X-RAY PHOTOELECTRON SPECTRA OF Rh(III) TRIFLUOROACETATE

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A study was made of the x-ray photoelectron spectra of Rh(I) and Rh(III) trifluoroacetate complexes. It was shown by using the C1s bond energies of the carboxylate carbon atom as a basis that bridging and monodentate coordination of the trifluoroacetate group could be distinguished with high resolution.

Keywords: *photoelectron spectra, Rh(III) trifluoroacetate.*

Rhodium and platinum trifluoroacetates are active in the oxidation reactions of hydrocarbons, including methane [1]. In addition, $Rh(CF_3COO)_3$ (**1**) is the starting compound for synthesizing Rh(I) complexes such as $Rh(CF_3COO)(PR_3)_3$ (R = Ph, $C_6H_4SO_3Na$) and $[Rh(NBD)CF_3COO]_2$ [2]. Since it has not been possible to obtain monocrystals of compound **1**, the most productive course is to make a comparative study of $Rh(CF_3COO)_3$ in a series of trifluoroacetate complexes of known structure.

In the present work we report the results of investigating the x-ray photoelectron spectra of $Rh(CF_3COO)_3$.

RESULTS AND DISCUSSION

Table 1 shows the x-ray photoelectron spectral data for compound **1** and other rhodium trifluoroacetate complexes. Comparing the $E_{\text{bond}}\text{Rh}3d_{5/2}$ values obtained in the present work with the analogous figures for a large number of rhodium complexes reported elsewhere [3], it is clear that as a ligand trifluoroacetate is a powerful electron acceptor. Evidence of this is provided by the fact that $E_{\text{bond}}\text{Rh}3d_{5/2}$ is greater for compound **1** than for the average value for Rh(III) (311.2 and 310.5 eV, respectively), which is in agreement with the increased electrophilic properties of Rh(III) in reactions with hydrocarbons. The ability of halogen-substituted radicals to draw away electron density from the rhodium atom is also borne out by the example of $Rh_2(CF_3COO)_4$, in which E_{bond} (310.2 eV) is close to its values in Rh(III) complexes [3].

The presence in the IR spectrum of compound **1** of bands having $\nu_{\text{asym}}(\text{COO})$ of 1670 and 1620 cm^{-1} and $\nu_{\text{sym}}(\text{COO})$ of 1450 and 1415 cm^{-1} points to the fact that the CF_3COO groups are nonequivalent. It is well known that in metal carboxylates CF_3COO^- is, as a rule, a bridging or monodentate group [4].

When rhodium trifluoroacetate complexes having a bridging CF_3COO group were investigated [5], it was found that $E_{\text{bond}}\text{C}1s$ for the carboxylate carbon atom in $[Rh(NBD)CF_3COO]_2$ was 289.0 eV (see Table 1).

Figure 1 shows the C1*s* x-ray photoelectron spectrum (unbroken line) of $Rh(CF_3COO)_3$. Component I (293 eV) corresponds to the CF_3 group and component II (289 eV) to the COO group, the 285.00 eV peak being caused by hydrocarbon adsorbate on the sample surface. The fact that component I exhibits a larger peak intensity than component II, given the same number of carbon atoms intrinsic to them, results from the greater half-width of component II. This is probably due to the varying types of coordination of the CF_3COO groups in compound **1**, as can be surmised from IR spectral data.

Data processing of the C1*s* spectrum of compound **1**, which comprised subtraction of the inelastically scattered electron background and deconvolution with the spectrometer apparatus function [6] showed (line 2, Fig. 1) that component II consists of two peaks with maxima at 289.9 and 289.2 eV, with an intensity ratio of 1.8:1.2. It may be assumed that the 289.9 and 289.2 eV peaks arise from the carboxylate carbon atom of the CF_3COO^- group having terminal and bridging types of coordination, respectively. The slight positive shift of the maxima for compound **1** compared to component II for compounds having only one type of CF_3COO^- coordination may be due to the fact that the central atom in **1** has a much larger positive charge than that on the metal atom in the compounds used for comparison.

