

ESCA (electron spectroscopy for chemical analysis) investigations of coordination compounds

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Abstract - A new method for the determination of effective atomic charge, extra-atomic relaxation energy and Madelung potential based on X-ray emission, ESCA and Auger spectroscopy data is described and applied to the study of coordinated donor ligands including $\text{SC}(\text{NH}_2)_2$, SO_3^{2-} , $\text{OS}(\text{CH}_3)_2$ and PPh_3 . The coordination leads to the decrease of electron density on the donor atom in ligand, this decrease being dependent on the mutual influence of ligands. The strong influence of metal-metal bond is demonstrated. The extra-atomic relaxation energy of the donor atom increases upon coordination.

INTRODUCTION

The binding energy values of inner electrons obtained by ESCA are widely used for the investigation of electronic structure and geometry of coordination compounds. The ESCA data are used, for example, for the determination of oxidation number and effective charge of atom under investigation and for the study of coordination type of ligands (ref.1). These investigations are based on experimental regularities and on some assumption concerning the connection between inner electrons binding energies and effective charge of atom under investigation.

Recently a new method for the determination of atomic effective charge, extra-atomic relaxation energy and Madelung potential in chemical compounds has been proposed (ref.2). This method is based on the experimentally measured energies of X-ray emission, ESCA and Auger transitions and allows to derive a quantitative description of the electron density changes in ligands upon their coordination. The main features of the method can be outlined as follows. The chemical shift of K_{α} -line ($\Delta E_{K\alpha}$) in compound in comparison with element, the binding energy of 2p-inner level (E_{2p}) and the energy (E_{KLL}) of Auger transition KLL can be expressed as follows (ref.2):

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

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

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

where $E_i(q)$ is ionization energy of i-level in free ion of investigated element with effective charge q, M- Madelung potential for the investigated compound and R_e -extra-atomic relaxation energy. The physical meaning of R_e is discussed in detail in refs. 2 and 3 and will be considered below. Using the experimental values $\Delta E_{K\alpha}$ as described in ref.2 and literature cited therein one can determine atomic effective charge q of the investigated atom in a compound. The $E_{2p}(q)$ and $E_{KLL}(q)$ values can be calculated with good accuracy using Hartree-Fock method. The R_e and M- φ values can be determined from Eqs. (2) and (3).

EXPERIMENTAL DATA

The experimental $\Delta E_{K\alpha}$, E_{2p} and E_{KLL} values are presented in Table 1. I. B. Baranovski, G. N. Dolenko, T. M. Ivanova and A. V. Churvaev have participated in the synthesis of compounds and in the investigations. The experimental details are similar to those described in ref. 2. The experimental errors were about ± 0.007 eV for $\Delta E_{K\alpha}$; $\pm 0,2$ eV for E_{2p} and $\pm(0,3-0.5)$ eV for E_{KLL} . Some regular features in experimental data will be discussed below using the calculated q , $M-\varphi$ and R_e values from Table 2. All the necessary theoretical values were taken from ref. 2 or calculated in the same manner.

TABLE 1. The experimental data (eV): $\Delta E_{K\alpha}$ - shift of K α line, E_{2p} - binding energy of 2p-level, E_{KLL} - energy of Auger KLL transition

N	Compound	$\Delta E_{K\alpha}$	E_{2p}	E_{KLL}
1	$SCC(NH_2)_2 \bar{=} ThIO$	-0,123	162,3	2112,7
2	$tr-[RhCl_2En_2]Cl_3ThIO$	-0.118	162,5	2112,9
3	$Rh_2(MeCOO)_4(ThIO)_2$	-0,104	162,6	2113,1
4	$[RhThIO_6]Cl(NO_3)_2$	-0,086	163,4	2113,0
5	$NiThIO_4Cl_2$	-0.079	162,9	2112,8
6	$cis-(PtEnThIO_2)(NO_3)_2$	-0,093	163,1	2112,8
7	$tr-[Pt(NH_3)_2ThIO_2]Cl_2$	-0,061	163,1	2112,6
8	$(CH_3)_2SO \bar{=} DMSO$	0,359	172,2*	2099,3*
9	$Rh_2(MeCOO)_4(DMSO)_2$	0,382	166,1	2110,9
10	$Na[RhCl_4(DMSO)_2]$	0,419	166,7	2109,6
11	Na_2SO_3	0,83	167,2	2108,2
12	$Na_3Rh(SO_3)_3 \cdot 3,5H_2O$	0,869	168,2	2109,2
13	$Na[Rh(NH_3)_4(SO_3)_2]$	0,870	167,1	2109,5
14	PPh_3	0.066	130,9	1853,3
15	$Rh(MeCOO)_4(PPh_3)_2$	0,114	131,1	1855,5
16	$cis-PtCl_2(PPh_3)_2$	0,122	131,9	1854,4
17	$tr-PtCl_2(PPh_3)_2$	0,105	131,9	1853,9

