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Isomerism of the Metal Complexes Containing Multidentate Ligands. VIII. Chromatographic Behavior of $[CoN_6]^{3+}$-type Complexes on an SP-Sephadex Column[1)]

Katsumi SAKAKIBARA, Yuzo YOSHIKAWA,* and Hideo YAMATERA
Department of Chemistry, Faculty of Science, Nagoya University, Chikusa-ku, Nagoya 464

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Synopsis. An empirical rule is presented for the elution order of $[CoN_6]^{3+}$-type complexes in chromatography on SP-Sephadex columns. The relative elution rates have been correlated with the number and the kind of the octahedral faces of the complex on which ion association with a phosphate ion occurs.

The application of ion-exchange Sephadex to the column-chromatographic separation of isomers of a metal complex was first described by Yoshikawa and Yamasaki, who successfully resolved the optical isomers[2)] of $[Co(en)_3]^{3+}$ and separated the three geometrical isomers[3)] of $[Co(dien)_2]^{3+}$. Subsequently the technique has been widely used to separate and resolve the isomers of many complexes. It is still difficult, however, to predict the elution order for a given mixture of isomers.

This note is concerned with a working hypothesis, which correlates the elution order with the structure of geometrical isomers of the $[CoN_6]^{3+}$-type complexes. The predictions from the hypothesis have been compared with the experimental results of isomer separation on several complexes with five-membered chelate rings.

Experimental

Materials. All Complexes,** $[Co(NH_3)_6]^{3+}$, $[Co(NH_3)_4(en)]^{3+}$, $[Co(NH_3)_2(en)_2]^{3+}$, $[Co(en)_3]^{3+}$, $[Co(dien)_2]^{3+}$,[3)] $[Co(en)(trien)]^{3+}$,[4,5)] $[Co(linpen)]^{3+}$,[6)] $[Co(hexaen)]^{3+}$,[7)] and $[Co(pn)_3]^{3+}$,[8)] were prepared according to the literature. For each complex in which geometrical isomerism occurs, an equimolar mixture of the geometrical isomers was prepared with the isomers isolated in advance.

Chromatography. The mixture of $[Co(dien)_2]^{3+}$ isomers was adsorbed at the top of an SP-Sephadex C-25 column (ϕ 1.4×*ca.* 130 cm) and eluted with 0.1 M Na_3PO_4. The elution curve was drawn by measuring the absorbance of each fraction of the eluate. Similar experiments were also made on the same column with 0.15 M Na_2SO_4, 0.15 M $Na_2\{(+)\text{-}C_4H_4O_6\}$ (sodium tartrate), 0.3 M NaCl, and 0.3 M $NaClO_4$ as eluents. The isomer contained in each band was identified by the IR spectra, the results of which are shown in Fig. 1, where the vertical lines indicate the peak positions (in elution volume) in each curve.

The mixtures of the isomers of $[Co(NH_3)_2(en)_2]^{3+}$, $[Co(dien)_2]^{3+}$, $[Co(en)(trien)]^{3+}$, $[Co(linpen)]^{3+}$, $[Co(hexaen)]^{3+}$, and $[Co(NH_3)_4(en)]^{3+}$ were examined for elution order on another column (ϕ 2.7×127 cm) with 0.1 M Na_3PO_4 as the eluent. In each experiment either $[Co(en)_3]^{3+}$ or $[Co(NH_3)_6]^{3+}$ was added as a reference, of which the peak position in each elution curve is shown by a dashed vertical line (Fig. 2). The separation of $[Co(pn)_3]^{3+}$ isomers was also made in a similar manner.

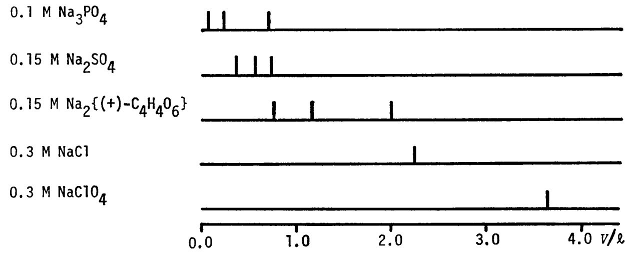

Fig. 1. Separation of the isomers of $[Co(dien)_2]^{3+}$ with different eluents. Column size: $\phi 1.4\times$*ca.* 130 cm (SP-Sephadex C-25).

