize unambiguously these properties. The theoretical estimate of these characteristics requires a certain "reference point," and the free fragments can naturally be used in this role. At present the following methods are used for description of donor–acceptor properties of coordinated ligands: EDA (Energy Decomposition Analysis) [2, 3], CDA (Charge Decomposition Analysis) [4–6], and NOCV (Natural Orbitals for Chemical Valence) [7–10], which are based on a priori partitioning of a complex into two fragments with formal charges assigned to them and on a sequential calculation of the electronic structure for the fragment-donor, fragment-acceptor, and complex.

The approach developed in the present work (valence-structural analysis, VSA) provides a possibility of a flexible partitioning of a complex into an arbitrary number of fragments and does not require a preliminary quantum-chemical calculation for each of them. This procedure was applied to characterize donor–acceptor properties of monodentate ligands in mono-nuclear ruthenium(II), platinum(II), and rhodium (I) complexes.

Bond order and its components. Within the limits of the qualitative molecular orbital theory the formal bond order (BO) in a diatomic molecule is defined by the number of electrons on bonding (N_{bond}) and antibonding (N_{anti}) MOs [Eq. (1)].

$$BO = \frac{N_{bond} - N_{anti}}{2}. \quad (1)$$

The "classical" bond order for linear molecules can be easily divided into contributions describing σ-, π-, and δ-components [Eq. (2)].

$$BO = \frac{(N^{\sigma} + N^{\pi} + N^{\delta})_{bond} - (N^{\sigma} + N^{\pi} + N^{\delta})_{anti}}{2}$$

$$= BO_{\sigma} + BO_{\pi} + BO_{\delta}. \quad (2)$$

Here N^{σ}, N^{π}, and N^{δ} are total numbers of electrons on bonding and antibonding MOs with appropriate symmetry.

In spite of the fact that molecular orbitals in nonlinear molecules cannot be classified as σ, π, and δ, in the chemical literature the concept of σ- and π-bonds between atoms is also widely used for molecules with other geometrical structures.

In 1968 formula (3) was introduced for the calculation of quantum-chemical bond orders (WBI, Wiberg Bond Index) between atoms A and B based on the density matrix **D** calculated in the orthogonal basis in the zero differential overlap approximation [11].

$$W(A - B) = \sum_{\mu \in A} \sum_{\nu \in B} |\mathbf{D}_{\mu\nu}|^2. \quad (3)$$

A series of works [11–16] was devoted to the evaluation of bond indices B(A–B) on the basis of *ab initio* calculations. The sum of orders of bonds formed by atom A defines its valence [Eq. (4)] [17].

$$V_A = \sum_{B \neq A} W_{AB}. \quad (4)$$

In [18] a correction for ionic character of bonds was introduced for the calculation of valences of atoms, and it was proposed to refer to the corresponding value calculated by formula (4) as the covalence.

By grouping together the molecular orbitals according to the irreducible representations Γ of the point group of the molecule Mayer bond order can be presented according to Eq. (5) [19].

$$B(A - B) = \sum_{\mu \in A} \sum_{\nu \in B} \sum_{\Gamma'} [\Sigma(DS)^{\Gamma}_{\mu\nu} \Sigma(DS)^{\Gamma'}_{\mu\nu}]. \quad (5)$$

Here Γ and Γ' are symbols of irreducible representations, by which a MO of a molecule is transformed. Such splitting is possible only in the case when no cross terms with $\Gamma \neq \Gamma'$ arise after multiplication of two sums in formula (5). For linear molecules this approach makes it possible to select σ-, π-, and δ-components of the bond order, whereas in other cases the resulting components $B(A - B)^{\Gamma}$ are hardly susceptible to the traditional chemical interpretation. The main drawback of bond indices B(A – B) is the pronounced dependence of their values on the basis set in use.

To calculate Wiberg indices within the limits of *ab initio* or DFT methods it is necessary to perform a transformation of the initial basis set to an orthogonal set, for example, to the basis of natural atomic orbitals (NAO) [20, 21]. The density matrix in the NAO basis is calculated by formula (6).

$$\mathbf{P}^{NAO} = \mathbf{T}^{+}(\mathbf{SDS})\mathbf{T}. \quad (6)$$

Here **S** is the overlap matrix and **T** is the matrix of the transformation from an AO basis to a NAO basis.

The procedure of the analysis of valence structure developed in this work is based on the **C** matrix of the expansion of molecular orbitals (MO or KS) over basis functions χ_{μ} (hereinafter referred to as AO), which is obtained from a quantum-chemical calculation. The matrix **C** defines the total spin-free density matrix **D** [Eq. (8)], which is constructed for open-shell systems as the sum of two contributions $\mathbf{D} = \mathbf{P}^{\alpha} + \mathbf{P}^{\beta}$.

$$\varphi_i = \sum_{\mu=1} \mathbf{C}_{\mu i}\chi_{\mu}, \quad (7)$$

$$\mathbf{D}_{\mu\nu} = 2 \sum_{i=1}^{occup} \mathbf{C}_{\mu i}\mathbf{C}_{\nu i}. \quad (8)$$

The first stage of VSA is the construction of a NAO basis and the calculation of Wiberg bond orders. We note that systems with open shells were considered within the limits of the UHF method, and W(A–B) values were calculated by formula (9) [13, 16].

$$W(A - B) = \sum_{\mu \in A} \sum_{\nu \in B} [(\mathbf{P}^{\alpha} + \mathbf{P}^{\beta})_{\mu\nu}]^2 + [(\mathbf{P}^{\alpha} - \mathbf{P}^{\beta})_{\mu\nu}]^2$$

$$= 2 [W^{\alpha}(A - B) + W^{\beta}(A - B)]. \quad (9)$$

For the decomposition of W(A–B) into σ-, π-, and δ-components the previously proposed AOSB (Atomic Orbitals Symmetry Based) scheme [22, 23] is applied, which uses local cylindrical symmetry for a diatomic fragment A–B of a polyatomic molecule and is based on the classification of matrix elements $\mathbf{P}_{\mu\nu}$ according to the symmetry of μ and ν AOs defined by the quantum number m. The splitting is carried out separately for each selected pair of atoms of the molecule under consideration. The coordinate system for this pair of atoms is displaced and rotated so that both atoms are located on the z axis, and matrixes **C** and **S** are correspondingly transformed. Bond orders were calculated as the sums of the σ-contribution ($m_{\mu} = m_{\nu} = 0$), π-contribution ($m_{\mu} = \pm 1$ and $m_{\nu} = \pm 1$), and δ-contribution ($m_{\mu} = \pm 2$ and $m_{\nu} = \pm 2$). For linear molecules the Wiberg index can be represented by formula (10).

