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REACTION OF AROMATIC NITRO COMPOUNDS

WITH TRANSITION METAL COMPLEXES

2. COMPLEXES OF PLATINUM(II) WITH AROMATIC NITRO COMPOUNDS: SYNTHESIS, PROPERTIES, SPECTRA, AND STRUCTURE

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By the method of resonance combination light scattering (RCLS) spectroscopy, we have already shown [1] that in solutions of K_2PtCl_4 , $PtCl_2(DMSO)_2$, and $Pt(M1)_2$, where M1 is 3-hydroxy-2-methyl-4-pyrone, in nitrobenzene, a coordination of the nitro group with the Pt atom takes place.

Synthesis and Catalytic Properties. Complexes of Pt(II) with aromatic nitro compounds were obtained by the reaction

 $\begin{array}{rl} \operatorname{PtCl}_2(\operatorname{DMSO})_2 + \operatorname{C_6H_4NO_2R} \rightarrow \operatorname{PtCl}(\operatorname{DMSO})(\operatorname{C_6H_3NO_2R}) + \operatorname{HCl+} \operatorname{DMSO} \\ (I) & (II)-(IV) \\ \operatorname{R} = \operatorname{H}(II); \ p\text{-Cl}(III); \ p\text{-CH}_3(IV); \ \text{Yield 4-8\%}. \end{array}$

A mixture of (I) and the aromatic nitro compound taken in a molar ratio of 1:100 was heated for 5-10 min at 180-230°C; dark red solutions were obtained. When cool, excess of nitro compound was removed by distillation [complex (II)] or sublimation [complexes (III) and (IV)] at reduced pressure. The residue was extracted by ether, and the extract evaporated to dryness. The residue was dissolved in a minimal amount of absolute acetone, and the impurities were precipitated by ether. After filtration and evaporation, red rhombic [(II)] or needlelike [(III) or (IV)] crystals were obtained (Table 1).

Complexes (II)-(IV) are readily soluble in acetone, ether, benzene, alcohols, halohydrocarbons, DMFA, DMSO, or nitro compounds; in aqueous solutions they decompose. Melting points of (II) 68°C, (III) 145°C (dec), of complex (IV) 160°C (dec).

During hydrogenation of (II)-(IV) by molecular H_2 it was found that they dissociate with the formation of the corresponding aniline and a Pt-containing compound, whose stability and catalytic activity depend on the solvent. In the presence of H_2 , (II)-(IV) are stable in benzene, DMFA, DMA, DMSO, but do not exhibit catalytic activity with the hydrogenation of aromatic nitro compounds. The addition of NaBH₄ leads to decomposition of (II)-(IV) with formation of Pt black. Compounds (II)-(IV) decompose similarly in acetone in the presence of H_2 .

In solutions of nitrobenzene, p-nitrotoluene, p-chloronitrobenzene, in a H₂ atmosphere at 20-80°C, compounds (II)-(IV) are catalytically active (specific activity 1.6-2.5 mole H₂/ mole Pt•min). The corresponding anilines are obtained as the reaction products. If instead of H₂, NaBH₄ is used, a mixture is formed consisting of N-arylhydroxylamine, azoxy and hydrazo derivatives.

Electronic and Infrared Absorption Spectra of Complexes (II)-(IV). During the study of the $PtCl_2(DMSO)_2 + C_6H_5NO_2$ system by the RCLS method [1], data were obtained showing that the

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	Found/Calculated, %							
Complex	с	N	CI	S	н	Pt		
PtCl (DMSO) ($C_{\theta}H_{4}NO_{2}$) (II)	22,6	3,3	8,4 8,25	7,3 7.4	2,5 2,3	45,1 45,3		
$PtCl(DMSO)$ (p- $ClC_{6}H_{3}NO_{2})$ (III)	20.2	3,1	15,2 15,3	7,0 6,9	2,0	41,2 41,9		
PtCl(DMSO) (p- $CH_3C_6H_3NO_2$) (IV)	24,1 24,3	3,1 3,15	7,9 8,0	7,1 7,3	2.6 2,8	44,0 43,9		

TABLE 1. Elemental Composition of (II)-(IV)

TABLE 2. Positions of Band Maxima (nm) in Electronic Absorption Spectra of (II)-(IV) and Corresponding Nitro Compounds (CH₃OH, C $\simeq 2 \cdot 10^{-4} - 5 \cdot 10^{-4}$ mole/liter)

(II)	C ₆ H ₅ NO ₂	(III)	p-ClC ₆ H ₄ NO ₂	(IV)	p-CH ₃ C ₆ H ₄ O ₂
253 280 338 520	207 244 261 280 *	209 328 373 508	207 215 272 280 *	$250 \\ 280 \\ 350 \\ 485$	207 218 275

*In heptane [2].

