Donor–Acceptor Properties of Ligands from the Natural Orbitals for Chemical Valence

Mariusz Mitoraj and Artur Michalak*

Department of Theoretical Chemistry, Faculty of Chemistry, Jagiellonian University, R.Ingardena 3, 30-060 Cracow, Poland

Natural orbitals for chemical valence (NOCV) have been used to characterize donor–acceptor properties of ligands in model nickel(II) complexes. NOCV allows for separation of ligand $\rightarrow$ metal and metal $\rightarrow$ ligand electron transfer processes (Dewar–Chatt–Duncanson model). Bonding between the ligand X = CN^-, PH_3, NH_3, C_2H_4, CO, CS, N_2, NO^+ and the metal-containing fragment in the $[Ni\ L_3]^{2+}$ complexes (L = NH_3, CO) have been discussed. For both σ-donation and π-back-bonding, the resulting orders of ligands are in a qualitative agreement with those commonly accepted. However, it was also demonstrated that the influence of the metal-containing fragment can be substantial, changing the relative donor–acceptor characteristics of different ligands.

Introduction

The "classical" Dewar–Chatt–Duncanson model[1,2] is of vital importance for inorganic and organometallic chemistry. The description of bonding in transition metal complexes in terms of synergic processes of the ligand $\rightarrow$ metal electron donation and the metal $\rightarrow$ ligand back-donation has influenced the way of thinking and speaking about transition-metal-based systems. Classification of ligands according to their donor–acceptor properties allows for understanding the electronic structure of metal complexes as well as for predicting and rationalizing their reactivity.[3-7]

However, separation of the donation/back-donation effects is often difficult on an experimental basis, although many techniques have been used in this area.[4-17] Conclusions on donor–acceptor properties are usually drawn indirectly; for example, the CO stretching frequency in carbonyl complexes is commonly used as an indicator of back-bonding.[3-7] Here, use of theoretical methods has been very helpful during the past

decades.[7,18-27] Numerous theoretical methods and concepts were applied in a description of donor–acceptor properties, including interaction-energy partitioning schemes,[27-29] charge decomposition analysis (CDA),[7,19-21] and constrained space orbital variation (CSOV)[22,23] techniques based on molecular orbital theory, localized orbitals/natural bond-orbital approaches,[31] or the analysis of molecular electrostatic potential.[27]

We have recently introduced[32] natural orbitals for chemical valence (NOCV), which lead to a very compact description of bonding in terms of only a few orbitals, localized in the bond region. This approach[32] for the first time allows for a direct separation of the contributions to the deformation density from the ligand $\rightarrow$ metal and metal $\rightarrow$ ligand electron transfer processes. Thus, in the NOCV framework, it is possible to directly address the Dewar–Chatt–Duncanson model.

The main purpose of the present study is to apply NOCV in a description of metal–ligand bonding in transition metal complexes. Donor–acceptor properties of a few typical ligands (CN^-, PH_3, NH_3, C_2H_4, CO, CS, N_2, NO^+) will be extracted from the results obtained for a series of model complexes with the same metal-based fragment. A variation in the donor–acceptor ability of considered ligands due to the change of the complex will also be investigated.

