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CYCLOPENTADIENYL COMPLEXES WITH HAFNIUM AND ZIRCONIUM CONTAINING NITRATE LIGANDS

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Only three examples of cyclopentadienyl complexes with Hf, containing NO_3 nitrate groups, are known: $CpHf(C_5H_7O_2)_2(NO_3)$ [1], $Cp_2HfCl(NO_3)$, and $Cp_2Hf(NO_3)_2$ [2]. The cyclopentadienyl nitrate derivatives of Zr have also been little studied [3]. The chemistry of Hf and Zr nitrates is of great practical importance, in particular for extractional separation of these elements [4, 5]. The study of the chemical reactions of the new nitrate complexes with Zr and Hf, for example clarification of the nature of the bond of the ligands with the metal, is also interesting.

In the present work, we studied the action of HNO_3 on several Hf and Zr complexes. The main path of the investigation was the synthesis of the nitrates of the monocyclopentadienyl complexes with these metals containing chelate (chel) ligands or Cl of the type $CpM(chel)_2(NO_3)$, $CpM(chel)(NO_3)_2$, and $CpMCl_2(NO_3)$. As starting materials for the synthesis of these compounds, complexes of type $CpM(chel)_2X$ and $[CpZrCl_2]_2O \cdot H_2O$ were mainly used, where X = chel, Cl, OC_6H_5, $OCOCH_3$, or NO_3. Cyclopentadienyl dibenzoylmethanate (DBM) complexes with Hf react with HNO_3 under mild conditions with exchange of only one ligand for the NO_3 group and the formation of complex (I)

$$\left.\begin{array}{l} CpHf(DBM)_3 \\ CpHf(DBM)_2(OC_6H_5) \\ CpHf(DBM)_2(OCOCH_3) \end{array}\right\} \xrightarrow[-35^{\circ}]{HNO_3} \begin{array}{c} CpHf(\text{ДБМ})_2(NO_3) \\ (I) \end{array}$$

where DBM = PhCOCHCOPh.

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TABLE 1. Composition of Complexes Obtained

Experiment	Initial reagents, mmoles	Compounds obtained	Yield,%	mp, deg C	Found/Calculated				
					C	H	Hf(Zr)	N	Cl
1	$CpHf(C_{15}H_{11}O_2)_3$ (1,42)	$CpHf(C_{15}H_{11}O_2)_2(NO_3)$	60	214	56,15/55,89	3,64/3,61	23,67/23,73	2,23/1,86	–
	HNO_3 (5,29)	$C_{15}H_{12}O_2$	58	72–73	–	–	–	–	–
2	$CpHf(C_{15}H_{11}O_2)_2Cl$ (0,57)	$CpHfCl_2(NO_3)\cdot 4H_2O$ *			13,91/13,38	3,06/2,70	39,76/39,79	2,69/3,12	14,87/15,81
	HNO_3 (2,2)	$CpHf(C_{15}H_{11}O_2)_2(NO_3)$ †	45	214,5	–	–	–	–	–
3	$CpHf(C_{15}H_{11}O_2)_2(OC_6H_5)$ (1,1)	$CpHf(C_{15}H_{11}O_2)_2(NO_3)$ †	77	214	–	–	–	–	–
	HNO_3 (4,0)	C_6H_5OH	98	42	–	–	–	–	–
4	$CpHf(C_{15}H_{11}O_2)_2(OCOCH_3)$ (1)	$CpHf(C_{15}H_{11}O_2)_2(NO_3)$ †	71	214	–	–	–	–	–
	HNO_3 (3,8)								
5	$CpHf(C_{15}H_{11}O_2)_2(NO_3)$ (1,4)	$CpHf(C_{15}H_{11}O_2)(NO_3)_2$	66	178	46,19/46,68	3,61/3,31	26,36/26,68	4,27/4,18	–
	HNO_3 (5)	$C_{15}H_{12}O_2$	53	72–73	–	–	–	–	–
6	$CpZr(C_5H_7O_2)_2(NO_3)$ (1,2)	$CpZr(C_5H_7O_2)(NO_3)_2$	71	105	32,31/31,68	3,32/3,18	23,86/24,30	7,07/7,38	–
	HNO_3 (4,4)								
7	$CpZr(C_5H_7O_2)_2(NO_3)$ (2,6)	$CpZrCl_2(NO_3)\cdot 4H_2O$ *	64	135–136	–	–	–	3,75/3,88	20,15/19,63
	HCl (14,4)	$CpZr(C_5H_7O_2)_2(NO_3)$		138–139,5	–	–	–	–	–
8	$CpHf(C_{15}H_{11}O_2)_2(NO_3)$ (0,9)	$CpHfCl_2(NO_3)\cdot 4H_2O$ *	77	139–140	13,27/13,38	2,91/2,70	40,31/39,79	–	15,83/15,81
	HCl (5,2)	$C_{15}H_{12}O_2$	77	72–73	–	–	–	–	–
		$CpHf(C_{15}H_{11}O_2)_2(NO_3)$ †		214,5	–	–	–	–	–
9	$CpZrCl_2(NO_3)\cdot 4H_2O$ (1,85)	$CpZr(C_{10}H_9O_2)_2(NO_3)$	35	192,5–194	55,84/55,53	4,62/4,28	16,97/16,87	2,84/2,58	–
	$C_{10}H_{10}O_2$ (3,6)								
	$(C_2H_5)_3N$ (3,6)								
10	Cp_2ZrCl_2 (1 g)	$[CpZrCl_2]_2O\cdot 11\,H_2O$	72	195	17,59/17,96	4,91/4,82	27,93/27,29	–	20,77/21,22
	H_2O (21 ml)								
11	$[CpZrCl_2]_2O\cdot 11H_2O$ (1,49)	$CpZrCl_2(NO_3)\cdot 4H_2O$ *	47	135–136	16,18/16,62	3,85/3,63	25,84/25,24	3,53/3,88	19,40/19,63
	HNO_3 (3,17)								