* Data for free molecule in gaseous phase (ref. 2)

EFFECTIVE CHARGE

The atoms S and P in the ligands $SCC(NH_2)_2$, $OSC(CH_3)_2$, SO_3^{2-} and PPh_3 act as electron donors upon coordination, that is why the negative charge on S atom in $SCC(NH_2)_2$ must decrease and positive charges on S or P atoms increase in $OSC(CH_3)_2$, SO_3^{2-} and PPh_3 . This is really the case (see Table 2). The differences in q values due to coordination are usually about 0.1 e. The essential point is the strong dependence of the charge difference on the mutual influence of ligands in the compounds. Let us consider this point using the thiourea compounds as an example.

In the compound 2 (Table 2) where molecule $SCC(NH_2)_2$ is not coordinated through transition metal atom, the q value for the S atom coincide within experimental error with that in free solid ligand. In compound 3 where the ligand is in trans-position with respect to Rh-Rh-bond, which is known to have a strong trans-influence and to prevent electron density transition from donor ligand to the metal atom (ref. 4), the essential electron density increase on S atom beyond possible experimental error is observed.

TABLE 2. The calculated values: q -effective charge, R_e -relaxation energy (eV), M -Madelung potential (eV), ϕ - work function (eV)

N	Compound	q	R_e	$M-\phi$
1	$SC(NH_2)_2 \bar{=} ThIO$	-0,33	4,1	-1,3
2	$tr-[RhCl_2En_2]Cl_3ThIO$	-0,31	4,4	-1,0
3	$Rh_2(MeCOO)_4(ThIO)_2$	-0,27	4,6	-1,3
4	$[RhThIO_6]Cl(NO_3)_2$	-0,22	5,0	-0,7
5	$NiThIO_4Cl_2$	-0,20	4,6	-1,8
6	$cis-(PtEnThIO_2)(NO_3)_2$	-0,24	4,7	-1,0
7	$tr-[Pt(NH_3)_2ThIO_2]Cl_2$	-0,15	4,7	-2,1
8	$(CH_3)_2SO \bar{=} DMSO$	0,70	3,76*	-5,9**
9	$Rh_2(MeCOO)_4(DMSO)_2$	0,73	6,4	-8,8
10	$Na[RhCl_4(DMSO)_2]$	0,79	6,1	-9,3
11	Na_2SO_3	1,35	6,1	-16,8
12	$Na_3Rh(SO_3)_3 \cdot 3,5H_2O$	1,40	7,2	-15,5
13	$Na[Rh(NH_3)_4(SO_3)_2]$	1,40	6,8	-17,0
14	PPh_3	0,16	4,8	-4,4
15	$Rh(MeCOO)_4(PPh_3)_2$	0,26	6,1	-4,1
16	$cis-PtCl_2(PPh_3)_2$	0,28	6,0	-3,7
17	$tr-PtCl_2(PPh_3)_2$	0,24	5,7	-3,5

* Data for free molecule in gaseous phase (ref.2)

** The M value in free molecule in gaseous phase (ref.2)

In the compounds 4-7 this increase of electron density in comparison with non-coordinated ligand is manifested quite clear.

It is worth noting, that the trans-influence of Rh-Rh-bond is well established for other ligands as well (compare compounds 9 and 10, 15 and 16,17): in all these cases the Rh-Rh bond diminishes the donor abilities of ligand in trans-position with respect to this bond, which is reflected by the decrease of the effective charge on S and P atoms in such compound in comparison with other coordination compounds (Table 2).

The trans-influence of Rh-Rh bond is well known and exhibit itself, for example, as the increase in Rh-Lig length in compounds containing this bond in comparison with that in $RhClO_4$ and $Rh(III)$ compounds (ref.5). For example, the Rh- PPh_3 length is 2,478 Å in compound 15, while the Rh- PPh_3 length is about 2,29 for Rh (III) compounds.

