Electron Effects of Adduct Formation by some Metal Halides*

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The results of NQR studies on electron density redistribution due to formation of adducts of various types of metal halides are reviewed and their consistency with X-ray data is discussed.

The problem of the influence of ligands in coordination chemistry is of traditional interest to our group. We performed a series of NQR studies with the aim of examining the redistribution of electron densities upon complexation of various types of metal halides.

The importance of the trans influence in the coordination chemistry of transition elements is widely known and we present here the results of NQR studies on reorganization of metal-halogen bonds due to the substitutional insertion of a ligand D capable of multiple bonding in osmium (ruthenium) hexahalide complexes.

Experimental data on ligand influences in the chemistry of main group elements are less extensive and we have performed a systematic NQR study on tin(IV) complexes of the type $[SnHal_6]^{2-}$ or $SnHal_4D_2$ where one or two acidoligands are substituted for σ-donor groups which considerably exceeded the halogen ligand in donating power. We start however with a short comment on NQR results concerning nonsubstituted group IV B element tetrahalide complexes limiting ourselves to chlori-compounds.

1. Group IVB Element Tetrachloride Complexes of Type $SnCl_4D_2$ and ACl_4D
(A = Si, Ge, Sn; D = donor ligand)

The asymmetry parameters (η) of the ^{35}Cl EFG have been measured in the chloro-compounds titled since i) the contribution of crystal field effects to their NQR spectra is relatively more important than in the related more covalent bromo- and iodo-complexes; ii) hexacoordinate $SnCl_4D_2$ adducts are known to exist as cis-trans isomers and neither frequency splittings (or line multiplicity) nor temperature dependence of frequencies are recognized [1, 2] as reliable criteria of isomerism; iii) the comparison of η in hexa- and pentacoordinate adducts was hoped to give more detailed information on Sn–Cl bonding.

The experimental determination [3] of the ^{35}Cl EFG asymmetry parameters based on the analysis [4] of slow beats of the spin-echo envelope in an external magnetic field has been performed in powder samples. As the results on hexacoordinate adducts showed (Table 1), the η values on axial Cl atoms (Cl–Sn–Cl fragment) appeared to be zero unless lattice contributions raised its value by several percent. On equatorial Cl atoms (Cl–Sn–D fragment) of both isomers the η values were usually noticeably higher, varying around 10% in the majority of the compounds. The attempt has further been made to reveal regularities of electron density redistribution between axial-equatorial bonds.

According to the X-ray data available on cis-$SnCl_4D_2$ compounds (Table 2) the axial Sn–Cl bond distances are shorter than equatorial in (1)–(7), while in (8)–(12) the relation is reversed. A partial reason might be secondary interactions involving axial Cl atoms in (8) and (10)–(12).

The regularities evidenced by NQR data are seen from the diagram of Fig. 1 which contains, along with the adducts where η is measured, those with unknown values of η but closely similar to the compounds of established cis configuration in type of ligands and spectral patterns. The total set of data shows that ^{35}Cl frequencies assigned to the two types of Cl sites, axial and equatorial, do not overlap, those of axial sites being relatively higher: $18.2\ \mathrm{MHz} < \nu_{eq} < 19.8\ \mathrm{MHz} < \nu_{ax} < 22.0\ \mathrm{MHz}$. Only the complexes with D =

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Table 1. ^{35}Cl NQR spectra of tin(IV), germanium(IV) and silicon(IV) chloro compounds[a] (relative intensities of lines in parentheses).