TABLE 3. IR Spectra of PtC1(DMSO)(C₆H₃NO₂R) Complexes

R	R=H	R	=n-Cl	$R = n - CH_3$			
ω, см-1	Assignment	ω, cm ⁻¹	Assignment	ω, CM- ¹	Assignment		
ω, cm ⁻¹ 451 m 463 m.sh 483 v.w 577 v.w 698 m 716 m.sh 727 s 787 m 863 m 918 w 963 w 978 m 1021 v.s 1091 s 1121 v.w 1142 v.w 1142 v.w 1142 v.w 1142 v.w 1142 v.w 1145 s 1342 w 1382 v.w 1404 m.sh 1419 m 1453 m 1523 v.s 1555 w.sh 1588 s 1616 w 2853 v.w 2909 w 2945 w 3009 w.sh 3022 w	Assignment v(Pt-S) 16b $v(C-S) \ AMCO$ $\gamma_s (NO_2)$ $\rho (CH_3) \ AMCO$ 17b 17a 18a 18b $v(S=O) \ AMCO$ 9a 9b $v_s NO_2$ 14 19b $\delta (CH_3) \ AMCO$ 19a $v_{as} (NO_2)$ 8a 8b $v_s (NO_2)$ 8a 8b $v_s (CH)$ $z_{as} (CH)$	ω, cM ⁻¹ 430 v.w 453 m 572 w 586 v.w 619 v.w 678 w 692 m 743 m 754 v.w 692 m 743 m 754 v.w 772 w 817 m 863 w 910 m 921 v.w 983 m 1023 s 1081 s 11023 s 1023 s 1081 s 1123 s 1208 s 1223 m.sh 1258 s 1233 v.w 1312 s 1333 v.w 1378 m 1408 m.sh 1402 m	Assignment v(Pt-S) 16b $v(C-S) \ AMCO$ $\gamma_s (NO_2)$ $p(CH_3) \ AMCO$ 17b 17a 18a 18b $v(S=O) \ AMCO$ $v_s (NO_2)$ $\delta (CH_3) \ AMCO$ $\frac{1}{4} \delta (CH_3)$ $\delta (CH_3)$ 19a $v_{as} (NO_2)$ Sa $v(CH) \ AMCO$	ω, см-1 433 m.sh 454 m 538 v.w 588 v.w 689 m 743 m 753 v.w. 825 v.w 901 w 921 w.sh 932 w 901 w 921 w.sh 932 w 979 m 1026 s 1100 m.sh 1134 m.sh 1150 v.s 1200 v.s 1223 m 1269 s 1311 w.sh 1324 m 1340 w.sh 1378 m 1433 w.sh 1433 w.sh 1266 m 2855 v.w 2918 w 2928 w.sh 2928 w.sh	Assignment v(Ft-S) 16b $v(C-S) \ \mbox{JMCO}$ $\gamma_{s}(NO)_{z}$ 17b $\delta(NO_{2})$ $\rho(CH_{3})$ 17a 18a $v(S=O) \ \mbox{JMCO}$ $v_{s}(NO_{2})$ 14 $\delta(CH_{3}) \ \mbox{JMCO}$ 19a $v_{as}(NO_{2})$ Sa		
3092 v.w	200	3025 w 3058 w 3080 m 3103 v·w	20b 20a	3030 w.sh 3078 v.w	v(CH) v(CH)		

Note: v.s., very strong; s, strong; m, medium; w, weak; v.w., very weak; sh, shoulder. Numbers and symbols a and b designate vibrations of phenyl ring according to Wilson [4].

