Stereochemistry effect of dicyclohexano-18-crown-6 on zinc isotope separation

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Zinc isotope fractionation is reported with the pure *cis-syn-cis* and *cis-anti-cis* stereoisomers of dicyclohexano-18-crown-6. These structures contribute differently to the enrichment of the Zn isotopes, and the best fractionation was obtained with the *cis-syn-cis* derivative.

Considered one of the most difficult technical problems to solve, isotope enrichment is governed by the mass, nuclear size and shape, and spin differences between isotopes according to the Bigeleisen theory,[1,2] and applied to the isotopic separation of elements with $Z > 38$ by

$$\ln\alpha = \varepsilon = a(\Delta m/mm') + b\nu_{\mathrm{fs}} + hf$$

where a is the weight contribution of the nuclear mass shift (sum of the vibrational energy shift and mass shift), m and m' are the nuclear masses of the isotopes, Δm is the difference in mass of the isotopes, and b is the weight of contribution of the field shift. The field shift (ν_{fs}) is a kind of isotope shift in orbital electrons that results from an isotopic difference in nuclear size and shape. The field shift gives an isotope effect *via* displacement of the electronic molecular state. The contribution of the hyperfine structure is represented by hf, induced by the coupling of the nuclear and electronic spin angular momenta (nuclear spin effect). This theory is now widely used among the scientific community to explain these unusual isotope effects. Isotopic separation has been carried out for nearly 60 years by industry, where separation methods such as gaseous diffusion, electromagnetic methods and ultracentrifugation have been employed. However, these expensive physical processes are only conceivable for applications in the nuclear industry, whose economical features are far different from other industrial and scientific areas (analysis, material science, medicine...). Thus, some processes are based on chemical exchange systems, such as liquid–liquid extraction experiments with dicyclohexano-18-crown-6 (DCH18C6) in chloroform.[3–11] With five stable isotopes, ^{64}Zn (48.6%), ^{66}Zn (27.9%), ^{67}Zn (4.1%), ^{68}Zn (18.8%) and ^{70}Zn (0.6%), natural zinc is considered to be a useful transition metal for cooling water treatment in light water nuclear power plants.[12] Already examined in liquid extraction experiments with DCH18C6,[5a,c] the mass-independent isotope fractionation of zinc was initially explained by odd/even isotope theory.[5c] DCH18C6 is traditionally purchased as a mixture of *cis-syn-cis* and *cis-anti-cis* stereoisomers in a 63 : 37 ratio. As far as we know, only Jepson and De Witt have reported a study of the pure stereoisomers in calcium isotope separation.[4] Unfortunately, no contribution from the stereochemistry on the separation data was observed with these ligands. However, it is well known that stereochemical factors play a significant role in determining the stability of both organic and metal cationic complexes in appropriately modified structures of 18-crown-6 derivatives, especially the stereoisomers of DCH18C6.[13] Here, we report the effect of the structure of DCH18C6 on zinc isotope separation, as permitted by precise analyses of the isotope ratios obtained by multiple-collector inductively-coupled plasma mass spectrometry (MC-ICP-MS, Nu Plasma 500 HR). In the present study, we measured the enrichment factors of ^{67}Zn and ^{68}Zn to ^{66}Zn. ^{64}Zn was not considered alongside other isotopes because of potential interference from ^{64}Ni.

The isotope separation factor (α_{m}) between the aqueous and the organic phases is defined as

$$\alpha_{\mathrm{m}} = \frac{([^{m}\mathrm{Zn}]/[^{66}\mathrm{Zn}])_{\mathrm{org}}}{([^{m}\mathrm{Zn}]/[^{66}\mathrm{Zn}])_{\mathrm{aq}}}$$

where ^{m}Zn indicates an isotope of zinc (^{67}Zn, ^{68}Zn, ^{70}Zn), and $([^{m}\mathrm{Zn}]/[^{66}\mathrm{Zn}])_{\mathrm{org}}$ and $([^{m}\mathrm{Zn}]/[^{66}\mathrm{Zn}])_{\mathrm{aq}}$ are the isotopic ratios obtained in the organic and aqueous phases. The enrichment factor (ε) is defined as $\varepsilon = \alpha - 1$. Since α is close to 1, the approximation $\varepsilon = \ln\alpha$ is often used. The experimental values of $([^{m}\mathrm{Zn}]/[^{66}\mathrm{Zn}])_{\mathrm{org}}$, corresponding to the extraction of zinc isotopes, respectively, with the mixture of DCH18C6 *cis-syn-cis* and *cis-anti-cis* stereoisomers, and $([^{m}\mathrm{Zn}]/[^{66}\mathrm{Zn}])_{\mathrm{aq}}$ (feed stock) are reported in Table 1. This allows the calculation of ε, defined as 10^{-4} units, which are illustrated in the Fig. 1 and Fig. 2.