D	ν [MHz]	Cl atoms[b]	η [%]
cis-$SnCl_4D_2$ [5, 6]			
$POCl_3$	21.132(2)	a	2.3 ± 0.5
	19.794	e	11.1 ± 2.0
	19.030	e	11.7 ± 2.4
$P_2O_3Cl_4$[c]	22.047	a	4.8 ± 1.6
	21.870	a	5.6 ± 1.6
	19.770	e	12.8 ± 3.0
	18.490	e	19.6 ± 2.1
MeCN	20.670	a	5.6 ± 1.5
	19.870	a	3.4 ± 1.5
	19.594	e	7.3 ± 2.2
	19.203	e	7.8 ± 2.2
Me_2CO	20.116(2)	a	0.8 ± 0.5
	18.786	e	4.7 ± 1.2
	18.770	e	4.7 ± 1.2
MeOH	20.316	a	2.1 ± 0.4
	19.871	a	3.1 ± 0.5
	17.866	e	13.1 ± 1.5
	17.499	e	12.0 ± 2.1
EtOH	20.568	a	3.8 ± 1.5
	20.120	a	3.9 ± 1.5
	17.750	e	19.4 ± 3.5
	17.498	e	23.2 ± 3.2
$(CH_2)_4(CN)_2$[c]	20.303	a	1.8 ± 0.5
	19.058	e	7.1 ± 1.8
CMA	21.820	a	1.7 ± 0.1
	18.530	a	1.7 ± 0.1
	19.510(2)	e	9.0 ± 1.6
BMA	21.910	a	1.1 ± 0.5
	18.570	a	1.7 ± 0.5
	19.590(2)	e	9.0 ± 1.6
trans-$SnCl_4D_2$ [5, 6]			
diox[c]	19.407	e	6.1 ± 1.5
DMF	17.766	e	5.7 ± 1.0
TMU	18.365	e	8.4 ± 0.5
	18.161	e	6.7 ± 1.9
THF	19.393	e	15.8 ± 3.0
	19.248	e	13.4 ± 1.1
	18.913	e	12.2 ± 1.1
	18.540	e	12.8 ± 1.2
DEE	19.438	e	13.6 ± 3.1
	19.472	e	13.6 ± 3.1
HMPT	18.045	e	10.4 ± 1.4
	17.774	e	10.8 ± 2.1
py	17.760	e	15.4 ± 2.6
	17.644	e	15.4 ± 2.6
DBS	18.480	e	15.2 ± 4.1
	18.180	e	15.5 ± 3.4
$SnCl_4D$ [7, 8]			
$MeNO_2$	24.390	e	10.6 ± 0.7
	24.260	e	14.0 ± 1.2
	24.010	e	8.4 ± 0.4
	20.100	a	4.5 ± 0.6
$4\text{-}MeC_6H_4COCl$	23.345	e	14.2 ± 1.0
	23.893(2)	e	9.6 ± 1.0
	19.908	a	1.5 ± 0.5
PhCOCl	24.222	e	5.5 ± 2.0
	24.382(2)	e	4.6 ± 1.5
	21.104	a	0.9 ± 0.5
$SnCl_4D$ [8]			
PhOMe	23.851	e	12.0 ± 1.0
	23.656	e	9.2 ± 1.0
	23.391	e	13.2 ± 1.0
	20.182	a	0.9 ± 0.5
$2,5\text{-}Me_2C_2H_3OMe$	23.904	e	13.0 ± 3.0
	23.557	e	12.5 ± 3.0
	23.186	e	10.5 ± 3.0
	20.109	a	0.0
$GeCl_4D$ [7]			
TMA	24.830(2)	e	25.3 ± 3.9
	24.660	e	24.2 ± 3.3
	20.590	a	2.0 ± 0.9
TMU	25.090	e	26.4 ± 5.0
	24.860	e	25.3 ± 4.2
	24.340	e	27.0 ± 3.8
	20.670	a	5.6 ± 1.0
HMPT	24.920	e	31.8 ± 5.0
	24.660	e	28.0 ± 4.3
	24.570	e	28.0 ± 4.3
	20.530	a	3.4 ± 0.5
$SiCl_4D$ [7]			
TMA	21.500	e	42.1 ± 7.2
	21.300(2)	e	36.6 ± 4.0
	18.860	a	1.7 ± 0.5
TMU	21.650	e	43.1 ± 4.1
	21.110	e	38.8 ± 2.6
	18.450	a	7.5 ± 2.0
	17.340	a	1.7 ± 0.5

[a] HMPT = hexamethylphosphortriamide, THF = tetrahydrofuran, TMU = tetramethyl urea, DBS = dibenzyl sulphide, DMF = dimethylformamide, py = pyridine, TMA = trimethylamine, DEE = diethyl ether, diox = dioxane, CMA = chloromethyl acetate, BMA = bromomethyl acetate.

[b] a = axial Cl atoms, e = equatorial Cl atoms.

[c] bidentate ligands.

Ph_3PO and Me_2SO made the exceptions to this rule due to high donor properties of the ligands. The area covered by ^{35}Cl signals of trans isomers is slightly shifted downwards: 17.5 MHz $< \nu_{eq} <$ 19.4 MHz.

