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Synthesis and Structure of Diaquo-tetra-μ-β-alaninatoniumdirhodium(II) Tetraperchlorate Dihydrate

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Tetra-μ-carboxylatodirhodium(II) complexes have been the subject of a number of investigations reported in recent literature. This renewed interest appears to result from the unusual nature of the rhodium–rhodium interaction [1–3], the axial bonding ability of these compounds [1–4], and the carcinostatic activity these complexes display [5, 6]. The only tetra-μ-carboxylatodirhodium(II) compounds that have been reported in the literature to date have not contained functional groups as part of the carboxylate side-chains. For some time we have had an interest in synthesizing amino acid derivatives of the rhodium(II) dimer in order to evaluate their biologic activity, as well as investigate their potential use as chelators of other metal ions. Recently, Cotton and co-workers reported on the successful synthesis and crystal structure of $Mo_2(gly)_4Cl_4 \cdot xH_2O$ [7], a compound structurally analogous to the dimeric rhodium (II) compounds. In this paper, we report the synthesis and crystal structure of the β-alanine complex of Rh_2^{4+}.

Experimental

Reagents

All solvents and organic chemicals were of the highest purity available from Aldrich Chemical Co., Milwaukee, Wis., and were used without subsequent purification. Rhodium(III) chloride trihydrate, purchased from Matthey Bishop Inc., Malvern, Pa., was recrystallized from ethanol before use in order to remove a contaminating ethanol-insoluble fraction.

Synthesis of t-Butyloxycarbonyl-β-alanine [$HOCO(CH_2)_2NHCOCOC(CH_3)_3$]

β-Alanine was reacted with excess 2-tert-butyloxycarbonyloxyimino-2-phenylacetonitrile (BOC-ON) and excess triethylamine for 1 hr at 45 °C in an acetone/water mixture in accordance with the procedure previously detailed by Itoh and co-workers [8]. Following removal of the acetone by distillation, the crude water-soluble product was purified by the method of Isowa and co-workers [9]. Briefly, an aqueous solution of the crude product was extracted with ethylacetate, acidified to pH 2 with dilute HCl and extracted into ethylacetate. The ethylacetate solution was washed with 5% HCl then with a NaCl-saturated aqueous solution and dried over anhydrous sodium sulfate. Pure product was obtained by crystallization from anhydrous diethylether. The product was characterized by ^1H NMR and melting point determination (mp 74–75 °C; Lit [10], 75–76 °C).

Synthesis of Tetra-μ-boc-β-alaninatodirhodium(II) [$Rh_2(OCO(CH_2)_2NHCOCOC(CH_3)_3)_4$]

t-Butyloxycarbonyl-β-alanine (1.5 g, 8.0 mmol) was added to 25 mL of absolute ethanol contained in a two neck 250 ml round bottom flask. While purging the reaction vessel with argon, sodium ethoxide, freshly prepared by reacting metallic sodium (0.18 g, 8.0 mmol) with 10 mL absolute ethanol, was added dropwise, followed by the addition of $RhCl_3 \cdot 3H_2O$ (0.70 g, 2.7 mmol). The resulting solution was heated to a gentle reflux for ninety minutes or until the solution became dark green in color. The crude product was then stripped of solvent, redissolved in 60 mL of diethyl ether, and washed with 15 mL portions of water until the aqueous layer was clear. Following removal of the diethyl ether, the crude product was redissolved in a minimal volume of ethyl acetate and loaded onto an alumina (80–200 mesh) column (40 × 2 cm). The pure product, blue-green in solution, was obtained using a methanol–ethyl acetate 1:1 eluent. Yield ~ 65%.

Synthesis of Diaquo-tetra-μ-β-alaninatoniumdirhodium(II) Tetraperchlorate Dihydrate [$Rh_2(OCO(CH_2)_2NH_3^+)_4(H_2O)_2](ClO_4)_4 \cdot 2H_2O$

To a 10 mL solution of methanol and tetra-μ-boc-β-alaninatodirhodium(II) (0.5 g, 0.5 mmol) at 0 °C was cautiously added 5.0 mL of 70–72% perchloric acid. This solution was then slowly warmed to 45 °C and maintained at that temperature until precipitation was completed. The finely divided blue-green crystals were collected and washed with three 10 mL portions of diethyl ether. Crystals for X-ray analysis were obtained from a methanol–water saturated ethyl acetate 1:1 solution.