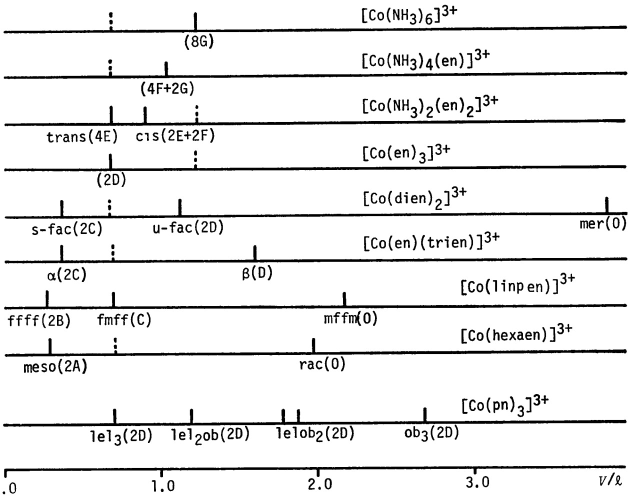

Fig. 2. The elution order of $[CoN_6]^{3+}$-type complexes. Column size: $\phi 2.7\times127$ cm (SP-Sephadex C-25). Eluent: 0.1 M Na_3PO_4.

Results and Discussion

The factors influencing the relative rates of elution of geometrical isomers of cationic Co(III) complexes on an SP-Sephadex column are probably two: the interaction between SP-Sephadex and the complex cation, and the interaction between the complex cation and the eluent anion. Different eluents were used to separate the isomers of $[Co(dien)_2]^{3+}$ (Fig. 1). The same elution order (*s-fac*, *u-fac*, and *mer*) was shown by 0.1 M Na_3PO_4, 0.15 M Na_2SO_4, and 0.15 M $Na_2\{(+)\text{-}C_4H_4O_6\}$ eluents, whereas 0.3 M NaCl and 0.3 M $NaClO_4$ resulted in no clear separation. These results indicate that the interaction of the complex cation with the eluent anion, not with SP-Sephadex, is the dominant factor in the separation of geometrical

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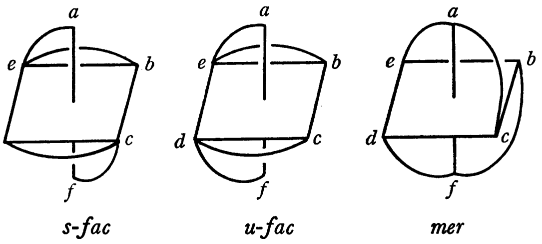
** The following abbreviations are used in this note: en, ethylenediamine; dien, diethylenetriamine; trien, triethylenetetramine; linpen, linear pentaethylenehexamine; hexaen, hexaethylenehexamine; pn, propylenediamine.



s-fac *u-fac* *mer*

Fig. 3. Three geometrical isomers of $[\mathrm{Co(dien)_2}]^{3+}$.

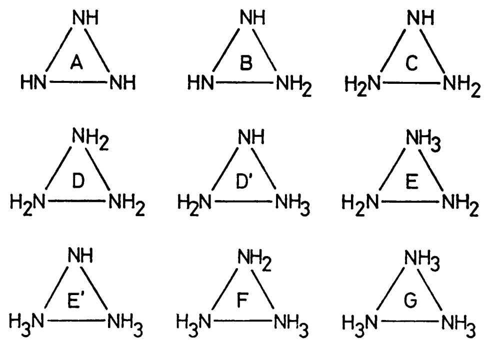


Fig. 4. Classification of the octahedral faces available for ion-pairing.