* Corresponding author. E-mail: michalak@chemia.uj.edu.pl.
(1) Dewar, M. J. S. *Bull. Soc. Chim.* **1951**, *18*, C71.
(2) Chatt, J.; Duncanson, J. A. *J. Chem. Soc.* **1953**, *3*, 2939.
(3) Cotton, F. A., Wilkinson, G. *Advanced Inorganic Chemistry*, Wiley: New York, 1998.
(4) Solomon, E. I.; Lever, A. B. P. *Inorganic Electronic Structure and Spectroscopy*; Wiley: New Jersey, 2006.
(5) Elschenbroich, C. *Organometallics*: Wiley-VCH: Weinheim, 2005.
(6) Pruchnik, F. *Organometallic Chemistry of Transition Metal Elements*; New York, 1990.
(7) Frenking, G.; Fröhlich, N. *Chem Rev* **2000**, *100*, 717, and references therein.
(8) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2656.
(9) Tolman, C. A. *J. Am. Chem. Soc.* **1970**, *92*, 2953.
(10) Bartik, T.; Himmler, T.; Schulte, H. G.; Seevogel, K *J. Organomet. Chem.* **1984**, *272*, 29.
(11) Gray, G.; Krainhazel, C. S. *J. Organomet. Chem.* **1983**, *241*, 201.
(12) Strohmeier, W. *Angew. Chem.* **1964**, *76*, 873.
(13) Strohmeier, W.; Müller, F. J. *Chem. Ber.* **1967**, *100*, 2812.
(14) Cotton, F. A.; Edwards, W. T.; Rauch, F. C.; Graham, M. A.; Perutz, R. N.; Turner, J. J. *J. Coord. Chem.* **1973**, *2*, 247.
(15) Cotton, F. A.; Darensbourg, D. J.; Ilsley, W. A. *Inorg. Chem.* **1981**, *20*, 578.
(16) Bodner, G. M.; Gagnon, C.; Whittern, D. N. *J. Organomet. Chem.* **1983**, *243*, 305.
(17) Russel, C.; Bush; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 681.

(18) Ziegler, T.; Autschbach, J. *Chem. Rev.* **2005**, *105*, 2695.
(19) Dapprich, S.; Frenking, G. *J. Phys. Chem.* **1995**, *99*, 9352.
(20) Ehlers, A. W.; Dapprich, S.; Vyboishchikov, S. F.; Frenking, G. *Organometallics* **1996**, *15*, 105.
(21) Frenking, G.; Wichmann, K.; Fröchlich, N.; Grobe, J.; Golla, W.; Le Van, D.; Krebs, B.; Läge, M. *Organometallics* **2002**, *21*, 2921.
(22) Pacchioni, G.; Bagus, P. S. *Inorg. Chem.* **1992**, *31*, 4391.
(23) Bagus, P. S.; Hermann, K.; Bauschlicher, C. W. *J. Chem. Phys.* **1984**, *80*, 4378.
(24) Fantucci, P.; Polezzo, S.; Sironi, M.; Bencini, A. *J. Chem. Soc., Dalton Trans.* **1995**, 4121.
(25) Gonzáles-Blanco, O.; Branchadell, V. *Organometallics* **1997**, *16*, 5556.
(26) Ruiz-Morales, Y.; Ziegler, T. *J. Phys. Chem A* **1998**, *102*, 3970.
(27) Suresh, C. H.; Koga, N. *Inorg. Chem.* **2002**, *41*, 1573.
(28) Morokuma, K. *J. Chem. Phys.* **1971**, *55*, 1236.
(29) Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1755.
(30) Ziegler, T.; Rauk, A. *Inorg. Chem.* **1979**, *18*, 1558.
(31) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1998**, *88*, 899.
(32) Mitoraj, M.; Michalak, A. *J. Mol. Model.* **2007**, *13*, 347.

Computational Details and the Model System

In all the calculations the Amsterdam Density Functional (ADF) program[33–37] was used. The Becke–Perdew exchange–correlation functional[38–40] was applied. A standard double-ζ STO basis with one set of polarization functions was used for main-group elements (H, C, N, O), while a standard triple-ζ basis set was employed for nickel. The 1s electrons of C, N, and O, as well as the 1s–2p electrons of S and Ni were treated as frozen core. Auxiliary s, p, d, f, and g STO functions, centered on all nuclei, were used to fit the electron density and obtain accurate Coulomb and exchange potentials in each SCF cycle.

The model systems investigated in the present work include square-planar nickel(II) complexes $[Ni(NH_3)_3X]^{2+}$ and $[Ni(CO)_3X]^{2+}$, with $X = CN^-$, PH_3, NH_3, C_2H_4, CO, CS, N_2, and NO^+. The two groups of complexes were compared, to characterize the influence of the metal-containing fragment. Thus, the NH_3 ligands (very weak π-acceptor character) was replaced by the CO ligands (σ-donor and π-acceptor character). In order to minimize the possible effect of the geometry/coordination changes, and the number of the metal d electrons, the model square-planar Ni(II) complexes were considered, even though some of them are not available experimentally.