Crystal Data

A transparent, dark green plate was cleaved into a smaller, nearly square cross-section, plate of dimensions *ca.* 0.5 × 0.5 × 0.25 mm. The latter was glued onto a glass fibre attached to a translation goniometer (x, y, z) head and mounted on a computer-controlled Enraf-Nonius CAD-4 diffractometer. The crystal was sprayed with an acrylic polymer layer (Krylon) to

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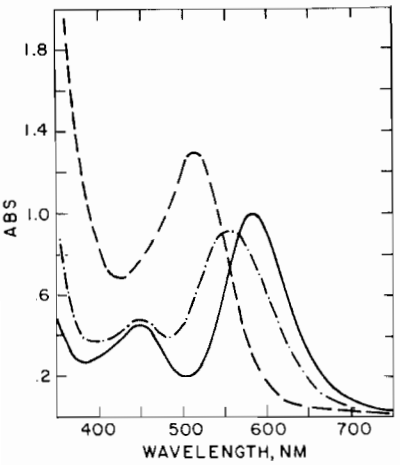

Fig. 1. The spectra illustrated above were obtained in aqueous solution on a Beckman Model 26 spectrophotometer equipped with one centimeter cells containing 3.0 m*M* $Rh_2(OCO(CH_2)_2NH_3)_4(ClO_4)_4$ and various mol ratios of pyridine; no pyridine, (——); 3.0 m*M* pyridine (–·–); large excess of pyridine, (– –).

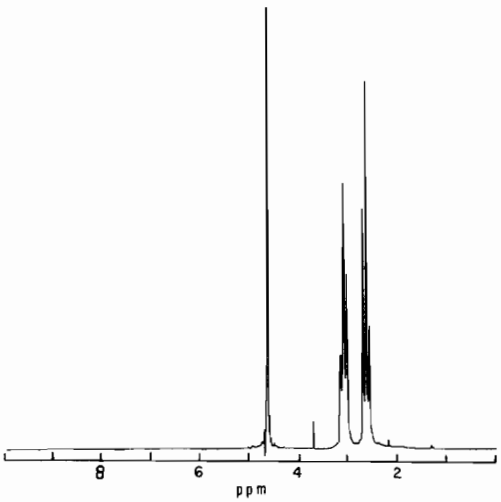

Fig. 2. The ^1H NMR spectra of $Rh_2(OCO(CH_2)_2NH_3)_4(ClO_4)_4$ obtained following three exchanges in D_2O was performed on a Varian model XL-100 NMR spectrometer in D_2O. The triplet positioned at 2.65 ppm is assigned to the β protons while the second triplet at 3.11 ppm is assigned to the α protons. All positions are relative to DSS.