It is to be noted that effective charges on Cl atoms estimated from NQR spectra appeared to be approximately the same on both, axial and equatorial Cl sites and in both kinds of isomers (Fig. 1e–g).

Several empirical indications of the type of isomerism are as follows: 1) the cis isomer may be identified by the presence in the spectrum of ^{35}Cl signals at frequencies above 19.8 MHz, the appropriate lines being assigned to Cl–Sn–Cl fragments; 2) more than 80% of trans isomers studied gave NQR spectra with ^{35}Cl average frequencies below 18.3 MHz while 80% of cis isomers had them above 19.3 MHz.

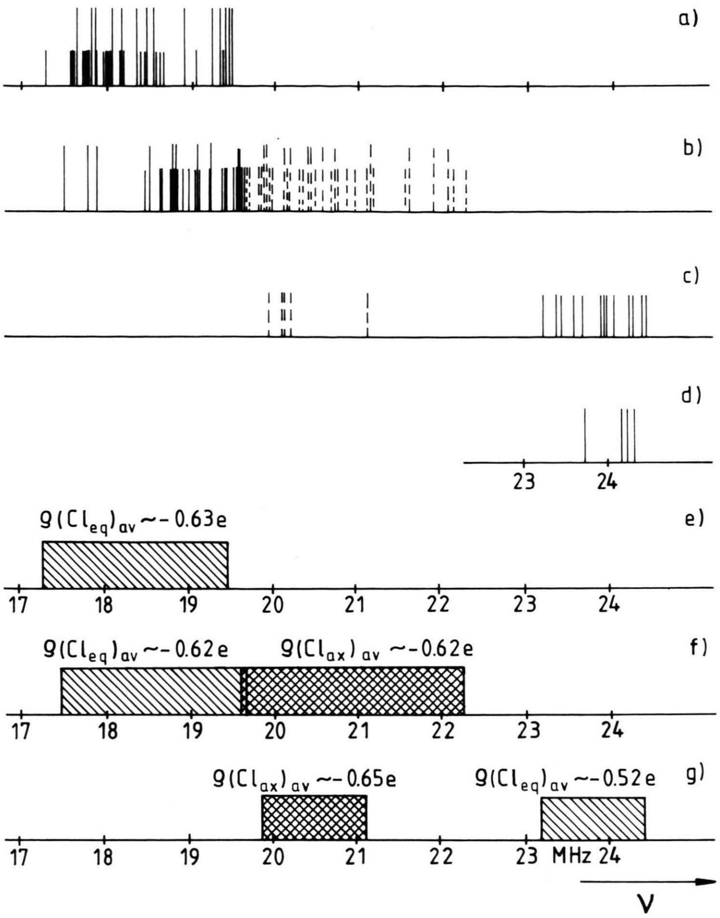

Fig. 1. The diagrams of ^{35}Cl NQR spectra of hexa- and pentacoordinate complexes of tin tetrachloride. Long bars – the ^{35}Cl frequencies with measured magnitudes of η [5, and refs. therein]; short bars – the ^{35}Cl frequencies with η values unknown. The dotted bars – axial Cl positions; the solid bars – equatorial Cl positions. The ^{35}Cl frequencies of (a) trans-$SnCl_4D_2$: the short bars correspond to the compounds with D=$(n\text{-}C_6H_{13})_2POH$, $(MeO)_2POH$, EtMeOPOH, Ph(iso-PrO)POH, $Et_2PO(SEt)$, Et_2POMe, $Et_2PS(SEt)$, Et_2POCl, Me_2PSCl, $(Me_2N)_2POPh$, $(Me_2N)_2POMe$, $(Me_2N)_2POEt$, $(Me_2N)_2PSPh$, $(Me_2N)_2PSEt$, $(Me_2N)POPh_2$, $(Me_2N)_2POOMe$, $Me_2NPSClEt$, Me_2NPSMe_2 [21], $MeCOOCHMe_2$ [23]. (b) cis-$SnCl_4D_2$: the short bars correspond to the compounds with D=CH_2CHCN, BuCN, $CH_2(CN)_2$, $C_6H_4(CN)_2$ [25], MeCOOEt, MeCOOPr [24], $(n\text{-}BuO)_2PO(SMe)$, $ClCH_2POCl_2$, $MeOPOCl_2$, $PhPOCl_2$ [21], $CHCH_2COOCHMe_2$, $Cl_2CHCOOMe$, $MeCOOC_2H_4Cl$, $ClCH_2\text{-}COOEt$ [23]; (c) $SnCl_4D$; (d) $SnCl_4$. The ^{35}Cl frequency ranges and average values of effective charges on equatorial ($\varrho(Cl_{eq})_{av}$) and axial ($\varrho(Cl_{ax})_{av}$) chlorine sites for (e) trans-$SnCl_4D_2$; (f) cis-$SnCl_4D_2$; (g) $SnCl_4D$.

