

OPTICALLY ACTIVE COORDINATION COMPOUNDS—51.¹ THE CIRCULAR DICHROISM OF *Λ*-*fac*-TRIS-(*S*- ALANINATO)RHODIUM(III)

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Abstract—The circular dichroism spectrum in solution of the non electrolyte Λ -*fac*-[Rh(*S*-ala-O⁻)₃], normally insoluble but salted-in to water, is reported and discussed.

The electroneutral tris-complexes of the bidentate anions of natural amino acids like *S*-alaninate, [M(*S*-ala-O)₃], with octahedral metal ions (M) like chromium(III),² cobalt(III)³ or rhodium (III),³ form four diastereoisomers. These are Λ - and Δ -meridional, and Λ - and Δ -facial.

Many among them are relatively poorly soluble in water. We find that, surprisingly, this limited solubility may in many cases be greatly enhanced by “salting-in”, using simple salts. This is behaviour reminiscent of the globular proteins like haemoglobin, more soluble in brine than in water, by contrast with many other proteins and most simpler organic non-electrolytes which are less soluble in brine than in water (they are “salted-out”). These surprising new effects on solubility are of potential significance because of the uniform ubiquity of amino acids in natural media.

Several such systems have been studied, though only two reports^{3,4} relate to the compounds of rhodium(III). For *S*-alaninate itself, it seems that the most accessible product which is essentially insoluble in water is Λ -facial-[M(*S*-ala-O⁻)₃], for M = Rh, Co and Cr (the three are isomorphous⁴). For “ β ” (i.e. facial)[Cr(glyO⁻)₃], the fact⁴ that its isotropic absorption maximum in the solid state differs from that in acid solution was taken to indicate chemical reaction for the chromium compound on dissolution. That glycinate is of course racemic.

A recent report² comments on the similar apparent variability of properties of the least soluble diastereoisomer of the homologous chromium(III) compound of *S*-alaninate. That is both thermally and photochemically fairly labile, so we report here our findings upon the relatively immutable rhodium analogue, studied in solutions made by the method, newly developed here, of “salting-in”. Its circular dichroism (CD) is reported for the first time, though the fact that the CD spectrum of a KBr disc and of fresh solutions in sulphuric or trifluoroacetic acids all differed, the last changing with time, had been mentioned.⁴

Spectroscopic properties for Λ -*fac*-[M(*S*-ala-O⁻)₃] had been reported,^{2,4} either for solids, dispersed in potassium halide discs, or (where M = Cr) for solutions² in DMSO, but not, of course, for neutral aqueous media. We are now able to remedy that, through “salting-in”.

EXPERIMENTAL

Electronic spectra were measured using a Uvikon 930 (Kontron) spectrophotometer. CD spectra were measured using a Roussel-Jouan “Dichrographe” Mark V, calibrated with camphor.

Materials

BDH reagent grade magnesium chloride and silver nitrate were used. Stock solutions of MgCl₂ (5 M) and AgNO₃ (3 M) were prepared in deionized water. The least soluble diastereoisomer of tris-*S*-

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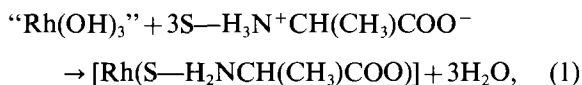
α -alaninorhodium(III) was prepared as described previously.³ The yields for the desired isomer were 17%. It had λ 338 and 283 nm (lit.⁴ 340 and 282 nm).

Procedure

A series of solutions of the compound of rhodium (4×10^{-4} – 2×10^{-3} M) were prepared in 5 M MgCl_2 . The UV and CD spectra of these solutions were scanned at 18°C. From the slope of the linear plot of absorbance at 338 nm against concentration, $\epsilon = 347$. Similarly, from the slope of the plot of CD absorbance, $\Delta\epsilon_{322} = 1.01$. The CD spectra of the same compound at various concentrations (4.6×10^{-4} – 2.3×10^{-3} M) in 3 M AgNO_3 were measured.