The typical example for the trans-influence of Pt- PPh_3 -bond is the compound of 16 and 17 type (ref.4). The length Pt-Cl is increased in cis-complex, while the length Pt-P is increased in tr-complex. In accordance with these results the charge on P atom in tr-complex is smaller than that in cis-complex.* (Table 2). Moreover, according to the chemical shifts of $ClK\alpha$ lines in cis-complex, -0,151(12)eV, and in tr-complex, -0,131(20)eV, one can expect the larger negative charge on Cl atom in cis-complex in comparison with tr-complex. This is consistent with the expected trans-influence but quite high experimental errors mentioned above do not allow us to make a definite conclusion on the base of $ClK\alpha$ line shift values only.

*The relative experimental error in q values for the compounds 16 and 17 was $\pm 0,01$ e.

The manifestation of tr-influence was also expected in the compounds 6 and 7, because the thiourea is known to have a strong trans-influence. The possible explanations for its absence in these cases are the difference in outer spherical anions and bidentate type of ethylenediamine ligand. The absence of data on the compound 6 structure did not allow us to find out how the trans-influence manifests itself in interatomic distances.

EXTRA-ATOMIC RELAXATION ENERGY

The extra-atomic relaxation energy R_e is the energy decrease in photoionization energy due to the relaxation of electron wave functions of the other B_1 -atoms in compound besides the A-atom under investigation. This relaxation is associated with a positive hole in photoionized atom and leads to the redistribution of the electron density between the atoms within the compound. According to this definition the R_e values are to correlate with the polarizability of A-B bond or of B_1 atom. This is really the case (see ref.2). The contribution of A- B_1 bond to the R_e value increases with the covalency of A- B_1 bond (refs. 2,3).

According to the definition the R_e value of donor atom in ligand is to increase upon coordination in comparison with a free ligand. This statement is valid for all the compounds from Table 2. In principle, the R_e value must be sensitive to trans-influence similar to q value. However, the large error of R_e experimental values, which has been estimated to be about $\pm 0,4$ eV, prevented us to analyze the experimental data in this respect.

(M - φ) VALUE

The (M- φ) value depends on the electron density distribution and interatomic distances in the whole crystal, that is why any simple regularities in the (M- φ) values are not expected. This fact is really proved by data from Table 2. Anyway, the data indicate that the main contribution to the (M- φ) value of coordinated ligand is associated with the ligand atoms, because coordination does not entail essential changes of (M- φ) values for ligands. In accordance with this result the (M- φ) value must be negative for the atom with a large positive effective charge q and the absolute [M- φ] value must increase with the decrease of electron density on the atom under investigation, i.e. with the increase of q value. These results follow from the increase (decrease) of negative (positive) q value on the neighboring atoms B with increasing the q value for A atom under investigation. The correlation between (M- φ) and q is really the case, especially for the large changes of q (Fig.1).

The dependence of (M- φ) on q is close to linear, which reflects the essential contribution to the (M- φ) value of the neighboring B_1 atoms. This contribution is equal to $\sum (1) q_1 / R_1$, where q_1 and R_1 are effective charges and interatomic distances A_1-B_1 correspondingly. In the first approximation the q_1 values must depend linearly on q. For example, in the molecule AB_n the value q_A is equal to nq_B .

In conclusion let us analyze the dependence of experimental $\Delta E_{K\alpha}$, E_{2p} and E_{KLL} values on q and R_e values.

The connection between E and q is quite simple (Eq.(1)): the increase in $\Delta E_{K\alpha}$ means the increase in q.

The dependence of E_{2p} value on q (Eq.(2)) is approximately linear (ref.1). In case of large differences in q values the difference in $E_{2p}(q)$ but not in R_e and (M- φ) determines the ΔE_{2p} value in chemical compounds (Fig.2). It

