X-Ray Crystallographic Approach to the Design of Phenolic Schiff Base Reagents for the Mutual Separation of Lanthanoids

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A novel mutual selectivity of lanthanoids in the *N,N'*-bis(5-nitrosalicylidene)ethylenediamine ($H_2Nsalen$)-KCl and *N,N'*-bis(5-nitrosalicylidene)-*o*-phenylenediamine ($H_2Nsaloph$)-KCl extraction systems was evaluated by the X-ray analysis of similar model complexes for extracted species. Cerium(IV) complexes with *N,N'*-bis(5-chlorosalicylidene)ethylenediamine ($H_2Clsalen$), *N,N'*-bis(salicylidene)-*o*-phenylenediamine ($H_2saloph$) and *N,N'*-bis(3,5-dibromosalicylidene)-*o*-phenylenediamine ($H_2Br_2saloph$) were selected as the models. The result of the X-ray analysis suggested that $[Ln(III)(Nsalen)_2]^-$ and $[Ln(III)(Nsaloph)_2]^-$ are meridional type (two ligands are oriented perpendicular to each other) and sandwich type (two ligands are oriented parallel to each other), respectively. It was suggested that the selectivity of the meridional structure is superior to that of the sandwich structure in these extraction systems.

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Lanthanoids have been utilized for magnetic and luminous materials, catalysts, or shift reagents, *etc.*¹ The mutual separation of lanthanoids in high purity, however, is very difficult owing to their remarkable chemical similarities. The only clue to their separation is a slight difference of their ion radii.²⁻⁴ Solvent extraction using a metal-complexing reagent is one of best choices as the separation method,^{5,6} and reagents having novel ion-size recognition ability have been desired. Several novel lanthanoids extraction systems have been investigated.⁷⁻⁹

Recently, we reported that quadridentate phenolic Schiff bases containing a nitro group, *N,N'*-bis(5-nitrosalicylidene)ethylenediamine ($H_2Nsalen$) and *N,N'*-bis(5-nitrosalicylidene)-*o*-phenylenediamine ($H_2Nsaloph$), can act as an effective extractant for the mutual separation of Ln^{3+} under the coexistence of a suitable counter cation.⁹ Furthermore, the mutual selectivity of lanthanoids on $H_2Nsalen$ was higher than that on $H_2Nsaloph$. The difference in the selectivity between these systems seems to result from the structure of the ligands or their complexes. We have aimed to design and construct a superior mutual separation system between lanthanoids. It is essential to evaluate the difference in the selectivity of the above two extraction systems from a structural viewpoint by X-ray crystallography. We tried to determine the structure of $M^+[Ln(III)(Nsalen)_2]^-$ or $M^+[Ln(III)(Nsaloph)_2]^-$ (for example, $M^+ = K^+$, Et_4N^+ , *etc.*) by single-crystal X-ray diffraction. However, the ion-pair Ln -complexes cannot be crystallized, but were merely precipitated, possibly owing to the existence of a nitro group in the ligands, or the difficulty in selecting a counter cation suitable for crystallization. Alternatively, the ligands containing an electron-attracting halogen group, $H_2Clsalen$ (*N,N'*-bis(5-chlorosalicylidene)ethylenediamine) and $H_2Br_2saloph$ (*N,N'*-bis(3,5-dibromosalicylidene)-*o*-phenylenediamine), or

non-substituted ligands, H_2salen (*N,N'*-bis(salicylidene)ethylenediamine) and $H_2saloph$ (*N,N'*-bis(salicylidene)-*o*-phenylenediamine), were selected as models of $H_2Nsalen$ and $H_2Nsaloph$, respectively. Ce^{4+} was selected as a central metal ion, because it can easily form a 1:2 uncharged crystalline complex with $H_2Clsalen$ or $H_2Br_2saloph$, rather than Ln^{3+} , and its ion size is almost the same as that of Lu^{3+} , which is the smallest cation in Ln^{3+} . The molecular structure of lanthanoid complexes, *e.g.* coordination number (CN), seems to be influenced mainly by the size of the central lanthanoid ions, rather than their charge. Actually, the typical CN of the smaller Ln^{3+} (heavy lanthanoid ions) and Ce^{4+} is eight, and it is considered that Ce^{4+} complexes with $H_2Clsalen$ or $H_2Br_2saloph$ can be used as a model of $[Ln(III)(Nsalen)_2]^-$ or $[Ln(III)(Nsaloph)_2]^-$ (Ln = small trivalent lanthanoids).

