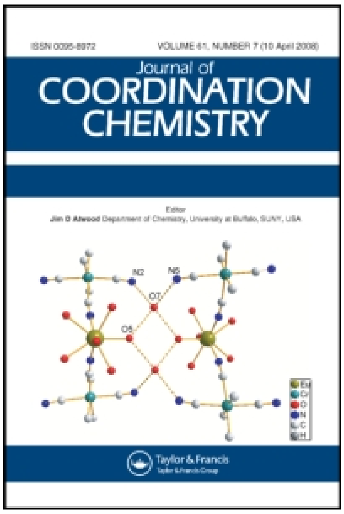

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

The Solubility of Optically Active Tris-α-diimine Ruthenium(II) Complexes in *1*-2-Methyl-1-Butanol

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To cite this Article Mizumachi, Kunikho(1973) 'The Solubility of Optically Active Tris-α-diimine Ruthenium(II) Complexes in *1*-2-Methyl-1-Butanol', Journal of Coordination Chemistry, 3: 2, 191 — 192

To link to this Article: DOI: 10.1080/00958977308073809

URL: http://dx.doi.org/10.1080/00958977308073809

J. Coord. Chem.
1973, Vol. 3, pp. 191–192

SHORT COMMUNICATION

The Solubility of Optically Active Tris-α-diimine Ruthenium(II) Complexes in *l*-2-Methyl-1-Butanol

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(*Received September 22, 1972*)

The difference of solubilities of the diastereomers of optically active complex ions has been widely utilized in the resolution of the complexes. The difference may arise from the fact that the dissymmetric ion of a resolving reagent has different interaction with the enantiomeric ions of the complex to be resolved mainly in the solid phase of diastereomers.

Bosnich *et al*[1] reported that the solubilities of the enantiomers of *cis*-$[Co(en)_2Cl_2]ClO_4$ in *l*-2,3-butanediol were different. This behaviour was explained that the interaction of the dissymmetric solvent and the enantiomeric cations are different between the *d*-cation and the *l*-cation.

This paper is to give a few examples in which the dextro, levo, and racemic isomers of inorganic complexes have different solubilities in an optically active solvent, *l*-2-methyl-1-butanol(active amylalcohl). The solutes are $[Ru(phen)_3](ClO_4)_2$, $[Ru(bipy)_3](ClO_4)_2$, and $[Ru(phen)_3]I_2$ isomers, (phen=phenanthroline, and bipy=bipyridine), which do not racemize under the conditions of measurement.

The solubilities of the complex perchlorates measured at 25.00 ± 0.02°C are shown in Table I, together with the solubilities in water determined by the present author.

TABLE I
Solubility at 25.00°C (10^{-5} M)

Complex Salt	in *l*-2-methyl-1-butanol	in water
d-$[Ru(phen)_3](ClO_4)_2$	4.00	169
l-$[Ru(phen)_3](ClO_4)_2$	4.70	
rac-$[Ru(phen)_3](ClO_4)_2$	0.584	65.3
d-$[Ru(bipy)_3](ClO_4)_2$	2.03	425
l-$[Ru(bipy)_3](ClO_4)_2$	1.85	
rac-$[Ru(bipy)_3](ClO_4)_2$	0.164	187

The following points are to be noted on the data:

1) The solubilities of the phenanthroline complexes in *l*-2-methyl-1-butanol are higher than those of the bipyridine complexes, while in aqueous solutions the order of the solubility is reverse.

The solubilities of the complexes in the organic solvent are much lower than in water. In this connection, it is worth noting that the water content in the organic solvent has a serious effect on the solubility data. A commercially available solvent would give higher solubilities than those shown in the table, careful drying and distillation of the solvent being indispensable.

2) With either complex, the solubilities of the isomers are different. Racemic complexes are the least soluble, and *l*-form is more soluble than *d*-form with the phenanthroline complex, the order is reverse, on the other hand, with the bipyridine complex.

The fact that there is the difference in the solubilities of the optical isomers in the optically active solvent can be attributed to the cation-solvent interaction in this system. The configuration of the complex ions may have an influence on the degree of the solvation in the solution which is reflected in turn in the solubility of the complexes.

The state of the solid phase which is in equilibrium with the saturated solution may also have some effects. If the number of the solvation of the complex salt in the solid phase would not be identical for both isomers, the consequent difference of the chemical potentials of the solid species should have influence on the solubility. This may arise from the interactions between the cations and the solvent, this time, in the solid phase.

Another point to be discussed is a cation-anion interaction (ion-association). It was reported that the enantiomers of $[Co(en)_3]^{3+}$ have different interactions with PO_4^{3-}, SO_4^{2-} in aqueous solutions.[2-4] Although for the complexes with phenanthroline or bipyridine as ligands the same effect may not be expected, the effect of ion-ion interactions might not be safely neglected. To avoid such ambiguity, the solubilities of $[Ru(phen)_3]I_2$ isomers in the same solvent were measured at 25.00°C.

The data in Table II shows that the *l*-isomer has higher solubility than the *d*-isomer, which is the same as in the case of the perchlorate. An iodide ion, which is regarded as spherical, should have the same degree of cation-anion interaction, if any, with either the *d*-cation or the *l*-cation. Consequently, the difference of the solubility of the iodide isomers can be exclusively ascribable to the difference of the cation-solvent interaction.

TABLE II
Solubility at 25.00°C (10^{-3} M)

Complex Salt	in *l*-2-methyl-l-butanol
d-$[Ru(phen)_3]I_2$	1.00
l-$[Ru(phen)_3]I_2$	1.50
rac-$[Ru(phen)_3]I_2$	0.136

The steric configuration of tris-α-diimine metal complexes has been discussed by some authors. Gillard *et al*[5] showed that *d*-$[Ru(phen)_3]^{2+}$ and *d*-$[Ru(bipy)_3]^{2+}$ have the same configuration on the basis of the circular-dichroism spectra and the reactions of the complexes. On the other hand, the solubility of the diastereomers with antimonyl-d-tartrate ion suggests that *d*-$[Ru(phen)_3]^{2+}$ and *l*-$[Ru(bipy)_3]^{2+}$ have the same configuration.

The solubility behaviour in the optically active solvent observed in this study is consistent with the latter information. Since the solubility should be related directly to the steric configuration, it may offer a good criterion on the configuration of the complexes.

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