In Search of the Purple Isomer of Tris(glycinato)-chromium(III)

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Red(facial) and purple(meridional) isomers of tris-(glycinato)cobalt(III) have been well known for some time [1, 2]. Most reports on the preparation of the analogous $Cr(gly)_3$ concern themselves with the red isomer only, and either do not mention the possible existence of the purple [3–5] or mention specifically a failure in attempts at its synthesis [6–9]. The facial geometry of the red isomer has been confirmed by an X-ray structure determination [10]. Nevertheless, two relatively obscure references to the purple isomer do exist. Israily [11] reported a purple monohydrate and Bhagwat, *et al.*, a trihydrate [12]. The first group used a synthesis based on reduction of dichromate in the presence of an excess of glycine, the second a stoichiometric mixture of Cr^{3+} and glycine (but no base!).

Gillard [8] was unable to reproduce Israily's synthesis, obtaining only the dihydroxy-bridged $[Cr_2(gly)_4(OH)_2]$. We too have been unable to obtain any purple $[Cr(gly)_3]$, even impure samples, using either prescription.

The very low solubility of all the complexes involved leads to problems in separation and in characterization of isomerically pure compounds. Once precipitated, a given fraction, representing conceivably a mixture of both isomers of $Cr(gly)_3$ and the dimer (of which nine isomers are possible), cannot be further separated. Chromatographic techniques (Sephadex G-10, ion exchange resins, *etc.*) have thus far not proved fruitful in separating components of the mother liquor.

The second part of the problem is that once a $Cr(gly)_3$ sample is obtained which is believed to be isomerically pure, it has been very difficult to confirm this. The infrared spectra are not sufficiently distinct, and absorption spectra, which must be obtained by reflectance on the solid, or using very long path lengths when dissolved in water, are not sensitive enough to reveal small amounts of the unwanted isomer. This problem applies as well to the red isomer as to the purple, and, in fact, we have found that most of the *fac*-$[Cr(gly)_3]$ products we obtained, using various literature methods [6, 9, 11], were contamined with the meridional isomer and even with the binuclear complex(es). This was true even when the samples were obtained only when a fraction could be crystallized out very slowly.

We have found the luminescence spectrum to yield the most sensitive test for isomeric purity. Both red [5] and purple $Cr(gly)_3$ complexes exhibit sharp line spectra, with $^2E \rightarrow {}^4A_2$ (in O_h notation) O–O transitions at 14478 cm^{-1} (red) and 14200 cm^{-1} (purple), each with associated (but mostly less intense) vibronic structure. The sharp line spectrum of the purple isomer at 10 K is also accompanied by a broad fluorescence. The fluorescence becomes relatively weaker at higher temperatures, but we found 10 K spectra preferable for isomer differentiation, because the sharp lines were narrower.

Thus isomeric impurities were recognizable by the presence of the appropriate O–O line in the spectrum. Binuclear complexes for the most part exhibited fluorescence, raising the general background level. The luminescence spectrum was also checked for independence of exciting wavelength as another test for purity [13]. In addition excitation spectra in the region of the ^2E and ^2T levels were recorded, monitoring different parts of the luminescence spectrum.

Even though we now have a reasonable means of identifying it, the purple isomer remains elusive. We could not reproduce synthetic procedures in the literature [10, 11], and the method we report below, which did at times lead to the purple isomer, was far from reproducible. Trying several methods, we did find one which reproducibly yielded substantially pure red isomer, and we therefore report this also.

For lack of other reliable spectroscopic methods, the luminescence spectrum may, in addition to the elemental analysis (and color), be brought to bear on the identification of the purple product as the meridional isomer of $Cr(gly)_3$. Since the empirical formula is correct, the primary concern is the replacement of amino groups by water in the coordination sphere. This would be expected to lower the energy of the $^2E_g \rightarrow {}^4A_{2g}(O_h)$ origin by about 200 cm^{-1} per H_2O [14, 15], and increase the splitting of the two components of this transition.

In fact, compared to the red isomer, the lowest doublet is found 278 cm^{-1} lower in energy in the purple product, while the splitting is increased from 73 to 113 cm^{-1}. Substantially these effects, however, are to be expected by lowering the symmetry from the nearly C_{3v} of the facial isomer to the (only very approximately) C_{2v} of the meridional isomer, establishing a first order splitting of the (octahedral) ^2E_g state. Thus the luminescence spectrum supports the

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complete coordination of all three glycinates, but does not rule out completely the incorporation of one water molecule.