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*The melting points were measured by lowering a sealed capillary into an apparatus heated to 130°C.

†A mixed probe with a compound obtained in experiment 1 does not show depression of melting point.

TABLE 2. Specific Electrical Conductivity of 0.01 M Solutions of Zr and Hf Complexes in THF at 20°C

Compound	κ, $\Omega^{-1}\cdot$ $cm^{-1}\cdot 10^{-4}$	Deg. of dissociation	Compound	κ, $\Omega^{-1}\cdot$ $cm^{-1}\cdot 10^{-4}$	Deg. of dissociation
$Cp_2ZrCl(NO_3)$	0,12	0,024	$CpZr(C_{15}H_{11}O_2)(NO_3)_2$	0,03	0,006
$CpZr(C_5H_7O_2)_2(NO_3)$	0,13	0,026	$CpHF(C_{15}H_{11}O_2)_2(NO_3)$	0,39	0,078
$CpZr(C_5H_7O_2)(NO_3)_2$*	0,3	—	$CpZr(C_{10}H_9O_2)_2(NO_3)$ *	0,05	—
$CpZr(C_{15}H_{11}O_2)_2(NO_3)$	0,1	0,02	$LiClO_4$	5	

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*Because of the limited solubility in THF, the measurements were carried out with 0.005 M solutions.

The complex of type (II) was synthesized by the reaction of HNO_3 with $CpHF(DBM)_2Cl$

$$CpHf(DBM)_2Cl \xrightarrow[-35^\circ]{HNO_3} \underset{(II)}{CpHfCl_2(NO_3)\cdot 4H_2O} + \underset{(I)}{CpHf(DBM)_2(NO_3)} \qquad (1)$$

On further action of HNO_3, complex (I) converts into complex.(III)

$$\underset{(I)}{CpHf(DBM)_2NO_3} \xrightarrow[20^\circ]{HNO_3} \underset{(III)}{CpHf(DBM)(NO_3)_2} \qquad (2)$$

In [3], a similar series of nitrate complexes with Zr was obtained as the result of the reaction of HNO_3 on $CpZr(acac)_2Cl$

$$CpZr(acac)_2Cl \xrightarrow[-35^\circ]{HNO_3} \underset{(IV)}{CpZrCl_2(NO_3)\cdot 4H_2O} + \underset{(V)}{CpZr(acac)(NO_3)_2} + \underset{(VI)}{CpZr(acac)_2(NO_3)} + HCl \qquad (3)$$

