Synthesis and Structure of the Complex Tetra-μ-prolinatodirhodium(II)

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Abstract

The dinuclear Rh^{II}–Rh^{II} complex with proline $[Rh_2(pro)_4][NEt_4]_2$ was synthesized and its structure studied by means of spectroscopic (IR, EPR and ESCA) and magnetochemical methods. It was shown that two proline molecules serve as bridging ligands, while the other two are only axially coordinated through their N atoms.

Introduction

Bear and co-workers [1–3] demonstrated that tetrakis-μ-acetatodirhodium(II), $[Rh_2(O_2CMe)_4]$, exhibits anticancer activity against many types of tumours. The interactions of this complex with several molecules of biological importance have also been studied by the same workers [3, 4]. They found that the complex inhibited DNA synthesis and that it reacted mainly with poly-A but not with poly-C and poly-G [3]. They also reported on the formation constants of the complexes with ado-5′-P, ado-5′-PP ado-5′-PPP (adenosine mono-, di- and triphosphate), imidazole, etc. [5–7]. The same group also found that cysteine causes the breakdown of the cage structure of the rhodium(II) complexes and reported on the behaviour after exposure to rhodium-(II) carboxylates [4] of free SH groups containing enzymes. Pneumatikakis and co-workers studied the interaction of $[Rh_2(O_2CMe)_4]$ with nucleosides and nucleotides and reported on the nature of the products formed and the binding sites of the ligands [8, 9]. They also found that cysteine and free SH-containing cysteine derivatives cause the breakdown of the carboxylate cage and isolated monomeric Rh(II)–cysteine complexes [10].

In this paper we report on the reaction of $[Rh_2(O_2CMe)_4]$ with L-proline in alkaline solution. The main objective was the breakdown of the carboxylate cage and the preparation of prolinato–Rh(II) monomeric or dimeric complexes.

Experimental

Materials

L-Proline and $RhCl_3 \cdot aq$ were purchased from Fluka A.G. and used without further purification. The complex $[Rh_2(O_2CMe)_4]$ was prepared according to the literature [11].

Preparation of Bis(tetraethylammonium)tetra-μ-prolinatodirhodate (Rh^{II}–Rh^{II})

L-Proline (0.441 g, 4 mmol) was dissolved in 10 ml water and neutralized with 8 ml 1 N KOH. $[Rh_2(O_2CMe)_4]$ (0.445 g, 1 mmol) was added to the solution and the mixture heated to 50 °C under nitrogen for 1 h. Tetraethylammonium bromide (1.051 g, 5 mmol) was then added and the solution evaporated to dryness at 50 °C under reduced pressure. The residue was taken up with DMF (10 ml) and filtered. The compound was precipitated from the filtrate with excess ether. Yield *ca.* 65%. *Anal.* Calc. for $Rh_2C_{52}H_{108}N_8O_8$: C, 52.91; H, 9.38; Rh, 17.45. Found: C, 53.12; H, 9.38; Rh, 17.25%. $\Lambda_M = 152$ $Ohm^{-1}\,cm^2\,mol^{-1}$ (10^{-3} M Rh in DMF).

Physical Measurements

The ESCA measurements were carried out in a UHV chamber of an ESCALAB-MkII electron spectrometer (VG Scientific). The sample to be studied was pressed in stainless steel sample holders, the pellets obtained being 12 mm in diameter, with a thickness of 1 mm. The pressure in the analysis chamber of the spectrometer during the measurements was 1×10^{-7} Pa. The photoelectron spectra were excited with Mg Kα radiation (1253.6 eV), the instrumental resolution being 1.0 eV as measured by full-width at half maximum (FWHM) of the Ag $3d_{5/2}$

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photoelectron peak. In order to reduce possible damage to samples by X-ray irradiation, they were cooled down to 180 K during the measurements. The accuracy of determination of the binding energy under these conditions was ±0.15 eV. The photoelectron peak intensities were evaluated as a ratio of photoelectron peak area and corresponding photoelectron cross-section [12]. No corrections for energy dependence of inelastic mean free paths of electrons and transmission function of the analyser were made.

During the measurements the sample surface was charged up to 4–5 eV positive as a result of the low conductivity of the samples studied. As an energy reference line, the 285.0 eV carbon peak was used [13].

The magnetic susceptibility measurements were carried out over the temperature range 140–300 K in an argon atmosphere, according to Faraday's method.

The IR and EPR spectra were obtained on a Perkin–Elmer 983 (CsI discs) in the range 4000–200 cm^{-1} and on an ERS 220 (GDR) [Mn(II) g-marker] spectrometer, respectively.

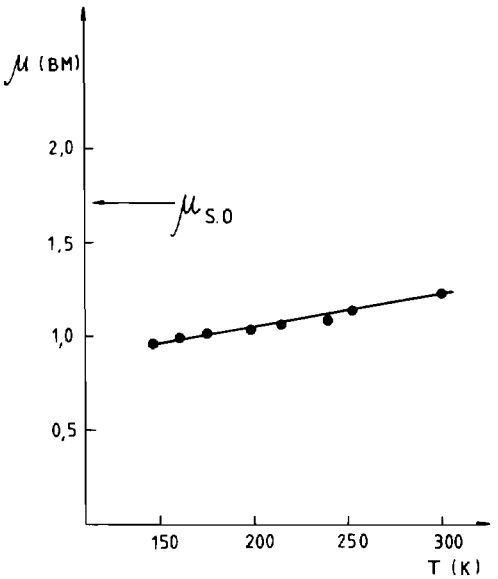


Fig. 1. The dependence of the effective magnetic moment (μ_{eff}) on temperature.

