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^{45}Sc NMR Study of Scandium Complexation by Podand Ligands

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The complexes of scandium trichloride with podand ligands (inorganic esters of polyoxaethylene glycols) were prepared and studied by ^{45}Sc NMR. The species formed were subjected to structural investigation and the effect of the ligand type was discussed.

Key words: NMR, ^{45}Sc NMR, scandium complexes, podand ligands

In earlier papers we reported on complexation of such cations as Li^+, Na^+ or Rb^+ by using some acyclic polyether ligands studied by multinuclear magnetic resonance spectroscopy, IR spectroscopy and electrochemical measurements [1–4]. The results of interactions of these ligands with transition metal ions were also published [5]. Some cations can form complexes of different types, because of their interactions with ether or X=O oxygen. The paramagnetic properties of Cu^{2+}, Fe^{3+}, Ni^{2+}, Co^{2+} ions are manifested in NMR spectra as strong signals broadening. Therefore, in solution a study on the mechanism of their formation or their structures is usually impossible.

Typical Sc^{3+} coordination number in complexes with monodentate ligands is 6. In solutions the equilibrium between species of different stoichiometry and structures was observed [6]. The ^{45}Sc nucleus is endowed with the spin 7/2 and a relatively low quadrupole moment. Because of 100% natural abundance the sensitivity of NMR experiments is high. The effects of solvent and other molecules complexation were studied by Kirakosyan [7] and Deakin [8]. The crown ethers complexes were investigated by Meehan [9]. This paper presents studies of complex formation between scandium ion and some podand ligands in nonaqueous solvents. The effect of the ligand structure on the complex geometry and coordination is discussed.

EXPERIMENTAL

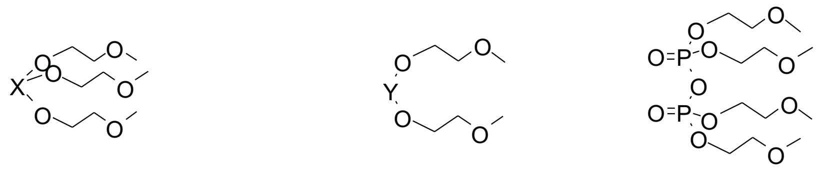
The ligands were prepared according to the procedure described previously [1–5]. All esters were distilled in vacuum before use. Scandium chloride (Aldrich, 99.9%) was used without purification. Scandium perchlorate was prepared from scandium dioxide (spectral pure) and perchloric acid (Aldrich). [^{2}H]$_3$-acetonitrile and [^{2}H]$_3$-nitromethane (Aldrich) was dried over 4A molecular sieves and distilled under argon atmosphere. Deuterium oxide (Aldrich) was also used without purification. Tetraethylammonium chloride (Aldrich) was used after crystallization from ethanol. Sc(trimethylphosphate)$_6$(ClO$_4$)$_3$ complex was prepared according to the procedure described by Pisaniello [10].

The ^{45}Sc NMR measurements were performed on Varian Gemini 300 spectrometer operating at 7.0 T using ^{1}H/^{31}P/BB inverse and standard ^{1}H/BB probeheads. The following parameters were used during acquisition: spectral frequency – 72.900 MHz; pulse width – 55° (8.0 μs); acquisition time – 1.5 s; spectral width – 40 kHz; number of points – 64 k; relaxation delay – 1.0 s; number of transients – 1024–2048. All spectra were recorded in 5 mm tubes by using 1.00 M $Sc(ClO_4)_3$ solutions in deuterium oxide as external standard. The temperature was 297.0±0.1 K. The half width of lines are measured from phosphor-decoupled ^{45}Sc NMR spectra.

The molar ratio of ligands to scandium trichloride was 3.5 and the concentration was 10 mg of $ScCl_3$ per 1 ml of solution. To attain a chemical equilibrium in the systems studied, the samples were kept overnight in room temperature. Preparations of all the samples were made in glove box under argon.