In the present work we showed that the unexpected formation of complex (IV) in reaction (3), and the corresponding Hf analog (II) in reaction (1), is the result of the action of HCl evolved in the course of these reactions on compounds (VI) and (I), respectively. This supposition was confirmed by model reactions (4) and (5)

$$\underset{(VI)}{CpZr(acac)_2(NO_3)} + HCl \rightarrow \underset{(IV)}{CpZrCl_2(NO_3)\cdot 4H_2O} \qquad (4)$$

$$\underset{(I)}{CpHf(DBM)_2(NO_3)} + HCl \rightarrow \underset{(II)}{CpHfCl_2(NO_3)\cdot 4H_2O} \qquad (5)$$

As a proof of the structure of (IV), its reaction with benzoylacetone in the presence of Et_3N is cited. This leads to the formation of (VII) with the exchange of two Cl atoms for the benzoylacetonate ligands

$$\underset{(IV)}{CpZrCl_2(NO_3)\cdot 4H_2O} \xrightarrow[Et_3N]{C_{10}H_{10}O_2} \underset{(VII)}{CpZr(C_{10}H_9O_2)_2(NO_3)} \qquad (6)$$

Complex (IV) was also obtained by an alternative route by the action of HNO_3 on dizirconoxane (VIII); the reaction is accompanied by decomposition of the dizirconoxane grouping

$$\underset{(VIII)}{[CpZrCl_2]_2O\cdot nH_2O} \xrightarrow{HNO_3} \underset{(IV)}{CpZrCl_2(NO_3)\cdot 4H_2O} \qquad (7)$$

The initial complex (VIII) was isolated during the hydrolysis of Cp_2ZrCl_2

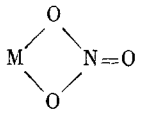
$$Cp_2ZrCl_2 \xrightarrow[20^\circ]{H_2O} \underset{(VIII)}{[CpZrCl_2]_2O\cdot nH_2O} \qquad (8)$$

The action of HNO_3 on complex (VI) at about 20°C leads to complex (V) in the same way as to the dibenzoylmethanate analog of Zr [3] or Hf in reaction (2)

$$\underset{(VI)}{CpZr(acac)_2(NO_3)} \xrightarrow[20^\circ]{HNO_3} \underset{(V)}{CpZr(acac)(NO_3)_2} \qquad (9)$$

The composition of all the Zr and Hf complexes obtained was confirmed by elemental analysis (Table 1). The IR, Raman, and ^{13}C NMR spectra, and also the electrical conductivity of certain nitrate complexes with Zr and Hf were studied. A comparison of the electrical conductivity of solutions of the complexes obtained with a limiting electrical conductivity of a 0.01 M solution of $LiClO_4$ in THF shows that the degree of dissociation of the complexes is very small (Table 2). From this we can assume that the ligands in the compounds obtained are bound to the metals by a nonionic bond.

The IR spectra of all the Zr and Hf β-diketonate complexes studied have strong bands in the 1500-1600 cm^{-1} region and do not have bands in the 1600-1800 cm^{-1} region. This indicates the bidentate character of the bonding of the chelate ligands with the metal. The η^5-Cp-ring is represented by absorption bands in the 830 and 3100 cm^{-1} regions. The remaining bands characteristic of this ligand are overlapped by the strong absorption bands of other ligands. The character of bonding of the nitrate group with the metal atom (mono- or bidentate) is interesting. In several papers, an attempt was made to find the type of coordination of the NO_3 group from the IR spectral data. An analysis of the available data leads to the conclusion that if IR spectra only are used, this is, in general, impossible ([6] and references in this paper).

The frequencies of the stretching vibrations lying in the 1050 cm^{-1} region (class A_1', inactive in the IR spectrum) and in the 1390 cm^{-1} region (class E', active in the IR spectrum) are the most characteristic of the NO_3 ion with D_{3h} symmetry. During the formation of a bond with the metal according to the monodentate type $M-O-NO_2$, as well as the bidentate type  the local symmetry of the NO_3 group decreases to C_{2v}, which has the following consequences: the NO symmetric vibration band becomes active in the IR spectrum (A_1 symmetry), while the degenerated vibration band (E') splits into two bands which are active in the IR spectrum ($A_1 + B_2$). The position of the first band changes little compared to that of the NO_3 ion band, while the splitting value of the second band is determined by a whole series of factors, including the type of coordination, charge on the metal, force coefficient of the M–O bond, etc. [6]. Thus, in many cases the frequency regions of mono- and bidentate forms are fairly close.