$$W(\mathrm{A}-\mathrm{B}) = \sum_{\substack{\mu\in \mathrm{A}\,\mu\in\sigma \\ \nu\in \mathrm{B}\,\nu\in\sigma}} (\mathbf{P}^{\mathrm{NAO}}_{\mu\nu})^2 + \sum_{\substack{\mu\in \mathrm{A}\,\mu\in\pi \\ \nu\in \mathrm{B}\,\nu\in\pi}} (\mathbf{P}^{\mathrm{NAO}}_{\mu\nu})^2 + \sum_{\substack{\mu\in \mathrm{A}\,\mu\in\delta \\ \nu\in \mathrm{B}\,\nu\in\delta}} (\mathrm{P}^{\mathrm{NAO}}_{\mu\nu})^2$$

$$= W^{\sigma}(\mathrm{A}-\mathrm{B}) + W^{\pi}(\mathrm{A}-\mathrm{B}) + W^{\delta}(\mathrm{A}-\mathrm{B}). \qquad (10)$$

In nonlinear molecules the σ-, π-, and δ-components are supplemented by a Cross Term Contribution W^{CTC}, which includes $\mathbf{P}_{\mu\nu}$ elements containing AOs with different symmetries [Eq (11)].

$$W(\mathrm{A}-\mathrm{B}) = W^{\sigma}(\mathrm{A}-\mathrm{B}) + W^{\pi}(\mathrm{A}-\mathrm{B}) + W^{\delta}(\mathrm{A}-\mathrm{B}) + W^{\mathrm{CTC}}(\mathrm{A}-\mathrm{B}). \qquad (11)$$

As a rule, appreciable cross term contributions point to electronic density delocalization over triatomic or polyatomic fragments. For such fragments an AOSB–P technique was developed, in which a bond index was split into two contributions: symmetric and antisymmetric in relation to a plane [22].

When considering transition metal complexes it is useful to elucidate the measure of the contribution of *s*-, *p*-, and *d*-AOs of a metal to σ- and π-interactions with ligands [24]. It is not difficult to separate these contributions when calculating σ-, π-, and δ-components of bond orders $W(\mathrm{M}-\mathrm{L})$ [Eq. (12)].

$$W(\mathrm{M}-\mathrm{L}) = W^{\sigma}_{s,s} + W^{\sigma}_{s,p} + W^{\sigma}_{s,d} + W^{\sigma}_{p,s} + W^{\sigma}_{d,s} + W^{\sigma}_{p,d} + W^{\sigma}_{p,p} + W^{\sigma}_{d,p} + W^{\sigma}_{d,d} + W^{\pi}_{p,p} + W^{\pi}_{p,d} + W^{\pi}_{d,p} + W^{\delta}_{d,d}. \qquad (12)$$

Valence atomic and molecular orbitals (VAO and VMOF). The following analysis is based on the $\mathbf{P}^{\mathrm{NAO}}$ density matrix and applies to molecular systems with closed electronic shells. We suggested to denote the hybrid atomic orbitals satisfying the requirements of the maximal or minimal valence activity as the valence atomic orbitals (VAO) of a specified atom in a specified molecule (VAO). The postulate of extreme valence activity is equivalent to the requirement of diagonality of all intraatomic blocks of the density matrix [25]. The extension of this approach is the construction of multicenter valence molecular orbitals VMOF (Valence Molecular Orbitals of Fragment), which satisfy the conditions of the maximal or minimal population and the valence activity of interfragment bonds [26, 27]. The transition to the VMOF basis ξ_i [Eq. (13)] is performed by diagonalizaton of the $\mathbf{P}^{\mathrm{NAO}}_{\mathrm{F}}$ block of $\mathbf{P}^{\mathrm{NAO}}$ matrix spanning over NAOs of this fragment, λ_μ.

$$\xi_i = \sum_{\mu\in \mathrm{F}} \mathbf{X}_{\mu i}\lambda_\mu. \qquad (13)$$

In this formula $\{\mathbf{X}_{\mu i}\}$ is the matrix of VMOF expansion over NAO. Eigenvalues of the $\mathbf{P}^{\mathrm{NAO}}_{\mathrm{F}}$ matrix represent populations of **VMOF** n_i.

In the framework of the outlined formalism the concept of valence or valence activity can be also extended to polyatomic fragments. In turn, the valence activity of a fragment **F**, V_{F}, can be presented as a sum of certain characteristics ν_i related to orbitals of this fragment (14) and be defined as partial orbital valences [Eq. (15)] reflecting the realized valence activity of each VMOF.

$$V_{\mathrm{F}} = \sum_{i\in \mathrm{F}} \nu_i, \qquad (14)$$

$$\nu_i = \sum_{\mathrm{G}\not\in \mathrm{F}} W_{i\mathrm{G}} = \sum_{\mathrm{G}\not\in \mathrm{F}} \sum_{k\in \mathrm{G}} (\mathbf{P}_{ik})^2 = \sum_{\mathrm{G}\not\in \mathrm{F}} \sum_{k\in \mathrm{G}} W_{ik}. \qquad (15)$$

It is natural to consider W_{ik} values as indices of bond orders between VMOFs ξ_i and ξ_k of F and G fragments, respectively. Using the known relation $(\mathbf{P}^{\mathrm{NAO}})^2 = 2\mathbf{P}^{\mathrm{NAO}}$ [16] valid for closed-shell systems, we can readily show that the expression $\nu_i = 2n_i - n_i^2$ is true. Thus, the valence activity of an orbital is maximal ($\nu_i = 1$) if $n_i = 1$, which is typical for a Lewis covalent bond, and is minimal ($\nu_i = 0$) in two cases: $n_i = 0$ (the orbital is not populated by electrons and does not participate in chemical bond) and $n_i = 2$ (for example, an orbital with a lone electron pair of an atom or an orbital responsible for covalent bonds inside a polyatomic fragment). Sequential application of this procedure to all structural blocks of a complicated molecule allows us to reduce the number of orbitals necessary for analyzing interfragment chemical bonds to a minimum, as it is sufficient to consider only active VMOFs.