Natural orbitals for chemical valence (NOCV) are defined[32] as the eigenvectors of the chemical valence operator of the Nalewajski–Mrozek theory,[41]

$$\hat{V}\varphi_i = v_i\varphi_i \quad i = 1...N \tag{1}$$

with the valence operator given by a matrix

$$V = \tfrac{1}{2}\Delta\mathbf{P} \tag{2}$$

where $\Delta\mathbf{P}$ corresponds to a difference between the *charge-and-bond-order* matrices of a molecule and promolecule (set of isolated atoms, or molecular fragments, ligands, etc.).

In the present work NOCV were determined in a fragment resolution; that is, in each case the bond between the ligand X and the transition-metal-containing fragment ($[Ni\, L_3]^{2+}$, $L = NH_3$, CO) was characterized. For this purpose the calculations were performed for the whole complex and the two fragments; NOCV were obtained from diagonalization of the corresponding $\Delta\mathbf{P} = \mathbf{P}(\text{complex}) - \mathbf{P}(\text{fragments})$ matrix. For each system the contours of NOCV were analyzed together with the corresponding NOCV eigenvalues and the NOCV contribution to the differential density, $\Delta\rho = \rho(\text{complex}) - \rho(\text{fragments})$.

Results and Discussion

We will start the discussion with thiocarbonyl complexes, as carbon monosulfide belongs to the category of ligands that are known to exhibit both σ-donor and π-acceptor properties.[3–6,20] Let us first present the interpretation of the natural orbitals for chemical valence (NOCV). Figure 1 presents the NOCV contours describing the bond between the transition metal
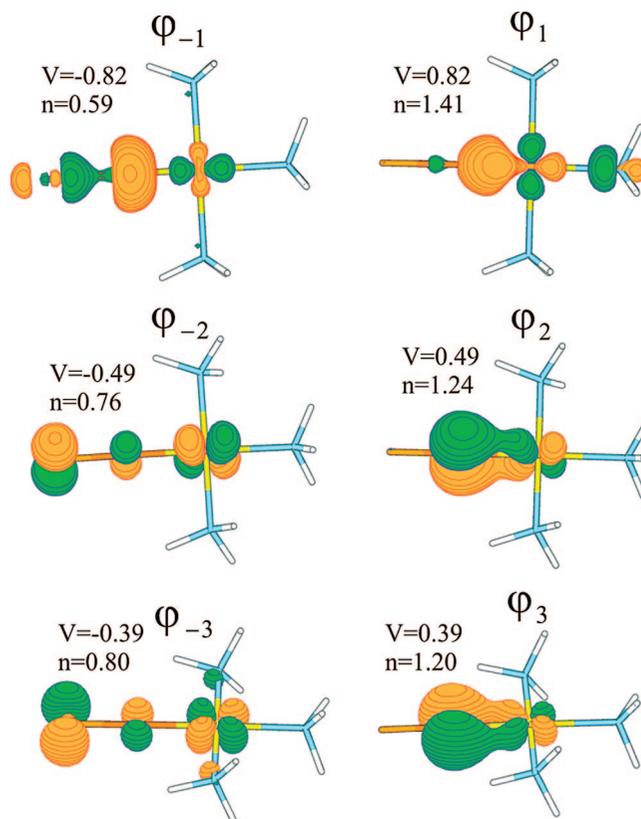
(33) TeVelde, G; Bickelhaupt, F. M.; Baerends, E. J.; Fonseca Guerra, C.; Van Gisbergen, S.J.A.; Snijders, J. G.; Ziegler, T. *J. Comput. Chem.* **2001**, *22*, 931,
and references therein.
(34) Baerends, E. J.; Ellis, D. E.; Ros, P. *Chem. Phys.* **1973**, *2*, 41.
(35) Baerends, E. J.; Ros, P. *Chem. Phys.* **1973**, *2*, 52.
(36) te Velde, G.; Baerends, E. J. *J. Comput. Phys.* **1992**, *99*, 84.
(37) Fonseca, C. G.; Visser, O.; Snijders, J. G.; te Velde, G.; Baerends, E. J. In *Methods and Techniques in Computational Chemistry, METECC-95*; Clementti, E., Corongiu, G., Eds.; STEF: Cagliari, Italy, 1995; p 305.
(38) Becke, A. *Phys. Rev. A* **1988**, *38*, 3098.
(39) Perdew, J. P. *Phys. Rev. B* **1986**, *34*, 7406.
(40) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822.
(41) Nalewajski, R. F.; Mrozek, J.; Michalak, A. *Int. J. Quantum Chem.* **1997**, *61*, 589.

