Short communication

# Chromatographic separation and characterization of the photoproduct of tris(L-cysteinesulfinato-N,S)cobaltate(III)

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## Abstract

The product of photolysis of $K_3(+)$-[Co(L-cysi-N,S)$_3$] (**1**, L-cysi=L-cysteinesulfinate(2−) ion, cysi= $NH_2CH(COO^-)CH_2SO_2^-$) was separated by column chromatography on DEAE-Sephadex A-25. The main band contained [Co(L-cysi-N,S)$_2$(L-cysi-N,O)]$^{3-}$ (**2**); linkage isomerization from sulfinato-*S* to sulfinato-*O* took place. This complex (**2**) is thermally unstable and reverts to the starting complex (**1**). An anion-exchange high-performance liquid chromatographic (HPLC) method was successfully applied to the kinetic study of this linkage isomerization reaction from **2** to **1**.   © 1997 Elsevier Science B.V.

*Keywords:* Linkage isomers; Kinetic studies; Cobalt complexes; Metal complexes; Tris(cysteinesulfinato(-N,S)cobaltate(III)

## 1. Introduction

The yellow complex potassium (+)-tris[L-cysteinesulfinato(2-)-N,S]cobaltate(III), $K_3(+)$-[Co(L-cysi-N,S)$_3$] (**1**, cysi=$NH_2CH(COO^-)CH_2SO_2^-$), is a very convenient and powerful resolving agent for 3+ complex cations [ML$_3$]$^{3+}$ (particularly where L= 1,10-phenanthroline and 2,2′-bipyridine) [1]. However, this complex is photo-labile; the surface of the solid becomes reddish in sunlight, and an aqueous solution, if left in sunlight, shows a marked change in the UV–Vis spectrum. The nature of the product of the photolysis has not been investigated. Dollimore and Gillard suggested that the complex was rather prone to form cobalt(II) [1].

Recently, Adamson and co-workers reported linkage isomerization from Co-S (sulfinato-S) to Co-O (sulfinato-O) in the photolysis of [Co{S(O)$_2$CH$_2$CH$_2$NH$_2$-N,S}(en)$_2$]$^{2+}$ (en=ethylene-diamine) [2,3]. Thus, we expected the color change of $K_3(+)$-[Co(L-cysi-N,S)$_3$] might be attributed to linkage isomerization from Co-S to Co-O (Fig. 1).

This paper deals with the column chromatographic separation of the photoproduct of (+)-[Co(L-cysi-N,S)$_3$]$^{3-}$ on DEAE-Sephadex A-25, characterization of the products, and the kinetic study of the thermal reverting reaction (linkage isomerization from Co-O to Co-S) of one of the products by a high-performance liquid chromatographic (HPLC) method. A part of this study has already been briefly reported [4].

## 2. Experimental

### 2.1. fac-Δ(R)-[Co(L-cysi-N,S)$_2$(L-cysi-N,O)]$^{3-}$ (2)

The $K_3(+)$-[Co(L-cysi-N,S)$_3$]·6H$_2$O complex (**1**) was prepared according to the literature [1]. An aqueous solution (400 ml) of $K_3(+)$-[Co(L-cysi-
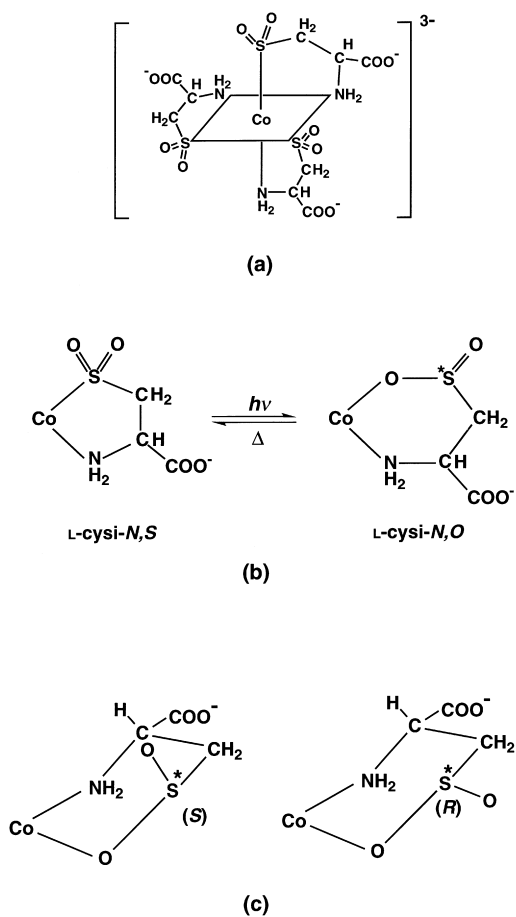
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Fig. 1. (a) Structure of *fac*-Δ-(+)-[Co(L-cysi-N,S)$_3$]$^{3-}$. (b) Reaction of the L-cysi chelate. (c) Two possible isomers (*R* and *S*) of the L-cysi-N,O chelate ring arising from the presence of a chiral sulfur atom.