Donor and acceptor abilities of ligands. Populations of active VMOFs can be used for estimating donor and acceptor abilities of ligands under the following conditions:

– A transition metal ion with a formal configuration d^n and ligands (anions or uncharged molecules) with a closed electronic shell[1] are considered as fragments of coordination compounds [28, 29]; for the free fragments the populations n_i^0 of all MOs are equal to 2 or 0;

– VMOFs and MOs of a free ligand are similar in composition, and a correspondence between them can be established; small (as practice of calculations shows) discrepancies can be considered as "preparation of a ligand to coordination;"

– A deviation of the n_i^0 value of a coordinated ligand from n_i^0 of a free ligand, Δq, characterizes donor ($n_i^0 = 2$) and acceptor ($n_i^0 = 0$) properties of the *i*th VMOF.

[1] This does not refer to the so-called "non-innocent" ligands.

Table 1. Populations n_i, orbital valence activities v_i, and orbital bond indices w_{ik} for the complex $[Ru^{II}(NH_3)_5(pz)]^{2+}$ (only VMOFs with valence activity exceeding 0.06 are shown; interligand w_{ik} indices are not given)

Parameter	Ligands						
	L^1	L^2	L^3	L^4	L^5	pz	pz
VMOF, ξ_i	ξ_5	ξ_6	ξ_7	ξ_8	ξ_9	ξ_{10}	ξ_{11}
n_i	1.76	1.74	1.74	1.74	1.74	1.71	0.09
v_i	0.42	0.44	0.44	0.44	0.44	0.50	0.19
				w_{ik}			
ξ_1 (n_k = 0.20)	0.06	0.06	0.06	0.06	0.06	0.05	
ξ_2 (n_k = 0.65)		0.21	0.21	0.21	0.21		
ξ_3 (n_k = 0.68)	0.27	0.07	0.07	0.07	0.07	0.34	
ξ_4 (n_k = 1.89)							0.18

These assumptions are within the framework of approximations explicitly or implicitly adopted by other theoretical methods used for the investigation of donor–acceptor properties. The analysis of atomic and partial valences and bond indices between atoms or fragments does not require such restrictions.

RESULTS AND DISCUSSION

Complexes $[Ru^{II}(NH_3)_5L]^{2+}$. As an example the application of the VSA procedure to $[Ru^{II}(NH_3)_5L]^{2+}$ [L = NH_3, py (pyridine), pz (pyrazine), and tz (tetrazine)] complexes is considered. Each complex was separated into seven fragments: the central metal atom and six ligands (L^1 = *trans*-NH_3; L^2, L^3, L^4, L^5 = *cis*-NH_3; L^6 = L). No assumptions about formal charges on fragments were made. Orbital bond order indices w_{ik} in the basis of active VMOFs are presented in Table 1 for the case of L = pz; these orbitals are four VAOs (ξ_1 - ξ_4) from the metal, one VMOF (ξ_5 – ξ_9) from each of NH_3 molecules, and two VMOFs (ξ_{10} and ξ_{11}) from the pyrazine molecule.

As ruthenium(II) in these compounds has the formal electronic configuration d^6 (t_{2g}^6 in terms of the *Oh* symmetry), populations of *s* and e_g orbitals in the absence of chemical bonds with ligands are equal to zero. Population of the VAOs ξ_i (i = 1, 2, 3) in the complex are nonzero owing to electronic density transfer from those VMOFs of ligands (μ) for which w_i values are nonzero. Such VMOFs are the orbitals of lone pairs of nitrogen atoms (Fig. 1), which are responsible for observed donor properties of ammonia and pyrazine molecules.

Populations of each of t_{2g}^6 AO of a d^6 ion in the octahedral crystal field are taken to be equal to two. In the case of coordinated pyridine, pyrazine, and tetrazine molecules, along with the lone electron pair of nitrogen (ξ_{10}), the π*-orbital (ξ_{11}) perpendicular to the ring plane has a nonzero valence activity. The population of this VMOF (0.09 for L = pyz) characterizes π*-acceptor properties of pyrazine, and the partial bond order $w_{11.4}$ = 0.18 points to the fact that ξ_{11} interacts with d_π-VAO ξ_4 (n_4 = 1.89). According to Table 2, the π*-acceptor ability of L decreases along the series: tz > pz > py > NH_3.

Along this series the energy of the lowest vacant MOs of nonbound ligands, which are considered to be responsible for the π*-acceptor properties, increases: –0.14 < –0.07 < –0.04 < 0.09 (eV). As a consequence, the energy (eV) of the electron transition with metal-to-ligand charge transfer increases [30, 31]: 2.33 (tz) < 2.62 (pz) < 3.06 (py).

The ratio $\Delta q(L\rightarrow M)/\Delta q(M\rightarrow L) \equiv D/A$ can be considered as a measure of donor–acceptor properties of a coordinated ligand. The separation of a complex into two fragments $\{Ru(NH_3)_5\}^{2+}$ and {L} practically does not affect the VSA results. The calculated characteristics are close to those obtained by the CDA procedure [32] (Table 3). We note, however, that for the CDA realization it has been necessary to carry out three quantum-chemical calculations for each compound: (1) for the whole $[Ru(NH_3)_5(L)]^{2+}$ complex, (2) for the $\{Ru(NH_3)_5\}^{2+}$ fragment, and (3) for the uncharged nonbound ligand L (the CDA procedure allows only for splitting into two fragments).