Table 2. Average values of axial (d_{ax}) and equatorial (d_{eq}) Sn–Cl bonding distances (pm) in cis isomers of $SnCl_4D_2$ complexes.

	D	d_{ax}	d_{eq}	Ref.
1	$(CH_2)_3(CN)_2$ [a]	235.1	236.1	[9]
2	CH_3CN	234.7	234.8	[10]
3	S_8O	233.6	238.2	[11]
4	$(CH_3)_2SO$	238.2	239.1	[12]
5	$(C_6H_5)_3PO$	238.2	239.3	[13]
6	$(C_2H_5NH)_2CS$	251.5	253.0	[14]
7	$POCl_3$	233.0	233.0	[15]
8	$(C_6H_5CO)_2NH$ [a] I	237.2	234.2	[16]
	II	237.2	234.9	
9	$[(CH_3)_2SiN]_2S$ [a]	238.5	234.1	[17]
10	Hpipox [a, b]	242.6	237.1	[18]
11	$SeOCl_2$	240.1	236.1	[19]
12	H_2O [c]	239.6	238.3	[20]

[a] Bidentate ligands.
[b] Hpipox = pyridoxal picolinoylhydrazone, the composition of the complex is $[SnCl_4 \cdot Hpipox] \cdot 2H_2O$.
[c] The composition of the complex is $[SnCl_4(H_2O)_2] \cdot 3H_2O$.

The related bromo- and iodo-compounds might show different spectral regularities due to different relationships between the electron-donating or withdrawing properties of the ligands D and Br or J as well as a different importance of crystal field effects as compared to the chlorides.

The results obtained yield more detailed information on the Sn–Cl bonding when compared to those on pentacoordinate adducts of trigonal bipyramidal configuration.

As one can see from Table 1 and Fig. 1, the axial Sn–Cl bonds differ insignificantly in $SnCl_4D_2$ and $SnCl_4D$ complexes. The η values on equatorial chlorines also vary in both of them within similar limits. The main difference between the adducts consists in relatively higher Cl 3Pσ orbital occupancy at equatorial Cl sites of hexacoordinate complexes. The contribution to nonzero η's on equatorial Cl sites of both types of adducts becomes evident from the trends displayed by the NQR spectra of ACl_4D complexes ($A = Sn, Ge, Si$). Considerable increase in η was found on those sites in the order $Sn > Ge < Si$, accompanied by a fall in ^{35}Cl frequencies in silicon adducts, inconsistent with electronegativity magnitudes in most scales (Table 1). This was understood [7] as an evidence for the increasing acceptance of Cl 3 Pπ electron density by the central element vacant orbitals, estimated as $\pi \cong 0.1$, $i \cong 0.47$ in silicon, $\pi \cong 0.08$, $i \cong 0.43$ in germanium and $\pi \cong 0.03$, $i \cong 0.52$ in tin tetrachlorocomplexes. The results unfortunately do not clarify the mechanism of π-interactions in those adducts.

2. Alkyl tin(IV) Halide Complexes of Type $LSnX_5$, $LSnX_3D_2$ and $L_2SnX_2D_2$ ($X = Cl, Br, I$; L = alkyl group; D = donor ligand)

The systems of type $Alk_xSnHal_{4-x}D_2$, in which the substituent group (Alk) considerably exceeds the halogen ligands in σ-donating power, have been predicted [26–29] to display a weakening of the Sn–Hal bonds at the cis position to the σ-substituent (cis weakening) accompanied by a relatively smaller trans influence, which might be strengthening. The experimental NQR data on the direction of the trans-influence as well as the comparison of the relative importance of the trans and cis effects could contribute to understanding this phenomenon. X-ray studies on nearly all the compounds of interest have been performed, which enable us to compare interatomic distances and NQR parameters as a measure of ligand influence.