TABLE 4. Vibration Frequencies (cm^{-1}) of Nitro Group in (II)-(IV) and in Corresponding Nitro Compounds

Assignment	(11)	C ₆ H ₅ NO ₂	(III)	p-ClC ₆ H ₄ O ₂	(IV)	p-CH ₃ C ₆ H.NO2
v _{as} NO2 v _s NO2	1523 v.s 1260 v.s 1208 v.s	1527 v.s 1351 v.s	1511 v.s 1258 s 1223 m.sh	1524 v.s 1343 v.s	1512 v.s 1269 s 1223m	1527 v.s 1345 v.s
δNO2 γsNO2 γasNO2	863 m 727 s	852 s 704 v.s 532 s	1208 s 863 w 743 m	855 s 741 s 535 m	1200 v.s 865 v.w 743 m	859 s 736 s 521 m

TABLE 5. Interatomic Distances and Valence Angles in (II)

Bond	d, Å	Angle	ω , deg
$\begin{array}{c} Pt-C^{i} \\ Pt-O^{i} \\ Pt-Cl \\ Pt-S \\ N-O^{2} \\ N-C^{6} \\ C^{i}-C^{2} \\ C^{3}-C^{4} \\ C^{4}-C^{5} \\ C^{5}-C^{6} \\ C^{i}-C^{6} \\ S-O^{3} \\ S-C^{7} \\ S-C^{8} \end{array}$	$\begin{array}{c} 1,96 (3) \\ 2,06 (2) \\ 2,357 (8) \\ 2,178 (6) \\ \hline 1,32 (4) \\ 1,19 (3) \\ 1,39 (4) \\ 1,38 (4) \\ 1,41 (4) \\ 1,42 (4) \\ 1,42 (4) \\ 1,39 (4) \\ 1,47 (4) \\ 1,39 (4) \\ 1,47 (2) \\ 1,76 (3) \\ 1,80 (5) \end{array}$	$C^{4}PtO^{4}$ $C^{4}PtS$ SPtCl $ClPtO^{1}$ $PtO^{4}N$ $O^{4}NC^{6}$ $O^{2}NC^{6}$ $NC^{6}C^{1}$ $NC^{6}C^{5}$ $C^{4}C^{6}C^{5}$ $C^{6}C^{1}Pt$ $PtC^{4}C^{2}$ $C^{4}C^{2}C^{2}$ $C^{4}C^{2}C^{4}$ $C^{3}C^{4}C^{5}$ $C^{4}C^{5}C^{6}$ $PtSO^{3}$ $PtSC^{7}$ $O^{3}SC^{7}$ $O^{3}SC^{8}$ $C^{7}SC^{8}$	

TABLE 6. Coordinates of Nonhydrogen Atoms $(10^4, \text{for C}, N, 0, \cdot 10^3)$ and Their Anisotropic Temperature Parameters $(\cdot 10^4)^*$ for (II)

		the second s					the second s			
Atom	X	Y	Z	B11	B_{22}	B_{33}	B ₁₂	B ₁₃	B_3	
$\begin{array}{c} {\rm Pt} \\ {\rm Cl} \\ {\rm S} \\ {\rm O}^1 \\ {\rm O}^2 \\ {\rm O}^3 \\ {\rm N} \\ {\rm C}^1 \\ {\rm C}^2 \\ {\rm C}^2 \\ {\rm C}^3 \\ {\rm C}^4 \\ {\rm C}^5 \\ {\rm C}^6 \\ {\rm C}^7 \\ {\rm C}^8 \end{array}$	$\begin{array}{c} 4245(1)\\ 4401(7)\\ 2769(5)\\ 560(2)\\ 668(1)\\ 252(2)\\ 438(2)\\ 438(2)\\ 381(2)\\ 403(2)\\ 403(3)\\ 554(3)\\ 525(2)\\ 188(2)\\ 257(3)\end{array}$	$5805 (1) \\7972 (8) \\6058 (6) \\548 (2) \\407 (3) \\528 (3) \\426 (3) \\395 (3) \\395 (3) \\305 (3) \\172 (3) \\123 (3) \\205 (3) \\342 (3) \\573 (4) \\772 (5)$	$\begin{array}{c} 1850(1)\\ 2763(12)\\ -6(9)\\ 369(3)\\ 478(3)\\ -156(3)\\ 375(3)\\ 153(4)\\ 42(4)\\ 43(4)\\ 154(5)\\ 281(3)\\ 262(4)\\ 109(3)\\ -64(6) \end{array}$	$\begin{array}{c} 37\\80\\40\\48\\42\\77\\38\\31\\42\\37\\99\\73\\44\\56\\65\end{array}$	56 61 62 102 196 179 92 89 81 91 62 94 107 155 115	$\begin{array}{c} 124\\ 229\\ 126\\ 177\\ 200\\ 160\\ 119\\ 164\\ 195\\ 238\\ 285\\ 137\\ 140\\ 129\\ 307\\ \end{array}$	$ \begin{array}{c} -1 \\ -11 \\ 11 \\ 14 \\ 21 \\ 101 \\ -6 \\ -28 \\ -22 \\ -35 \\ 49 \\ 105 \\ 48 \\ -60 \\ 93 \end{array} $	$\begin{array}{c} 6\\ 44\\ 22\\ -27\\ -19\\ -82\\ 7\\ 25\\ 23\\ 98\\ 235\\ -5\\ 30\\ 21\\ 46\\ \end{array}$	$ \begin{array}{c} -6 \\ -51 \\ 1 \\ -55 \\ 97 \\ -186 \\ -136 \\ -92 \\ -70 \\ -170 \\ 64 \\ 42 \\ -133 \\ 25 \\ 84 \end{array} $	