The contour map shown in Fig. 2 was constructed by the Chemissian program [33] for the electron density deformation upon the formation of the

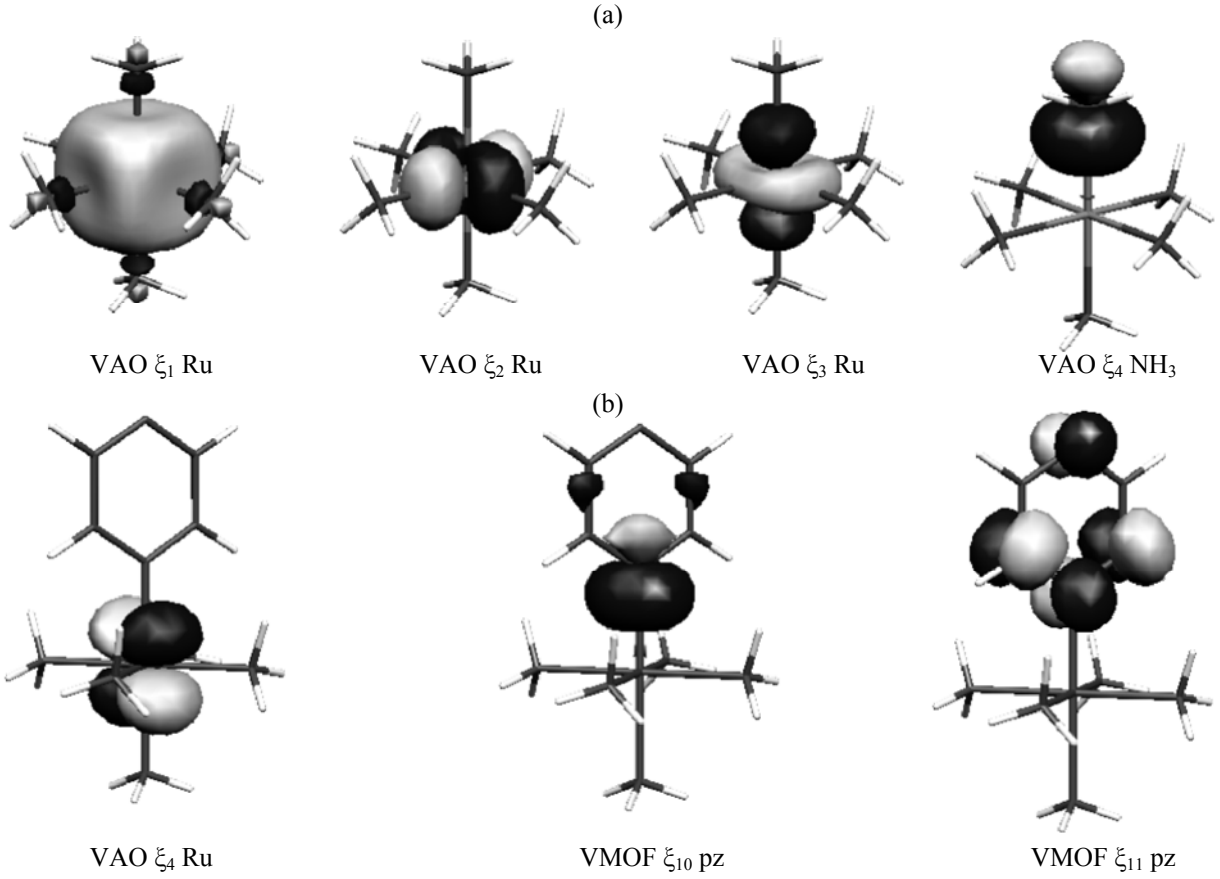

Fig. 1. VAOs ($\xi_1 - \xi_3$) of the metal and VMOF of ammonia molecules for (a) $[Ru(NH_3)_5(L)]^{2+}$ complexes, (b) VAO ξ_4 of ruthenium and VMOF of the pyrazine molecule in the $[Ru(NH_3)_5(pz)]^{2+}$ complex.

$[Ru(NH_3)_5(pz)]^{2+}$ complex from two fragments, $\{Ru(NH_3)_5\}^{2+}$ and a pyrazine molecule. The electron density transfer from the metal d_π-AO to the ligand π-orbital perpendicular to the ring plane can be clearly seen. The increase in the density on the Ru–NH_3 (*trans*) bond upon pyrazine coordination to the $\{Ru(NH_3)_5\}^{2+}$ fragment with a coordination vacancy reflects a competition between *trans*-ligands for the charge transfer from lone pairs of nitrogen atoms to σ-orbitals of the central atom, which forms the basis for the static *trans*-influence.

Scale of donor–acceptor **abilities of coordinated ligands.** Metal-ligand donor–acceptor interactions in the complexes $[NiL_3X]^q$ (L = NH_3, CO; X = CN^-, PH_3, NH_3, C_2H_4, CO, CS, N_2, NO^+) were studied in [7] within the framework of the NOCV method. It was found that for L = NH_3 the charge transfer X→$[NiL_3]^q$ (X = CN^-, PH_3, NH_3, C_2H_4) approaches one electron and for X ligands considered in the present study it decreases in the series: $CN^- \approx PH_3 > NH_3 \approx C_2H_4 > CO > NO^+$, and the Ni→X charge transfer diminishes in the series: $NO^+ > CO > C_2H_4 \approx PH_3 > CN^- > NH_3$, whereas, for example, Δρ (Ni > NH_3) reaches 0.28. Such results were attributed to the synergetic charge transfer (Δρ) X→Ni and Ni→X; it was pointed out

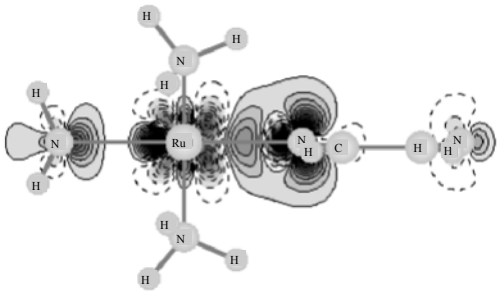

Fig. 2. Deformation of electronic density of $[Ru(NH_3)_5]^{2+}$ fragments and pyrazine molecule upon their combining in the $[Ru(NH_3)_5(pz)]^{2+}$ complex. $\Delta\rho = \rho\{[Ru(NH_3)_5(pz)]^{2+}\} - \rho(pz)$. Regions of negative values (electron density is decreasing) are shown by dashed lines, Δρ values for contour lines vary from –0.035 up to +0.035, and regions of the largest changes are marked by darker color.