Unfortunately, it was not possible to distinguish precisely the position of the C1*s* spectral components corresponding to the carbon atoms of the CF_3COO monodentate group in $(PPh_3)_3Rh(CF_3COO)$ and $(PPh_3)_2Rh(CO)CF_3COO$ because of the intensity and width of the attendant peak from the PPh_3 carbon atoms (π—π^* transition). It was found that for platinum (II)

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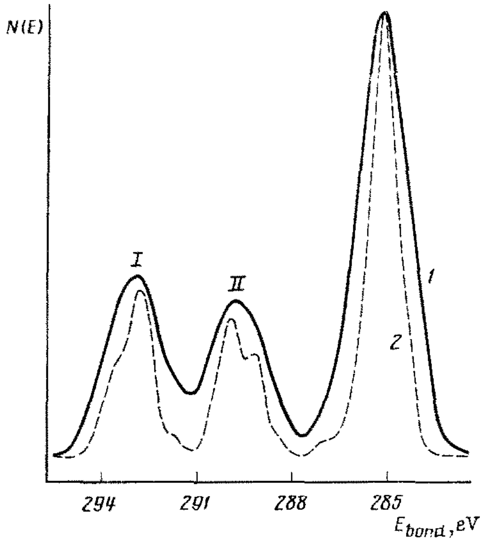

Fig. 1. C1*s* x-ray photoelectron spectrum of $Rh(CF_3COO)_3$ before (1) and after (2) data processing; component I (293 eV) corresponds to the CF_3 group and component II (289 eV) to the COO group.

TABLE 1. Bond Energies (eV) in Complex Rhodium Compounds

No.	Compound	$Rh3d_{5/2}$	F 1s	C 1s	
				CF_3	COO
1	$Rh(CF_3COO)_3$	311.2	688.5	292.9	289.7
2	$[Rh(NBD)CF_3COO]_2$*	308.8	688.3	292.7	289.0
3	$Rh(CF_3COO)CO(PPh_3)_2$	308.5	687.9	–	–
4	$Rh(CF_3COO)(PPh_3)_3$	307.8	687.7	–	–

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*NBD — norbornadiene.

trifluoroacetate, $Pt(CF_3COO)_2$, the C1*s* peak corresponding to the carboxylate carbon atom in the case of end coordination occurred at 289.7 eV. This can be viewed as additional confirmation of the assignment made.

The half-width of the $Rh3d_{5/2}$ peak in compound **1** was also greater than that in individual rhodium complexes (Nos. 2-4, Table 1). This may result from the presence in **1** of rhodium compounds of identical composition but different molecular structure.

In summary, it was found that in $Rh(CF_3COO)_3$ coordination occurs partly through bridging of the CF_3COO groups and partly through bonding with a single rhodium atom. This bridging and monodentate coordination can be distinguished with high energy resolution using x-ray photoelectron spectroscopy.

EXPERIMENTAL

$Rh(CF_3COO)_3$ was synthesized using the method described in [2] and $[Rh(NBD)CF_3COO]_2$ using that reported in [7], while $Rh(CF_3COO)(PPh_3)_3$ and $Rh(CF_3COO)(CO)(PPh_3)_2$ were obtained by heating **1** with PPh_3 in ethyl alcohol.

$Rh(CF_3COO)(PPh_3)_3$. Found, %: C 67.4; H 4.90. Calculated, %: C 67.1; H 4.52. IR spectrum (ν, cm^{-1}): 1670 (COO).

$Rh(CF_3COO)(CO)(PPh_3)_2$. Found, %: C 61.3; H 4.3. Calculated, %: C 60.93; H 3.9. IR spectrum (ν, cm^{-1}): 1690 (COO), 1990 (CO). Nucleus parameters: a = 14.737(3), b = 12.253(2), c = 20.248(4), β = 109.34(1)°, V = 3450(1). Spatial group $P2_{1/c}$, monoclinic, Z = 4.

X-ray photoelectron spectrum samples were prepared by applying the complex to an aluminum substrate, which had just been cleaned by mechanical means and oxidized in air until a solid layer of Al_2O_3 (20-30 Å) was formed to prevent the applied complex reacting with the substrate. Spectra were recorded on a VIEE-15 instrument with a magnesium anode ($h\nu$ = 1253.6 eV). These were calibrated relative to the C1*s* line (285.0 eV) of the hydrocarbon condensate from the residual gases in the vacuum chamber. Spectrometer resolution, defined as the width at half the height of the Au $4f_{7/2}$ peak, was 1.17 eV over the whole range of energies investigated.

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