RESULTS AND DISCUSSION

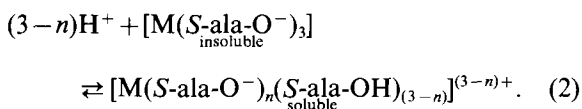
We confirm that, following reaction (1) of "rhodium(III) hydroxide" with *S*-alanine,



a mixture of isomers forms.³ The least water-soluble was obtained after exhaustive washing with water: typical yields were 17% (the original report³ had 16%). This *Λ-fac*- $[\text{Rh(S-ala-O}^-)_3]$ had properties agreeing well with those reported originally,³ including solubility in 50% (v/v) sulphuric acid.

A $4d^6$ chromophore $[\text{RhN}_3\text{O}_3]$ of the kind studied here would indeed be expected from the baricentre rule (averaging RhN_6 of $[\text{Rh(en)}_3]^{3+}$ at 300 nm and RhO_6 of $[\text{Rh(C}_2\text{O}_4)_3]^{3-}$ at 400 nm) to absorb at *ca* 340 nm in its lowest energy spin-allowed *d-d* bands, as was found (Fig.1).

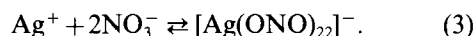
The cobalt and rhodium eutropes are essentially insoluble in water, but dissolve in 50% sulphuric acid, presumably through one or both of two causes. The first would be protonation of one or more of the peripheral oxygen atoms (2):



The protonated forms ($3 \geq n \geq 1$) would be soluble. Because the facial isomer has three-fold equivalence of the possible sites of protonation, there is only one chemical species with $n = 1$, one with $n = 2$ and one with $n = 3$. The situation for the less symmetrical *mer*-isomer would be less simple: for $n = 3$, there is one micro-equilibrium only. Lifschitz commented⁵ on the marked solvent effects on the Cotton effect (in optical rotatory dis-

persion) of the α (meridional) isomers of $[\text{Co(S-ala-O)}_3]$ in 50% sulphuric acid as against water.

The second possible reason for the dissolution is not chemical reaction as in (2), but specific cybotactic solvation, whereby the solvated protons of the acid $(\text{H}_{2n+1}\text{O}_n)^+$, with $1 \leq n \leq 6$, act much like the ammonium salt of that same acid in producing structured regions in the water which surrounds the ions. These structured regions in turn fit (solvate) the tris-amino acid solute $[\text{M(S-ala-O}^-)_3]$ better than unperturbed water does. The latter phenomenon, acids exerting a "salt effect" on solubility, albeit of salts rather than the kinetically inert quasi-organic non-electrolyte salted-in here, had been described⁶ in accounting for the increase in solubility of silver chloride in nitric acid. This was classically compared to the enhancement by sodium nitrate, i.e. ascribed to the effect on activity of hydroxonium nitrate. This may indeed be a major influence. However, that classical explanation of the analytical phenomena in terms of activity coefficients may need revision, at least in part. Silver dinitrate ions exist:⁷ their salt with the *trans*-dibromotetrapyridinerhodium(III) cation has been characterized, and it is conceivable that the extra equilibrium (3) in solution may underlie at least part of the effect on the solubility of silver chloride (via its K_{sp}),



As we have found⁸ for many other stable uncharged "inner" complexes of amino acids, $[\text{M}(\alpha)_n]$, where n is equal to the oxidation state of the metal ion, it is not only protons which cause their dissolution. Typically, for $\text{M} = \text{Cu}$, $n = 2$, $\alpha = \text{glyO}^-$ etc. the solubility in water increases sharply⁹ on adding simple salts like MgCl_2 , CaCl_2 , KBr or AgNO_3 . From such solutions, numerous representatives of a new class of compound have crystallized. This class embodies the combination of a non-electrolyte complex compound, $[\text{M}(\alpha)_n]$, with a simple salt $\text{M}'\text{X}_6$. Examples include $[\text{Cu}(\text{glyO}^-)_2] \cdot 2\text{AgNO}_3$,⁹ $[\text{Cu}(\text{glyO}^-)_2] \cdot \text{MgCl}_2 \cdot 7\text{H}_2\text{O}$ ⁸ and $[\text{Cu}(\text{picO})_2] \cdot \text{KNCO}$ ¹⁰ (picO denotes α -picolinate, i.e. 2-carboxylatopyridine). In these labile cupric systems (though they are stable in pure water), the environment of the copper ion may alter. For instance, the second compound is actually⁹ the salt $[\text{Mg}(\text{OH})_2]_6[\text{Cu}(\text{glyO}^-)_2\text{Cl}_2] \cdot \text{H}_2\text{O}$. However, in others, the added metal salt causes no change in the first coordination sphere of the copper ion.