Table 2. Bond orders and donor-acceptor abilities of ligands (L = NH_3, py, pz, tz) in $[Ru(NH_3)_5(L)]^{2+}$ complexes as determined by VSA

L	W(Ru–L)				Δq			q(L)
	W	W^σ	W^π	W^σ/W^π	L→Ru	Ru→L	D/A	
NH_3	0.36	0.35	0.02	22.00	0.25	0.02	13.21	0.23
py	0.44	0.38	0.06	7.00	0.30	0.09	3.28	0.21
pz	0.46	0.38	0.08	4.97	0.31	0.12	2.48	0.18
tz	0.59	0.40	0.19	2.12	0.36	0.30	1.18	0.06

that the sum of these values correlated with the ΔE_{orb} value calculated by the EDA method.

Using the procedure of valence-structural analysis described in the previous sections, we have studied donor–acceptor properties of ligands L in $[Pt(L)(Cl)_3]^{q-1}$ and $[Ru(L)(NH_3)_5]^{2+q}$ complexes (q is the formal charge of the free ligand L with a closed electronic shell) (Table 4, Fig. 3). According to our data, ligands Cl^- and NH_3 have no π-acceptor ability; ligands L are selected so that their donor and acceptor properties vary in the widest range. These properties depend on the composition and structure of the inner coordination sphere, nevertheless, a correlation between Δq(Ru→L) and Δq(Pt→L) is easily observed (Fig. 3b). The greatest discrepancies in the order of Δq(Ru→L) and Δq(Pt→L) variations in the series of selected ligands L were observed for phosphorus-containing ligands. It is not improbable that they also participate in nonclassical interactions inside the coordination sphere.

The obtained sequences of variation of donor and acceptor activities of coordinated ligands coincide with the data of [7], however the values of charge transfer between ligands L and the metal are essentially different: the NH_3→M charge transfer is far from one, and the NH_3←M charge transfer is absent, which is in better agreement with the generally accepted views on the properties of this ligand.

Table 3. Donor, Δq(L→M), and acceptor, Δq(M→L), properties of ligands in $[Ru(NH_3)_5(L)]^{2+}$ complexes as determined by CDA (electron-charge units)

L	Δq(L→M)	Δq(M→L)	D/A
NH_3[a]	0.28	0.01	27.6
py	0.32	0.08	4.1
pz	0.28	0.08	3.3
tz	0.28	0.10	2.6

[a] $(NH_3)_{trans}$ in $[Ru(NH_3)_5(pz)]^{2+}$.

Tertiary phosphines constitute an important class of ligands, and the description of the nature of their bonds with metals and quantitative characteristics of these bonds attract attention over many years. To construct a scale of their donor–acceptor properties, experimental data were usually used. A review of theoretical studies in this field is given in [34], where σ-donor and π-acceptor properties of phosphine ligands were characterized within the framework of the NOCV method. The σ-donor properties of ligands L were found to decrease in the series: $P(CH_3)_3$=$P(OCH_3)_3$ > $PH(CH_3)_3$ > $PH_2(CH_3)_3$ > PH_3 > PCl_3 > PF_3 $[Ni(CO)_3L]$, $P(CH_3)_3$ > $PH(CH_3)_3$ > $PH_2(CH_3)_3$ > $P(OCH_3)_3$ > PH_3 > PCl_3 > PF_3 $[Mo(CO)_5L]$; and the π-acceptor properties, in the series: PF_3 > PCl_3 >> $P(OCH_3)_3$ > PH_3 > $PH_2(CH_3)_3$ > $PH(CH_3)_3$ > $P(CH_3)_3$ $[Ni(CO)_3L]$, PCl_3 > PF_3 >> $P(OCH_3)_3$ > PH_3 > $PH_2(CH_3)_3$ > $PH(CH_3)_3$ > $P(CH_3)_3$ $[Mo(CO)_5L]$.

In addition to Pt(II) compounds, donor–acceptor abilities of PX_3 ligands have also been analyzed in this work for *trans*-$[Rh(CO)(COOH)(L)_2]$ complexes (Table 5), where the following sequences of variation of donor and acceptor properties have been found.

Δq(L→M):

$P(OMe)_3 \geq PMe_3 \geq P(OPh)_3 \approx PF_3 \geq PPh_3 \geq PH_3 \approx P(NC_4H_4)_3$ $[Pt(L)(Cl)_3]^-$;

$P(i\text{-}Pr)_3 \approx P(Cy)_3 \geq PMe_3 \geq PF_3 \geq PPh_3 > PH_3$ $[Rh(CO)(COOH)(L)_2]$.

Δq(M→L):

$PF_3 \approx P(NC_4H_4)_3 \approx P(OMe)_3 \approx P(OPh)_3 \geq PPh_3 \geq PMe_3 \approx PH_3$ $[Pt(L)(Cl)_3]^-$;

$PF_3 >> PH_3 \approx PPh_3 \geq P(iPr)_3 \approx P(Cy)_3 \geq PMe_3$ $[Rh(CO)(COOH)(L)_2]$.

The correlation between the charge transfer along L→Pt σ-bond and the Pt–Cl_{trans} bond order in square planar $[Pt(L)(Cl)_3]^{q-1}$ complexes (Fig. 4) indicates that

Table 4. Donor and acceptor valence abilities of monodentate ligands L in $[Pt(L)(Cl)_3]^{q-1}$ and $[Ru(L)(NH_3)_5]^{2+q}$ complexes (q is a formal charge on free ligand L with closed electronic shell)