Table 3 lists some selected NQR and X-ray data. The main sources of inaccuracy in the derivation of the spectral and structural parameters as well as the reliability of their interpretation have been discussed [30, 31]: both methods yield complementary pieces of valuable information provided the necessary caution is taken. Having estimated from NQR spectra the magnitude of the σ-electron density $NPz = 2 - Up = |\delta| + 1$ at halogen sites, we then looked how it changed ($+\Delta\delta$) at positions cis and trans to the alkyl substituents. Similarly, the relative lengthening (shortening) of the Sn–Hal bonds ($+\Delta d$) was estimated from the X-ray data. As seen from Table 3, the influence of the alkyl group is reflected in large NQR frequency shifts with respect to the parent compounds. Thus, introduction of an alkyl group into a regular octahedron $[SnHal_6]^{2-}$ with a singlet NQR spectrum

Table 3. Ligand influence as found[a] by ^{35}Cl, ^{81}Br, ^{127}I NQR ($\pm\Delta\delta$) and X-ray analysis ($\pm\Delta d_{Sn-Hal}$); cis weakening, $+\Delta\delta$ ($+\Delta d$); trans strengthening, $-\Delta\delta$ ($-\Delta d$).

Compound	Assignment	ν [MHz] aver.	$\pm\Delta\delta$ (%)	d [pm] aver.	$\pm\Delta d$ [pm] (%)
$(NMe_4)_2SnCl_6$	Cl–Sn–Cl	16.68		242.2	
$(NMe_4)_2EtSnCl_5$[b]	Cl–Sn–Cl	12.30	+0.079 (11.3)	251.6	+9.2 (3.8)
	Cl–Sn–C	18.04	−0.025 (3.6)	241.0	−1.4 (0.6)
D = HMPT					
tr-$SnCl_4D_2$	Cl–Sn–Cl	17.90		238.8	
tr-$EtSnCl_3D_2$	Cl–Sn–Cl	–		249.1	+10.3 (4.3)
	Cl–Sn–C	20.02	−0.038 (5.6)	237.9	−0.9 (0.4)
tr-$Me_2SnCl_2D_2$	Cl–Sn–Cl	9.45	+0.155 (23.0)	257.0	+18.2 (7.6)
D = TMU					
tr-$SnCl_4D_2$	Cl–Sn–Cl	18.24		239.1	
tr-$EtSnCl_3D_2$	Cl–Sn–Cl	13.47	+0.087 (13.0)	249.1	+10.1 (4.2)
	Cl–Sn–Cl	19.35	−0.02 (2.9)	237.4	−1.7 (0.7)
D = DMSO					
cis-$SnCl_4D_2$	Cl–Sn–Cl(O)			238.6	
cis-$EtSnCl_3D_2$	Cl–Sn–O	13.52	+0.076 (11.2)	245.6	+6.95 (2.9)
	Cl–Sn–C	16.96	+0.013 (1.9)	239.8	+1.15 (0.5)
cis-$Me_2SnCl_2D_2$	Cl–Sn–O	10.40	+0.133 (19.7)	251.1	+12.35 (5.2)
$(NMe_4)_2SnBr_6$	Br–Sn–Br	115.07		260.5	
$(NMe_4)_2BuSnBr_5$	Br–Sn–Br	80.55	+0.107 (16.7)	269.9	+9.4 (3.6)
	Br–Sn–Br	130.79	−0.05 (7.6)	256.6	−3.9 (1.5)
D = HMPT					
tr-$SnBr_4D_2$	Br–Sn–Br	127.75		255.0	
cis-$BuSnBr_3D_2$	Br–Sn–O	93.80	+0.105 (17.4)	263.3	+8.3 (3.3)
	Br–Sn–C	132.60	−0.015 (2.5)	252.9	−2.1 (0.8)
tr-$Me_2SnBr_2D_2$	Br–Sn–Br	60.60	+0.208 (34.5)	274.0	+19.0 (7.4)
D = py					
tr-$SnBr_4D_2$	Br–Sn–Br	122.66			
tr-$Me_2SnBr_2D_2$	Br–Sn–Br	65.76	+0.177 (28.7)	272.0	
		QCC[c] ($\eta = 0$) QCC ($\eta = 10\%$)			
cis-SnI_4Bipy	I–Sn–I(N)	1076.5 1065.0		280.2	
D = HMPT					
cis-$EtSnI_3D_2$	I–Sn–I(O)	753.0	+0.144–0.149 (26.90–27.9)	289.3	+0.091 (3.2)
	I–Sn–C	1109.3	−0.014–0.019 (2.6–3.5)	263.4	−0.168 (6.0)
tr-$Et_2SnI_2D_2$	I–Sn–I	467.9	+0.261–0.266 (48.8–50.2)	301.6	+0.214 (7.6)

