Mendeleev Commun., 1991, 1(1), 3–4

Effective Atomic Charge and Extraatomic Relaxation Energies in Coordinated Ligands

Vadim I. Nefedov,*[a] Igor B. Baranovskii,[a] Aleksei V. Chuvaev,[a] Georg N. Dolenko[b] and Tatyana M. Ivanova[c]

[a] *Institute of General and Inorganic Chemistry, Academy of Sciences of the USSR, 117907 Moscow, USSR*
[b] *Institute of Organic Chemistry, Siberian branch of the Academy of Sciences of the USSR, 664033 Irkutsk, USSR*
[c] *Research Institute for Organic Intermediates and Dyes, 107787 Moscow, USSR*

The effective atomic charge and extraatomic relaxation energies of donor atoms in ligands change as expected on coordination and depend on the strength of the metal—ligand bond which is governed mainly by the mutual influence of ligands in the coordination compounds investigated.

Recently a new method for the determination of effective atomic charge, extraatomic relaxation energy and Madelung potential in chemical compounds has been proposed.[1] This method is based on the experimentally measured energies of X-ray emission, ESCA and Auger transitions and allows one to derive a quantitative description of electron density changes in ligands upon coordination. The main features of the method can be outlined as follows. The chemical shift ($\Delta E_{K\alpha}$) of the $K\alpha$ line in the X-ray spectrum of a compound compared with that of an element, the binding energy (E_{2p}) of the 2p inner level of an atom and the energy (E_{KLL}) of Auger transition KLL can be expressed as in eqns. (1)–(3) where $E_i(q)$ is the ionization energy

$$\Delta E_{K\alpha} = \Delta[E_{1s}[(q) - E_{2p}(q)] \quad (1)$$

$$E_{2p} = E_{2p}(q) + (M - \phi) - R_e \quad (2)$$

$$E_{KLL} = E_{KLL}(q) - (M - \phi) + 3R_e \quad (3)$$

of the *i*th state of a free ion of a particular element, with effective charge *q*. *M* is the Madelung potential for the atom under investigation, ϕ is the work-function of the compound and R_e is the extraatomic relaxation energy. For a bond A—B between atoms in a given compound, R_e is the decrease in photoionization energy connected with the relaxation of electron wave functions of other atoms B_i owing to the positive hole in atom A. According to this definition the R_e values should correlate with the polarizability of the A–B bond or of atoms B_i. The physical meaning of R_e is discussed in detail elsewhere.[1,2] Using the experimental values $\Delta E_{K\alpha}$ as described[1] and literature cited therein one can determine the effective atomic charge *q* of atom under investigation in a compound. $E_{2p}(q)$ and $E_{KLL}(q)$ values can be calculated with good accuracy using the Hartree–Fock method. R_e and $M - \phi$ values can be determined from eqns. (2) and (3).

It should be emphasized that eqn. (1) is a consequence of eqn. (2) in the case of the 1s and 2p levels. Eqns. (2) and (3) are valid for free atoms, ions and atoms in chemical compounds.

The experimental $\Delta E_{K\alpha}$, E_{2p} and E_{KLL} values for various free ligands and coordination compounds are presented in Table 1. The experimental details are similar to those described in ref. 2. The experimental errors were about ± 0.007 eV for $\Delta E_{K\alpha}$, ± 0.2 eV for E_{2p} and $\pm$ (0.3–0.5 eV) for E_{KLL}.

The S and P atoms in the ligands $SC(NH_2)_2$, $OSMe_2$, SO_3^{2-} and PPH_3 act as electron donors upon coordination. The negative charge on the S atom in $SC(NH_2)_2$ should therefore decrease and the positive charges on S or P atoms in $OSMe_2$, SO_3^{2-} and PPH_3 should increase on coordination. This is indeed the case (Table 1). The changes in *q* values on coordination are usually of the order of + 0.1 e. The essential point is the strong dependence of the change in charge on the mutual influence of the ligands. Let us consider this point using the thiourea compounds as examples.

In compound **2** (Table 1), where $SC(NH_2)_2$ is not coordinated to a transition metal atom, the *q* value for the S atom coincides with that for the molecule in the solid state within the limits of experimental error. In compound **3**, the ligand is in a position *trans* to the Rh—Rh bond, which is known to have a strong *trans* influence[3] and to prevent electron density transfer from the donor ligand to the metal atom. In this case the observed increase in electron density on the S atom is already outside the possible limits of experimental error, but is still small. In compounds **4**–**7** this increase of electron density in comparison with the non-coordinated ligand is manifested quite clearly.

The *trans* influence of the Rh—Rh bond is also well established for other ligands, as shown by a comparison of compounds **9** and **10**, **15** and **16**, **17**. In all these cases the Rh—Rh bond diminishes the donor abilities of the ligand *trans* to this bond and this effect is reflected by a decrease of effective charge on the S and P atoms in such compounds in comparison with other coordination compounds (Table 1).

The *trans* influence of the Pt—PPh_3 bond in compounds **16** and **17** is manifested by a smaller charge on the P-atoms in the *trans* complex than that in the *cis* complex (the relative experimental error in determining *q* for these compounds was $\pm$ 0.01 e).