Ligand	$[Pt(L)(Cl)_3]^{q-1}$				$[Ru(L)(NH_3)_5]^{2+q}$			
	Δq(L→M)	Δq(M→L)	D/A	Q(L)	Δq(L→M)	Δq(M→L)	D/A	Q(L)
				$q = -1$				
CN	0.60	0.16	3.77	–0.56	0.61	0.12	5.02	–0.51
CCH	0.60	0.16	3.86	–0.55	0.61	0.12	5.18	–0.51
Cl	0.37	0.01	>10	–0.64	0.33	0.01	>10	–0.62
OH					0.38	0.01	>10	–0.62
CH_3OO					0.31	0.02	>10	–0.68
SCN	0.46	0.05	8.44	–0.60	0.43	0.02	>10	–0.59
CNS					0.56	0.13	4.37	–0.57
NCS					0.34	0.07	5.15	–0.72
CH_3	0.70	0.01	>10	–0.35				
CF_3	0.60	0.14	4.42	–0.54				
CCPh	0.58	0.20	2.96	–0.62				
Ph	0.65	0.12	5.28	–0.49				
PhCN	0.62	0.19	3.26	–0.57				
				$q = 0$				
H_2O	0.17	0.05	3.67	0.12	0.14	0.01	>10	0.13
NH_3	0.28	0.06	5.00	0.22	0.25	0.02	>10	0.23
py	0.28	0.15	1.91	0.12	0.30	0.09	3.28	0.21
pyz	0.29	0.24	1.19	0.04	0.30	0.12	2.48	0.18
tz					0.36	0.30	1.18	0.06
DMSO[a]					0.20	0.02	>10	0.18
DMSO[b]	0.41	0.16	2.63	0.25	0.46	0.10	4.67	0.36
N_2					0.32	0.26	1.20	0.05
C_2H_4	0.34	0.37	0.94	–0.02	0.35	0.27	1.31	0.08
C_2H_2	0.32	0.35	0.90	–0.04	0.32	0.24	1.32	0.08
CO	0.47	0.46	1.01	0.01	0.56	0.36	1.53	0.19
PH_3	0.48	0.18	2.77	0.31				
PF_3	0.51	0.27	1.85	0.22				
PMe_3	0.56	0.17	3.30	0.39	0.58	0.08	6.86	0.50
PPh_3	0.51	0.20	2.52	0.31	0.59	0.10	5.98	0.49
$P(OMe)_3$	0.57	0.25	2.29	0.32	0.65	0.14	4.60	0.51
$P(OPh)_3$	0.53	0.24	2.15	0.27	0.65	0.14	4.53	0.51
$P(NC_4H_4)_3$	0.48	0.26	1.84	0.22	0.64	0.16	4.02	0.48
				$q = +1$				
$pyzH^+$					0.30	0.36	0.83	0.94
NO^+					0.36	0.93	0.39	0.43

[a] DMSO is coordinated through the sulfur atom. [b] DMSO is coordinated through the oxygen atom.

the *trans*-influence of the ligand L is defined first of all by the σ-donor activity of L.

Electronic interactions between *cis*-ligands in *trans*-[Rh(CO)(PY$_3$)$_2$(OCOH)] (Y = CH$_3$, *i*-Pr, Cy, and Ph) complexes. The stretching vibration frequency ν(CO) is a useful source of information on donor–acceptor interactions in the inner coordination spheres of carbonyl complexes and on effects of mutual influence of ligands. It is caused by the

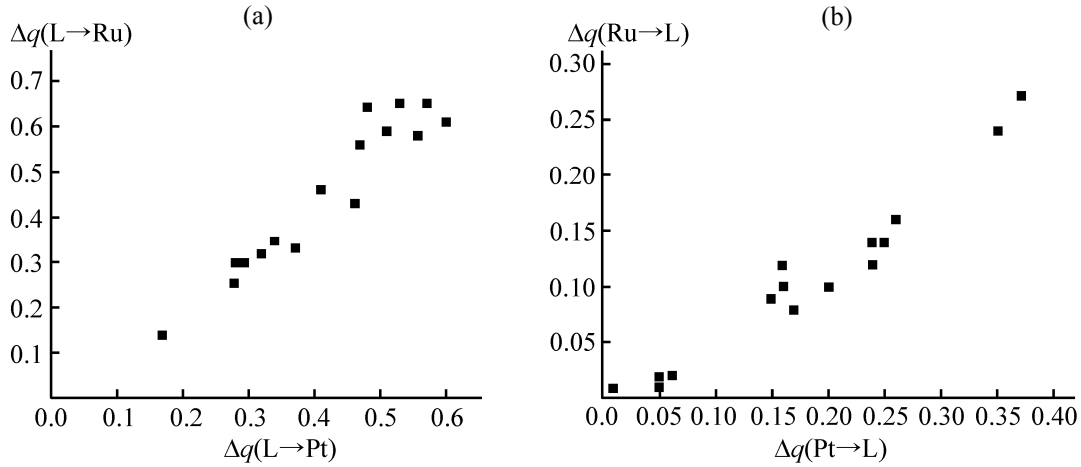

Fig. 3. Correlation between (a) donor and (b) acceptor ability of ligands L in $[Pt(L)(Cl)_3]^{q-1}$ and $[Ru(L)(NH_3)_5]^{2+q}$ complexes.

sensitivity of carbonyl ligands to the composition and structure of complexes and by a high degree of vibrational independence nature of ν(CO) frequencies. It was suggested in [35] that the characteristics describing metal-CO bonds [bond length and spin-spin interaction constant *J*(CRh)] are defined by the nature of the ligand in *trans*-position relative to the carbonyl group, and the characteristics, which are defined by the population of π-antibonding orbitals of carbonyl groups, depend first of all on *cis*-ligands in the coordination sphere. The analysis of electronic structure of *trans*-$[Rh(CO)(PY_3)_2(OCOH)]$ complexes shows that only the carbonyl ligand in these compound has an appreciable π-acceptor ability, phosphines exhibit pronounced donor and weak acceptor abilities, which are caused first of all by the population of *p*- (instead of *d*-) phosphorus orbitals, and in the case of triphenylphosphine, by the population of Ph π*-orbitals. In the *trans*-$[Rh(CO)(PPh_3)_2(OCOH)]$ complex the

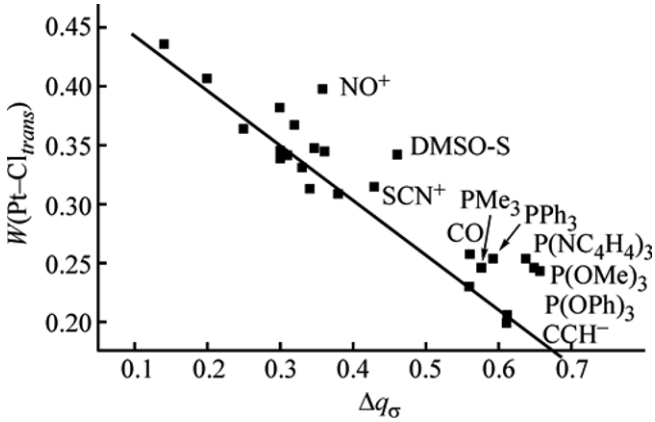

Fig. 4. Correlation between Δq(L→Pt) and W(Pt–Cl_{trans}) in $[Pt(L)(Cl)_3]^{q-1}$ complexes.

