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The Cinnamate Complex of Rhodium(II) and some of its Adducts

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Rhodium cinnamate and some of its adducts were synthesized and characterized through IR and visible spectroscopy, thermogravimetry and magnetic susceptibility. The compounds have the general formula $Rh_2(Cin)_4 \cdot 2L$ *(Cin = cinnamate ion and L = pyridine, imidazole or dimethylamine). The IR spectra show that the carboxylate ions function as bridges between two rhodium atoms. Only one band appears in the visible spectra (600 nm region); this band follows the spectrochemical series reported previously for rhodium acetate adducts [1, 2]. When these compounds are heated under nitrogen atmosphere the final product at 310 °C is rhodium metal. Rhodium cinnamate is diamagnetic at 25 °C.*

Introduction

The rhodium carboxylates whose structure have been determined present a spacial arrangement analogous to that of copper acetate [3]. As indicated in Fig. 1, the L position can be occupied by a great variety of ligands, the color of the compounds being dependent on the donor atom. When this atom is oxygen, the color is green or blue-greenish; with nitrogen, the color is violet or pink, and with sulphur, orange.

The order of the wavelength shifts with respect to the donor atoms is: $O < S < sp^3N < sp^2N \cong As < S=O$

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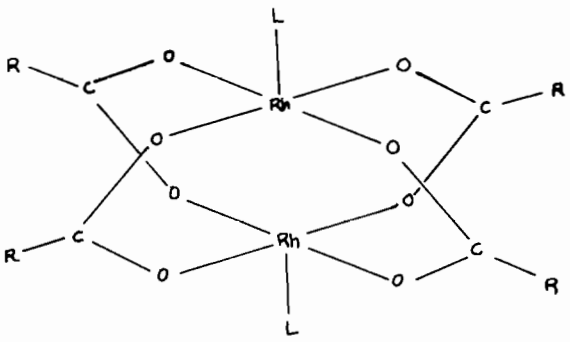

Fig. 1. The spatial arrangement of the rhodium carboxylates.

[2, 4, 5]. Bear *et al.* have reported evidence for anticancer activity of rhodium carboxylates [6–8] and the importance of these compounds as catalysts has been pointed out [16–18]. Most of the literature concerning rhodium carboxylates has, with some exceptions [5, 9, 10], focused on rhodium acetate. In this paper we report the synthesis and study of some of the properties of rhodium cinnamate and of its adducts with pyridine (Py), imidazole (Im) and dimethylamine (DMA).

Experimental

Synthesis of Rhodium Cinnamate

Sodium cinnamate was obtained by the following procedures: approximately 2.4 g (16 mmol) of cinnamate acid in 10 ml of water were neutralized with 25% aqueous sodium hydroxide, using phenolpthalein as indicator. The resulting aqueous solution was concentrated to a thick slurry on a hot plate and, after cooling slightly, approximately 100 ml of acetone were added with stirring. The salt was collected by filtration using a medium fritted-glass crucible, washed with 50 ml of acetone and dried under vacuum at room temperature. Rhodium cinnamate was synthesized by 1.5 hr reflux of 1.0 g (3.8 mmol) of $RhCl_3 \cdot 3H_2O$ (Fluka AG) and 6.5 g (38 mmol) of sodium cinnamate in 100 ml of absolute ethanol. During the course of the reaction the initially red solution gradually changed into a suspension of a green solid. After cooling to room temperature, the green solid was collected and washed three times by resuspension in 60 ml portions of water. After drying in a desiccator for 24 hours, the product was treated with ether and filtered. The solid was then dissolved in acetonitrile, the solution was filtered and evaporated to dryness under an air flux. The residual greenish-brown solid was heated under vacuum at 76 °C for 8–10 hours to yield a green solid. The compound is practically insoluble in alcohol, water and most common solvents. It is, however, soluble in acetonitrile, dimethylformamide and dimethylsulfoxide.

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Synthesis of the Adducts

$Rh_2(Cin)_4 \cdot 2Py$

100 mg (0.13 mmol) of rhodium cinnamate was treated with pyridine (approximately 1.5 ml, Merck), giving a brick-red solid. After sedimentation, the supernatant was removed with a pipette and the solid residue washed several times with ether and dried under vacuum. The compound is insoluble in acetonitrile, methanol, acetone and water, but soluble in dimethylformamide.