Thus, from the position of the bands it is impossible to distinguish between the two types of coordination. They also cannot be distinguished by using the selection rule in the IR and Raman spectra, since the two forms have the same C_{2v} symmetry. However, the solution can be obtained by studying the polarization lines in the Raman spectra. In the case of a monodentate coordination, the highest frequency band belongs to class B_2, i.e., it should be depolarized in the Raman spectrum, while in the case of the bidentate coordination it belongs

TABLE 3. Vibration Frequencies of the NO_3 Group in IR Spectra of Zr and Hf Complexes

Compound	Frequency, ν, cm^{-1}			
$Cp_2ZrCl(NO_3)$	1566 v.s	1260 s	1016 s	761 m
$Cp_2HfCl(NO_3)$	1562 s	1263 s	1010 m	772 w
$CpZr(acac)(NO_3)_2$*	1550 s	1270 v.s	1025 s	770 m
$CpZr(DBM)(NO_3)_2$	1560 †	1265 s	1018 s	780 m
$CpZrCl_2(NO_3)\cdot 4H_2O$	1570 s	1265 s	1030 s	770 m
$CpHfCl_2(NO_3)\cdot 4H_2O$	1575 v.s	1265 s	1025 s	775 m
$CpZr(DBM)_2(NO_3)$	1558 †	1277 s	1032 s	769 m

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*In the $(acac)_3Zr(NO_3)$ complex [8], the bidentate character of the NO_3 ligand was shown by x-ray diffraction analysis [9]. The reported frequencies in the IR spectra of this compound are similar to those observed for complexes described in the present work.

†Overlaps by strong $\nu_{C=O}$ bands.

TABLE 4. ^{13}C NMR Spectra of Zr Complexes (saturated solutions)

Compound	Conditions of measurement		$\delta\,^{13}C$, ppm with reference to TMS		
	solvent	T., °C	C_5H_5	CH	CO
$Cp_2ZrCl(NO_3)$ (IX)	$CH_2Cl_2+CDCl_3$ (30%)	30	115,6	–	–
		–95	114,9	–	–
		–120	114,8	–	–
	THF	30	114,0	–	–
		–30	113,7	–	–
		–130	113,0	–	–
$CpZr(DBM)(NO_3)_2$ (X)	CH_2Cl_2	26	117,9	97,1	*
	CH_2Cl_2	–80	117,5	96,2	186,0 179,9
	$CH_2Cl_2+CDCl_3$ (30%)	–100	117,1	95,7	185,2 179,1
$CpZr(DBM)_2(NO_3)$ (XI)	$CH_2Cl_2+CDCl_3$ (30%)	27	116,5	96,4 95,1	183,9 183,6 183,6 183,2
		–115	116,0	95,6 93,7	182,3 181,6 181,6 181,2

*No signal is observed.

to class A_1, i.e., it should be polarized. For complexes with β-diketonate ligands, it is difficult to measure the polarization of the Raman lines of the nitrate group, since the 1500-1600 cm^{-1} region is overlapped by strong bands of the chelate ligand (stretching vibrations of the $C=O$ group). Therefore, as a model, we selected a complex which does not contain β-diketonate ligands, $Cp_2ZrCl(NO_3)$ [3, 7]. In contrast to the IR spectra, where strong bands correspond to the NO_3 group vibrations, in the Raman spectra, the corresponding lines are very weak, but in the case of $Cp_2ZrCl(NO_3)$, their polarization could be measured in CH_2Cl_2 and THF solution. The 1560 and 1021 cm^{-1} lines were found to be polarized, and the 1268 cm^{-1} line depolarized, which corresponds to the case of a bidentate coordination. The frequencies corresponding to the vibrations of the NO_3 ligand are practically equal in the IR spectra of the Hf and Zr complexes studied (Table 3), so that it is possible to assume that the character of bonding of NO_3 with the metal is the same in all these compounds. Since the Raman spectra indicate a bidentate coordination for $Cp_2ZrCl(NO_3)$, it is possible that the coordination in the remaining compounds is also bidentate. It can be assumed that the $Cp_2ZrCl(NO_3)$ and $CpM(chel)(NO_3)_2$ complexes are penta- and heptacoordinated, respectively.