For the present rhodium(III) system, very inert indeed, we take this to be the case for several reasons: (i) the solubility changes remarkably, but in much the same degree for several salts; (ii) the rhodium(III) compounds [and indeed their

cobalt(III) eutropes] are recovered unchanged by adding water to their solutions in magnesium chloride, silver nitrate and so on. The molar CD (Fig. 1) of Λ -*fac*-[Rh(S-ala-O⁻)₃] in 5 M magnesium chloride or in 3 M silver nitrate is independent of its concentration (i.e. it obeys the chiroptical counterpart of the Beer–Lambert law).

The CD spectrum in 3 M silver nitrate solution for the longest wavelength band is very similar quantitatively to that in Fig. 1: the second band (of ¹A₁g → ¹T₂g parentage in the O_h point group but assigned to ¹A₁ → ¹E_g here) could not be measured in the concentrated silver nitrate solutions because of the high background absorption due to nitrate. The CD spectrum of the other facial isomer, soluble in water, β(+)[Rh(S-ala-O)₃] had (λ, Δε): 338 nm, -1.35; 278 nm, +0.52.

We have seen in 5 M MgCl₂, 3 M AgNO₃ or 50% H₂SO₄, no clear Cotton effect arising from spin-forbidden transitions within the spin-paired 4d⁶

manifold. Indeed, such absorptions seem not to have been observed for any rhodium(III) chromophore, other than for the isotropic absorption in water of *trans*-dichloro-bis-1,2-diaminoethane-rhodium(III) chloride, *trans*-[Rh(en)₂Cl₂]Cl, where¹¹ a band at 488 nm has ε = 1.0. There is a shoulder with weak intensity at lowest energy in the present isotropic spectrum. Isotropic spin-allowed absorption bands here are at 338 and at 287 nm. The bands in Fig. 1 under the *d-d* electronic absorption at ca 338 nm arise from the ¹A₁ → ¹E_g + ¹A₂ components in the C₃ point group. Since we know the configuration to be Λ at rhodium(III), this defines the E transition as having a positive Cotton effect.

In the present case, the negative CD band at 267 nm is associated with a component of the band of parentage (in O_h) ¹A₁g → ¹T₂g, i.e. with ¹A₁ → ¹E_g + ¹A₂. We see only one Cotton effect for band 1, which corresponds to the ¹E_g component.

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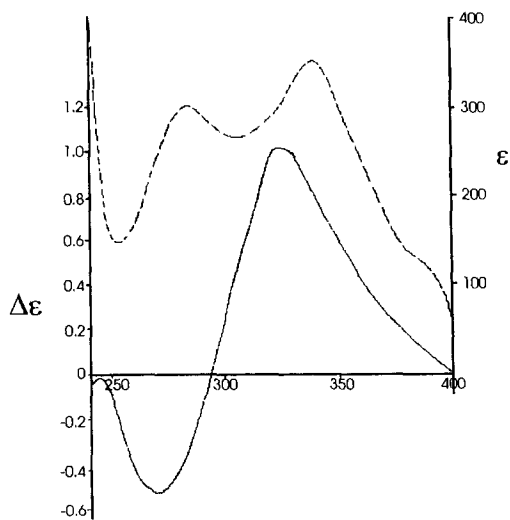


Fig. 1. The isotropic electronic absorption (---) and CD (—) spectra of Λ -*fac*-[Rh(S-ala-O)₃] measured in a 5 M solution of MgCl₂ in water at 18°C.