long-wave absorption band arising during the reaction in this system at 520 nm may be a band of charge transfer between the platinum atoms and the nitro group in the complex of Pt(II) with nitrobenzene formed. It is probable that the long-wave bands in the 485-520 nm region have a similar nature also in complexes (II)-(IV) (Table 2). The bands in the UV region of the spectrum of (II) probably correspond to transitions in coordinated nitrobenzene.



Fig. 1. Molecular structure of PtC1(DMS0)(C₆H₄NO₂) complex.

A qualitative assignment of the bands in the IR absorption spectra of (II)-(IV) (Table 3) was made by comparison with the spectra of the initial complex (I) [3, 4], free nitrobenzene and its derivatives [5], and also of compounds with different forms of coordination of the nitro group [6]. In the IR spectra of (II)-(IV) in the 400-3200 cm^{-1} region bands appear corresponding to the vibrations of coordinated DMSO and the corresponding nitro compound. The very intense IR bands at 1511-1523 cm⁻¹ corresponding to the antisymmetric stretching vibration v_{as} NO₂, the very intense bands at 1200-1269 cm⁻¹ corresponding to fully symmetric stretching vibrations v_s NO₂, the medium intensity bands at 863-865 cm⁻¹ corresponding to the scissoring vibrations δ (NO₂), and the bands at 723-743 cm⁻¹ corresponding to the twisting vibrations γ_s (NO₂) can be reliably assigned to the vibrations of the nitro group (Table 4). The IR bands in the 3100-3000 cm⁻¹ (stretching vibrations of CH-bonds, vCH) and in the 1620-1580 cm⁻¹ region (vibrations with preferential contribution of the stretching of the C = C bonds in the ring, vC = C) are assigned to the vibrations of a substituted phenyl ring. The assignment of the remaining IR bands is less definite because of the complex influence of the coordination of the nitro compound on its electronic structure, and hence on its vibration spectrum, including the characteristic vibrations of the phenyl ring. Thus, the vibrations of the phenyl ring in (II)-(IV) do not in fact give any definite information on its state in these complexes. However, decrease in the frequency of the fully symmetrical stretching vibration v_s NO_2 by 76-145 cm⁻¹ and the inappreciable increase in the frequencies of the deformational vibrations δ NO₂ by 6-9 cm⁻¹ and $\gamma_{\rm S}$ NO₂ by 2-23 cm⁻¹, with simultaneous absence of the rocking vibration of the nitro group γ_{as} NO₂ in the 521-535 cm⁻¹ region [4] in (II)-(IV), compared with the case with free nitro compounds (see Table 3), are characteristic indicators of the coordination of the nitro group with Pt(II) atom via the 0 atom of the nitro group [6].

