Heteroatom Chemistry
Volume 11, Number 3, 2000

Ligand Effect on Chlorine Electron Density Distribution in Titanium Tetrachloride Complexes

G. N. Dolenko,[1] B. A. Gostevskii,[2] O. Kh. Poleshchuk,[3] J. Latosinska,[4] M. Ostafin,[4] M. A. Belogolov,[1] and M. V. Grechneva[2]

[1]Department of Natural Sciences, East Siberian Institute of Russian Ministry for Internal Affairs, 110 Lermontov St., 664077 Irkutsk, Russian Federation

[2]Institute of Chemistry, Siberian Division, Russian Academy of Sciences, 664033 Irkutsk, Russian Federation

[3]Department of Chemistry, State Pedagogical University, 75 Komsomol'sky Av., 634041 Tomsk, Russian Federation

[4]Institute of Physics, Adam Mickiewicz University, 85 Umultowska St., 61-614 Poznan, Poland

Received 21 January 1999; revised 4 August 1999

ABSTRACT: *C1 Kα line shifts and ^{35}Cl NQR frequencies have been measured for series of titanium tetrachloride complexes. Nonempirical calculations of corresponding free ligands have been carried out on the MP2/6-31G* level. Dependencies of the experimental data obtained on experimental and calculated parameters of ligand donor ability have been analyzed. It is shown that the electron density on acceptor chlorine atoms and the electric field gradient on their nuclei are determined at first by the polarizing effect of the ligand.* © 2000 John Wiley & Sons, Inc. Heteroatom Chem 11:177–181, 2000

INTRODUCTION

It is known that Kα line shifts (ΔKα) of the 3d period elements are proportional to effective charges on these atoms [1–3]. As this takes place, the electron density on corresponding atoms increases linearly with the growth of negative ΔKα values. Previously [4–6] we showed that the dependence of effective charges of chlorine atoms on ligand donor numbers (DN) [7] in $TiCl_4L_2$ complexes differs essentially from that in $SnCl_4L_2$ and $SbCl_5L$ complexes. Although, in chloride complexes of non-transition elements, the electron density on chlorine atoms increases linearly with the growth of the ligand's DN and with the ^{35}Cl NQR frequency motion in the low-frequency field, there are no similar dependencies for $TiCl_4L_2$ complexes.

To investigate the particularities appropriate to $TiCl_4$ complexation, we have measured in the present work Cl Kα shifts and ^{35}Cl NQR frequencies for a large series of titanium tetrachloride complexes and correlated the data obtained with different parameters of ligand donor ability.

METHODS

$TiCl_4L_2$ complexes are produced by direct conjugation of near stoichiometric quantities of the corresponding components in a vacuum, in a special glass

---

Correspondence to: G. N. Dolenko.
Tel.: +7-395-2-46-35-62; Fax: +7-395-2-46-64-34; E-mail: *vlad@irioch.irk.ru*
© 2000 John Wiley & Sons, Inc. CCC 1042-7163/00/000000-00

system [8]. The synthesis is carried out in a small excess of organic ligands, which are subsequently frozen. The composition and cleanliness of complexes obtained are tested by IR spectra and element analysis.

Kα fluorescence spectra were obtained by use of X-ray spectrometer "Stearate". The spectra were excited by AgL radiation (X-ray tube operated at 0.2–0.4 A and 6-10 kV), analyzed by a quartz crystal (plane of rhombohedron, bend radius 500 mm) and recorded by a proportional counter filled with an argon-methane mixture (P-10). Samples were prepared by rubbing them on nickel plates. During the exposure time (about 0.5 minute for one Cl Kα spectrum), the samples were maintained at liquid nitrogen temperature. Measurements of Cl Kα spectra were repeated 16–20 times and averaged by the technique described in Ref. [2].

^{35}Cl NQR frequencies were measured at liquid nitrogen temperature using Fourier transform at the pulse spectrometer of the Institute of Physics of Adam Mickiewicz University [9].