$Rh_2(Cin)_4 \cdot 2Im$

100 mg (0.13 mmol) of rhodium cinnamate dissolved in a minimum volume of acetonitrile (clarified by decantation) was treated with a concentrated solution of 0.04 g of imidazole (Aldrich), in absolute ethanol. After standing overnight in the refrigerator, the supernatant was removed with a pipette and the residual solid washed several times with 2 ml of ether. The product was maintained in a desiccator over anhydrous $CaCl_2$. The compound is practically insoluble in most common solvents, exceptions being acetonitrile and dimethylformamide.

$Rh_2(Cin)_4 \cdot 2DMA$

300 mg (0.39 mmol) of rhodium cinnamate dissolved in 18 ml of dimethylformamide (clarified by decantation) were treated with about 0.2 ml of dimethylamine (40% solution, Riedel–De Haën AG). After stirring, the solid product was washed several times with alcohol followed by ether.

Carbon, hydrogen and nitrogen were determined by the Microanalytical Laboratory, Instituto de Química, Universidade de São Paulo. Infrared spectra were recorded on a Perkin Elmer-180 spectrometer using fluorolube mulls contained between KBr windows. Visible absorption spectra were recorded on a Zeiss DMR-10 spectrometer. Thermogravimetric analyses were performed on a Perkin-Elmer TGS-1 apparatus at a heating rate of 10 deg min^{-1} under a nitrogen atmosphere. Magnetic susceptibility measurements were made by the Gouy method using an external weighing device [12].

Results and Discussion

Elemental analysis for rhodium cinnamate and its adducts, all of which are air stable, are reported in Table I. Thermogravimetric curves for rhodium cinnamate and its adducts are shown in Fig. 2.

Rhodium cinnamate is stable up to about 200 °C, where rapid decomposition takes place. The pyridine adduct exhibits liberation of axial ligands up to 200 °C. After the pyridine molecules have been completely liberated, the compound becomes practically stable up to the point of cage break-down, which occurs between 290–310 °C. For the other adducts, axial ligand loss is not so sharp. In all cases, the final residue is rhodium metal.

Infrared spectra

Figure 3 reproduces the infrared spectrum of $Rh_2(Cin)_4$, the frequencies of the principal IR bands being shown in Table II.

The difference between ν_{asym} and ν_{sym} for the carboxylate group indicates that these groups act as bridges joining two rhodium atoms [1, 13]. As in the acetate amine adducts [4], the ν_{asym} (CO_2^-) band, which occurs at 1545 cm^{-1} in the anhydrous rhodium cinnamate, shifts 10–13 cm^{-1} to higher wavenumbers in the adducts. On the other hand, the ν_{sym} band is displaced 5–10 cm^{-1} towards lower wavenumbers. In all the spectra, there is a characteristic absorption in the 1640 cm^{-1} region attributed to the C=C stretching mode [13]. The 1575, 1490 and 1445 cm^{-1} bands can be assigned to ring vibrations.

Electronic Spectra

As noted above, the colors of rhodium carboxylates depend on the nature of the donor atom of the axial ligand (L), O-donors giving green or blue-greenish compounds, N-donors pink compounds and S-donors orange complexes. Generally, the visible spectra present one (*ca.* 600 nm) or two (*ca.* 600 and 450 nm) bands. The lower energy band has been assigned to the transition $\pi^*(Rh-Rh) \rightarrow \sigma^*(Rh-Rh)$ [14]. The position of the band at *ca.* 600 nm depends

TABLE I. Analytical Data.

	Carbon		Hydrogen		Nitrogen	
	calc.	found	calc.	found	calc.	found
$Rh_2(Cin)_4$	54.43	54.08	3.55	3.48		
$Rh_2(Cin)_4 \cdot 2Py$	58.00	57.84	4.02	4.09	2.94	3.14
$Rh_2(Cin)_4 \cdot 2Im$	54.21	54.19	3.90	3.91	6.02	5.93
$Rh_2(Cin)_4 \cdot 2DMA$	54.31	53.85	4.79	4.98	3.17	3.40