RESULTS AND DISCUSSION

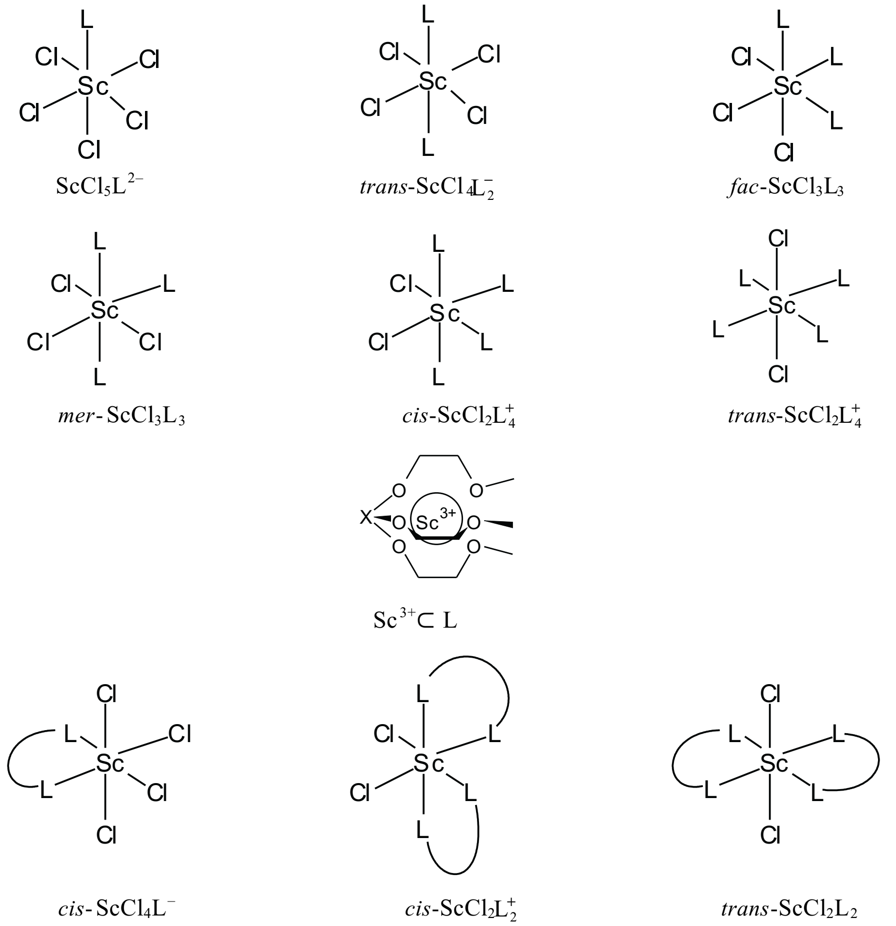
The structures of the ligands studied are presented in Fig. 1. The chemical shifts, intensities and coupling constants of ^{45}Sc NMR signals are collected in Table 1. The structures of complexes, forming in solution, are shown in Fig. 2.



X = B (**B23**); P (**P23**); OP (**OP23**); As (**As23**) Y = OS (**OS22**); OPH (**OPH22**) **OP$_2$24**

Figure 1. Ligands structures.

^{45}Sc NMR spectrum of the OP23/$ScCl_3$ system revealed a series of signals, differing in the line width, chemical shift, multiplicity and intensity. The change of solvent, from acetonitrile to nitromethane, did not cause a change in the spectrum (except shifts smaller than the measurements' accuracy). Therefore, it is clear that the solvent molecules do not bond to scandium(III) ion in the experimental conditions. Because of scandium atom is quadrupolar and hexacoordinate, the line width and, in some cases, line multiplicity arises from the scalar coupling, could be used to assign the signals to specific species existing in solution. The line width of quadrupolar nuclei signal is strongly depended on the symmetry of electric field gradient around the atom, therefore it brings the information on the symmetry of coordination sphere. An increase in the complex symmetry (hence, a decrease in the field anisotropy) results in decrease in $\Delta\nu_{1/2}$ of the signal. The effect of chemical exchange on the line width, in this case, could be neglected, because of strong interactions between O=P group and scandium ion. The chemical shifts of $ScCl_6^{3-}$ ion (measured in $ScCl_3$ + Et_4NCl 1:3 mixture in CD_3CN) and Sc(trimethylphosphate)$_6$(ClO_4)$_3$ in the same solvent, which are 248.0 and –21.0 ppm, respectively, determined the range of shifts for $ScCl_nL_{6-n}^{(3-n)^+}$ (where L is OP ligand), what is helpful in spectrum analysis. The *fac*-$ScCl_3L_3$ complex has the highest (C_{3v}) symmetry among species observed in this system. For high



ScCl$_5$L^{2-} *trans*-ScCl$_4$L$_2^-$ *fac*-ScCl$_3$L$_3$

mer-ScCl$_3$L$_3$ *cis*-ScCl$_2$L$_4^+$ *trans*-ScCl$_2$L$_4^+$

Sc$^{3+}\subset$ L

cis-ScCl$_4$L$^-$ *cis*-ScCl$_2$L$_2^+$ *trans*-ScCl$_2$L$_2$

Figure 2. Structures of complexes of scandium ion with the ligands studied.

