The Structure of the Methanol Adduct of Tris-(8-quinolinolato)-chromium(III)

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ADDITION compounds of tris-(8-quinolinolato)-chromium(III) with alcohols and amines have been reported[1] to be formed only with the *cis*-stereoisomer. This property might be useful as a general method for separating *cis*- and *trans*-isomers of octahedral complexes containing unsymmetrical bidentate ligands. For instance, the *cis*- and *trans*-tris-glycinato-complexes of cobalt-(III) form mono- and di-hydrates respectively,[2] which might be separable by this technique. These compounds are also notable because of the high temperature (~200°) which is required to remove the alcohol from the adduct.[1]

By following the synthesis reported by Umland and Adam,[1] as well as the more common precipitation from aqueous solution[3] we have been able to prepare only one isomer of tris-(8-quinolinolato)-chromium(III). The i.r. and u.v. visible spectra of material which had been heated for 6 hr. at 200° were identical with those of the unheated compound. Both heated and unheated compounds readily form solvates with methanol. The *trans*-structure of this methanol adduct has been verified by a single-crystal *X*-ray study.[4] Our results indicate that only the *trans*-isomer has been prepared.

Crystal data for Cr(oxine)$_3$,MeOH; M = 516·2; monoclinic, a = 16·904(2), b = 13·209(2), c = 10·959(1) Å, and β = 97·40 ± 0·05°; Z = 4; space group $P2_1/n$, Mo-K_α radiation (λ = 0·71069). In the range $0 \leqslant 2\theta \leqslant 30°$ a total of 2213 unique reflections were recorded. The structure was solved by a combination of the symbolic addition method[5] and standard Fourier techniques. The structure was refined using the full-matrix least-squares program of Busing and Levy,[6] until R was 0·085 for 1657 reflections. All hydrogen atoms except those on the methanol were evident in a difference synthesis. The geometry of the metal co-ordination and the relative position of the methanol is shown in the Figure; the oxine carbon atoms are omitted for clarity.

The Cr is octahedrally co-ordinated. Three positions are taken up by oxine nitrogen atoms and three oxine oxygen atoms complete the co-ordination. The octahedron is distorted owing to the forced configuration in the five-membered chelate rings. The configuration is *trans*- and the methanol does not take part in the co-ordination. The methanol molecule is hydrogen bonded to a *trans*-oxygen in the second oxine. The O(oxine) · · · H–O(methanol) distance is 2·81 ± 0·01 Å.

The difficulty in removing methanol from the adduct is best explained in terms of crystal packing. Two methanol molecules related to each other by a centre of symmetry (at 0, $\frac{1}{2}$, 0) are trapped in a "cage-like" cavity, whose walls are formed by oxine molecules. The cavity is quite large and easily accommodates the large thermal motion of the methanol molecule. The C_{MeOH}–C_{MeOH} distance is 5·32 ± 0·05 Å, which is 1·3 Å larger than the sum of the van der Waals radii. Since the cavity is closed on all six sides, a major reorganization of the structure is necessary in order to remove the methanol. This factor, rather than strong hydrogen bonding, accounts for the high temperatures necessary to destroy the alcohol adducts.

The cavity containing the methanol molecules appears to be large enough to accommodate ethanol also. Preliminary *X*-ray investigations of crystals of Cr(oxine)$_3$,H$_2$O and Cr(oxine)$_3$,EtOH indicate that the compounds are isomorphous with Cr(oxine)$_3$,MeOH, indicating that the H$_2$O, MeOH, or EtOH molecules occupy the same site. The unit-cell dimensions agree to within 0·3 Å and intensity distributions are very similar. Attempts at crystallizing the propanol or any higher adducts have so far been in vain.

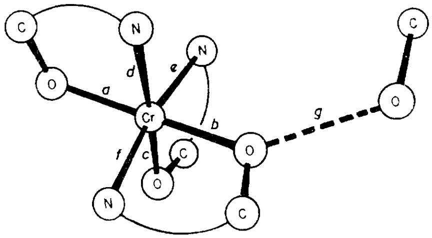

FIGURE. *Configuration of* Cr(oxine)$_3$,MeOH.
Bond lengths and angles are: *a* = 1·944(7); *b* = 1·968(7); *c* = 1·935(7); *d* = 2·075(9); *e* = 2·053(8); *f* = 2·061(9); *g* = 2·81(1) Å; ∠*ad* = 81·40 ± 0·3°; ∠*ae* = 94·0 ± 0·3°; ∠*af* = 92·9 ± 0·3°; ∠*ac* = 93·3 ± 0·3°; ∠*bf* = 82·1 ± 0·3°; ∠*bc* = 95·2 ± 0·3°; ∠*be* = 92·0 ± 0·3°; ∠*bd* = 90·4 ± 0·3°; ∠*cf* = 90·0 ± 0·3°; ∠*ce* = 82·4 ± 0·3°; ∠*de* = 94·2 ± 0·3°; ∠*df* = 93·2 ± 0·3°. The bonds in the 8-hydroxyquinoline group are normal. The average values are: C–C = 1·41 (1), C–N = 1·36 (1) C–O = 1·34 (1) Å.

We conclude that separation of stereoisomers on the basis of their solvate-forming capacity as described by Umland and Adam[1] will not be useful as a general method. Unfortunately, it appears that the solvate-forming capacity is strictly related to the crystal packing and may vary greatly from one case to another.

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