[a] [30] and refs. therein.
[b] [31]. – [c] QCC-quadrupole coupling constant (MHz).

results in a spectroscopic splitting of the order of 6 MHz between equatorial (Cl–Sn–Cl) and axial (Cl–Sn–C) chlorine sites and in a splitting of about 51 MHz in bromine sites.

The prevailing effect of alkyl substituent is, according to both NQR and X-ray results, a weakening (lengthening) of the Sn–Hal bonds at position cis to the alkyl group, i.e. cis weakening. According to NQR, its magnitude amounts to 10–13% in monoalkyl-substituted chlorides, 14–18% in the analogous bromides and about 28% in $EtSnI_3(HMPT)_2$ (Table 3). The second alkyl substituent increases the cis weakening nearly additively, making the effect in $Alk_2SnHal_2(HMPT)_2$ complexes about 23%, 34% and 49% in the chloride, bromide and iodide, respectively. This means that the cis weakening influence of alkyl group increases the σ-electron density at the appropriate Hal site in the order $Cl < Br < I$. The X-ray data, however, give a relative cis-lengthening nearly independent of the acido-ligands. In $AlkSnHal_3(HMPT)_2$ it appeared to be 4.3% and 3.3% for Hal = Cl and Br, respectively. For Hal = I the lengthening was about 3.8% when compared to SnI_4.bipy (the structure of $SnI_4(HMPT)_2$ is not yet known). In $Alk_2SnHal_2(HMPT)_2$ the situation is similar, Δd being 7.6% and 7.4% for chloride and bromide, respectively, and 7.6% for the iodide (also compared to SnI_4.bipy). The discrepancy between the results of the two methods originates in the fact that a small absolute elongation of the Sn–Hal bonds occurs in those systems in the order $Cl < Br < I$ against a background of increasing Sn–Hal bond distances in the parent compounds. In NQR the situation is reversed, so that the considerable absolute increase in σ-electron density on the halogen atoms in the order $Cl < Br < I$ is accompanied by its decrease on the halogen atoms in the corresponding unsubstituted compounds due to increasing covalency. Hence there is evidence of a relatively higher sensitivity of NQR to the effects of ligand influence.

The trans influence is reflected in X-ray as a rather weak (within 2 pm) change in the appropriate Sn–Hal bond distance (Table 3). Shortening by approximately 5 pm has only been found for $[BuSnBr_5]^{2-}$ anion. It is, however, reliably detected by NQR, the direction of the effect being always trans strengthening. The high frequency shift at trans halogen (compared to the initial complex) exceeded 2 MHz in $EtSnCl_3(HMPT)_2$ and 15 MHz in $[BuSnBr_5]^{2-}$, which of course exceeded crystal field contributions [31].

Table 3 reveals the combined effect of the alkyl group and the ligands D on the Sn–Hal bonds, which depends on both the donor properties and the mutual arrangement of the ligands. Thus in the complexes $Me_2SnBr_2D_2$ $\Delta\delta = 34\%$ for D = HMPT and $\Delta\delta = 29\%$ for D = py the corresponding ^{81}Br downward shifts are 67.1 MHz and 56.9 MHz, respectively. One can also see that the strong σ-donor ligand DMSO cancels out the trans shortening caused by the ethyl group in cis $EtSnCl_3D_2$.

In general, NQR parameters seem to be more sensitive to the influence of ligands than interatomic distances, which is not unexpected considering that the phenomenon is governed by electronic effects, and the NQR parameters are determined directly by the electron density distribution.

The X-ray data, although relatively less influenced by the effects of complexation, give valuable information on the spatial arrangement of atoms and atomic groups and are helpful for the correct assignment of resonances and hence for reliable conclusions on the effects of complexation.

