Inorganica Chimica Acta, 40 (1980) 203–206

Properties and Structure of $Rh_2(HCOO)_2(CO)_4$

FLORIAN PRUCHNIK and KATARZYNA WAJDA

Institute of Chemistry, University of Wrocław, 50-383 Wrocław, Joliot-Curie 14, Poland

Received October 18, 1979

$Rh_2(HCOO)_2(CO)_4$ was prepared and its properties were investigated. The dimeric structure of this compound was determined from its mass spectrum. IR spectra were measured in the 50–4000 cm^{-1} region and the electronic spectra were measured in various solvents. The dimer–monomer equilibrium was examined in methanol–benzene solutions.

Introduction

Lawson and Wilkinson examined a number of bridged carbonyl rhodium(I) compounds, prepared in petroleum ether solution at room temperature from the reaction between di-μ-chlorotetracarbonyldirhodium(I) and suitable silver salts [1]. Among the rhodium(I) carboxylate complexes only $Rh_2(CH_3COO)_2(CO)_4$ has been known until now. Its infrared spectrum was examined in the 400–4000 cm^{-1} region [1]. No electronic spectra of this compound were measured.

The present paper deals with the properties and structure of the hiterto unknown $Rh_2(HCOO)_2(CO)_4$ compound.

Experimental

$Rh_2(HCOO)_2(CO)_4$

Gaseous CO was passed through a $Rh_2(CH_3COO)_4$ or $Rh(NO_3)_3$ solution in anhydrous formic acid at 80 °C. After 12 hours a golden-brown precipitate with metallic lustre was formed. The precipitate was filtered off, washed with methyl alcohol and dried in an argon stream. The yield for $Rh_2(CH_3COO)_4$ as initial complex was 80% and for $Rh(NO_3)_3$ was 30%.

$Rh_2(CH_3COO)_2(CO)_4$ was prepared according to the method described in [1].

Results of analysis:
$Rh_2(HCOO)_2(CO)_4$
Melting point 115–119 °C (decomposition)

Calc: %C = 17.67, %Rh = 50.46, %CO = 28.92

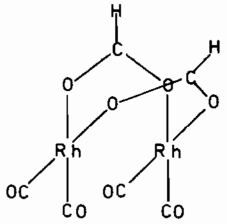

Fig. 1. Structure of $Rh_2(HCOO)_2(CO)_4$.

Found: %C = 18.1, %Rh = 49.8, %CO = 29.6

$Rh_2(CH_3COO)_2(CO)_4$
Melting point 160 °C (decomposition)

Calc: %C = 22.04, %H = 1.38
Found: %C = 22.4, %H = 1.3

Results and Discussion

A crystalline golden-brown complex with metallic lustre whose colour is altered on grinding into green-blue, was prepared with a high yield (80%) from $Rh_2(CH_3COO)_4$ [2] in anhydrous formic acid under carbon monoxide. As $Rh_2(CH_3COO)_2(CO)_4$, the compound prepared by us is fairly well soluble in alcohols, acetone, CCl_4, chloroform and slightly less in anhydrous formic acid yielding orange-yellow solutions. It is stable in air, decomposes under humid conditions and sublimes.

The molecular weight of $Rh_2(HCOO)_2(CO)_4$ determined by the mass spectroscopy method is 408 which proves its dimeric structure (Fig. 1). The mother ion is formed at m/e = 408 which corresponds to $Rh_2(HCOO)_2(CO)_4^{\dot{+}}$. In the first stage of fragmentation the H atom and then the CO molecule are split off. The pattern of fragmentation is as follows:

$$Rh_2(HCOO)_2(CO)_4$$
$$\xrightarrow{-e} Rh_2(HCOO)_2(CO)_4^{\dot{+}} \ (m/e = 408)$$
$$\xrightarrow{-H} Rh_2(HCOO)(COO)(CO)_4^{\dot{+}} \ (m/e = 407)$$

TABLE I. Frequencies and Band Assignments for the Complexes $Rh_2(RCOO)_2(CO)_4$. Frequency region 500–4000 cm^{-1} (in KBr).

Compound	$\nu C(O)$	$\nu_{as}(COO)$	$\nu_s(COO)$	Other Bands
$Rh_2(HCOO)_2(CO)_4$	1830vw 2010vs 2080vs	1568vs	1318s	533vw, 625w, 720vw, 772m, 780m, 803vw, 1300s, 1347vs, 1365vs, 1615s, 1631s, 2875s, 2925m, 2960m
$Rh_2(CH_3COO)_2(CO)_4$	1836vw 1980w,sh 2020vs 2067s,sh 2083vs	1560vs	1439s	612vw, 622vw, 680vw, 1020vw, 1336vw, 1344vw, 2920vw

TABLE II. Frequencies and Band Assignment for the Complexes $Rh_2(RCOO)_2(CO)_4$. Frequency region 50–500 cm^{-1} (in nujol).