A *trans* influence was also expected in compounds **6** and **7**, because thiourea is known to have a strong *trans* influence. Possible explanations for its absence in these cases are the difference in outer sphere anions and the bidentate character of the ethylenediamine ligand in **6**. The absence of data on the structure of compound **6** prevented us from discovering how the *trans* influence manifests itself in interatomic distances.

According to the definition the value of R_e for a donor atom in a ligand should increase on coordination in comparison with that in a free ligand. This statement is valid for all the compounds in Table 1. In principle, the value of R_e should be sensitive to the *trans* effect in a similar way to that of *q*. However, the large experimental error for the R_e values, which was estimated as about $\pm$ 0.4 eV, prevented us from analysing the experimental data in this respect.

In conclusion let us analyse the dependence of the experimental E_{2p} and E_{KLL} values on *q* and R_e values. The dependence of E_{2p} on *q* [eqn. (2)] is approximately linear.[1] In the case of a large change in *q* values the difference in $E_{2p}(q)$, but not in R_e and $(M - \phi)$, determines the value of ΔE_{2p} in coordination compounds. It is noteworthy that the values of ΔE_{2p} between coordinated and free ligands usually correlate with changes in *q* values, although the difference Δq is quite small in this case. The correlation between ΔE_{2p} and Δq holds especially well where a *trans* influence is present (*e.g.* corresponding values for compounds **1**, **3** and **4**–**7**; **8**, **9** and **10**; **14**, **15** and **16**, **17** in Table 1). However, no *trans* influence was observed for the P_{2p} binding energy values in compounds **16** and **17**, although it is well manifested in the *q* values. The *trans* influence of metal–metal bonds on the binding energy of neutral and acidic ligands has been studied in detail.[4,5]

Received in USSR, 13th June 1990
Received in UK, 31st August 1990; Com. 0/03032E

Table 1 Experimental and calculated energy parameters/eV

No.	Compound	$\Delta E_{K\alpha}$	E_{2p}	E_{KLL}	q[a]	R_e	$M - \phi$
1	$SC(NH_2)_2$ (thio)	−0.123	162.3	2112.7	−0.33	4.1	−1.3
2	*trans*-$[RhCl_2(en)_2]Cl_3$(thio)[b]	−0.118	162.5	2112.9	−0.31	4.4	−1.0
3	$Rh_2(MeCO_2)_4(thio)_2$	−0.104	162.6	2113.1	−0.27	4.6	−1.3
4	$[Rh(thio)_6]Cl(NO_3)_2$	−0.086	163.4	2113.0	−0.22	5.0	−0.7
5	$[Ni(thio)_4]Cl_2$	−0.079	162.9	2112.8	−0.20	4.6	−1.8
6	*cis*-$[Pt(en)(thio)_2](NO_3)_2$	−0.093	163.1	2112.8	−0.24	4.7	−1.0
7	*trans*-$[Pt(NH_3)_2(thio)_2]Cl_2$	−0.061	163.1	2112.6	−0.15	4.7	−2.1
8	Me_2SO (dmso)	0.359	172.2[c]	2099.3[c]	0.70	3.76[c]	−5.9[d]
9	$Rh_2(MeCO_2)_4(dmso)_2$	0.382	166.1	2110.9	0.73	6.4	−8.8
10	$Na[RhCl_4(dmso)_2]$	0.419	166.7	2109.6	0.79	6.1	−9.3
11	Na_2SO_3	0.83	167.2	2108.2	1.35	6.1	−16.8
12	$Na_3Rh(SO_3)_3 \cdot 3.5H_2O$	0.869	168.2	2109.2	1.40	7.2	−15.5
13	$Na[Rh(NH_3)_4(SO_3)_2]$	0.870	167.1	2109.5	1.40	6.8	−17.0
14	PPh_3	0.066	130.9	1853.3	0.16	4.8	−4.4
15	$Rh(MeCO_2)_4(PPh_3)_2$	0.114	131.1	1855.5	0.26	6.1	−4.1
16	*cis*-$[PtCl_2(PPh_3)_2]$	0.122	131.9	1854.4	0.28	6.0	−3.7
17	*trans*-$[PtCl_2(PPh_3)_2]$	0.105	131.9	1853.9	0.24	5.7	−3.5

[a] In the units of elementary charge. [b] en = $H_2N(CH_2)_2NH_2$. [c] Data[2] for the free molecule in the gaseous phase. [d] *M* value[2] was that for the free molecule in the gaseous phase.

References

1 V. I. Nefedov, V. G. Yarzhemsky, A. V. Chuvaev and E. M. Trishkina, *J. Electron Spectrosc. Relat. Phenom.*, 1988, **46**, 381.

2 V. I. Nefedov, *Z. Anorg. Allg. Chem.*, 1989, **577**, 179.

3 G. G. Christoph and Y. B. Koch, *J. Am. Chem. Soc.*, 1979, **101**, 1422.

4 V. I. Nefedov, Ya. V. Salyn, I. B. Baranovskii and A. G. Maiorova, *Zh. Neorg. Khim.*, 1980, **25**, 216 (English translation in *Russ. J. Inorg. Chem.*, 1980, **25**, 116).

5 V. I. Nefedov, Ya. V. Salyn, A. V. Shtemenko and A. S. Kotelnikova, *Inorg. Chim. Acta*, 1980, **45**, L49.