3. Osmium (Ruthenium) Nitrido- and Nitrosohalogeno-complexes of Type $R_2[LAX_5]$ ($L = Os, Ru$; $L = N\equiv$, $NO\equiv$; $X = Cl, Br, I$; $R = K^+, Rb^+, (NH_4)^+$)

The substituent (L) substituted into a transition element hexahalide octahedron $[AX_6]^{2-}$ is known to alter the metal-halogen bonds in such a way that the prevailing effect is a trans influence. Its type depends considerably on the bonding properties of the ligand L. Both weakening and strengthening are possible according to the X-ray data and we have attempted to observe the spectral evidence of both effects. The nitrido- ($N\equiv$), and nitroso- ($NO\equiv$) ligands, both capable of triple bonding, were substituted into hexahaloosmate (ruthenate) anions to give pseudooctahedral $[OsNX_5]^{2-}$ (1) and $[MNOX_5]^{2-}$ (2) having $M\equiv L$ bonds of very different electronic structure. All three components of the $Os\equiv N$ bond are covalent and hence strongly trans weakening while the quasi-triple $M\equiv NO$ bond is known to have only one covalent π-component, the other being of dative and the σ-component of donor-acceptor character. The trans influence of such a bond is expected to be weak, which is confirmed by the X-ray data available. Strong trans lengthening (about 20 pm) was found in (1) for X = Cl [32] and a weak trans influence was observed in (2), varying between shortening (~1.3 pm for M = Ru;

Table 4. ^{35}Cl, ^{81}Br, ^{127}I NQR (MHz) average spectra of anion species at 300 K [36]; the X-ray (pm) [32, 33, 36, 37] and the ESCA (ev) data [38, 39]; ϱ, (e) = effective charges on atoms and atomic groups according to NQR; a = axial, e = equatorial halogen atom.

Anion	Hal. atom	ν [a], MHz	ϱ (Hal)	π (M-Hal)	(M≡N) ϱ (M) (NO≡)	*d* (M-Hal)	∢(L-M-Hal$_e$) [a]	*d* (Os≡N)	Os 4f$_{7/2}$ Ru 3p$_{3/2}$
$[OsNCl_4]^-$	e	22.26	−0.59	0	+1.380	231.0	104.6	160.4	54.8
$[OsNCl_5]^{2-}$	e	20.40	−0.62	0	+1.390	236.2	96.2	161.4	55.1
	a	7.00 [b]	−0.87	0		260.5			
$[OsCl_6]^{2-}$		16.84	−0.57	0.08	+1.438	240.0			54.0
$[OsNOCl_5]^{2-}$	e	18.15	−0.64 ÷ −0.60	0.02 ÷ 0.05		238.0	92.7		53.7
	a	14.10	−0.64 ÷ −0.60	0.07 ÷ 0.10		238.6			
$[OsNBr_4]^-$	e	149.50	−0.53	0	+1.136	245.7	104.3	158.3	54.3
$[OsNBr_5]^{2-}$	e	140.50	−0.56	0	+1.116				54.6
	a	44.95	−0.86	0					
$[OsBr_6]^{2-}$		111.80	−0.53	0.08	+1.180				53.1
$[OsNOBr_5]^{2-}$	e	122.10	−0.59 ÷ −0.54	0.02 ÷ 0.05	−0.23 ÷ −0.48	251.9	92.0		53.2
	a	91.08	−0.59 ÷ −0.54	0.08 ÷ 0.11		252.1			
$[OsNI_4]^-$ [c]	e	1366.50	−0.41	0	+0.640	266.2	103.7	162.6	53.6
$[OsI_6]^{2-}$ [c]		942.33	−0.47	0.08	+0.814				52.1
$[OsNOI_5]^{2-}$	e	1033.50	−0.52 ÷ −0.47	0.02 ÷ 0.05		271.9	91.5		53.0
	a	782.20	−0.62 ÷ −0.57	0.03 ÷ 0.06		274.0			
$[RuCl_6]^{2-}$		17.34	−0.56	0.08	+1.384				464.6
$[RuNOCl_5]^{2-}$	e	18.20	−0.64 ÷ −0.59	0.02 ÷ 0.05	−0.20 ÷ −0.45	237.2	8.3 pm [d]		464.8
	a	14.00	−0.63 ÷ −0.57	0.08 ÷ 0.11		235.9			
$[RuNOBr_5]^{2-}$	e	120.80	−0.59 ÷ −0.55	0.02 ÷ 0.05		251.7	6.3 pm [d]		
	a	91.90	−0.59 ÷ −0.55	0.08 ÷ 0.11		251.1			
$[RuNOI_5]^{2-}$ [c]	e	1020.80	−0.52 ÷ −0.48	0.02 ÷ 0.05		271.7	4.7 pm [d]		
	a	789.4	−0.53 ÷ −0.49	0.08 ÷ 0.11		272.2			

[a] For the iodides the values of QCC, MHz are given. – [b] Estimated by recalculation from ^{81}Br frequencies in $Rb_2[OsNBr_5]$. [c] at 77 K. – [d] The elevation of the Ru atom above equatorial plane.