The infrared spectrum, however, is not consistent with an uncoordinated amino group, lacking the bend and twist modes near 1500 and 1100 cm^{-1}, respectively, but exhibiting the coordination-shifted frequencies [16] of 1590 and 1150 cm^{-1}.

An X-ray powder diffraction spectrum was recorded [17], but could not be used to establish isomorphism, since the Co(III) complex, with which it should be most similar, crystallizes with two waters of hydration [1] or in anhydrous form [18], depending on the preparation.

Experimental Section

mer-Cr(gly)$_3$

Glycine (10 g) and $CrCl_3 \cdot 6H_2O$ (4 g) were dissolved in H_2O (30 mL), after which methanol (120 mL) was added. The solution was refluxed for 2 h, then $NaHCO_3$ (5.7 g) was added and the solution was reduced in a volume by heating a further 30 min, and allowed to cool. The purple material which settled out was filtered off, and consisted primarily of binuclear complex(es), as would be expected from the 1:9:4:5 molar ratio of Cr^{3+} to Hgly to HCO_3^-. The mother liquor was left for several days, and each day the deposited solid material was collected. After 3–5 days a purple product was sometimes observed, which was recognizably different in that it was clearly crystalline. This was collected (sometimes as two or three fractions) and analyzed for isomeric purity using luminescence spectroscopy. Very few of the fractions were isomerically pure. The analysis reported is for the sample used to obtain Fig. 1. Calcd for $Cr(C_2H_4NO_2)_3 \cdot 3H_2O$: C, 21.95; H, 5.53; N, 12.81; Cr, 15.84. Found: C, 21.88; H, 4.40; N, 12.57; Cr, 15.94.

fac-[Cr(gly)$_3$]

$CrCl_3 \cdot 6H_2O$, glycine, and NaOH were dissolved in water in a mol ratio of 1:3:3 and heated 4 h at 90–100 °C. The reddish precipitate formed on cooling overnight contained a substantial amount of the binuclear complex(es). This precipitate was filtered off and added to a mixture of 10% Me_2SO in water, along with a small amount of zinc dust and ferrous sulfate (to provide a reduction pathway), and an amount of glycine equal to that used in the first step. This solution was refluxed overnight and filtered hot. Upon coooling, dark red crystals of [Cr(gly)$_3$] appeared which, from the luminescence spectra, were isomerically pure.

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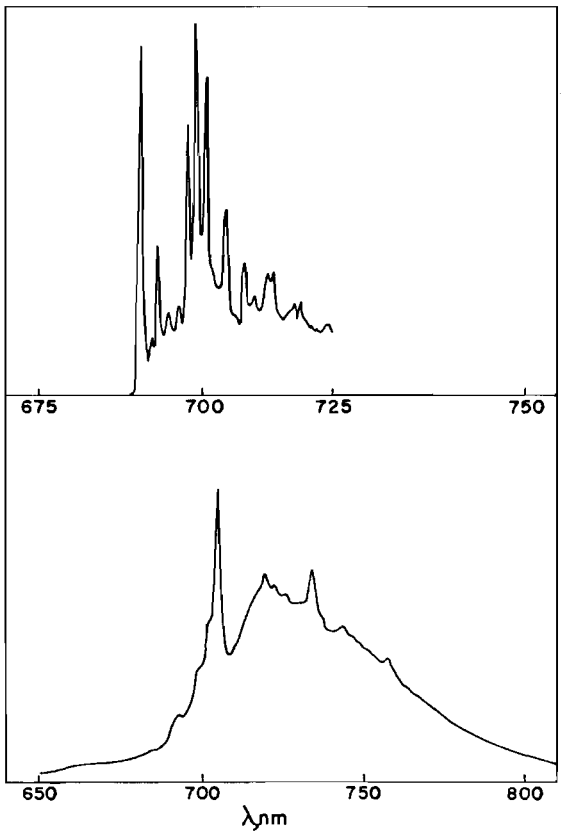

Fig. 1. Luminescence spectra at 10 K of facial (top) and meridional (bottom) isomers of Cr(gly)$_3$. Intensity (ordinate) is in arbitrary units.

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