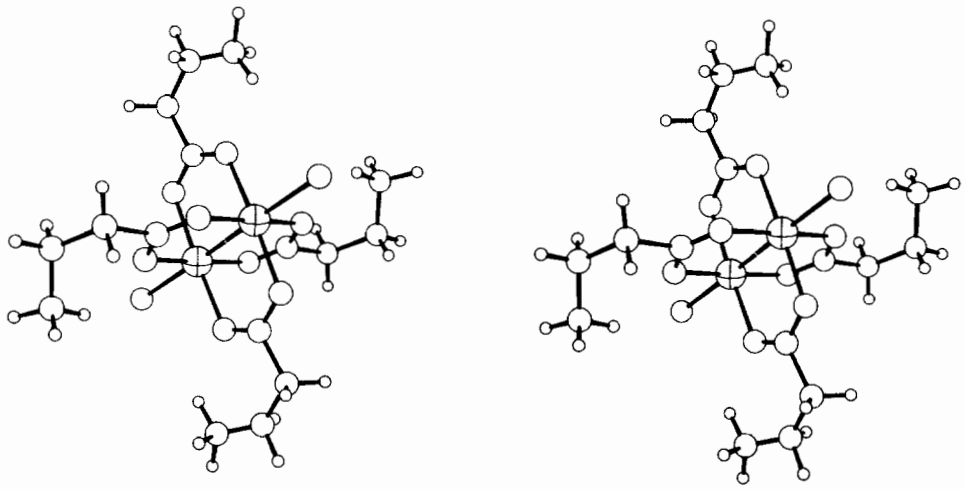

Fig. 3. This is an ORTEP sterio plot of the configuration of the $Rh_2(H_2O)_2(OCO\text{-}CH_2\text{-}CH_2\text{-}NH_3^+)_4^{4+}$ cation found in the lattice of $[Rh_2(H_2O)_2(OCO\text{-}CH_2\text{-}CH_2\text{-}NH_3)_4](ClO_4)_4 \cdot 2H_2O$. For the sake of clarity and to avoid overlapping of atoms in the viewer's line of sight, we have used thermal parameters of arbitrary size. Hydrogen atoms are depicted at their theoretical positions. The Rh–Rh distance is 2.38 Å, the mean Rh–O (carbox.) distance is 2.05 Å and the Rh–O(H_2O) distance is 2.34 Å. The angle between adjacent planes (O_2C) of carboxylate ligands is 90°. Distances and angles in the amino acid ligands are normal. Finally, the distance of closest approach between the terminal –NH functional groups, as found in the lattice, is 5.60 Å. However, using scaled models, one can show that they can approach as closely as 2.8 Å, making them, at least potentially, good bidentate ligands for other metal atoms.

prevent it from decomposing in the X-ray beam, which apparently occurs because of the loss of water of hydration found in the lattice (see chemical formula). The unit cell dimensions were obtained from the automatic centering of 25 reflections: a = 14.431(17), b = 19.176(5), c = 13.369(15) Å; V = 3699.65 Å, d(calc.) = 1.788 g cm^{-3} for Z = 4 molecules/unit cell. The space group is Pccn. The data (a total of 2846 reflections) were collected in the range of $4.0° < 2\theta < 45.0°$, of which 1143 were found to have $I > 3\sigma(I)$ and were, therefore, used in data processing and refining of the structural parameters. The techniques employed in data collection and processing have been described in detail else-

where [13, 14]. MoKα radiation was used throughout. The current value of the agreement index, R(F), is 0.085.

Results and Discussion

The visible spectra of an aqueous solution of diaquo-tetra-μ-β-alaninatoniumdirhodium(II) tetraperchlorate, illustrated in Fig. 1, reveals an absorption maxima, λ_1, centered at 582 nm and a second weaker band, λ_2, at 447 nm. These two absorption bands are typical of tetra-μ-carboxylatodirhodium(II) compounds. For example, the acetato complex displays absorption maxima at 587 nm and 447 nm [11], while all tetra-μ-carboxylatodirhodium(II) complexes show a characteristic blue shift of λ_1 upon the formation of axial adducts with nitrogen donor ligands [12]. As seen in Fig. 1, the addition of pyridine to an aqueous solution of the β-alanine derivative resulted in a shift of the absorption maxima of λ_1 to shorter wavelengths, typical of all carboxylate bridged rhodium(II) species. Also, the magnetic equivalence of the carboxylato ligands is illustrated by the expected ^{1}H NMR (Fig. 2) of the β-alanine derivative.

The results of X-ray analysis on this compound (Fig. 3) show that the molecule contains a tetravalent cation consisting of a pair of Rh(II) axially bound by a pair of H_2O molecules and bridged by four β-alanine ligands. This cation, shown in Fig. 3, has a nearly perfect-square pyramidal arrangement around each of the Rh(II) cations, if one does not count the potential Rh–Rh interaction. There is a set of three independent perchlorate anions in the asymmetric unit: (a) one located at a general position of the lattice, (b) two located at special positions of the space group; namely, at 1/4, 1/4, 0.879 and 3/4, 1/4, 0.096. Finally, the Rh(II) cations are located at inversion centers (1/2, 0, 0). There is an interesting kind of disorder in all the perchlorates which, much to our surprise, are not hydrogen-bonded to the terminal $-NH_3^+$ moieties. The reader can see that, instead, the hydrogen bonds involving the $-NH_3^+$ are to the oxygens of the carboxylic groups of the amino acids.

Acknowledgements

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