N,S)$_3$]·6H$_2$O (0.5 g) was irradiated at ca. 5°C for 50 min using a 400-W high-pressure mercury lamp (internal irradiation type) fitted with a Pyrex glass filter. The color of the solution changed from yellow to red. The reaction mixture was passed through a DEAE-Sephadex A-25 column (50×5 cm I.D.). Since the photoproducts are likely to isomerize, chromatography was performed in a cold room (ca. 5°C). Upon elution with 0.23 *M* Na$_2$SO$_4$, the column showed six bands; green (band I), green (band II), dark green (band III), reddish green (band IV), red (band V), and yellow (band VI), in the order of elution. The slowest-moving yellow band (band VI)

contained the unreacted starting complex (**1**). The eluate containing band V was used for kinetic measurements.

The acid form of complex **2**, *fac*-Δ(*R*)-[Co(L-Hcysi-N,S)$_2$(L-Hcysi-N,O)]·0.5H$_2$O, was isolated by the method reported previously [4].

### 2.2. Apparatus

The chromatographic system consisted of a Jasco 880-PU HPLC pump and a Jasco 875 UV–Vis detector. Chromatograms were recorded on a Jasco 807-IT integrator. UV–Vis and circular dichroism (CD) spectra were recorded on a Jasco Ubest V-550 spectrophotometer and a Jasco J-720 spectropolarimeter, respectively.

### 2.3. Chromatographic system

#### 2.3.1. Stationary phase
The anion-exchange column used in this study was a YMC-Pack IES-AX A-AX-12-46-35 (250×4.6 mm I.D.) from YMC (Kyoto, Japan). This support is a silica-based material (particle size, 5 μm; pore size, 120 Å) and has covalently bonded polyethylenimine as weak anion-exchange groups.

#### 2.3.2. Mobile phase
The eluent was a 0.4 *M* aqueous solution of NaCl and the flow-rate was 1.0 ml min$^{-1}$.

#### 2.3.3. Sample solutions
The eluate containing band V (complex concentration, ca. 0.4 m*M*) was heated at 45°C, and portions of the reaction mixture were withdrawn at timed intervals. The injected volume was 5 μl. The complexes were detected at 333 nm where complexes **1** and **2** give the same molar absorption coefficient. The chromatography was carried out at 20°C.

### 2.4. Molecular mechanics calculations

Strain-energy minimization calculations were carried out for two possible isomers, *fac*-Δ(*R*)- and *fac*-Δ(*S*)-[Co(L-cysi-N,S)$_2$(L-cysi-N,O)]$^{3-}$ with a modified MM2 computer program [5,6] in order to obtain their relative strain energies and to estimate the stable structure between the isomers. The param-

eters for the present force fields were mainly adopted from those of MM2 (1985), MM2 and MMP2 (1986), and the literature ( [7], and references cited in [5]). The electrostatic interactions were not considered for these calculations.

## 3. Results and discussion

When an aqueous solution of $(+)$-[Co(L-cysi-N,S)$_3$]$^{3-}$ was irradiated with visible light, the color of the solution changed from yellow to red. The progress of the reaction was followed by the anion-exchange HPLC method. Complex **2** reached its maximum concentration after 50 min of irradiation, and after that the concentrations of the other species increased. Although we tried to separate the photoproduct by ion-pair chromatography (for the separation of anionic metal complexes by ion-pair chromatography see, for example, [8]), the separation was not so good as that by the anion-exchanger. Only a limited number of studies have been reported for the separation of anionic metal complexes by ion-exchange chromatography (for example, [9]).

Column chromatography of the reaction mixture on DEAE-Sephadex A-25 showed six bands (Fig. 2). HPLC revealed that bands I–IV involved more than one species, while band V involved only one species (complex **2**). We could isolate the most abundant complex **2** as the acid form. However, since this complex is likely to isomerize to complex **1** (the starting complex), the isolated complex was contaminated with a small amount of complex **1** as evidenced by the $^1$H NMR spectrum. Thus, the eluate containing complex **2** (band V) was used for the kinetic study (vide infra).