isomers.[9)]

The structure of each geometrical isomer may or may not favor ion association. Experimental results so far reported on $[\mathrm{Co(en)_3}]^{3+}$–oxo anion systems have indicated that three hydrogen bonds can be formed between a trigonal-pyramidal or tetrahedral oxo anion and a set of three N–H bonds extending along a direction perpendicular to an octahedral face of the complex. Two faces of the $[\mathrm{Co(en)_3}]^{3+}$ octahedron are suitable for such ion association, whereas chelate rings will sterically interfere with ion association on the six other faces of the octahedron.[10)]

In the three geometrical isomers of $[\mathrm{Co(dien)_2}]^{3+}$ (Fig. 3), ion association will occur on the two faces, *abc* and *def*, in the *s-fac* isomer and on the two faces, *abc* and *bcf*, in the *u-fac* isomer. Each octahedral face of the *mer* isomer, however, is hindered from ion association by the chelate ring, which is consistent with the experimental results that the *mer* isomer was the final one to be eluted.

The elution behavior of the *s-fac* and *u-fac* isomers will be discussed in connection with the tendency for hydrogen bonding of the N–H protons with an oxo anion. That tendency will be in the order: secondary amine>primary amine>ammonia.[9)] Consequently the octahedral faces may be classified according to the types of amine groups on the faces, in effect, according to the number of hydrogen atoms attached to the nitrogen atoms; the face containing three secondary amine groups is designated A, the face containing two secondary and one primary amine groups is designated B, *etc.* (Fig. 4). In this way a letter of the alphabet is affixed to each face in the order of increasing number of total hydrogen atoms attached to the nitrogen atoms on the face. This serves as an index. In the situation that two types of faces exist with an equal number of attached hydrogen atoms, the designation is D and D′ for example. A face carrying a prior alphabetical name will have a greater tendency to ion-pair formation. The *s-fac* isomer of $[\mathrm{Co(dien)_2}]^{3+}$ has two C faces, and the *u-fac* isomer has two D faces. Consequently the tendency to associate with eluent anions will be in the order: *s-fac*>*u-fac*>*mer*. This order agrees with the order found experimentally.

Based on the preceding discussion, the elution order for $[\mathrm{CoN_6}]^{3+}$-type complexes can be predicted and explained. Figure 2 gives the experimental results, where the position of the peak is shown for each isomer together with the number and type of octahedral face on which ion association with a phosphate ion occurs. The experimental elution results agreed completely with the prediction for the isomers of each complex investigated. There are however some cases where comparison is not straight-forward, *e.g.*, *trans*-$[\mathrm{Co(NH_3)_2(en)_2}]^{3+}$ (4E), $[\mathrm{Co(en)_3}]^{3+}$(2D), and *fmff*-$[\mathrm{Co(linpen)}]^{3+}$ (C) were eluted at similar positions, a fact attributed to the counterbalance of the effect of decreasing number of faces available for ion-pairing and that of the increasing tendency of the faces to ion-pairing. Elution was slower for *u-fac*-$[\mathrm{Co(dien)_2}]^{3+}$(2D) than for $[\mathrm{Co(en)_3}]^{3+}$(2D), which has been attributed to the fact that the two D faces of the former complex cannot simultaneously have suitable N–H orientations for hydrogen bonding with the eluent anion.

$[\mathrm{Co(pn)_3}]^{3+}$(2D) represents an example of a special case where the conformational effect is important; in this complex, the conformation of the chelate rings are not as flexible as in other complexes. Combination of the asymmetries at the ligands and the central cobalt gives rise to four enantiomeric pairs of isomers, in which the flexibility of the chelate rings is restricted by steric interaction of the bulky methyl group of pn. The N–H bonds at the both ends of a *lel* chelate ring are suitably oriented for hydrogen bonding, while those of the *ob* chelate ring are not.[8)] The experimental result for $[\mathrm{Co(pn)_3}]^{3+}$ indicates that the N–H orientation greatly affects the rate of elution.

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