	CO	OCOH	PPh_3
Δq (from a ligand)	0.51	0.33	0.48
Δq (onto a ligand)	0.51	0.02	0.10

charge transfer Δq between each of ligands and the remaining metal fragment has the following values.

As the donor ability of PX_3 ligands in *cis*-positions in relation to the carbonyl group increases, ν(CO) decreases [36]. As Δq[Rh(CO)$(PY_3)_2$(OCOH)→CO] decreases, the frequency of C–O stretching vibrations increases (Table 6), which can be considered as an evidence of reliability of calculated characteristics of donor–acceptor properties. Nonzero total Wyberg indices, W(P–C) ~ 0.09, and partial Wyberg indices, w[σ(PY_3)–π*(CO)] ~ 0.05, point to a possibility of direct nonclassical interactions between PY_3 and CO ligands (Table 6).

Valence-structural analysis developed in the present work is based on the results of a quantum-chemical calculation for the molecule (complex) under study and includes the following stages: transition to the basis of natural atomic orbitals (NAO); calculation of Wyberg bond indices; their decomposition into σ-, π-, and δ-components; analysis of contributions of separate (*s, p, d*)-AOs to these values; construction of single-center (VAO) and multicenter valence molecular orbitals (VMOF) and their sorting by the valence activity realized inside a fragment or directed to interfragment bonds; characterization of donor and acceptor valence activities of VMOFs; construction of a table of indices for bonds between orbitals of fragments and analysis of VMOFs responsible for the formation of intrafragment and interfragment bonds.

Table 5. Donor and acceptor abilities of ligands L in complexes $[PtCl_3L]^-$ and *trans*-$[Rh(CO)(COOH)(L)_2]$

L	$[PtCl_3L]^-$				$[Rh(CO)(COOH)(L)_2]$	
	Δq(L→M)[a]	Δq(M→L)[a]	Δq(L→M)[b]	Δq(M→L)[b]	Δq(L→M)[a]	Δq(M→L)[a]
$P(Cy)_3$					0.51	0.09
$P(i\text{-}Pr)_3$					0.51	0.09
PMe_3	0.56	0.17	0.55	0.19	0.50	0.08
PPh_3	0.51	0.20	0.51	0.23	0.48	0.10
PH_3	0.48	0.18	0.50	0.18	0.44	0.10
$P(OMe)_3$	0.57	0.25	0.57	0.25		
$P(OPh)_3$	0.53	0.24	0.54	0.28		
$P(NC_4H_4)_3$	0.48	0.26	0.48	0.26		
PF_3	0.51	0.27	0.55	0.26	0.49	0.18

[a] B3LYP/LanL calculation. [b] PBE1PBE/SDD+DZVP.

Table 6. Donor and acceptor abilities of the carbonyl ligand in *trans*-$[Rh(CO)(PY_3)_2(OCOH)]$ complexes, characteristics of the interaction between *cis*-ligands CO and PY_3, and frequencies of stretching vibrations C–O[a]

Parameter	Cy	*i*-Pr	Me	Ph
$\Delta q[Rh(PY_3)_2(OCOH) \leftarrow CO]$	0.524	0.530	0.517	0.512
$\Delta q[Rh(PY_3)_2(OCOH) \rightarrow CO]$	0.578	0.566	0.527	0.506
W(P–C)	0.097	0.098	0.089	0.083
$W[\sigma(PY_3)–\pi^*(CO)]$	0.055	0.059	0.048	0.040
$\nu(CO)_{calc}$ [36][a]	1936	1945	1966	1975
$\nu(CO)_{exp}$ [36]	1948	1954		1980

[a] Calculated frequencies for all complexes were multiplied by an empirical calibrating factor 1.02455.

The VSA is carried out by means of specially developed software. As compared to other procedures focused on solution of similar problems, VSA has the following advantages: considerably smaller computational complexity; results of the analysis are linked both with charge characteristics and with bond orders; a flexible splitting into fragments (the number of fragments can be arbitrary, which makes it possible to consider interfragment ligand–ligand interactions); only the formal configuration of the metal atom is used to describe donor–acceptor interactions, and complexes are classified according to it without any speculations about the charges of fragments.

The application of the VSA technique describes metal-ligand bonds in the considered complexes in complete agreement with the previously proposed model [1] and allows donor–acceptor bonds to be characterized in terms of charge transfers M←L [$\Delta q(\sigma)$] and M→L [$\Delta q(\pi)$]. This description is supplemented by the calculation of bond orders and their component-wise analysis.

DETAILS OF CALCULATIONS

Quantum-chemical calculations were carried out in the framework of density functional theory with the B3LYP hybrid functional [37]. The LanL2DZ valence basis set [38, 39] was supplemented by polarizing *d* orbitals and diffuse *p* orbitals for P, S, and Cl atoms [40]. In the case of phosphorus-containing Pt(II) complexes the exchange-correlation functional PBE0 (also known as PBE1PBE) [41] was used in combination with the basis sets SDD and DZVP for the Pt atom and the H, C, N, O, and P atoms [42], respectively. For all compounds the calculations were performed with the full geometry optimization without symmetry limitations. The calculations were carried out using the GAUSSIAN-03 program [43] on the high-performance computer complex of St. Petersburg State University.