Herein, we report on the result of an X-ray structural analysis of lanthanoid complexes with halogen-substituted H_2salen or $H_2saloph$ as model complexes, whose structure is presumed to be the same as that of extracted species in the mentioned Ln^{3+} - $H_2Nsalen$ or Ln^{3+} - $H_2Nsaloph$ system, and evaluate the difference of the selectivity of the above two extraction systems, and mention the design of a superior mutual separation reagent.

Experimental

Reagents

The ligands $H_2Clsalen$ and $H_2Br_2saloph$ (Fig. 1) were synthesized from 5-chlorosalicylaldehyde and ethylenediamine, and 3,5-dibromosalicylaldehyde and *o*-phenylenediamine, respectively, according to literature methods.¹⁰

Preparation of the model complexes

Ce^{4+} complexes with $H_2Clsalen$ and $H_2Br_2saloph$ were prepared by a modifying a literature method.¹¹

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Fig. 1 Structure of Schiff base ligands.

Table 1 Crystallographic data of complexes **1** and **2**

	Ce(Cl ₂ salen) ₂ (1)	Ce(Br ₂ saloph) ₂ (2)
Formula	C ₃₂ H ₂₄ CeCl ₄ N ₄ O ₄	C ₄₀ H ₂₀ Br ₈ CeN ₄ O ₄
Formula weight	810.50	1139.83
Crystal size (mm)	0.25 × 0.30 × 0.35	0.35 × 0.10 × 0.10
Crystal system	orthorhombic	triclinic
Space group	P2 ₁ 2 ₁ 2 ₁	P $\bar{1}$
<i>a</i> (Å)	15.47(1)	12.89(1)
<i>b</i> (Å)	16.79(1)	15.74(2)
<i>c</i> (Å)	13.38(3)	12.14(4)
α (°)	90	100.2(1)
β (°)	90	99.4(1)
γ (°)	90	82.99(8)
<i>V</i> (Å ³)	3475(7)	2381(7)
<i>Z</i>	4	2
<i>D</i> _{cal} (g cm ⁻³)	1.549	1.590
<i>F</i> (0 0 0)	1608	1080
λ (Mo K α) (Å)	0.71069	0.71069
μ (Mo K α) (mm ⁻¹)	1.657	6.781
Temperature (K)	293	293
Max 2 θ (°)	55.1	55.0
No. reflections measured	4461	11422
No. independent reflections	4461	10933
No. observed reflections	1824	4614
No. parameters	406	514
<i>R</i>	0.0511	0.0670
<i>wR</i>	0.0315	0.0740
(Δ/σ) _{max}	0.00	0.00
(Δ/ρ) _{max} (e Å ⁻³)	0.00	0.00
(Δ/ρ) _{min} (e Å ⁻³)	-0.69	-1.33

Ce(Cl₂salen)₂ (1**).** A solution of cerium(III) chloride heptahydrate (559 mg, 1.5 mmol) in methanol (20 cm³) was added while being stirred to a hot solution of ligand, H₂Clsalen (843 mg, 2.5 mmol), in acetonitrile (150 cm³). A yellow solid of Ce(III)-complex was deposited, after which the complex was gradually oxidized by air, changed to a brownish Ce(IV) solid, and then dissolved. An ammonia solution (6 mol dm⁻³, 1 cm³) was added in order to complete the oxidation, and then stirred at 80°C for 0.5 h. The reaction mixture was allowed to stand at

Fig. 2 Molecular structure of Ce(Cl₂salen)₂ (**1**) showing the labeling of the non-H atoms. Displacement ellipsoids are drawn at the 50% probability level.

room temperature for *ca.* 1 day to produce dark-brown crystals of (**1**). Yield: 720 mg (71.3%). *Anal.* Calcd. for C₃₂H₂₄CeCl₄N₄O₄: C, 47.42; H, 2.98; N, 6.91. Found: C, 47.26; H, 3.00; N, 7.63%.