Figure 1. Contours of the natural orbitals for chemical valence characterizing the bond between the $[Ni(NH_3)_3]^{2+}$ fragment and the CS ligand. The numbers denote the corresponding NOCV eigenvalues (*V*) and their populations (*n*). Only the orbitals participating in bonding ($|V| > 0.1$) are shown. The contour value is $|\varphi_i(r)| = 0.1$ au.

fragment $[Ni(NH_3)_3]^{2+}$ and the CS ligand in the $[Ni(NH_3)_3(CS)]^{2+}$ complex. There exist six orbitals participating in bonding, i.e., exhibiting nonzero eigenvalues. One of the features of NOCV is that they can be grouped in pairs of complementary orbitals corresponding to the same eigenvalue with the opposite sign:[32]

$$\hat{V}\varphi_{-k} = -v_k\varphi_{-k}, \quad \hat{V}\varphi_k = v_k\varphi_k, \quad k = 1...N/2 \tag{3}$$

Thus, the bond between the $[Ni(NH_3)_3]^{2+}$ fragment and the CS ligand is described by three pairs of complementary NOCV. The contours shown in Figure 1 clearly demonstrate that all six NOCV are strongly localized in the bond region. Within each pair, the orbital with negative eigenvalue exhibits antibonding character, while that corresponding to the positive eigenvalue is a bonding orbital. The first pair of NOCV (φ_{-1}, φ_1), characterized by $|v| = 0.82$, describes formation of a σ-component of the bond between CS and the metal. The second pair (φ_{-2}, φ_2), characterized by $|v| = 0.49$, describes a π-bond formed by the virtual orbital of CS and the occupied d orbital of the metal. The last pair (φ_{-3} and φ_3), corresponding to $|v| = 0.39$, has a similar π-character.

In the NOCV representation, the deformation density, $\Delta\rho = \rho(\text{complex}) - \rho(\text{ligand}) - \rho(\text{metal--fragment})$, can be expressed as a sum of the pair contributions:[32]

$$\Delta\rho(r) = \sum_{k=1}^{N/2} v_k[-\varphi_{-k}^2(r) + \varphi_k^2(r)] = \sum_{k=1}^{N/2} \Delta\rho_k(r) \tag{4}$$

Interpretation of NOCV follows from eq 4: an eigenvalue v_k corresponds to a fraction of electron density that is being

transferred from the φ_{-k} orbital to the φ_k orbital when the molecule is created from the fragments. It should be pointed out that within each pair both natural orbitals have a fractional occupation number in the promolecule (without a bond between fragments) and in the molecule (after the bond is formed). The occupation numbers of the two orbitals in a molecule are related to the eigenvalue: $n_{-k} = 1 - \nu_k/2$ and $n_{+k} = 1 + \nu_k/2$. An occupation number of the bonding orbital equal to 2 corresponds to a "single"-bond component.

The bond formation is thus realized by a decrease in the occupation number of the antibonding orbital by ν_k and an increase in the occupation number of its bonding partner by the same amount, i.e., a transfer of ν_k electrons from the former orbital to the latter. This certainly corresponds as well to a charge transfer between the two fragments, since both orbitals comprise contributions from both fragments. The charge flow between the fragments is visualized in the $\Delta\rho$ contribution.

Figure 2 shows such $\Delta\rho$ contributions from the complementary pairs of NOCV for the $[Ni(NH_3)_3(CS)]^{2+}$ complex. It is clearly seen that the contribution from the first pair, φ_{-1} and φ_1, describes transfer of electron from the ligand to nickel. The second pair of NOCV describes the electron back-donation: CS → metal.