symmetry species, the line multiplicity could be observed, so for the complex, where L = OP23 in which the scalar interactions of ^{45}Sc nuclei with three equivalent ^{31}P atoms occur, the quartet is expected, such a signal was observed at 146.3 ppm ($^2J_{45Sc\text{-}31P}$ = 30 Hz). Width line at 95.6 ppm (quintet), which in enhanced resolution is divided into a triplet of triplets with similar coupling constants ($^2J_{45Sc\text{-}31P}$ = 33 and 39 Hz), should be assigned to *cis*-ScCl$_2$L$_4^+$ complex (C_{2v} symmetry) containing two pairs of non-equivalent phosphorus atoms. The *trans*-ScCl$_2$L$_4^+$ complex with D_{4h} symmetry gives the broadest line at 80.9 ppm with residual multiplicity (quintet because of four equivalent OP groups in coordination sphere; $^2J_{45Sc\text{-}31P}$ = 28 Hz). The strongest signal was observed in ^{45}Sc NMR spectrum as a triplet of doublets ($^2J_{45Sc\text{-}31P}$ = 27 and 35 Hz), that is characteristic of *mer*-ScCl$_3$L$_3$ structure, containing two non-equivalent groups of phosphorus atoms. Other signals in the spectrum did not present a multiplicity, so the assignment could be performed only on the basis of chemical shifts and the full width at half maximum. The signal at 167.3 ppm, with relatively small $\Delta\nu_{1/2}$ parameter originates from the complex with two ligand molecules: *trans*-$ScCl_4L_2^-$. Mathematical analysis of this resonance line (zero filling and apodisation with gaussian window function) permits the estimation of a value of ^{45}Sc-^{31}P coupling constant at 30–35 Hz. The signal shifted to the highest frequency (177.0 ppm) with the lowest intensity was assigned to $ScLCl_5^{2-}$ complex.

The spectrum of complexes with OPH22 ligands was very similar to that obtained for the OP23/$ScCl_3$ system. The signal assignments are collected in Table 1. Because of smaller symmetry and the weakest donor properties of the ligand molecule, the signals are broader than for phosphate ester complexes, due to a higher field anisotropy around central ion and the exchange rate of ligands. Only for two species coupling constants could be measured.

For P23 ligand, that is P-donor but is not O-donor, the series of signals arise from complexes with analogical structures to these formed in $ScCl_3$ – OP systems were observed. All signals are shifted to the highest frequency in comparison to the shifts observed for phosphate and phosphonate complexes and the signals in the spectrum are much more broadened. This effect precludes the possibility of coupling constants observation. Therefore, it is difficult to determine a *cis/trans* isomery of the complexes. The signals are assigned on the basis of the half width analysis. An additional, broad signal at 230.0 ppm was noted. In the spectrum of $ScCl_3$ with $P(OMe)_3$ mixture, prepared under the same conditions, the species with such spectral properties are not formed, so it could be explained as a signal corresponding to an inclusion complex of Sc^{3+} ion. The strong broadening of them is the effect of scandium ion exchange, fast molecule reorientation and small symmetry of the coordination sphere.

Because of weak donor character of the O=S group, in comparison to that of the O=P group, the variety of forming scandium complexes with sulphite esters is much more smaller and only some of them appear in solution (see Table 1). For assignments the line width and chemical shifts are used. The borate and arsenate ligands could not interact with scandium ion *via* atom, which connect chains together, therefore for them only inclusion compounds have formed and only the lines at about 230 ppm were observed in the spectrum. It is not clear, whether the free Sc^{3+} ion or some chloride complexes are bounded in the ligand's cavity. The chemical shifts of scandium inclusion complexes, prepared in other solvents, did not differ from these for acetonitrile, so it is clear that the complexated species do not contain a solvent molecule. The using of $ScBr_3$ instead of $ScCl_3$ in the complex preparation, does not solve this problem, because of strong line broadening and overlapping.

Tetraalkyl pyrophosphate in the reaction with scandium ion behaved as bidentate ligands, forming only complexes with 1:1 and 1:2 stoichiometry. The signal arising from $ScCl_4L^-$ was observed at 182.5 ppm, *e.g.* it was shifted downfield in comparison to the position of the signal for the equivalent complex with OP23 (*i.e.* $ScCl_4L_2^-$). This effect is forced by the ligand structure, *cis* – configuration of O=P group connected with the central ion.