Ce(Br₂saloph)₂ (2**).** A dark-brown crystalline product was obtained by using the same procedure as that described for complex **1**, except for replacing H₂Clsalen with H₂Br₂saloph. Yield: 0.85%. *Anal.* Calcd. for C₄₀H₂₀Br₈CeN₄O₄: C, 34.32; H, 1.44; N, 4.00. Found: C, 33.41; H, 1.51; N, 3.54%.

Crystallography

Each of prismatic dark-brown crystal complexes **1** and **2** was mounted in a glass fiber. Data were collected on a Rigaku AFC-7R diffractometer. Lorentz and polarization corrections were applied. An absorption correction based on Ψ -scans was introduced. The structure was solved by heavy-atom Patterson methods¹² and expanded using Fourier techniques.¹³ The structure was refined by a full-matrix least-squares procedure on *F* using the teXsan package.¹⁴ All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included with idealized geometry, but not refined. The details of data collection and crystallographic data are summarized in Table 1.

Results and Discussion

Molecular structure of model complexes

The molecular structure of complex **1**, indicating the numbering of the atoms, is shown in Fig. 2. Positional parameters and temperature factors for non-H atoms are listed in Table 2. The cerium atom is in a distorted square antiprism environment, being bonded to four oxygen atoms and four nitrogen atoms in two quadridentate Clsalen²⁻ dianions, which are oriented perpendicular to each other (meridional type). The meridional structure was also reported for that of [Hpipe][Er(salen)₂] (Hpipe = piperidinium).¹⁵ The radius of the tetravalent cerium cation is the smallest in the stable lanthanoides, nearly equal to that of Lu³⁺. Therefore, the H₂Nsalen complex with heavy lanthanoid ions seems to have a meridional structure.

A complex of Ce⁴⁺ with monochloro- or bromo-substituted H₂saloph, (H₂Clsaloph or H₂Br₂saloph) was prepared. However, a single crystal suitable for X-ray analysis has not been obtained. Therefore, complexes Ce⁴⁺ with dibromo-substituted and non-substituted ligands were used as models.

X-ray analysis of Ce(saloph)₂ has been already reported by Terzis *et al.*¹¹ The complex is eight-coordinated by two quadridentate ligands, forming a distorted square antiprism (Fig. 3). The two saloph²⁻ ligands are oriented parallel to each other