Thus, this example shows that NOCV allows for discussion of bonding in terms of the Dewar–Chatt–Duncanson model[1,2] of the ligand → metal donation and the metal → ligand backdonation. The corresponding eigenvalues can be used as measures of these synergic electron transfer processes: σ-donation can be quantified by $V_d = \nu_1$, and the π-back-donation by $V_{bd} = \nu_2 + \nu_3$. It was shown[32] that V_d and V_{bd} are in qualitative agreement with other measures of donation/back-donation processes, such as orbital interaction energy or changes in Mulliken electron populations of frontier orbitals. It should be pointed out, however, that in general one should not rely solely on the eigenvalues; an inspection of the NOCV shapes, and especially their $\Delta\rho$ contributions, is always necessary to make sure that donation/back-donation are separated, to verify which orbitals correspond to donation and which to back-bonding, etc.

In Figure 3 we display NOCV describing the bond between the $[Ni(NH_3)_3]^{2+}$ fragment and the NH_3 ligand in the tetra-amine nickel(II) system. In this case we describe a bond involving the ligand with very poor π-acceptor ability. However, there still exist three pairs, one corresponding to a σ-component and

Figure 3. Contours of NOCV characterizing the bond between the $[Ni(NH_3)_3]^{2+}$ fragment and the NH_3 ligand. The numbers denote the corresponding NOCV eigenvalues (V) and their populations (n). Only the orbitals participating in bonding ($|V| > 0.1$) are shown. The contour value is $|\varphi_i(r)| = 0.05$ au.
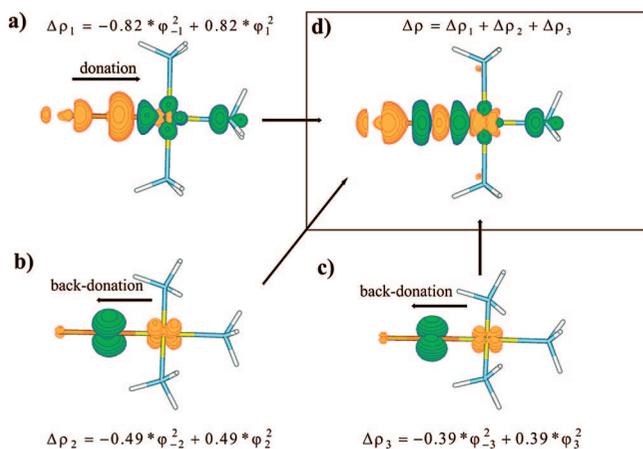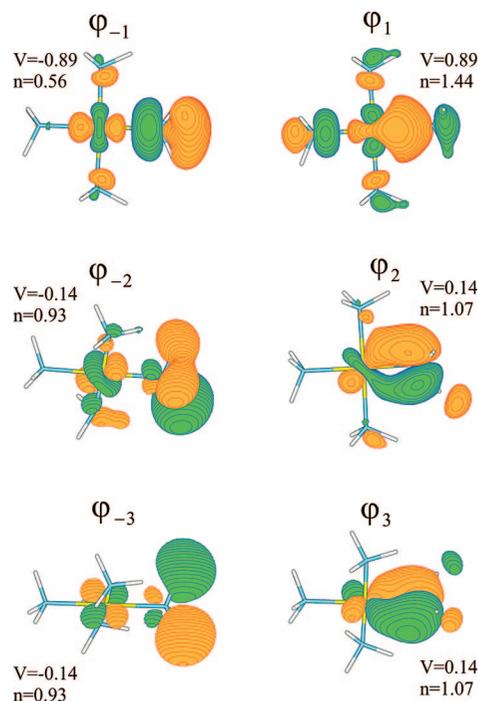

Figure 4. Contributions from the pairs of complementary NOCV (panels a–c) to the deformation density $\Delta\rho$, shown in panel d, for the bond between $[Ni(NH_3)_3]^{2+}$ and the NH_3 ligand. The corresponding orbitals are shown in Figure 3. The contour value is $\Delta\rho(r) = 0.005$ au.

two describing π-components. The first pair (φ_{-1}, φ_1) is characterized by $|\nu| = 0.82$, while the π-components (φ_{-2}, φ_2 and φ_{-3}, φ_3) are described by relatively small eigenvalues $|\nu| = 0.14$. The corresponding contributions to deformation density are shown in Figure 4. It is clearly seen from the figure that in this case the overall deformation density $\Delta\rho$ is practically determined by the $\Delta\rho_1$ contribution (σ-donation). In this case the back-donation contributions, $\Delta\rho_2$ and $\Delta\rho_3$, have a minor effect.