Compound	$\nu(Rh–C) + \delta(Rh–C)$	$\nu_s(Rh–O)$	$\nu_{as}(Rh–O)$	Other Bands
$Rh_2(HCOO)_2(CO)_4$	500vs 479s 450vs	360vs	388vs	75w, 118vw, 167s, 221m, 311vs
$Rh_2(CH_3COO)_2(CO)_4$	499s 477m 455vs	321w	342vw	216vw, 168m

$$\xrightarrow{-CO} Rh_2(HCOO)(COO)(CO)_3^+ \ (m/e = 379)$$

$$\xrightarrow{-CO} Rh_2(HCOO)(COO)(CO)_2^+ \ (m/e = 351)$$

$$\xrightarrow{-CO} Rh_2(HCOO)(COO)(CO)^+ \ (m/e = 323)$$

$$\xrightarrow{-CO} Rh_2(HCOO)(COO)^+ (m/e = 295)$$

The spectrum exhibits very strong peaks at m/e = 12, 16, 28, 44 which correspond to the C, O, CO, CO_2 molecules. The dimeric structure of the complex with bridging formate groups is confirmed by the IR spectra (Table I).

In the 500–4000 cm^{-1} region it differs only slightly from that of $Rh_2(HCOO)_4$ [3]. A small difference between the $\nu_s(COO)$ and $\nu_{as}(COO)$ frequencies indicates that the formate groups are bound symetrically with the rhodium atoms as the acetate groups in $Rh_2(CH_3COO)_2(CO)_4$. A similar structure of both these compounds may be evidenced by the far infrared spectra. In the formate complex the $\nu(Rh–C)$ and $\delta(Rh–C)$ valence bands are in the same positions (Table II) as in the case of the acetate complex [4]. The $\nu_{as}(Rh–O)$ and $\nu_s(Rh–O)$ bands for the formate complex lie at higher energies than for the acetate complex as might have been expected.

Because of a low spin–orbit coupling constant the electronic spectra of the rhodium(I) compounds are relatively simple [5]. Above 20000 cm^{-1} there are the M–L charge transfer bands from the orbitals: $a_{1g}(z^2) \rightarrow a_{2u}(^1A_{1g}–^{1,3}A_{2u})$, $e_g(xz, yz) \rightarrow a_{2u}(^1A_{1g}–^{1,3}E_u)$, $b_{2g}(xy) \rightarrow a_{2u}(^1A_{1g}–^{1,3}B_{1u})$. The electronic spectra of the formate and acetate complexes in various solvents are similar (Table III). The first band appearing in methanol solutions at about 38000 cm^{-1} results probably from the $^1A_1–^1B_1$, $^1B_2$ transition and that at about 31000 cm^{-1} from the $^1A_1–^1A_{2u}$ transition. The spectra in alcohol solutions differ from those in benzene solutions (Table III).

Because of the rhodium–rhodium interaction the spectral band at about 31000 cm^{-1} is shifted to lower energies and the band at 23000 cm^{-1} is observed in alcohols. The absorption was studied over the 18200–35000 cm^{-1} region for the $Rh_2(HCOO)_2(CO)_4$ complex solutions depending on the composition of the solvent consisting in methyl alcohol and benzene. The 31300 cm^{-1} band intensity was found to increase with increasing methanol concentration in benzene and the 23000 cm^{-1} band intensity

TABLE III. Electronic Absorption Spectra of $Rh_2(RCOO)_2(CO)_4$.

Compound	Methanol $cm^{-1} \times 10^{-3}$ (ϵ, $dm^3\ mol^{-1}\ cm^{-1}$)	Benzene $cm^{-1} \times 10^{-3}$ (ϵ, $dm^3\ mol^{-1}\ cm^{-1}$)
$Rh_2(HCOO)_2(CO)_4$	27.7sh, 31.3(6.6×10^3), 38.4(1.13×10^4)	23.0(5.5×10^3), 31.3(1.3×10^3)
$Rh_2(CH_3COO)_2(CO)_4$	27.8sh, 30.9(6.4×10^3), 38.0(1.35×10^4)	22.7(6.2×10^3), 31.0(1.8×10^3)

TABLE IV. Thermodynamic Data for the Equilibrium: $Rh_2(RCOO)_2(CO)_4 + 2\ CH_3OH = Rh(RCOO)(CO)_2(CH_3OH)$.