Signals in the ^{31}P, ^{13}C or ^1H NMR spectra of the systems studied were broad and overlapped, thus their interpretation was impossible.

Table 1. ^{45}Sc NMR data for complexes of $ScCl_3$ with podand ligands in acetonitrile.

Ligand	^{45}Sc NMR data* [ppm]	Half width [Hz]	Complex structure	Molar fraction
OP23	177.0	70	$ScCl_5L^{2-}$	0.05
	167.3	60	*trans*-$ScCl_4L_2^-$	0.05
	146.3 (q; $^2J_{Sc-P}$=30 Hz)	30	*fac*-$ScCl_3L_3$	0.2
	130.9 (td; $^2J_{Sc-P}$=35 Hz, $^2J_{Sc-P}$=27 Hz)	65	*mer*-$ScCl_3L_3$	0.45
	95.6 (tt; $^2J_{Sc-P}$=33 Hz, $^2J_{Sc-P}$=39 Hz)	35	*cis*-$ScCl_2L_4^+$	0.15
	80.9 (qu, $^2J_{Sc-P}$=28 Hz)	120	*trans*-$ScCl_2L_4^+$	0.10
OPH22	166.8	75	*trans*-$ScCl_4L_2^-$	0.5
	154.5 (q; $^2J_{Sc-P}$=32 Hz)	35	*fac*-$ScCl_3L_3$	0.2
	140.7	80	*mer*-$ScCl_3L_3$	0.2
	103.9 (tt, $^2J_{Sc-P}$=24 Hz)	45	*cis*-$ScCl_2L_4^+$	0.03
	91.8	180	*trans*-$ScCl_2L_4^+$	0.07
P23	230.5	500	$Sc^{3+} \subset L$	0.4
	210.3	120	*trans*-$ScCl_4L_2^-$	0.15
	187.9	70	$ScCl_3L_3$	0.25
	166.4	75	$ScCl_2L_4^+$	0.2
OS22	160.2	40	*fac*-$ScCl_3L_3$	0.8
	119.4	75	*mer*-$ScCl_3L_3$	0.15
	105.3	45	*cis*-$ScCl_2L_4^+$	0.05
As23	232.5	600	$Sc^{3+} \subset L$	1
B23	230.0	540	$Sc^{3+} \subset L$	1
OP_224	182.5	60	*cis*-$ScCl_4L^-$	0.1
	87.5 (tt; $^2J_{Sc-P}$=35 Hz, $^2J_{Sc-P}$=39 Hz)	45	*cis*-$ScCl_2L_2^+$	0.3
	75.2 (qu, $^2J_{Sc-P}$=31 Hz)	130	*trans*-$ScCl_2L_2^+$	0.6

*)q – quartet; td – triplet of doublets; tt – triplet of triplets; qu – quintet.

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REFERENCES

1. Gierczyk B., Schroeder G., Wojciechowski G., Różalski B., Brzezinski B. and Zundel G., *Phys. Chem. Chem. Phys.*, **20**, 4897 (1999).
2. Schroeder G., Gierczyk B., Łęska B., Wojciechowski G., Pankiewicz R., Brzezinski B. and Bartl F., *J. Mol. Struc.*, **607**, 9 (2002).
3. Bełtowska-Brzezinska M., Łuczak T., Gierczyk B., Eitner K., Brzezinski B., Pankiewicz R. and Schroeder G., *J. Mol. Struct.*, **607**, 77 (2002).
4. Pankiewicz R., Schroeder G., Gierczyk B., Brzezinski B. and Bartl F., *Biopolymers (Biospectroscopy)*, **65**, 95 (2002).
5. Schroeder G., Gierczyk B. and Łęska B., *J. Incl. Phenom.*, **35**, 327 (1999).
6. Crawford N.P. and Melsol G.A., *J. Chem. Soc. A*, 141 (1970).
7. Kirakosyan G.A., Tarasov V.P. and Buslaev Y.A., *Magn. Reson. Chem.*, **27**, 103 (1989).
8. Deakin L., William L., Popham M.C., Reid G. and Webster M., *J. Chem. Soc., Dalton Trans.*, **14**, 2439 (2000).
9. Meehen P.R. and Willey G.R., *Inorg. Chim. Acta*, **284**, 71 (1999).
10. Pisaniello D.L., Linkoln S.F. and Williams E.H., *J. Chem. Soc., Dalton Trans.*, 1473 (1979).