Results and Discussion

The elemental analysis and conductivity data are indicative of the formation of the tetra-μ-prolinato-dirhodate(II) complex.

The complex is paramagnetic, showing a slightly asymmetric EPR singlet line at ambient temperature ($g = 1.95 \pm 0.01$, polycrystalline sample), thus proving the oxidation state +2 for rhodium. As no hyperfine splitting due to ^{103}Rh ($S = 1/2$) was observed, no definite conclusions could be drawn concerning the existence of either mono- or dinuclear Rh(II), or mixed valence Rh^{II}–Rh^{III} complexes. For that reason, magnetochemical and ESCA measurements were performed. The temperature dependence of the effective magnetic moment (μ_{eff}) is presented in Fig. 1. Its value varies slightly with temperature and is rather lower than the spin-only value ($\mu_{s.o.} = 1.73$ BM).

The data obtained show antiferromagnetic exchange, thus ruling out both monomeric and mixed valence structures and suggest a direct Rh^{II}–Rh^{II} bond formation.

The ESCA data (Table I) are in agreement with this conclusion. Only two peaks due to Rh $3d_{5/2}$ and Rh $3d_{3/2}$ are present, while for Rh^{II}–Rh^{III} two doublets should be observed [14, 15]. Both the binding energy values (309.4 and 314.0 eV respectively) and the line-width ($E_{1/2}$) of the Rh $3d_{5/2}$ peak (2.5 eV) observed are typical of Rh^{II}–Rh^{II} complexes [14].

The ESCA and IR data (Table II) provide additional information concerning the coordination modes of the ligand and its structure in the solid state as well. The data obtained for the free ligand show the existence of two forms of the amino acid in the solid state: the appearance of two peaks for N 1s in the ESCA spectrum; the presence of $\nu(COO^-)_s$, $\nu(COO^-)_{as}$ and $\nu(^+NH_2)$ assigned to a zwitterion structure, and ν(CO) of the –COOH group and ν(NH) in the IR spectrum. The ESCA data allow the percentage of the zwitterion structure to be roughly evaluated, the latter being approx. 80%.

TABLE I. Selected IR Frequencies for L-Proline and $[Rh_2(pro)_4]^{2-}[Et_4N]_2$

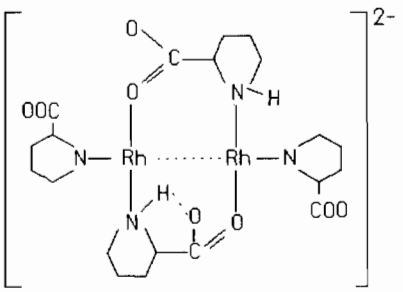
	$\nu(COO^-)_s$	$\nu(COO^-)_{as}$	$\nu(C{=}O)^a$	$\nu(^+NH_2)$	ν(NH)	ν(NH···O)
L-Proline	1445	1600br	1700sh	2960	3110	
$[Rh_2(pro)_4][Et_4N]_2$	1460 1480sh 1490sh	1580sh 1610 1630sh				3430v.br

[a]–COOH group.

TABLE II. ESCA Data for the Free Ligand and the Complex [Binding Energies (eV ±0.15 eV]

	C 1s (O=C(O))	C 1s (O=C(O–M))	C 1s (O=C(O–H)(O–M))	Rh $3d_{5/2}$	Rh $3d_{3/2}$	N 1s(>NH)	N 1s(>$^+$NH$_2$)	N 1s($^+$NEt$_4$)
L-Proline	287.0					399.3 (20%)	400.4 (80%)	
$[Rh_2(pro)_4][Et_4N]_2$	287.4	292.6	295.4	309.4	314.0	399.6 (70%)		401.8 (30%)

The ESCA data for the complex show the coordination through both the N atom and the carboxyl group of the ligand. The presence of only one N 1s peak* due to the ligand indicates that all four nitrogen atoms (from the four ligands present in the inner coordination sphere) are coordinated to the metal ions. The binding energy of the peak (399.6 eV) corresponds to that of other coordinated N-containing ligands [15–17]. Rather surprisingly, however, three different C 1s peaks (assigned to different –COOH groups) were observed. Most probably the lowest peak (287.4 eV) is due to the –COO– group from two equatorially coordinated proline molecules, which act as monodentate ligands (Structure **I**). The other two C 1s peaks might be assigned to the carboxyl groups of the two proline molecules which act as bridging ligands (Structure **I**).



I

In one of the bridging proline molecules, intra-hydrogen-bond formation should be assumed too, as indicated by the IR data obtained (see Table II). It should be mentioned that due to steric reasons intra-hydrogen-bond formation is possible only in coordinated D-proline. The latter might be formed as a result of racemization of the initial L-proline when neutralized with 1 M KOH. Evidently the peak with the highest binding energy (295.4 eV) should be assigned to the carboxyl group engaged both in coordination and hydrogen bonding.

The IR data obtained (see Table I) are also in agreement with this assumption. The lack of >$^+$NH$_2$ and >NH vibrations in the IR spectrum of the complex indicates the proton replacement, *i.e.* on N–M bond formation. At the same time a set of three different symmetric and asymmetric C=O vibrations are present, as well as a very broad band in the range 3500–3200 cm^{-1}, typical for hydrogen-bond formation.

*Evidently the peak with higher binding energy corresponds to the $[N(CH_3)_4]^+$, characterized with electron deficiency and being approx. one-third of the total N content of the complex.

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