The uncertainties of ^{67}Zn/^{66}Zn and ^{68}Zn/^{66}Zn were 0.2–0.3 and 0.1‰, respectively, depending on the extractant type. Because of the very low abundance of ^{70}Zn (0.6%), we could not obtain precise enough ^{70}Zn/^{66}Zn data for assessment of the isotope fractionation, and we have reported a theoretical enrichment factor based on a predictive odd isotope effect, as already assumed in the Bigeleisen theory. Although the excessive enrichment of ^{67}Zn was observed, as already described in

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Table 1 Measurement results of stock solutions, back-extraction solution and enrichment factors

	$^{m}Zn/^{66}Zn$		$\varepsilon_{m/66}$ ($\times 10^{-4}$)		
	$^{68}Zn/^{66}Zn$	$^{67}Zn/^{66}Zn$	$\varepsilon_{67/66}$	$\varepsilon_{68/66}$	$\varepsilon_{70/66}$[a]
Feedstock	0.6607752	0.1452924	—	—	—
Mixture	0.6602225	0.1453459	3.68223	−8.36442	−16.7289
cis-syn-cis	0.6602109	0.1454610	11.60419	−8.53997	−17.0789
cis-anti-cis	0.6603549	0.1452944	0.13765	−6.36071	−12.7249

[a] Theoretical.

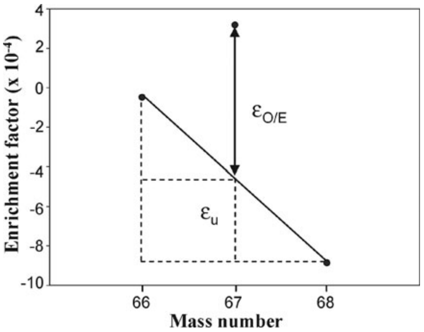

Fig. 1 Isotopic enrichment factor of zinc with the mixture of *cis-syn-cis* and *cis-anti-cis* DCH18C6.

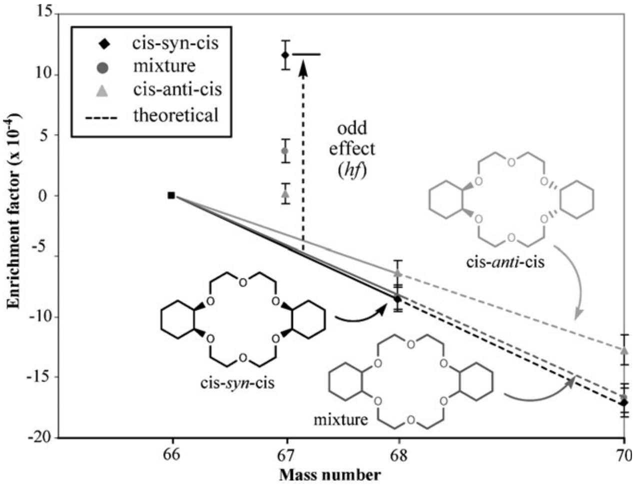

Fig. 2 Isotopic enrichment factors of zinc with DCH18C6 (pure or mixture of *cis-syn-cis* and *cis-anti-cis* stereoisomers). Error bars correspond to the level precision of the RSD <10%. They were calculated from the measurements of isotope ratios (40 measurements by sample).

Fujii's and Nishizawa's previous studies,[5a,c,d] a correlation of ε to DCH18C6 was observed with the isotopes of even mass. According to previous work,[5c] an enrichment of light even isotopes is obtained in the organic phase, but the measured values were lower than those already determined.[5c] To describe the unusual behavior of the odd mass number isotopes, unit mass enrichment (ε_u) and odd/even enrichment factor ($\varepsilon_{O/E}$) terms are generally introduced. By combining the observed enrichment factors of the even mass number isotopes (Fig. 1), ε_u represents the isotope separation effect per one mass number difference, corresponding to the slope of the line. The $\varepsilon_{O/E}$ corresponds to the difference between the expected value (on the line) and the experimental value. With the mixture of DCH18C6, the unit mass enrichment factor was surprisingly $\varepsilon_u = 0.00042$ for 2 M $ZnCl_2$ and 0.7 M HCl, while it was evaluated to be 0.006 in previous work (14 times higher).[5c] As already noticed in the literature, the odd/even atomic mass effects were usually much larger than the isotope separation of unit mass difference.[5] Here, the odd/even atomic mass effect value was determined as $\varepsilon_{O/E} = 0.00079$, two times larger than that of ε_u and of opposite sign, which was also lower than the effect observed by Fujii *et al.* (0.045).[5d]

Moreover, a correlation of ε to the stereoisomers of DCH18C6 was also clearly observed (Fig. 2). The *cis-syn-cis* macrocycle appeared to be the most efficient ligand, with experimental $\varepsilon_{68,66} = -0.00085$, close to the value determined with the mixture of stereoisomers (−0.00084), but with $\varepsilon_{67,66} = 0.00116$, clearly higher than the value obtained with the mixture of stereoisomers (0.00037). Finally, the fractionation of zinc isotopes with the *cis-anti-cis* isomer was less pronounced, with $\varepsilon_{67,66}$ and $\varepsilon_{68,66}$ values of 0.00001 and −0.00064, respectively.