Nonempirical calculations on the MP2/6-31G* level were made using two-exponential wave functions by means of the GAUSSIAN-94 program package [10] at the RS/6000 workstation. Some spatial parameters of investigated molecules were taken from Ref. [11] (see Table 1); all the remaining spatial parameters were optimized. Nefedov and Gofman (1978) [12] assumed that the dependence of a characteristic T of M-X bond in MX_nL compounds can be presented as

$$T(L) = T(0) + CP \tag{1}$$

with T(0) and C being constants for considered characteristic T of M–X bond; P being a value called influence parameter depending mostly on L. The authors considered many physical characteristics of M–X bonds and found by the least-squares-method of analysis such P values which suit best to the equation (1) for all the characteristics T and the compounds MX_nL.

RESULTS AND DISCUSSION

The table presents experimental values of Cl Kα line shifts in $TiCl_4L_2$ complexes with respect to Cl_2 (ΔCl Kα), ^{35}Cl NQR frequencies, ligand's donor numbers (DN), ligand's influence parameters ($\langle P \rangle$) [12]*, and ionization potentials (IP) of the corresponding donor molecular orbital of the ligand. One can see that in this case, in fact, there is no dependence of Cl Kα shifts on DN values (see Figure 1a), unlike that for $SnCl_4L_2$ and $SbCl_5L$ complexes [4,5]. Examination of the dependence ΔCl Kα on ^{35}Cl NQR frequencies (Figure 1b), and on such widely used parameters of the ligand's donor ability as influence parameters (Figure 1c) and ionization potentials (Figure 1d), shows similar results.

It is well known that the ligand's donor ability is determined by a set of parameters: IP of the corresponding donor MO, degree of its localization on the coordinating atom, effective charge of the coordinating atom, etc. [12]. The absence of simple depen-

TABLE 1 Experimental and Calculated Parameters of Electron Structure of $TiCl_4L_2$ Complexes

		Complexes		*Free Ligands*							
				Experimental Data			*Calculated Data*				
N	*L*	*−ΔCl Kα, eV·1000, with respect to Cl₂*	ν³⁵ Cl, MHz	DN [7], kcal/mol	⟨P⟩ [12]	IP, eV	Fixed Bond Lengths (Å)	Fixed Valence Angles (°)	−ε, eV	α	qx
1	$(Me_2N)_3PO$	271 (10)[a]	9.49	38.6	—	10.44 [13]	—	—	12.17	0.418	−0.597
2	$(CH_2)_4O$	211 (11)	8.59	20.0	—	9.43 [14]	—	—	10.82	0.453	−0.520
3	PPh_3	210 (12)	8.64	26[b]	10.00	7.92 [14]	—	—			—
4	Py	203 (11)	8.37	33.1	0.00	9.65 [14]	—	—	11.05	0.497	−0.423
5	Me_2NCOH	195 (13)	9.04	26.5	−5.96	10.46 [14]	—	—	11.73	0.497	−0.422
6	NBz_3	187 (9)	—	29[b]	—	8.0 [14]	—	—			—
7	Me_2CO	175 (14)	8.59	17.0	−9.75	9.71 [14]	CC 1.52 CO 1.22	OCC 120	11.09	0.448	−0.393
8	MeCN	173 (10)	8.40	14.1	0.51	12.18 [15]	CC 1.468 CN 1.159	—	9.04	0.548	−0.166
9	Me_2S	154 (9)	8.65	23.5	1.76	8.65 [15]	CS 1.802	CSC 98.9	9.04	0.720	0.096
10	PhCN	143 (14)	9.27	11.9	−5.52	9.73 [16]	—	—	12.87	0.261	−0.353

[a] Here and below, the numbers in parentheses on the right-hand side are the mean square errors in the last significant digit, taken for the 95% confidence interval by Student's criterion.

[b] The DN values are estimated by correlation analysis for $SbCl_5L$ complexes [4].