The Pt atom has a square planar coordination typical of Pt(II) [7, 8] and forms a fivemembered metallo-ring with the nitrogenzene molecule, in which one of the 0 atoms of the nitro group and the C atom in the ortho position with respect to the nitro group enter the coordination sphere of Pt (Fig. 1, Table 5). The Pt atom protrudes from the plane of four

TABLE 7. Coordinates of Hydrogen Atoms $(\cdot 10^3)$ * and Bond Length with Corresponding C Atom for (II)

Atom	X	Y	Z	СН, А	Atom	X	Y	Z	С—Н, Å
H ² H ³ H ⁴ H ⁵ H ⁷	308 354 507 623 132	340 105 31 170 560		$\begin{array}{ c c c } 1,2 \\ 1,1 \\ 1,0 \\ 1,1 \\ 0,9 \end{array}$	H7 H7 H8 H8 H8	188 198 250 196 320	647 489 810 767 811	180 175 36 -166 -91	1,0 1,0 0,9 1,0 1,0

*The numbers of the corresponding carbon atoms were assigned to the hydrogen atoms.

atoms Cl, S, 0^1 , C^1 by 0.05 Å, and this plane is coplanar with the plane of the nitro group. The plane of the nitro group forms a dihedral angle of 3° with the plane of the phenyl ring.

It should be noted that the complex of Pt(IV) with o-nitrotoluene, in which a $Pt-C \sigma$ bond of 2.06(2) Å was also found, has a completely different structure, and the nitro group does not enter the coordination sphere of Pt [9]. The coordination of one of the atoms of the nitro group with the metal, and the formation of a six-membered metallo-ring were found recently in the dimeric methoxo-complex of Cu(II) with 2,4-dinitrophenol [10].

From the similarity between the chemical and spectral properties of (Ii)-(IV), it can be assumed that the molecular structures of (III) and (IV) are similar to that of complex (II).

EXPERIMENTAL

Nitrobenzene, twice distilled at reduced pressure, p-chloronitrobenzene and p-nitrotoluene, twice recrystallized from ethanol, were used. The hydrogenation was carried out as described in [11]. The hydrogenation products were analyzed by TLC (Silufol, eluent acetone:benzene = 1:4).

The electronic absorption spectra were measured on a Specord UV VIS spectrophotometer. The samples were used in the form of solutions in methanol $(2 \cdot 10^{-4} - 5 \cdot 10^{-4} \text{ mole/liter})$. The IR spectra were recorded on the UR-20 spectrophotometer, and the samples were used in the form of tablets of (II)-(IV) with KBr.

Intensities of 1519 independent reflections with $I \ge 3\sigma$ were measured on a Syntex $P\bar{I}$ diffractometer from a single crystal $0.08 \times 0.18 \times 0.25$ mm in size with monochromatized MoK_{α}-radiation in an interval up to $(\sin \theta/\lambda)_{max} = 0.743$. No correction for the absorption was introduced. The structure was determined by the heavy atommethod and refined by the method of least squares in an anisotropic approximation. Part of the hydrogen atoms were found from the differential synthesis, and part were calculated geometrically. The hydrogen atoms were included in the refinement with fixed positional and isotropic temperature parameters. All the calculations were carried out according to the complex of Roentgen-75 programs.

The final R = 0.085. The coordinates of nonhydrogen atoms and their anisotropic temperature parameters are given in Table 6, and the coordinates of hydrogen atoms are given in Table 7.

The authors wish to express their gratitude to L. P. Rozenberg for selecting the crystals for the experiments, for their examination by the photometric method, and for help in carrying out the calculations on the BÉSM-6 computer.

CONCLUSIONS

1. Complexes of platinum(II) with aromatic nitro compounds of the general formula $PtCl(DMSO)(C_6H_3NO_2R)$, where R = H, Cl, CH_3 , were synthesized. Their electronic and IR spectra were measured and discussed. The catalytic activity of the complexes in the hydrogenation reaction of the aromatic nitro compounds was shown.

2. An x-ray investigation of the $PtCl(DMSO)(C_6H_4NO_2)$ complex was carried out, and it was shown that the platinum atom has a square planar coordination and forms a five-membered metallo-ring, which includes one of the oxygen atoms of the nitro group and a carbon of the benzene ring at the ortho position with reference to the nitro group.

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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 NO₃ 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)

 $\left. \begin{array}{c} Cp Hf(\ \text{DBM})_3 \\ Cp Hf(\ \text{DBM}) \ _2(OC_6H_5) \\ Cp Hf(\ \text{DBM}) \ _2(OCOCH_3) \end{array} \right\} \xrightarrow[-35^c]{\text{HNO}_4} Cp Hf(\ \Pi EM)_2(NO_3) \\ (I) \end{array}$

where DBM = PhCOCHCOPh.

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