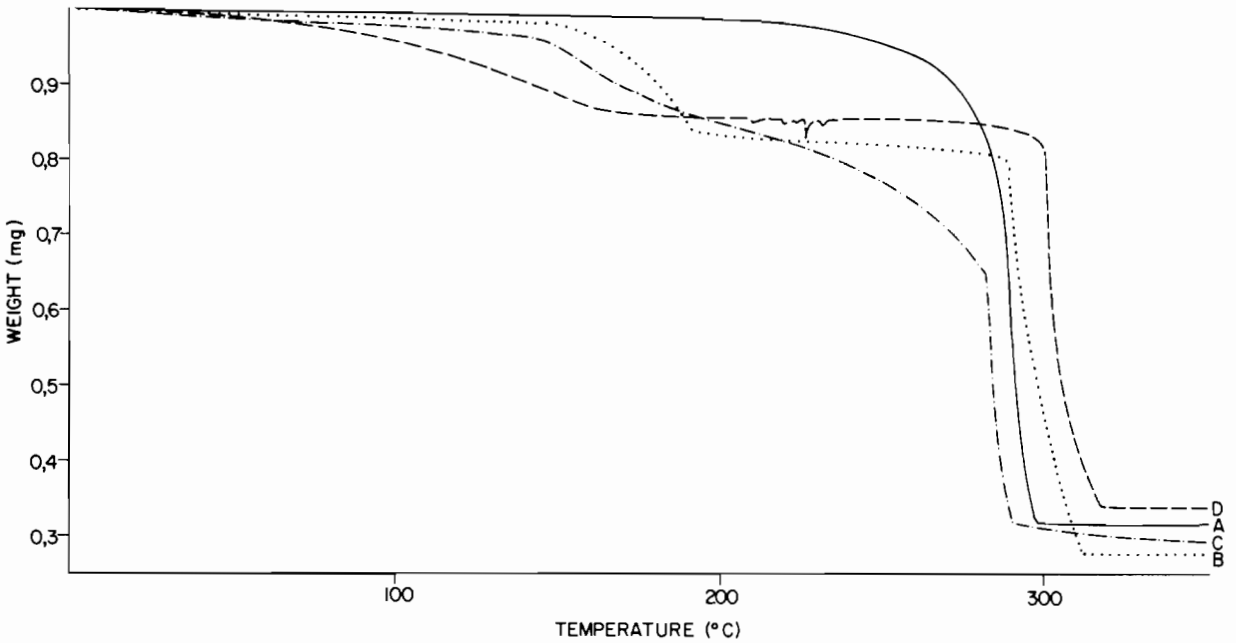

Fig. 2. Thermogravimetric curves for: A, rhodium cinnamate (0.948 mg); B, pyridine adduct (0.923 mg); C, imidazole adduct (0.907 mg) and D, dimethylamine adduct (0.868 mg).

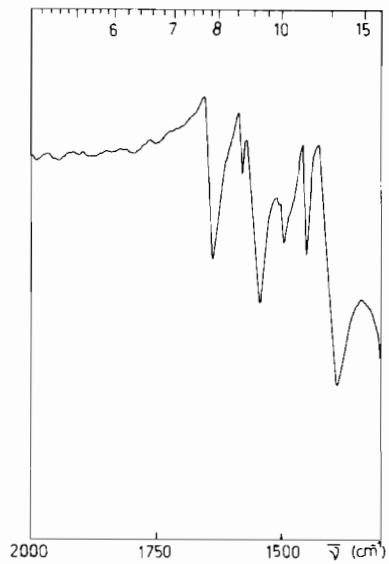

Fig. 3. IR spectrum of $Rh_2(Cin)_4$ in the 2000–1200 cm^{-1} region.

on the axial ligand because the σ^* orbital is directed outwards along the metal–metal bond. The other band, at *ca.* 450 nm, is dependent on the nature of the bridging ligand ($RCOO^-$), as indicated by a comparison of literature values for acetate [1] and salicylate [5]. The electronic absorption spectral data for rhodium cinnamate and its adducts are listed in Table III.

Although not soluble in most common solvents, anhydrous rhodium cinnamate is soluble in coordinating solvents such as DMF, DMSO, acetonitrile, pyridine, *etc.* The solution in DMF is green while those in acetonitrile and pyridine are pink, consistent with the progressive shift of λ_1 to shorter wavelength going from DMF to acetonitrile to pyridine (Table III). The shift to shorter wavelength upon changing the donor atom from oxygen to nitrogen is consistent with the fact that this absorption arises from a d–d transition with the orbital splitting following the usual spectrochemical series, *i.e.*, the spectral shifts being related to the donor atom in the general order:

TABLE II. IR Data in cm^{-1} for $Rh_2(Cin)_4 \cdot 2L$.