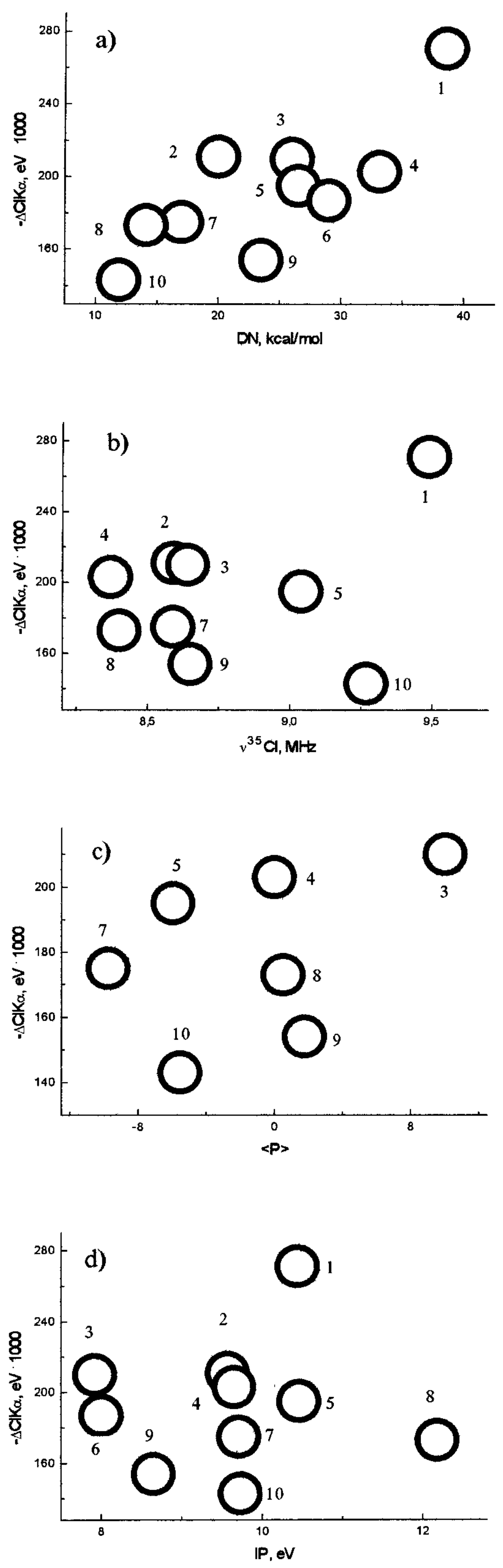

FIGURE 1 The Cl Kα shifts in $TiCl_4L_2$ complexes versus (a) ligand's donor numbers DN, (b) ^{35}Cl NQR frequencies, (c) ligand's influence parameters $\langle P \rangle$, (d) ionization potentials of free ligands. Radii of circles correspond to the errors of ΔCl Kα measurements. Numbering of points corresponds to that in Table 1.

dencies presented in Figure 1 shows that no single one of the parameters mentioned above is predominant.

Taking into account that the DN is substantially an integral parameter, we have examined the dependence of ΔCl Kα on two parameters simultaneously, DN and IP, which, being taken together, can characterize definitely the ligand's donor ability. As a result, we have obtained the following two-parameter correlation:

$$-\Delta \text{Cl K}\alpha = 3.8(7)\text{DN} + 10(2)\text{IP} + 2(14)$$

$$(r = 0.973,\ s = 21,\ n = 10) \qquad (2)$$

One can see from this correlation that the electron density on the chlorine atoms in $TiCl_4L_2$ complexes is determined firstly by the ionization potential of the ligand molecule orbital conjugated effectively with the vacant orbitals of the acceptor and depends considerably on the DN. The positive sign at the main IP term shows that the electron density of the chlorine atoms of the acceptor increases with the ligand's donor ability decreasing, which is opposite to that for $SnCl_4L_2$ and $SbCl_5L$ complexes. Correlation (2) supposedly shows that the chlorine atom electron density in $TiCl_4L_2$ complexes is defined firstly by the polarization effect of the ligand:

$$\ddot{A} \rightarrow \text{Ti-Cl} \Rightarrow \ddot{A} \rightarrow \text{Ti}^{+\delta}\text{-Cl}^{-\delta} \qquad (3)$$

with Ä being the ligand's coordinating atom containing valence n- or π- electron density capable of donation. This effect may be illustrated by the essential weight of the resonance structure (III):

$$\underset{\text{(I)}}{\overset{\curvearrowright}{A} \rightarrow \overset{\curvearrowright}{\text{Ti}-\text{Cl}}} \leftrightarrow \underset{\text{(II)}}{\overset{\curvearrowleft}{A^+}-\text{Ti Cl}^-} \rightarrow \underset{\text{(III)}}{A \rightarrow \text{Ti}^+ \ \text{Cl}^-}$$

We should note that in this case the increase of the polarity of the Ti–Cl bond (see correlation 3) is accompanied by the decrease of this bond order.