Table 2 Positional parameters and B_{eq} Ce(ClSalen)₂ (1)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq}
Ce	0.17956(4)	0.10542(3)	0.00604(6)	5.92(1)
Cl(1)	-0.2962(2)	0.0535(2)	-0.1360(3)	11.7(1)
Cl(2)	0.5766(3)	0.2636(3)	0.2894(3)	13.6(2)
Cl(3)	0.4304(2)	0.3498(2)	-0.3953(3)	12.0(1)
Cl(4)	-0.1750(2)	-0.1933(2)	0.0261(3)	12.7(1)
O(1)	0.0784(5)	0.0761(5)	-0.1063(5)	6.2(2)
O(2)	0.3071(6)	0.0858(5)	0.0840(6)	8.3(3)
O(3)	0.2292(4)	0.2119(4)	-0.0653(5)	6.4(2)
O(4)	0.0983(6)	0.0377(5)	0.1130(6)	7.0(3)
N(1)	0.0501(5)	0.2012(5)	0.0302(6)	5.8(3)
N(2)	0.1887(7)	0.1958(5)	0.1615(7)	6.4(3)
N(3)	0.2787(7)	0.0630(6)	-0.1430(8)	7.4(4)
N(4)	0.2001(6)	-0.0434(5)	-0.0191(8)	7.2(3)
C(1)	-0.0059(8)	0.0757(7)	-0.1127(8)	5.6(3)
C(2)	-0.043(1)	0.0155(9)	-0.1739(9)	8.1(5)
C(3)	-0.1327(9)	0.0107(8)	-0.177(1)	8.9(5)
C(4)	-0.1867(9)	0.0638(7)	-0.1320(9)	7.6(4)
C(5)	-0.1511(7)	0.1232(6)	-0.0758(7)	5.2(3)
C(6)	-0.0616(8)	0.1311(6)	-0.0651(7)	5.5(3)
C(7)	-0.0269(6)	0.1926(5)	-0.0028(9)	5.0(2)
C(8)	0.0675(7)	0.2667(7)	0.0961(9)	6.6(4)
C(9)	0.1086(8)	0.2347(8)	0.1890(9)	7.0(4)
C(10)	0.253(1)	0.2190(9)	0.212(1)	7.3(5)
C(11)	0.341(1)	0.193(1)	0.194(1)	7.2(5)
C(12)	0.407(1)	0.230(1)	0.247(1)	8.3(5)
C(13)	0.493(1)	0.214(1)	0.229(1)	9.7(6)
C(14)	0.516(1)	0.153(1)	0.166(1)	9.5(6)
C(15)	0.454(1)	0.1093(8)	0.1153(9)	8.6(5)
C(16)	0.3657(9)	0.1303(9)	0.132(1)	6.9(5)
C(17)	0.2726(8)	0.2416(7)	-0.142(1)	5.8(4)
C(18)	0.2725(6)	0.3232(8)	-0.1627(9)	6.2(4)
C(19)	0.3185(9)	0.3572(6)	-0.2394(9)	6.9(4)
C(20)	0.3680(8)	0.3072(8)	-0.299(1)	7.3(4)
C(21)	0.3702(8)	0.2276(9)	-0.2833(9)	7.0(4)
C(22)	0.320(1)	0.1928(8)	-0.2066(8)	5.9(4)
C(23)	0.3211(9)	0.1096(8)	-0.2022(8)	6.9(3)
C(24)	0.2837(9)	-0.0224(7)	-0.1626(9)	9.2(5)
C(25)	0.2778(8)	-0.0669(6)	-0.067(1)	9.3(4)
C(26)	0.1381(8)	-0.0952(6)	-0.007(1)	6.9(3)
C(27)	0.0529(8)	-0.0825(7)	0.0331(9)	6.6(4)
C(28)	-0.0123(9)	-0.1374(7)	0.0152(9)	7.3(4)
C(29)	-0.0921(9)	-0.1280(8)	0.0533(9)	8.4(5)
C(30)	-0.1089(9)	-0.0635(9)	0.113(1)	8.3(5)
C(31)	-0.045(1)	-0.0110(8)	0.1356(9)	7.0(4)
C(32)	0.0377(9)	-0.0153(7)	0.0964(9)	5.8(4)

$$B_{\text{eq}} = (8/3) \pi^2 (U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha.$$

(sandwich type). A 1:2 complex with Ln and a planar quadridentate ligand, such as H₂saloph, seems to prefer a sandwich orientation rather than a meridional one, because of the rigidity of the phenylenediamine bridge in the ligand.

The molecular structure of complex **2**, indicating the numbering of the atoms, is shown in Fig. 4. The positional parameters and temperature factors for non-H atoms are listed in Table 3. The cerium atom is in a distorted square antiprism environment, belonging to two largely distorted Br₂saloph²⁻, which are oriented in a meridional structure in a similar manner as complex **1** (Fig. 5). The dihedral angles between two cerium coordination least-squares planes (Ce–O(1)–N(1)–N(2)–O(2) and Ce–O(3)–N(3)–N(4)–O(4)) in complex **1** and complex **2** are 92.64° and 92.40°, respectively. Here, the ideal dihedral angles between their planes in the meridional type and the sandwich type are 90° and 0°, respectively. The conformation of Br₂saloph²⁻ in the complex differs from that of Ce(saloph)₂,

Fig. 3 Molecular structure of Ce(saloph)₂. Fig. 4 Molecular structure of Ce(Br₂saloph)₂ (**2**) showing the labeling of the non-H atoms. Displacement ellipsoids are drawn at the 50% probability level.

against our expectation. A steric repulsion between Br atoms at the 3-position of salicylidene groups in the two ligands appears to cause the meridional orientation. In the conformation of Ce(Br₂saloph)₂, assuming the same sandwich orientation as that of Ce(saloph)₂, the interatomic distance between Br(1) and Br(5) (or Br(7)) should be shorter than the van der Waals distance. H₂Nsaloph is a mono-substituted molecule for H₂saloph, at the 5-position of salicylidene group, and the substituent cannot cause a steric repulsion between the two ligands in the complex. Therefore, the complex with the heavy lanthanoids seems not to be a meridional structure but a sandwich one.