For the other ligands investigated in the present study, the contours of NOCV look qualitatively similar: in each case there exist a pair of NOCV corresponding to the ligand → metal
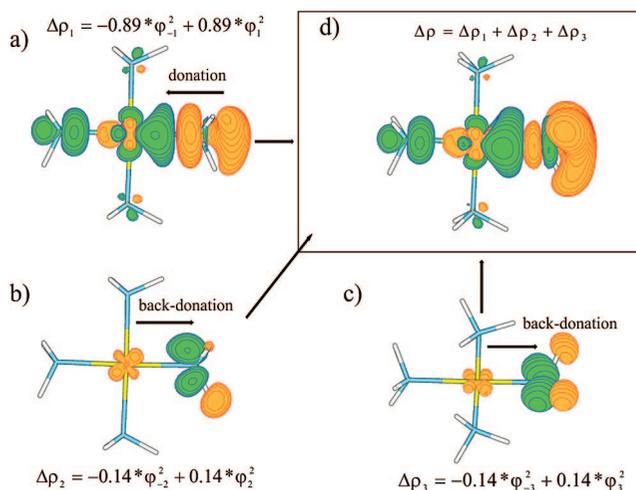

Figure 2. Contributions from the pairs of complementary NOCV (panels a–c) to the deformation density $\Delta\rho$, shown in panel d, for the bond between $[Ni(NH_3)_3]^{2+}$ and the CS ligand. The corresponding orbitals are shown in Figure 1. The contour value is $\Delta\rho(r) = 0.01$ au.
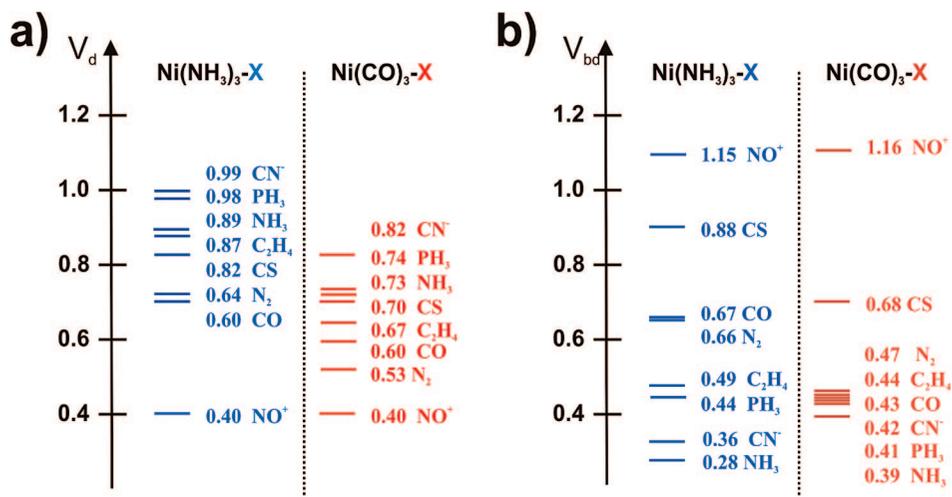
Figure 5. σ-Donor (panel a) and π-acceptor (panel b) properties of ligands X in Ni(NH$_3$)$_3$–X and Ni(CO)$_3$–X complexes, measured by the NOCV eigenvalues (V_d and V_{bd}, respectively).

σ-donation and two pairs of NOCV describing metal $\rightarrow$ ligand π-back-donation. This is also true for the orbitals characterizing the complexes with another metal-based fragment considered here, [Ni(CO)$_3$]$^{2+}$. Therefore, we will not show those orbitals and limit the discussion to the NOCV eigenvalues, providing a quantitative measure of donation/back-donation processes.