For the further examination of the dependence of the chlorine-electron density on the ligand effect, we have carried out nonempirical calculations of free ligand electron structure. As a result, we have obtained some parameters of the ligand's donor ability, presented in Table 1. These are the one-electron energy (ε) of the highest occupied MO interacting with the vacant acceptor orbitals, degree of localization (α) of this MO on the ligand's coordinating atom ($\alpha = 1$ for one-central MO), and the effective charge (q_A) on the ligand's coordinating atom. Performed correlation analysis shows that Cl Kα shifts depend on the effective charge of the ligand's coordinating atom and the degree of localization of the donor MO, and do not depend on ε:

$$-\Delta\mathrm{Cl}\ K\alpha = -227(24)q_A + 234(23)\alpha - 0(10)\ (r = 0.987,\ s = 17,\ n = 8) \qquad (4)$$

The obtained correlation (4) completely confirms the previous conclusion that the chlorine atom electron density does not depend substantially on the ligand's donor ability and increases with the growth of the ligand's polarization effect depending mostly on the effective charge of the ligand's coordination atom and the degree of localization of the main ligand donor MO on this atom.

Fig. 2 presents the dependencies of the ^{35}Cl NQR frequency on DN, IP, and ⟨P⟩. We can see that there are no simple satisfactory dependencies here as well as in Figure 1. Nevertheless, one can see the tendency of the increase of the ^{35}Cl NQR frequency with the growth of the ligand's donor ability. This is opposite to that for non-transition metal complexes [5]. Correlation analysis performed leads to two two-parameter relations:

$$\nu^{35}\mathrm{Cl} = 0.014(7)\ (-\Delta\mathrm{Cl}\ K\alpha) + 0.6(1)\mathrm{IP} + 0.2(5) \quad (r = 0.981,\ s = 0.8,\ n = 9) \qquad (5)$$

$$\nu^{35}\mathrm{Cl} = 0.06(3)\mathrm{DN} + 0.72(9)\mathrm{IP} + 0.2(5)\ (r = 0.979,\ s = 0.8,\ n = 9) \qquad (6)$$

It is shown from the equations (5) and (6) that IP is the principal parameter defining ν^{35}Cl NQR values. As this take place, IP's increase (indicating a decrease of ligand donor ability) leads to an increase of ν^{35}Cl NQR. The positive sign at the $-\Delta$Cl Kα term indicates the increase of the gradient of the electric field at chlorine nuclei with the growth of the chlorine-electron density. However, in $\mathrm{SnCl_4L_2}$ and $\mathrm{SbCl_5L}$ complexes, we saw ^{35}Cl NQR frequencies to be decreased with the growth of the electron density on the chlorine atom [4,5]. This effect is associated with the essential influence of the change of the TiCl bond order on the ^{35}Cl NQR frequencies.

Townes-Dailey's approximation [17] for the chlorine atom leads to the following relation:

$$e^2Qq_{zz}/e^2Qq_{at} = 0.5(N_x + N_y) - N_z = (1 - s^2)(1 - i) - (1.5 - s^2)\pi \qquad (7)$$

with e^2Qq_{zz} being the quadrupole coupling constant of interaction; e^2Qq_{at} being the quadrupole coupling constant of interaction of one 3p electron; N_x, N_y and N_z being electron populations of $3p_x$, $3p_y$, $3p_z$ chlorine atom orbitals respectively; s^2 being the degree of sp hybridization; i being the bond ionicity; π being the bond order. Usually, the increase of the ^{35}Cl NQR frequency on complexation of non-transition metal halogenides was explained by the decrease of