From the result of the comparison between the molecular structures of Ce(ClSalen)₂ and Ce(saloph)₂, we consider that the difference in the mutual separability of the small Ln³⁺ (Lu³⁺, Yb³⁺, Tm³⁺, *etc.*) in the H₂Nsalen-KCl and H₂Nsaloph-KCl extraction systems results from the orientation of two coordinating ligands. Namely, the formation of a meridional structure as extracted species can give a higher separability than that of the sandwich structure. Here, the superiority of the ligands which can form the meridional complexes seems to be observed not only in small (heavy) lanthanoid ions, but also in large (light) lanthanoid ions. In the meridional complexes, a larger ion obviously causes a larger distortion of the ligand molecules and, namely, a lower stability constant and extraction constant.

Table 3 Positional parameters and B_{eq} $\text{Ce}(\text{Br}_2\text{saloph})_2$ (2)

Atom	x	y	z	B_{eq}
Ce	0.69472(5)	0.25106(5)	0.83175(6)	2.48(2)
Br(1)	0.7263(1)	0.3978(1)	0.5110(1)	5.01(4)
Br(2)	1.1611(1)	0.43540(9)	0.6275(1)	4.45(4)
Br(3)	0.4127(1)	0.0539(1)	0.7301(1)	8.24(6)
Br(4)	0.6377(2)	-0.2065(1)	0.9608(2)	11.08(8)
Br(5)	0.9799(1)	0.0195(1)	0.8603(2)	9.62(6)
Br(6)	0.7752(2)	-0.2281(1)	0.5280(2)	9.73(7)
Br(7)	0.6449(1)	0.40626(9)	1.2127(1)	4.30(4)
Br(8)	0.2013(1)	0.4632(1)	1.1048(1)	5.58(5)
O(1)	0.7614(6)	0.3302(5)	0.7328(6)	3.5(2)
O(2)	0.5902(6)	0.1582(5)	0.8584(6)	3.9(2)
O(3)	0.7984(6)	0.1409(6)	0.7720(6)	3.9(2)
O(4)	0.6253(5)	0.3500(5)	0.9597(6)	3.0(2)
N(1)	0.8734(7)	0.3022(6)	0.9420(8)	2.7(2)
N(2)	0.7692(7)	0.1851(6)	1.0149(7)	2.4(2)
N(3)	0.6209(7)	0.1844(7)	0.6241(8)	3.4(3)
N(4)	0.5161(7)	0.3233(5)	0.7410(7)	2.7(2)
C(1)	0.8509(8)	0.3513(7)	0.7110(9)	2.6(3)
C(2)	0.8543(9)	0.3850(8)	0.612(1)	3.3(3)
C(3)	0.9453(9)	0.4082(7)	0.5853(9)	3.0(3)
C(4)	1.0396(8)	0.4020(8)	0.6632(9)	3.0(3)
C(5)	1.0386(8)	0.3689(8)	0.758(1)	3.3(3)
C(6)	0.9464(8)	0.3443(8)	0.7852(9)	2.8(3)
C(7)	0.9499(9)	0.3232(8)	0.897(1)	3.6(3)
C(8)	0.8912(8)	0.2954(8)	1.063(1)	3.1(3)
C(9)	0.957(1)	0.3499(8)	1.139(1)	4.0(4)
C(10)	0.970(1)	0.340(1)	1.251(1)	5.3(4)
C(11)	0.916(1)	0.2807(9)	1.287(1)	4.5(4)
C(12)	0.853(1)	0.2282(8)	1.210(1)	3.5(3)
C(13)	0.8375(9)	0.2349(8)	1.0959(9)	2.7(3)
C(14)	0.758(1)	0.1078(9)	1.029(1)	4.2(4)
C(15)	0.683(1)	0.0485(9)	0.963(1)	3.7(4)
C(16)	0.691(1)	-0.0378(9)	0.986(1)	4.9(4)
C(17)	0.621(2)	-0.093(1)	0.937(2)	9.9(7)
C(18)	0.541(2)	-0.069(1)	0.857(1)	7.8(6)
C(19)	0.529(1)	0.012(1)	0.835(1)	5.3(4)
C(20)	0.599(1)	0.0821(9)	0.884(1)	4.6(4)
C(21)	0.794(1)	0.062(1)	0.719(1)	4.5(4)
C(22)	0.867(1)	-0.012(1)	0.741(1)	6.0(5)
C(23)	0.862(1)	-0.096(1)	0.687(1)	6.8(5)
C(24)	0.777(1)	-0.114(1)	0.606(1)	7.9(5)
C(25)	0.706(1)	-0.0508(9)	0.576(1)	4.8(4)
C(26)	0.708(1)	0.0357(8)	0.629(1)	4.1(4)
C(27)	0.6335(9)	0.0998(9)	0.583(1)	3.8(3)
C(28)	0.5544(8)	0.2417(8)	0.558(1)	3.1(3)
C(29)	0.541(1)	0.2327(9)	0.437(1)	4.1(4)
C(30)	0.481(1)	0.2915(9)	0.379(1)	4.5(4)
C(31)	0.433(1)	0.363(1)	0.437(1)	4.7(4)
C(32)	0.4446(9)	0.3756(8)	0.558(1)	3.5(3)
C(33)	0.5047(8)	0.3139(8)	0.619(1)	3.0(3)
C(34)	0.4373(8)	0.3593(7)	0.799(1)	2.8(3)
C(35)	0.4424(9)	0.3802(7)	0.9116(8)	2.0(3)
C(36)	0.3463(9)	0.4089(7)	0.948(1)	2.5(3)
C(37)	0.3355(9)	0.4315(7)	1.053(1)	2.8(3)
C(38)	0.428(1)	0.4320(7)	1.136(1)	3.4(3)
C(39)	0.5209(9)	0.4070(8)	1.099(1)	3.3(3)
C(40)	0.5341(9)	0.3770(7)	0.9901(9)	2.3(3)