The ^{13}C NMR spectra of the Zr nitrate complexes (Table 4) show that on the time scale of ^{13}C NMR, the bidentate bonds of the NO_3 group are fairly labile and, therefore, the isomers rapidly convert one into another over the whole temperature range available for the measurements, and give an averaged spectrum, as if the NO_3 group occupied one coordination site. For complex (IX), a single narrow signal of the Cp group is observed in the spectrum, which remains unchanged when the temperature is decreased to –130°C. In the spectrum of complex (X) in CH_2Cl_2, one signal of the Cp group and one of the CH group were observed at 26°C. With decrease in the temperature to –80°C, besides these two signals in the spectrum, two CO signals were observed of an equal intensity. At –100°C, another two sets of low-intensity signals appear: Cp (δ 116.7 and 116.2 ppm), CO (δ 180.7 and 183.2 ppm), and CH (δ 94.6 and 94.7 ppm). With increase in temperature, the spectrum of (X) becomes more simple, and the observed temperature-dependent changes have a reversible character.

In the spectrum of (XI) at 27°C the following set of signals is observed: one signal of the Cp ligand, two signals of the CH groups, and four signals of the CO group, two of them merged. With decrease in temperature to –115°C, the spectrum practically does not change. Table 4 shows that the rigidity of the complexes studied increases with increase in the number of the β-diketonate ligands.

EXPERIMENTAL

The reactions were carried out with dry solvents, without access to moisture from the air. The experimental results and the analysis of the compounds not yet described in the literature are given in Table 1. Experiments 9-11 were carried out at 20°C (experiment 9 in

CH_3CN); the remaining experiments at −35°C (in CH_2Cl_2) for 3-6 h; 54% HNO_3 and 36% HCl were used. The molecular weight of $Cp_2ZrCl(NO_3)$, determined in a THF solution by the sedimentation method in an ultracentrifuge, is 340, calculated 318.8.

To determine the degree of ionic character of the M—ligand bonds, the values of electrical conductivity ($\varkappa$) of 0.01 M solutions of Zr and Hf complexes in THF were measured on an "Impulse" conductometer ($\varkappa$THF = $1\cdot10^{-8}\Omega^{-1}\cdot cm^{-1}$). The degree of dissociation was found as the ratio of equivalent electrical conductivity of a given compound λ ($\lambda = \varkappa\cdot1000/C$, where C is concentration; $\lambda = \varkappa\cdot10^5$) to the equivalent electrical conductivity of a $LiClO_4$ solution in THF at the same concentration. Since THF is a solvent with a low dielectric constant, even a typically ionic compound such as $LiClO_4$ is not completely dissociated in it. Nevertheless, by comparing with $LiClO_4$, it is still possible to evaluate the bond character in the complexes. The data in Table 2 show that the degree of dissociation of the complexes studied is in all cases lower by a factor of several tens than the degree of dissociation of lithium perchlorate, i.e., the complexes are practically nonelectrolytes.

The IR spectra were obtained on an UR-20 Zeiss IR spectrometer in KBr tablets, or in the form of a paste in mineral oil; the Raman spectra were measured on a Ramanor HG-2S spectrometer with an excitation by a 5145 Å line of an argon ionic laser. The ^{13}C NMR spectra were obtained on a HX-90 Fourier spectrometer (22.635 MHz) in a Fourier transformation and a protonic suppression regime with noise modulation Buildup number 30,000.

CONCLUSIONS

1. New types of hafnium monocyclopentadienyl nitrate complexes, $CpHf(DBM)(NO_3)_2$ and $CpHfCl_2(NO_3)\cdot4H_2O$ (DBM is dibenzoylmethane residue) were synthesized.

2. Dichlorides $CpMCl_2(NO_3)$ are formed in the reaction of monochlorides $CpM(chel)_2Cl$ with HNO_3 as the result of the reaction of HCl thus evolved with the exchange product $CpM\cdot(chel)_2(NO_3)$.

3. From a study of the electrical conductivity, IR, and Raman spectra, the nonionic character of the metal—nitrate bonds and bidentate character of the nitrate ligands in $Cp_2M\cdot(NO_3)Cl$ have been assumed.

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