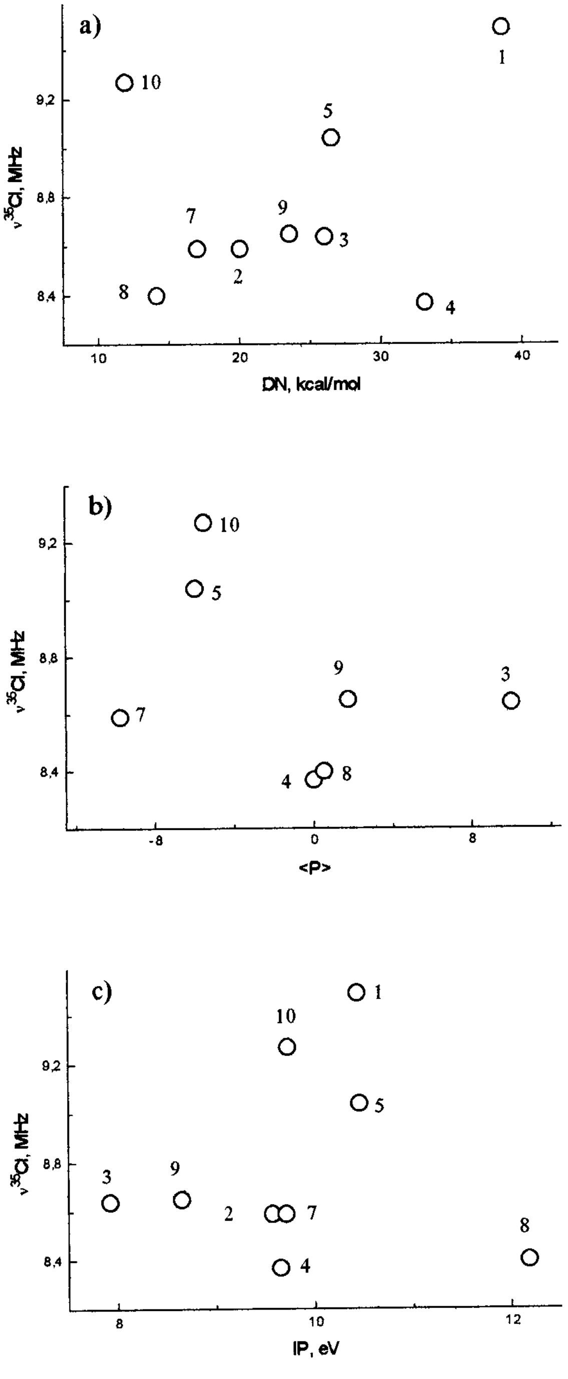

FIGURE 2 ^{35}Cl NQR frequencies in $\mathrm{TiCl_4L_2}$ complexes versus (a) ligand's donor numbers, (b) ligand's influence parameters, (c) ionization potentials of free ligands. Numbering of points corresponds to that in Table 1.

the transfer of n_{Cl} electron density to the vacant metal d orbitals caused by the competition donation of the ligand's electron density on these orbitals, that led to the decrease of the MCl bond order [18].

We showed previously [19], as a result of carried out nonempirical quantum chemical calculations, that there is a decrease of the order of the TiCl bond on $TiCl_4$ complexation. This effect must lead to an increase of ^{35}Cl NQR frequency according to equation (8). Therefore, one can think that the change of the ^{35}Cl NQR frequency in the $TiCl_4L_2$ series is firstly due to differences of the order of the TiCl bond.