Fig. 3 compares the UV–Vis and CD spectra of complex **2** with those of the starting complex, *fac*-Δ-$(+)$-[Co(L-cysi-N,S)$_3$]$^{3-}$ (**1**). Complex **2** has been assigned to *fac*-Δ-[Co(L-cysi-N,S)$_2$(L-cysi-N,O)]$^{3-}$ mainly on the basis of its reactivity and spectroscopic data (UV–Vis, CD, and $^1$H NMR spectra) [4]. The sulfur atom becomes chiral (*R* and *S*) upon photoisomerization (Fig. 1), and the number of possible isomers increases. The molecular mechanics calculations of the two possible isomers, *fac*-Δ(*R*)- and *fac*-Δ(*S*)-[Co(L-cysi-N,S)$_2$(L-cysi-N,O)]$^{3-}$, revealed that the former is more stable than the latter
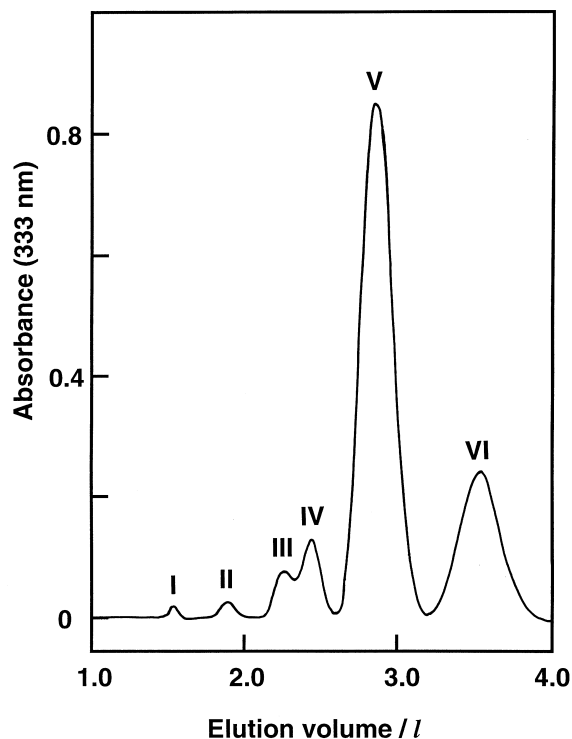


Fig. 2. Elution curve of the product of photolysis of K$_3$(+)-[Co(L-cysi-N,S)$_3$]. Chromatographic conditions: column, DEAE-Sephadex A-25 (50×5 cm I.D.); eluent, 0.23 *M* Na$_2$SO$_4$ in water; flow rate, 2.5 ml/min; UV detection, 333 nm.

by 5.0 kJ mol$^{-1}$ (Table 1). On the basis of this energy difference, the relative abundance of *fac*-Δ(*R*)/*fac*-Δ(*S*) at equilibrium is calculated to be 7.4. Thus, complex **2** can be assigned to *fac*-Δ(*R*)-[Co(L-cysi-N,S)$_2$(L-cysi-N,O)]$^{3-}$. The less abundant isomer (*fac*-Δ(*S*)) may be involved in either of the bands I–IV. The starting complex (**1**) contains three sulfinate-S groups and if linkage isomerization proceeds stepwise, three isomeric products are expected, i.e., [Co(L-cysi-N,S)$_2$(L-cysi-N,O)]$^{3-}$ (first step), [Co(L-cysi-N,S)(L-cysi-N,O)$_2$]$^{3-}$ (second step), and [Co(L-cysi-N,O)$_3$]$^{3-}$ (third step). Moreover, since each L-cysi-N,O chelate ring has a chiral sulfur atom, the number of possible isomers becomes very large. Probably, bands I–IV involve these isomers.

Kinetics of linkage isomerization from *fac*-Δ(*R*)-[Co(L-cysi-N,S)$_2$(L-cysi-N,O)]$^{3-}$ (**2**) to *fac*-Δ-[Co(L-cysi-N,S)$_3$]$^{3-}$ (**1**) were studied in 0.23 *M* Na$_2$SO$_4$ at 45°C using the HPLC method. As Fig. 4 shows, the

Table 1
Final energy terms (kJ mol$^{-1}$) from the minimization for two isomers of *fac*-Δ-[Co(L-cysi-N,S)$_2$(L-cysi-N,O)]$^{3-}$ (complex **2**)