Figure 5 collects V_d and V_{bd} values calculated for all the complexes studied in the present work. Let us first discuss the σ-donor properties of ligands (Figure 5a). The V_d eigenvalues calculated for [Ni(NH$_3$)$_3$X]$^{2+}$ complexes are shown in the left-hand side of Figure 5a. The highest values of V_d were obtained for CN$^-$ and PH$_3$ ligands (0.99, 0.98). Ammonia, ethylene, and carbon monosulfide are characterized by relatively close values of V_d (0.89, 0.87, 0.82); molecular nitrogen and carbon monoxide form the next group, according to decreasing V_d. A significantly lower σ-donation eigenvalue was observed for NO$^+$ (0.40).

Thus, the folowing ligand order was determined for ligand $\rightarrow$ metal σ-donation in the case of [Ni(NH$_3$)$_3$X]$^{2+}$ complexes:

$$\text{CN}^- > \text{PH}_3 > \text{NH}_3 > \text{C}_2\text{H}_4 > \text{CS} > \text{N}_2 > \text{CO} > \text{NO}^+$$

The right-hand side of Figure 5a shows the V_d eigenvalues determined for [Ni(CO)$_3$X]$^{2+}$ complexes. In the carbonyl complexes, the eigenvalues are in general decreased compared to the [Ni(NH$_3$)$_3$X]$^{2+}$ systems; the only exception is NO$^+$, for which the (lowest) value $V_d = 0.4$ remains unchanged. The following order of ligands,

$$\text{CN}^- > \text{PH}_3 > \text{NH}_3 > \text{CS} > \text{C}_2\text{H}_4 > \text{CO} > \text{N}_2 > \text{NO}^+$$

looks quite similar. Only the position of ligands characterized by close σ-donation eigenvalues are exchanged: CS and C$_2$H$_4$, as well as CO and N$_2$; we have used color font here to emphasize the differences and similarities in the two sequences.

In general the results of NOCV analysis allow us to classify CN$^-$, PH$_3$, and NH$_3$ as strong σ-donors and CS and ethylene as intermediate, followed by CO and N$_2$. Finally, NO$^+$ was found to be definitely the weakest σ-donor from the group of ligands studied here. This general classification is in agreement with the previous study of Frenking et al.[20]

However, for some ligands the shift due to the change in the metal-containing fragment is visibly larger than for others. Thus,

the example presented here demonstrates that σ-donor properties of a ligand depend on the actual complex. Not only is the magnitude of electron transfer influenced by the metal-containing fragment, but also the relative σ-donor ability of different ligands may change.

Let us now discuss the π-acceptor properties of the same group of ligands. Figure 5b collects the V_{bd} values determined in the [Ni(NH$_3$)$_3$X]$^{2+}$ and [Ni(CO)$_3$X]$^{2+}$ complexes.

The following π-acceptor order was found from the calculations for [Ni(NH$_3$)$_3$X]$^{2+}$:

$$\text{NO}^+ > \text{CS} > \text{CO} > \text{N}_2 > \text{C}_2\text{H}_4 > \text{PH}_3 > \text{CN}^- > \text{NH}_3$$

For the [Ni(CO)$_3$X]$^{2+}$ complexes the corresponding ligand order is

$$\text{NO}^+ > \text{CS} > \text{N}_2 > \text{C}_2\text{H}_4 > \text{CO} > \text{CN}^- > \text{PH}_3 > \text{NH}_3.$$
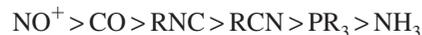
Again, the positions of neighbors in the orders change. In both cases, NO$^+$ is the strongest π-acceptor ($V_{bd} = 1.15$, 1.16), followed by CS (0.88, 0.68). {N$_2$, C$_2$H$_4$, CO} and {PH$_3$, CN$^-$} form two groups of ligands with an intermediate π-acceptor character, and NH$_3$ is characterized by lowest V_{bd} values (0.28, 0.38).