REFERENCES

1. Chatt, J. and Duncanson, J.A., *J. Chem. Soc*., 1953, p. 2939.
2. Kitaura, K. and Morokuma, K., *Int. J. Quantum Chem*., 1976, vol. 10, no. 2, p. 325.
3. Ziegler, T. and Rauk, A., *Theor. Chim. Acta*, 1977, vol. 46, no. 1, p. 1.
4. Dapprich, S. and Frenking, G., *J. Phys. Chem*., 1995, vol. 99, no. 23, p. 9352.
5. Dapprich S.and Frenking, G., *Angew. Chem. Int. Ed. Engl*., 1995, vol. 34, no. 3, p. 354.
6. Mitoraj, M.P., Michalak, A., and Ziegler, T., *J. Chem. Theory Comput*., 2009, vol. 5, no. 4, p. 962.
7. Mitoraj, M. and Michalak, A., *Organometallics*, 2007, vol. 26, no. 26, p. 6576.
8. Mitoraj, M. and Michalak, A., *J. Mol. Model*., 2007, vol. 13, no. 2, p. 347.
9. Michalak, A., Mitoraj, M., and Ziegler, T., *J. Phys. Chem. A*, 2008, vol. 112, no. 9, p. 1933.
10. Mitoraj M, P., Michalak, A., and Ziegler, T., *Organometallics*, 2009, vol. 28, no. 13, p. 3727.
11. Wiberg, K.B., *Tetrahedron*, 1968, vol. 24, no. 3, p. 1083.
12. Mayer, I., *Chem. Phys. Lett*., 1983, vol. 97, p. 270.
13. Mayer, I., *Chem. Phys. Lett*., 1985, vol. 117, p. 396.
14. Mayer, I., *Int. J. Quant. Chem*., 1986, vol. 29, p. 73.
15. Mayer, I., *Int. J. Quant. Chem*., 1986, vol. 29, p. 477.
16. Mayer, I., *Simple Theorems, Proofs, and Derivations in Quantum Chemistry*, New York: Kluwer/Plenum, 2003.
17. Borisova, N.P. and Semenov, S.G., *Vestn. Leningr. Gos. Univ*., 1973, no.16 , p. 121.
18. Evarestov, R.A. and Veryazov, V.A., *Theor. Chim. Acta*, 1991, vol. 81, p. 95.
19. Bridgeman, A.J., Cavigliasso, G., Ireland, L.R., and Rothery, J., *J. Chem. Soc. Dalton Trans*., 2001, no. 14, p. 2095.
20. Reed, A.E., Weinstock, R.B., and Weinhold, F., *J. Chem. Phys*., 1985, vol. 83, no. 2, p. 735.
21. Reed, A.E., Curtiss, L.A., and Weinhold, F., *Chem. Rev*., 1998, vol. 88, no. 6, p. 899.
22. Sizova, O.V., Skripnikov, L.V., and Sokolov, A.Yu., *Theochem.*, 2008, vol. 870, no. 1, p. 1.
23. Sizova, O.V., Skripnikov, L.V., Sokolov, A.Yu., and Sizov, V.V., *Int. J. Quant. Chem*., vol. 109, no. 11, p. 2581.
24. Sokolov, A.Yu. and Sizova, *Zh. Obshch. Khim*., 2010, vol. 80, no. 7, p. 1057.
25. Ruedenberg, K., *Revs. Modern Phys*., 34, 326-376, 1962.
26. Sizova, O.V. and Baranovskii, V.I., *Teor. Eksper. Khim*., 1975, vol. 11, no. 2, p. 147.
27. Baranovskii, V.I., Sizova, O.V., and Ivanova, N.V., *Zh. Strukt. Khim*., 1976, vol. 17, no. 3, p. 549.
28. Jцrgensen, C.K., *Coord. Chem. Rev*., 1966, vol. 1, nos. 1–2, p. 164.
29. Jörgensen, C.K., *Oxidation Numbers and Oxidation States*, Berlin, Springer Verlag, 1969.
30. Tfouni, E., *Coord. Chem. Rev*., 2000, vol. 196, p. 281.
31. Cacelli, I., Campanile, S., Denti, G., Ferretti, A., and Sommovigo, M., *Inorg. Chem*., 2004, vol. 43, no. 4, p. 1379.
32. Dapprich, S. and Frenking, G., *CDA. Version 2.1.2. 29.04.2010*, Philipps-Universitдt Marburg, AK Computerchemie.
33. *Chemissian Program http://www.chemissian.com.*
34. Mitoraj, M, P. and Michalak, A., *Inorg. Chem*., 2010, vol. 49, no. 2, p. 578.
35. Sizova, O.V., Sokolov, A. Yu., and Skripnikov, L.V., *Koord. Khim*., 2007, vol. 33, no. 11, p. 814.
36. Sizova, O.V., Varshavskii, Yu.S., and Skripnikov, L.V., *Koord. Khim*., 2007, vol. 33, no.5, p. 323.
37. Becke, A.D., *J. Chem. Phys*., 1993, vol. 98, no. 7, p. 5648.
38. Wadt, W. R. and Hay, P. J., *J. Chem. Phys*., 1985, vol. 82, no. 1, p. 284.
39. Hay, P. J. and Wadt, W. R., *J. Chem. Phys*., 1985, vol. 82, no. 1, p. 299.
40. Check, C.E., Faust, T.O., Bailey, J.M., Wright, B.J., Gilbert, T.M., and Sunderlin, L.S., *J. Phys. Chem. A*, 2001, vol. 105, p. 8111.
41. Adamo, C. and Barone, V., *J. Chem. Phys*., 1999, vol. 110, p. 6158; Perdew, J, P., Burke, K., and Ernzerhof, M., *Phys. Rev. Lett*., 1996, vol. 77, p. 3865.
42. Andrae, D., Haussermann, U., Dolg, M., Stoll, H., and Preuss, H., *Theor. Chim. Acta (Berlin),* 1990, vol. 77, p. 123; Godbout, N., Salahub, D. R., Andzelm, J., and Wimmer, E., *Can. J. Chem*., 1992, vol. 70, p. 560.
43. Frisch, M.J., Trucks, G.W., Schlegel, H.B., Scuseria, G.E., Robb, M.A., Cheeseman, J.R., Montgomery, J.A. Jr., Vreven, T., Kudin, K.N., Burant, J.C., Millam, J.M., Iyengar, S.S., Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G.A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J.E., Hratchian, H.P., Cross, J.B., Bakken, V., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R.E., Yazyev, O., Austin, A.J., Cammi, R., Pomelli, C., Ochterski, J.W., Ayala, P.Y., Morokuma, K., Voth, G.A., Salvador, P., Dannenberg, J.J., Zakrzewski, V.G., Dapprich, S., Daniels, A.D., Strain, M.C., Farkas, O., Malick, D.K., Rabuck, A.D., Raghavachari, K., Foresman, J.B., Ortiz, J.V., Cui, Q., Baboul, A.G., Clifford, S., Cioslowski, J., Stefanov, B.B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R.L., Fox, D.J., Keith, T., Al-Laham, M.A., Peng, C.Y., Nanayakkara, A., Challacombe, M., Gill, P.M.W., Johnson, B., Chen, W., Wong, M.W., Gonzalez, C., and Pople, J.A., *Gaussian 03*, Revision B.05, Gaussian, Inc., Wallingford.