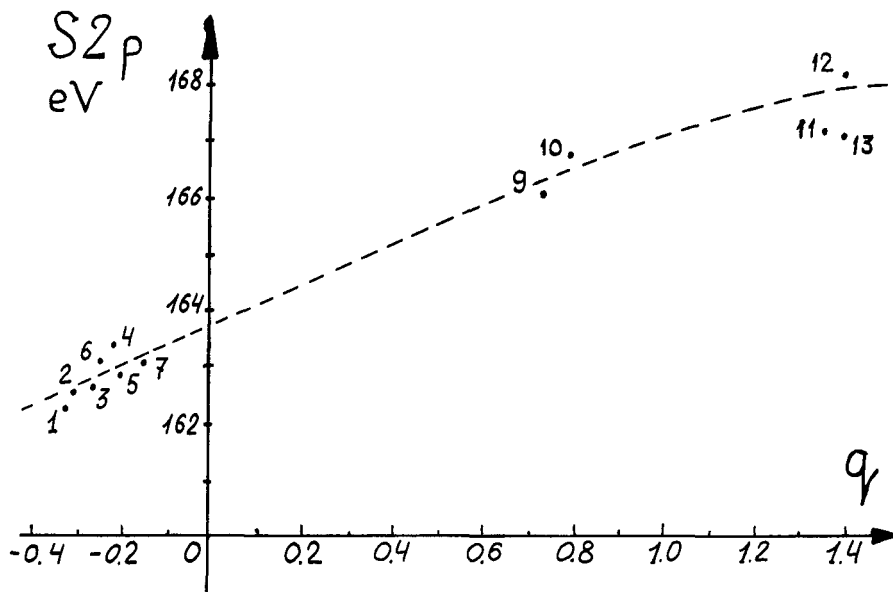


Fig.1. The dependence of E on q. The numbers correspond to the compounds in Table 2

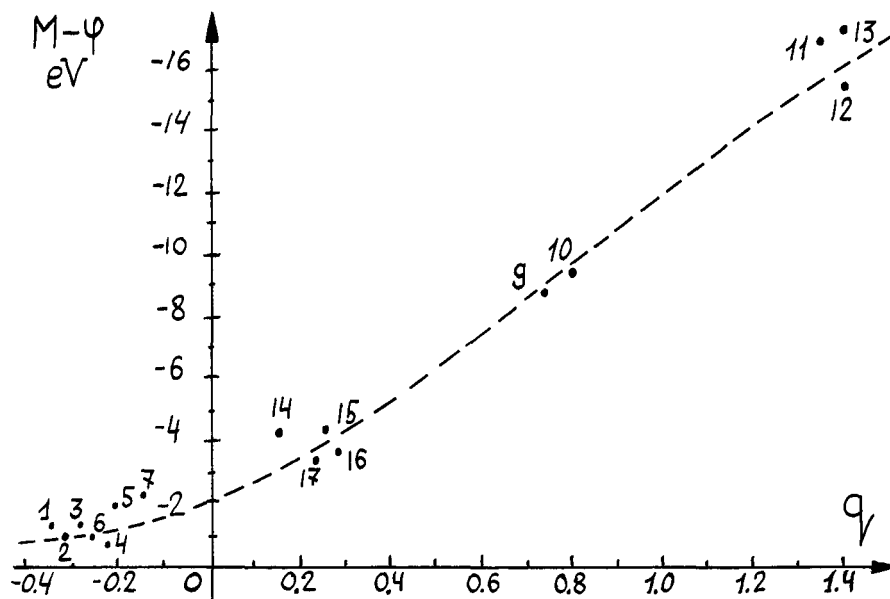


Fig.2. The dependence of (M - φ) on q. The numbers correspond to the compounds in Table 2

is noteworthy that the ΔE_{2p} values between coordinated and free ligand 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 for the case of trans-influence (the corresponding values for the compounds 1,3 and 4-7; 8,9 and 10; 14,15 and 16,17). However no trans-influence was observed for P2p binding energy values in compounds 16 and 17, although it is well manifested in q values. The trans-influence of metal-metal bond on binding energy of neutral and acidoligands has been studied in detail in ref.6 and 7. In these papers the binding energies of donor atoms in ligands in trans-position with respect to metal-metal bond are proved to be lower than those in other coordination compounds. This is accordance with expected changes in electron density distribution due to the trans-influence.

The E_{KLL} value of ligand atom usually increases in coordinated ligand, although the q value also increases upon coordination. The increase of the positive q value is known to lower the E_{KLL} value (ref.2). These results indicate the main role of ΔR_e and not $\Delta E_{KLL}(q)$ for ΔE_{KLL} in these cases. Indeed, analyzing the data from tables 1 and 2 one can see the increase of E_{KLL} values with increasing R_e values for a given ligand.

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