	$Rh_2(HCOO)_2(CO)_4$				$Rh_2(CH_3COO)_2(CO)_4$		
C_{MeOH}	1.23 *M*				1.23 *M*		
$C_{comp.}$	9.8×10^{-4} *M*				9.2×10^{-4} *M*		
ΔH kJ mol^{-1} K^{-1}	−24.5				−21.1		
ΔS J mol^{-1} K^{-1}	−26.6				−18.7		
	$Rh_2(RCOO)_2(CO)_4$						
T (K)	273	283	293	303	313	323	333
$-\Delta G$ kJ mol^{-1} R = H	17.1	17.2	16.7	16.4	16.2	15.7	15.7
$-\Delta G$ kJ mol^{-1} R = CH_3	16.0	15.8	15.7	15.4	15.2	15.1	14.6

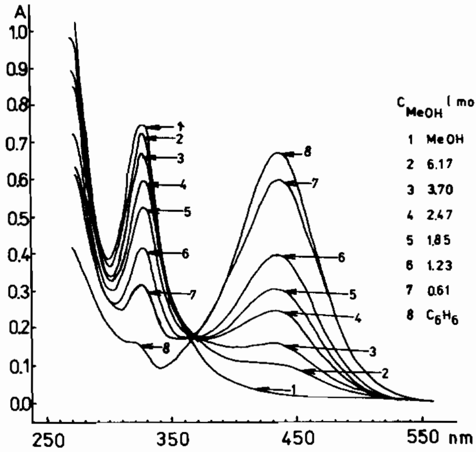

Fig. 2. Absorption spectra of $Rh_2(HCOO)_2(CO)_4$ in benzene–methanol solutions. $C_{complex} = 1.22 \times 10^{-3}$ *M*.

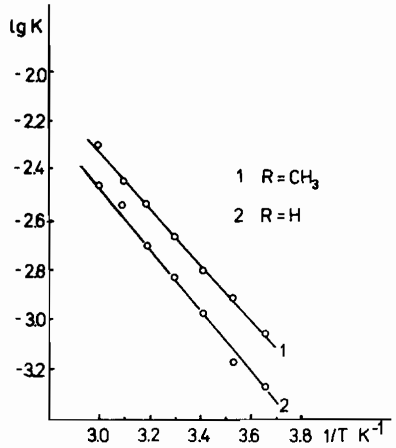

Fig. 3. Dependence of lg K on 1/T for the equilibrium: $Rh_2(RCOO)_2(CO)_4 + 2CH_3OH = 2Rh(RCOO)(CO)_2(CH_3OH)$.

decreases (Fig. 2). One isosbestic point is found at 27200 cm^{-1}.

The same correlation was observed for $Rh_2(CH_3COO)_2(CO)_4$. The band at about 23000 cm^{-1} is characteristic of the dimeric form since the molecular weight measured for the formate complex in benzene solution is 420. The conductivity in benzene was also measured and it was found that the $Rh_2(HCOO)_2(CO)_4$ complex solution in this solvent is non-ionic. The band at about 31000 cm^{-1} appearing in alcohols corresponds to a monomeric form as is found from a decrease in band intensity at 23000

cm^{-1} after treating the complex solution in benzene with a stoichiometric amount of *p*-toluidine which, as a Lewis base, is capable of splitting the M–L–M bridges. The conductivity of $Rh_2(HCOO)_2(CO)_4$ in methanol solution was measured. It is 4.6 cm^2 ohm^{-1} mol^{-1} which indicates that the monomeric form is partially dissociated. The monomer/dimer ratio was found to depend on the amount of methanol present in the mixture and on temperature in argon atmosphere (Fig. 3), but such dependence was not found in CO atmosphere because of the reaction between CO and complex. The thermodynamic data obtained from the temperature dependence for the equilibrium:

$$\text{dimer} + CH_3OH \rightleftharpoons \text{monomer}$$

are summarized in Table IV.

$Rh_2(RCOO)_2(CO)_4$ (R = H or CH_3) occurs in two forms, as a dimer in crystalline state, in benzene, CCl_4 *i.e.* in non-polar solvents and as a monomer in alcohol solutions in which the bridge is split and the solvent molecule is attached.

References

1 D. N. Lawson and G. Wilkinson, *J. Chem. Soc.*, 1900 (1965).

2 P. Legzdins, R. W. Mitchell, G. Rempel, J. O. Ruddick and G. Wilkinson, *J. Chem. Soc. A*, 3322 (1970).

3 Yu. Ya. Kharitonov, T. Ya. Mazo and W. A. Knyazeva, 'Kolebatelnye Spektry Neorg. Khim.', 1971 (314), Nauka, Moscow, U.S.S.R.

4 P. M. Adams and P. J. Chandler, *J. Chem. Soc. A*, 588 (1969).
Yu. S. Varshavskii, M. M. Singh and N. A. Buzina, *Zh. Neorg. Khim.*, *16*, 1372 (1971).

5 H. Isci and W. R. Mason, *Inorg. Chem.*, *16*, 1950 (1977).