With the contribution of the theoretical values of $\varepsilon_{70,66}$, it was possible to obtain three equations for the isotope pairs $^{67}Zn/^{66}Zn$, $^{68}Zn/^{66}Zn$ and $^{70}Zn/^{66}Zn$, allowing the contribution of the nuclear mass-dependent effect ($a(\Delta m/mm')$), the field shift effect ($b\nu_{fs} = b\delta\langle r^2\rangle$, where $\delta\langle r^2\rangle$ is the isotopic change in the mean-square radius) and the hyperfine shift *hf* to the enrichment factor to be evaluated.

The nuclear mass effect and the field shift effect can be separated by using the experimental contribution of $\varepsilon_{68,66}$ and the theoretical $\varepsilon_{70,66}$ value, irrespective of interference from the nuclear spin (*hf*), because the nuclear spins of the even atomic mass isotopes ^{66}Zn, ^{68}Zn and ^{70}Zn is zero. The field shifts of zinc, the relative values of $\delta\langle r^2\rangle$ and the reduced masses are listed in Table 2.[14] The relative values were used to calculate the scaling factors *a* and *b*.

Whatever the ligand, we observed that the nuclear mass effects were larger than the field shift effects and showed identical signs (Table 3), which is different to those observed for the enrichment of zinc isotopes in a chemical exchange reaction by cryptands.[5d,14] Thus, the contribution of the nuclear mass effect is about 2.70 times larger than the field shift effect for the mixture of DCH18C6 stereoisomers: the *cis-syn-cis* and the *cis-anti-cis* derivatives. For $\varepsilon_{67,66}$, the contribution of the nuclear spin effects *hf* due to the nuclear spin $\frac{5}{2}$ of ^{67}Zn, means that it has an opposite sign to the nuclear mass and the field shift effects. With significant values

Table 2 Reduced masses and field shifts of zinc

	Isotope		
	66,67	66,68	66,70
$(\Delta m/mm')/10^{-4}$	2.21	4.456	8.658
$(\Delta m/mm')_{rel}$[a]	0.5074	1	1.9430
Field shift ν_{fs}/GHz[b]	−0.140	−0.620	−1.332
$(\delta\langle r^2\rangle)_{rel}$[b]	0.2262	1	2.1548

[a] Rel = relative value. [b] Ref. 14.

Table 3 Evaluation of scaling factors a and b, and values of hf

	Crown ether		
	Mixture	*cis-syn-cis*	*cis-anti-cis*
a	−6.136	−6.247	−4.6329
b	−2.228	−2.293	−1.7278
a/b	2.754	2.724	2.681
hf	7.300	7.916	2.878

of 7.300 and 7.916, respectively for the mixture of DCH18C6 stereoisomers and the *cis-syn-cis* derivative, it represents the largest effect on ^{67}Zn/^{66}Zn fractionation.

In conclusion, we have shown that a slight difference in ligand structure has a large effect on the separation of transition metal isotopes, and this observation opens up new possibilities for the design of ligands for isotope separation. Zinc isotopes were fractionated using liquid/liquid extraction with DCH18C6, and its pure *cis-syn-cis* and *cis-anti-cis* stereoisomers. In this study, we observed that the structure of the stereoisomers of DCH18C6 contributes significantly to the enrichment of Zn isotopes, with the best fractionation by the *cis-syn-cis* derivative. The mass-dependent effect is larger than the field shift effect, and both effects are identical towards the enrichment of Zn isotopes. Finally, the nuclear spin effect is recognized to enhance the enrichment factor of ^{67}Zn in the opposite direction to the sum of the contribution of the nuclear mass and field shift effects. Taking into account the potential interest in preparing pure stable isotopes of metals in the fields of physics and materials sciences, these observations could open new opportunities to design ligands for practical isotope separation.

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Experimental section

General procedure for zinc isotope fractionation

20 mL of an aqueous solution (0.7 M HCl in de-ionized water) containing zinc chloride (99.999%, 2 M) and 20 mL of an organic solution containing the DCH18C6 (0.2 M) as a mixture of both stereoisomers (63 : 37) or pure *cis-syn-cis* and *cis-anti-cis* ligands, previously obtained as described in the literature,[13e] were vigorously stirred for 30 min at 300 K in a flat-bottomed flask. The solution mixture was then transferred to a separating funnel and stood still for 30 min so that the phases could separate. The organic phase was isolated and then scrubbed with 20 mL of pure water to back-extract the $ZnCl_2$ into the water. The zinc chloride salt in the back-extraction solutions were then dried by heating. In order to decompose residual organic substances, 5 mL of 14 M nitric acid was added to the dried salt and it was heated for 45 min. 1 mL of 30% hydrogen peroxide was then added and the solutions heated to dryness to prepare the sample for measurement of $Zn(NO_3)_2$ concentration (ICP-AES) and isotopic composition (MC-ICP-MS). 500 ppb solutions of zinc in 0.05 M HNO_3 were prepared for isotopic analysis and introduced into the Nu Plasma 500 HR.

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