X = Cl [32]) and lengthening (~2.1 pm for M = Os; X = I [33]).

Using NQR we have studied a number of osmium (ruthenium) nitroso- and osmium nitridohalo-compounds [34–36]. Table 4 lists the NQR data together with the estimated bonding characteristics, the X-ray data whenever available, and the ESCA data. The results of alternative methods appeared useful for obtaining reasonable and self-consistent sets of interpretations of the NQR results. The value of the latter lies of course not in the absolute magnitudes but in their relative trends within the series of related compounds.

The X-ray data [34 and refs. therein] show that the halonitridoosmates have the central atom noticeably elevated above the equatorial plane, which justifies the σ-approximation generally accepted to describe the Os–X bonds. This is supported by a good linear correlation of ^{35}Cl frequencies vs. Os–Cl bonding distances [34]. Estimation of the effective charges on atoms and atomic groups was made, using the well-known relation $Up = e^2Q\,q_{zz}/e^2Q\,q_o = (NPz + NPy)/2 - NPz = 1 - i - 3/2\pi$ (Table 4), and enabled us to conclude that: 1) The introduction of the nitrido-ligand into $[OsX_6]^{2-}$] weakens all the Os–X bonds, with the trans weakening being extraordinarily large. This is reflected in the increase of about 0.3 e^- in the effective charge on the trans Br atom (the corresponding ^{81}Br downward frequency shift exceeds 95 MHz). 2) The effective charge on the Os≡N group remains nearly constant within the various nitridoanions of each halogen. Thus (1) and $[OsNX_4]^-$, although considerably differing from each other in their crystal chemistry, show very similar charges on those groups. 3) As one can see from Table 4, the positive charge on the Os≡N group is slightly smaller than that on the Os atom in the initial $[OsX_6]^{2-}$. At the same time the ESCA results [38] show the Os $4f_{7/2}$ binding energy to be higher in nitridohalo-anions than in the $[OsX_6]^{2-}$ anions. This may be evidence for negative charge being borne by the nitrido-ligand in these compounds.

Crystallographically, the difference between nitrido- and nitroso-pentahalo-anions consists in a reduction (from 96° to 92°) of the angles ∠ L≡Os–X (equatorial) accompanied by a slight elongation of the distances Os–X (equatorial) (Table 4). In agreement with those changes the results of quantum chemical calculations [40] on $[RuNOX_5]^{2-}$ give evidence for nonzero π-character of the Ru–X bonds, while the NQR shows the reduced (with respect to nitrido pentahalides) frequences assigned to equatorial halogens. Strong π-acceptor and weak σ-donor properties of the NO-group along with $\sigma+\pi$ donor properties of the trans halogens are expected [41] to shorten the Ru–Cl axial bonds, the contribution of the σ-system to trans-strengthening being considered relatively more important than that of the π-system. The spectral patterns of nitrosopentahalides, however, show reduction of axial NQR frequencies with respect to equatorial. Considering nearly equivalent M–X axial and equatorial distances, this undoubtedly indicates the prevailing contribution of the axial halogen π-system to trans strengthening. Table 4 gives the limits of variation of effective charge values on halogen sites and NO-groups consistent with the X-ray data on M–X axial and equatorial bond distances.

According to the ESCA results [38, 39] the Os $4F_{7/2}$ (Ru $3p_{3/2}$) binding energies have nearly the same values in $[OsNX_5]^{2-}$ and $[MNOX_5]^{2-}$, which could justify the use of the same positive charges on the central atoms in the pairs of compounds. Consistent with the currently accepted view, we then obtain negative values for the charges on nitrose-groups. In spite of a very simplified approach to correlation of the NQR parameters with bonding characteristics, the results obtained appear to be in reasonable agreement with those of other methods.

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