	ν_{asym} (OCO)	ν_{sym} (OCO)	$\Delta\nu$	C=C stretch.	Ring
$Rh_2(Cin)_4$	1545	1395	150	1640	1580, 1495, 1445
$Rh_2(Cin)_4 \cdot 2Py$	1552	1385	167	1635	1570, 1490, 1445
$Rh_2(Cin)_4 \cdot 2Im$	1555	1390	165	1635	1575, 1490, 1445
$Rh_2(Cin)_4 \cdot 2DMA$	1558	1385	173	1635	1575, 1490, 1445

TABLE III. Visible Absorption Spectral Data for Rhodium Cinnamate and its Adducts.

Compound	Solvent	Absorptions λ_1	λ_2	ϵ
$Rh_2(Cin)_4$	DMF	583		329
	Acetonitrile	545	455(s)[a]	276
	Pyridine	517		295
$Rh_2(Cin)_4 \cdot 2Py$	DMF	538		285
$Rh_2(Cin)_4 \cdot 2Im$	DMF	550		250
$Rh_2(Cin)_4 \cdot 2DMA$	DMF	550		235

[a]s = shoulder.

$O < S < sp^3N < sp^2N \cong As < \overset{\diagdown}{S}=O$ [1]. Of particular interest is the behavior of the adducts in DMF solutions. The fact that the colors are maintained implies that there are no substitutions of the axial positions. The wavelength change from 538 nm in the py adduct to 550 nm in the Im and DMA adducts suggests that the higher electron acceptor capability of py is a prevailing factor [19]. The magnetic moment of 0.4 MB at 25 °C demonstrates that rhodium cinnamate is diamagnetic, like other rhodium carboxylates [15], with strong interaction between the two rhodium atoms.

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References

1 S. A. Johnson, H. R. Hunt and H. M. Newmann, *Inorg. Chem., 2*, 960 (1963).
2 J. Kitchens and J. L. Bear, *J. Inorg. Nucl. Chem., 31*, 2415 (1969).
3 M. A. Porai-Koshits and A. S. Antsyshkina, *Dokl. Akad. Nauk SSSR, 146*, 1102 (1962).
4 G. Pneumatikakis and N. Hadjiliadis, *J. Chem. Soc. (Dalton), 4*, 596 (1979).
5 R. N. Shchelokov, A. G. Maiorova, G. N. Kuznetsova, I. F. Golovaneva and O. N. Evstaf'eva, *Russ. J. Inorg. Chem., 25*, 1049 (1980).
6 R. G. Hughes, J. L. Bear and A. P. Kimball, *Proc. Amer. Assoc. Cancer Res., 13*, 120 (1972).
7 A. Erck, L. Rinen, J. Whileyman, I. M. Chang, A. P. Kimball and J. L. Bear, *Proc. Soc. Exp. Biol. Med., 145*, 1278 (1974).
8 J. L. Bear, H. B. Gray, Jr., L. Rainen, I. M. Chang, R. Howard, G. Serio and A. P. Kimball, *Cancer Chemother. Rep., 59*, 611 (1975).
9 R. N. Shchelokov, A. G. Maiorova, S. S. Abdullaev, O. N. Evstaf'eva, I. F. Golovaneva and G. N. Emel'yanova, *Russ. J. Inorg. Chem., 26*, 1774 (1981).
10 M. D. Joesten, R. Najjar and G. Hebrank, *Polyhedron, 1*, 637 (1982).
11 A. I. Vogel, Textbook of Practical Organic Chemistry (edited by Longman, London), 4th ed., p. 800 (1978).
12 H. E. Toma, A. M. C. Ferreira and V. L. Osorio, *J. Chem. Educ., 60*, 600 (1983).
13 N. Kumar and A. K. Suri, *J. Indian Chem. Soc., LVIII*, 738 (1981).
14 D. S. Martin, Jr., T. R. Webb, G. A. Robbins and P. E. Fanwick, *Inorg. Chem., 18*, 475 (1979).
15 V. I. Belova and Z. S. Dergacheva, *Russ. J. Inorg. Chem., 16*, 1626 (1971).
16 A. J. Anciaux, A. J. Hubert, A. F. Noels, N. Petiniot and P. Teyssié, *J. Org. Chem., 45*, 695 (1980).
17 A. J. Anciaux, A. Demonceau, A. F. Noels, A. J. Hubert, R. Warin and P. Teyssié, *J. Org. Chem., 46*, 873 (1981).
18 A. Demonceau, A. F. Noels, A. J. Hubert and P. Teyssié, *J. Chem. Soc. Chem. Commun.*, 688 (1981).
19 R. J. Sundberg and R. B. Martin, *Chem. Rev., 74*, 471 (1974).