This general classification of the ligand acceptor properties is in qualitative agreement with the orders presented in the well-known inorganic/organometallic textbooks. For example, the order in Cotton's book is

$$\text{C}_2\text{H}_4, \text{CO} > \text{CN}^- > \text{SCN}^- > \text{I}^- > \text{Br}^- > \text{Cl}^- > \text{NH}_3$$

and in Elschenbroich's book:

$$\text{NO}^+ > \text{CO} > \text{RNC} > \text{RCN} > \text{PR}_3 > \text{NH}_3$$

According to Pruchnik, CS and NO$^+$ are classified as strong π-acceptors, CO and C$_2$H$_4$ as medium-strong, N$_2$ and PH$_3$ as medium-weak, and CN$^-$ and NH$_3$ as weak:

$$\text{NO}^+, \text{CS} > \text{C}_2\text{H}_4, \text{CO} > \text{N}_2, \text{PH}_3 > \text{CN}^-, \text{NH}_3$$

Our results show, however, that in [Ni(CO)$_3$X]$^{2+}$ complexes the differences in V_{bd} values for all the intermediate and weak π-acceptors (N$_2$, C$_2$H$_4$, CO, PH$_3$, CN$^-$, NH$_3$) become much smaller (range from 0.29 to 0.47) than in the case of
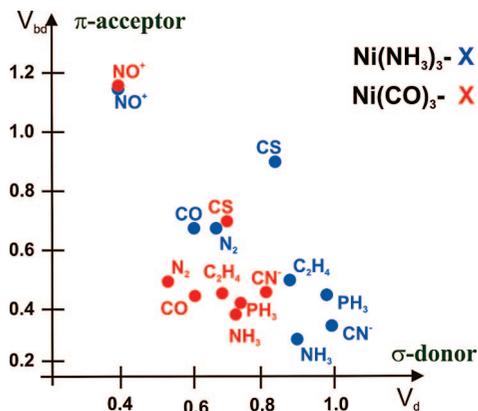
Figure 6. Donor–acceptor map of ligands X in Ni(NH$_3$)$_3$–X and Ni(CO)$_3$–X complexes.

[Ni(NH$_3$)$_3$X]$^{2+}$ (range from 0.28 to 0.67). This may result from the competition for the metal d orbitals by four π-accepting ligands in [Ni(CO)$_3$X]$^{2+}$, as opposed to [Ni(NH$_3$)$_3$X]$^{2+}$, in which three NH$_3$ ligands are very weak π-acceptors. Thus, this example strengthens our previous conclusion on the importance of the metal-based fragment.

In order to conclude the results of the present study, Figure 6 shows a map of σ-donor and π-acceptor properties of investigated ligands, measured by the corresponding NOCV eigenvalues. A two-dimensional map allows for a direct inspection of both donor and acceptor properties. A common intuitive way of thinking of the ligand properties is that the better the ligand's σ-donor ability, the worse its π-acceptor character. Figure 6 clearly demonstrates that it is a very rough simplification. Depending on the nature of the other ligands in the metal-containing fragment, a deviation from the expected trend can be substantial. This is especially pronounced in the case of [Ni(CO)$_3$X]$^{2+}$.

Concluding Remarks

In the present study natural orbitals for chemical valence were used to describe bonding between the ligand X and the metal-containing fragment in the model nickel(II) complexes. The main purpose was to characterize donor–acceptor properties of ligands X. The approach applied here offers a new, *direct* measure of the donor–acceptor properties of ligands that is obtained in a natural way from the results of calculations for the whole system and the fragments. Thus, it allows one to directly address the Dewar–Chatt–Duncanson model, as NOCV in a natural way lead to a separation of the ligand → metal and metal → ligand electron transfer processes.

For both σ-donation and π-back-donation, the resulting orders of ligands are in a qualitative agreement with those commonly accepted. However, it was also demonstrated that the influence of the metal-containing fragment can be substantial, changing not only the magnitude of electron transfer but also the relative donor–acceptor characteristics of different ligands. It has been recently emphasized by Frenking et al.[21] that the relative π-acceptor strength of ligands can be established only with respect to a given complex fragment. Our results demonstrate that this is as well true for σ-donor ability of the ligands. However, the effect is indeed more pronounced for back-bonding.

The analysis presented in this article demonstrated that NOCV can be useful in rationalizing experimental donor–acceptor characteristics, based on the indirect, spectroscopic measures. This can be especially valuable in problematic cases, when experiment does not provide definite answers or it is hard to carry out.