The least-squares-method of analysis of ν^{35}Cl NQR dependence on calculated parameters of ligands shows that these frequencies do not depend on the effective charge of the ligand's coordinating atom and are determined by the parameters of the main donor ligand MO:

$$\nu^{35}\mathrm{Cl} = 0.63(3)(-\varepsilon) + 4.0(7)\alpha + 0.0(2)$$
$$(r = 0.997,\ s = 0.3,\ n = 8) \tag{8}$$

The first term (at $-\varepsilon$) of the obtained correlation shows that ^{35}Cl NQR frequencies increase when the donor ligand ability decreases, and the second term shows the opposite effect. This leads to the conclusion that the hypothesis about the dominant influence of competition transfer of the ligand electron density to the Tid orbitals on the increasing of ν^{35}Cl NQR is wrong. It seems likely that the correlation (8) indicates ^{35}Cl NQR frequencies to be determined firstly by the change of TiCl bond order associated with the ligand polarization effect but not with Ap → Tid electron transfer. As this takes place, the polarization ligand effect on the electric-field gradient at chlorine nuclei is softer than that on the chlorine-effective charge because it is determined firstly by the distribution of the ligand boundary electron density, and does not depend on q_A.

Equations 5–8 allow us to make the conclusion that, in $TiCl_4L_2$ complexes, the gradient of the electric field on the chlorine nuclei is determined firstly by the TiCl bond order (which decreases with the growth of the polarization effect of the ligand boundary electron density), but not by total-electron density on the chlorine atoms as it is in complexes of non-transition metal chlorides.

REFERENCES

[1] Mazalov, L. N.; Yumatov, V. D.; Murakhtanov, V. V.; Gelmukhanov, F. Kh.; Dolenko, G. N.; Gluskin, E. S.; Kondratenko, A. V. Rentgenovskie Spektry Molekul; Nauka: Novosibirsk, 1977.

[2] Dolenko, G. N. J Mol Struct 1993, 291, 23.

[3] Dolenko, G. N.; Latajka, Z.; Ratajczak, H. Heteroat Chem 1995, 6, 553.

[4] Dolenko, G. N.; Poleshchuk, O. Kh.; Koput, J. Heteroat Chem 1998, 9, 543.

[5] Poleshchuk, O. Kh.; Nogaj, B.; Dolenko, G. N.; Elin, V. P. J Mol Chem 1993, 297, 295.

[6] Dolenko, G. N.; Poleshchuk, O. Kh.; Elin, V. P.; Litvin, A. L.; Udachin, I. V.; Ivanovsky, A. V. Bull Akac Sci USSR Div Chem Sci 1989, 38, 2314 (English translation).

[7] Gutmann, V. Coord Chem Rev 1975, 15, 207.

[8] Vyazankin, N. S.; Razuvaev, G. A.; Krugkaya, O. A.; Semchikova, G. S. J Organometal Chem 1966, 6, 474.

[9] Poleshchuk, O. Kh.; Nogaj, B.; Latosinska, J. N.; Glaser, A.; Ostafin, M. J Mol Struct 1997, 415, 153.

[10] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheseman, J. R.; Keith, T.; Peterson, G. A.; Montgomery, J. A.; Raghavachan, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayata, P. Y.; Chen, W.; Wong, M. W.; Andres, J. I.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. GAUSSIAN 94, Revision B.1, Gaussian Inc., Pittsburg, 1995.

[11] Vilkov, L. V.; Mastryukov, V. S.; Sadova, N. I. Opredelenie Geometricheskogo Stroeniya Svobodnykh Molekul, Khimiya, Leningrad, 1978.

[12] Nefedov, V. I.; Gofman, M. M. Koordinacionnaya Khimiya 1978, 4, 820.

[13] Zverev, V. V.; Kitaev, Yu. P. Uspekhi Khimii 1977, 46, 1515.

[14] Vovna, V. I. Elektronnaya Struktura Organicheskikh Soedinenii po Dannym Photoelektronnoi Spektroskopii; Nauka: Moscow, 1991.

[15] Vovna, V. I.; Vilesov, F. I. Uspekhi Photoniki, 1975, 3.

[16] Rabalais, J. W.; Colton, R. J. J Electron Spectrosc Relat Phenomen 1972, 1, 83.

[17] Townes, C. H.; Dailey, B. P. J Chem Phys 1949, 17, 782.

[18] Buslaev, Yu. A.; Kravchenko, E. A.; Kolditz, L. Coord Chem Rev 1987, 82, 1.

[19] Poleshchuk, O. Kh.; Latosinska, J. Koordinacionnaya Khimiya 1996, 22, 33.