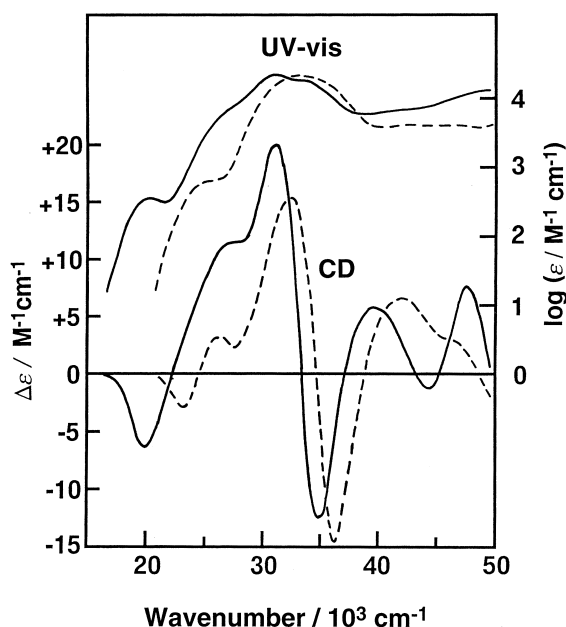| Complex | Total | Bond | Angle | Nonbonded | Torsion |
|---|---|---|---|---|---|
| *fac*-Δ(*R*)-[Co(L-cysi-N,S)$_2$(L-cysi-N,O)]$^{3-}$ | 121.9 | 8.0 | 81.6 | 12.0 | 20.2 |
| *fac*-Δ(*S*)-[Co(L-cysi-N,S)$_2$(L-cysi-N,O)]$^{3-}$ | 126.9 | 6.6 | 85.4 | 10.0 | 24.8 |



Fig. 3. UV–Vis and circular dichroism (CD) spectra of the starting complex, *fac*-Δ-(+)-[Co(L-cysi-N,S)$_3$]$^{3-}$ (**1**, – – –) and *fac*-Δ(*R*)-[Co(L-cysi-N,S)$_2$(L-cysi-N,O)]$^{3-}$ (**2**, ———).
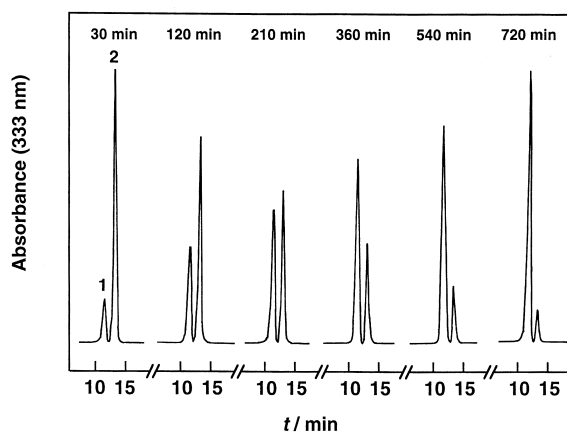


Fig. 4. Chromatograms obtained at various reaction times (30, 120, 210, 360, 540, and 720 min) during the linkage isomerization from *fac*-Δ(*R*)-[Co(L-cysi-N,S)$_2$(L-cysi-N,O)]$^{3-}$ (**2**) to *fac*-Δ-(+)-[Co(L-cysi-N,S)$_3$]$^{3-}$ (**1**) at 45°C in 0.23 *M* Na$_2$SO$_4$ aqueous solution. Chromatographic conditions: column, YMC-Pack IES-AX A-AX-12-46-35 (250×4.6 mm I.D., particle size 5 μm); eluent, 0.4 *M* NaCl in water; flow rate, 1.0 ml/min; UV detection, 333 nm.

area of band 1 increases, whereas that of band 2 decreases with time as the result of linkage isomerization. The plot of ln $S_t$ vs. time gave a straight line for three half-lives ($S_t$ denotes the area of band 2 at time *t*). The slope gave the first-order rate constant $k = 5.1 \times 10^{-5}$ s$^{-1}$.

## 4. Conclusions

A high-performance liquid chromatographic (HPLC) method was successfully applied to the kinetic study of the linkage isomerization from *fac*-Δ(*R*)-[Co(L-cysi-N,S)$_2$(L-cysi-N,O)]$^{3-}$ (**2**) to *fac*-Δ-[Co(L-cysi-N,S)$_3$]$^{3-}$ (**1**). This method has the great advantages that only a short elution time is required

and that only microquantities of samples are necessary.

## References

[1] L.S. Dollimore, R.D. Gillard, J. Chem. Soc. Dalton Trans. (1973) 933.
[2] H. Mäcke, V. Houlding, A.W. Adamson, J. Am. Chem. Soc. 102 (1980) 6889.

[3] V.H. Houlding, H. Mäcke, A.W. Adamson, Inorg. Chem. 20 (1981) 4279.

[4] M. Kojima, I. Sugimoto, Y. Shimizu, Y. Yoshikawa, Proc. Jpn. Acad. 70B (1994) 101.

[5] Y. Yoshikawa, J. Comput. Chem. 11 (1990) 326.

[6] N.L. Allinger, Y.H. Yuh, QCPE 11 (1980) 295.

[7] G.R. Brubaker, D.W. Johnson, Coord. Chem. Rev. 53 (1984) 1.

[8] G. Ma, T. Hibino, M. Kojima, J. Fujita, Bull. Chem. Soc. Jpn. 62 (1989) 1053.

[9] R.M. Cassidy, L. Sun, J. Chromatogr. A 654 (1993) 105.