Inorganica Chimica Acta, 25 (1977) L93–L94
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Tris-Complexes of (–)-1,2-Diamino-propane: A Comment

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Received September 13, 1977

A recent note [1] in this Journal referred to the relative abundance of isomers of the tris-(R)-(–)-propylenediaminerhodium(III) cation, and pointed out that the earliest descriptions [2] of the circular dichroism had not agreed well quantitatively.

The explanation offered was in terms of the varying distributions of isomers, in samples made by the interaction of (–)pn with rhodium(III) halo-species, under various conditions. This is almost certainly correct. However, the number of isomers suggested [1] by Hearson, Mason, and Wood is too small because they overlook the well-known geometric isomers. The present note collects relevant information to give a revised picture of the isomerism. In addition to our original work [2] on the rhodium system, we had commented [3] on this isomerism in a subsequent resolution.

Jaeger was conscious of the value of stereoselective interaction between a resolved 1,2-diamine and an octahedral ion in evaluating relative configurations of metal ions. He however did *not* use 1,2-diaminopropane but only such 1,2-diamines (LL) as (–)1,2-cyclohexanediamine, (–)chxn, which possess two-fold symmetry. As discussed again [4] by Galsbol, Steenbol, and Sondergard Sorensen, there are only 2 isomers of $[M\{(-)LL\}_3]$, *i.e.* $\Delta[M\{(-)LL\}_3]^{n+}$ and $\Lambda[M\{(-)LL\}_3]^{n+}$. Using optically pure 1,2-cyclohexanediamine, they found [4] that the ratio of more stable to less stable diastereoisomer for the tris-complex with rhodium(III) was around 8:5.

The situation for optically active bidentate ligands which lack two-fold symmetry is entirely different and less simple. The best-known of such ligands are the natural L series of α-amino-acidates. The isomerism of their complexes has been discussed [5] at length. The 4 possible isomers are: D-*fac*-$[M(L\alpha)_3]$, L-*fac*$[M(L\alpha)_3]$, D-*mer*-$[M(L\alpha)_3]$ and L-*mer*-$[M(L\alpha)_3]$. 1,2-propylenediamine manifests [6] identical (but less obvious) geometric isomerism. The spread of standard free energies from most to least stable for $[Co(pn)_3]^{3+}$ is [6] about 7 kJmol.

The statistical proportion of *fac*:*mer*, assuming that *no* stereoselective effects of any kind operate, is 1:3. MacDermott found [7] this *cis*:*trans* ratio of 1:3 for the corresponding cobaltic pair. That is, if one could separate out the two D-isomers of $[Rh(-pn)_3]^{3+}$, then, statistically, they should be 75% abd and 25% abc. It is only the *less* abundant abc-isomer which has the true C_3-axis (shown in formulae I and II of reference 1).

Attempts at the actual separation of the isomer Λ-abc-$[M(+\ pn)_3]^{n+}$ from Λ-abd-$[M(+\ pn)_3]^{n+}$ have failed. Dwyer, Sargeson and James could not tell [8] (for the enantiomeric pairs: $D[Co(+)_3]$ and $L[Co(-)_3]$; $D[Co(++-)]$ and $L[Co(--+)]$; $D[Co(+--)]$ and $L[Co(-++)]$, and $D[Co(-)_3]$ and $L[Co(+)_3]$) whether each enantiomer was *cis*(abc) or *trans*(abd) or a mixture. MacDermott [7], and later [9] Crossing and Snow, found that the physical properties of abc(*cis*) and abd(*trans*) isomers of $\Delta[Co(-pn)_3]Cl_3$ are very similar.

Some while ago, we noticed [3] that the same precipitating agent [in our case the (+)tris-[L-cysteinesulphinato(2–)-SN] cobaltate(III)] caused the crystallization of different (Δ) isomers of $[Rh(pn)_3]^{3+}$ and $[Cr(pn)_3]^{3+}$ as opposed to cobalt(III) (where a Λ isomer – or some Λ isomers – formed). We had also noticed, in our early work [2], that the chiroptical properties of "stereoselectively synthesized" samples of $[Rh(-pn)_3]^{3+}$, as say, iodide salts, varied considerably, depending upon the detailed purification procedure. It is, of course, not too surprising that different gegen ions (say nitrate and iodide) cause the enrichment in their solid salts of differing isomers, quite apart from any selective ion-pairing effects which polarizable anions like iodide may have upon the *d–d* chiroptical spectra of rhodium ions.

We had assumed that the variability [2] in chiroptical properties of various samples of tris-{(R)(–)-diaminopropane}rhodium(III) stemmed from the presence in these samples of greater or smaller amounts of *meridional* or *facial* isomers, such variability arising either from kinetic factors in the synthesis or, more likely, from slightly differing solubilities of the salts with a given gegen ion of the *facial* and *meridional* isomers.

The "ratio of lel:ob isomers" reported recently [1] (based on fractional crystallization* to constant properties of the iodide and the chloride (+)tartrate) is 62:38 (*i.e.* 1.63). The "ratio of more stable:less stable" (*i.e.* Λ:Δ) for the two cyclohexanediamine isomers is [4] about 8:5 (*i.e.* 1.6). It seems likely that the measured ratio [1] for $[Rh(pn)_3]^{3+}$ is in fact (total of Λ forms):(total of Δ forms). All four forms (Λ*fac* and Λ*mer*; Δ*fac* and Δ*mer*) are present: the suggestion [1] that only the (*facial*) forms with the 3-fold axis are involved is incorrect.

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*It had earlier been found [6] that, even by careful paper and column chromatography, only a very partial separation of isomers could be achieved.

References

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