$$B_{\text{eq}} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}(aa^*bb^*)\cos\gamma + 2U_{13}(aa^*cc^*)\cos\beta + 2U_{23}(bb^*cc^*)\cos\alpha).$$

View of the design of the superior mutual separation reagent

As mentioned above, the formation of a lanthanoid complex having a meridional structure is greatly affected by its ion size and, therefore, H_2Nsalen seems to show a high mutual extraction selectivity of lanthanoids. From this reason, the cavity (the space in which metal ion can be fitted with the ligand) in the meridional structure may be preferable for recognizing the ion size. The efficient separation of a specific size of lanthanoids can be realized by varying the cavity size in the H_2Xsalen type ligands.

Fig. 5 Coordination geometry about the Ce atom in a meridional-type complex showing the atom labeling scheme: (a) $\text{Ce}(\text{ClSalen})_2$ (1); (b) $\text{Ce}(\text{Br}_2\text{saloph})_2$ (2).

On the other hand, $\text{H}_2\text{Br}_2\text{saloph}$ can also form meridional type complexes with heavy lanthanoid ions because of a steric repulsion between Br atoms at the 3-position of the salicylidene groups. This fact suggests that, in forming Ln complexes with the H_2saloph type ligands, the substituent at the 3-position of salicylidene groups can affect the conformation of the ligand. The introduction of various substituents at the 3-position of the salicylidene groups in those ligands may give a novel mutual separation ability of lanthanoids.

The separation systems discussed here are based on “structural control on the orientation of the ligand” in the extracted complex according to ion size, and the mutual separability of Ln^{3+} can be extremely improved in this extraction system. The separation in a new category system must be interesting and will be useful in the future.

Single-crystal X-ray diffraction is an effective method for the design of analytical reagents, though there is a restriction in that only crystalline samples can be used.

Supplementary Material

The detailed crystallographic data of the structure described in this paper are available from the authors.

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