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Anion receptor functions of lanthanide tris(β-diketonate) complexes: naked eye detection and ion-selective electrode determination of Cl^- anion

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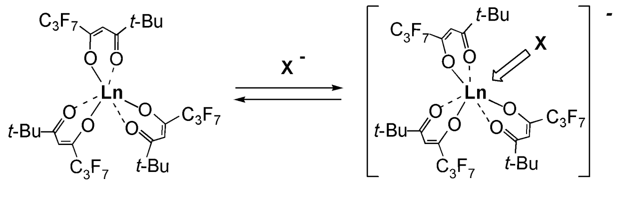
Lanthanide tris(fluorinated β-diketonates) acted as effective receptors of Cl^- anion in luminescence sensing and ion-selective electrode systems *via* highly coordinated complexation.

Since various inorganic anions play fundamental roles in chemical and biological systems,[1] their specific receptors have been extensively developed to monitor the targeted anions of biological, environmental, clinical, and industrial interest.[2] Lanthanide complexes have recently been recognized as effective sensory materials,[3] because one or more additional substrates can be bound upon highly coordinated complexation. A series of macrocyclic lanthanide complexes have attracted considerable attention as luminescent sensory materials.[4] Parker and Gunnlaugsson presented lanthanide cyclen complexes for selective detection of HCO_3^- anion.[5] Furthermore, acyclic pyridine derivatives were employed as useful multidentate ligands for anion-responsive lanthanide complexes.[6,7]

We describe here lanthanide tris(β-diketonates) applied for the first time as effective anion receptors in naked eye detection and ion-selective electrode determination. Although various colorimetric reagents and electrochemical devices have already been developed for use in anion sensing processes,[8,9] our employed lanthanide tris(β-diketonates) **1–4** have unique receptor characteristics (Fig. 1): (1) several vacant coordination sites on the lanthanide center are available for anion recognition;[3] (2) both selectivity and sensitivity in anion coordination are modified by a proper selection of lanthanide center;[7] (3) intense and steady lanthanide luminescence is provided by bidentate β-diketonate ligands; and (4) stability and solubility of the lanthanide receptor in the electrode membrane are enhanced by use of fluorinated ligand. Therefore, this type of lanthanide complex is expected to offer visual sensing of anionic guests and rapid determination of aqueous samples.

The highly coordinated complexation between lanthanide tris(β-diketonate) and inorganic anion was monitored in $CDCl_3$ by the ^{1}H-NMR method. The addition of lanthanide receptor to a solution of Bu_4NCl, Bu_4NBr, Bu_4NI or Bu_4NClO_4 salt caused characteristic shifts of proton signals for $(CH_3CH_2CH_2C\mathit{H_2})_4N^+$ cation. The obtained titration curves showed saturation in the presence of excess lanthanide complex and gave good fits for 1 : 1 complexation.[10] Table 1 summarizes the estimated stability constants for lanthanide tris(β-diketonates) **1–4** with four kinds of anions, indicating that each lanthanide receptor preferred smaller (harder) Cl^- anion to larger (softer) Br^-, I^- or ClO_4^- anion.[11] The estimated *K* values for Cl^- anion depended on the natures of lanthanide centers but exhibited a different trend from that of ionic radii: for stability constant (*K* value), Pr^{3+} (450) < Eu^{3+} (600) = Dy^{3+} (610) > Yb^{3+} (94); for ionic radius of octacoordinated lanthanide center,[12] Pr^{3+} (1.13 Å) > Eu^{3+} (1.07 Å) > Dy^{3+} (1.03 Å) > Yb^{3+} (0.99 Å). These probably mean that a smaller lanthanide center provides shorter coordination from the Cl^- anion but larger steric repulsion between β-diketonates and Cl^- anion.



1: $Ln^{3+} = Pr^{3+}$, **2**: $Ln^{3+} = Eu^{3+}$, **3**; $Ln^{3+} = Dy^{3+}$, **4**: $Ln^{3+} = Yb^{3+}$.

Fig. 1 Structures of lanthanide tris(β-diketonates) **1–4** and their highly coordinated complexes with anion (X^-).

Typically, when 3 equivalent Cl^- anion was added to a CH_3CN solution of europium tris(β-diketonate) **2**, the europium luminescence observed at 611 nm was enhanced 2.0-fold.[13] Since the addition of Br^-, I^- or ClO_4^- anion slightly influenced the luminescence intensity (< 1.3-fold), the anion-enhanced luminescence was recorded in a similar trend to that of *K* values. The addition of F^- anion greatly changed UV spectrum of europium tris(β-diketonate) **2**. Although this anion formed the highly coordinated complex, the europium luminescence was suppressed.[14] The Cl^- anion-responsive luminescence was large enough to be recognized by the naked eye (see Graphical abstract), though Br^-, I^- and ClO_4^- anions offered undetectable luminescence under the employed conditions.[15] These provide a possibility that lanthanide tris(β-diketonate) receptors allow anion-selective detection without use of any spectroscopic instrumentation.

The lanthanide tris(β-diketonates) acted as Cl^- anion-specific receptors in ion-selective electrode systems when they were incorporated in poly(vinyl chloride) (PVC) membrane.[16] The potentiometric cell used was Ag/AgCl/1.0×10^{-2} M NaCl/PVC membrane/test solution/Ag/AgCl. Their potentiometric response profiles were characterized by fixed interference method at 1.0×10^{-2} M of interfering anions (Fig. 2). All the lanthanide tris(β-diketonates) exhibited near Nernstian re-

Table 1 Lanthanide tris(β-diketonates) and their highly coordinated complexation[a]

	Stability constant (K: M^{-1}) in $CDCl_3$			
Ln^{3+} Complex	Cl^-	Br^-	I^-	ClO_4^-
1	450[b]	79	[c]	[c]
2	600	84	[c]	[c]
3	610[b]	28	20	15
4	94[b]	11[b]	[c]	[c]

[a] Conditions: tetrabutylammonium salt, 0.0200 mol L^{-1}; Ln^{3+} complex, 0–0.0600 mol L^{-1}; at 25 °C. [b] Slightly cloudy. [c] Too small to be determined.

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sponses for Cl^- anion, and the slope (mV $decade^{-1}$) was measured as −56.0 for Pr^{3+} complex **1**, −57.6 for Eu^{3+} complex **2**, −51.8 for Dy^{3+} complex **3**, and −55.9 for Yb^{3+} complex **4**, respectively. The response time of each electrode, tested by measuring the time required to achieve a steady state potential (with ±1 mV), was less than 30 seconds. These lanthanide receptors operated well within the range of pH 2–6, and their response stability was maintained for two months. Fig. 2 indicates that the employed lanthanide-based electrodes are highly selective towards Cl^- anion in comparison with many common anions: F^-, Br^-, I^-, SCN^-, OH^-, HCO_3^-, $CH_3CO_2^-$, NO_3^-, ClO_4^- and SO_4^{2-} anions. Although Br^-, I^- and SCN^- anions competed with Cl^- anion in the Pr^{3+}, Dy^{3+} and Yb^{3+} complex systems, Eu^{3+} complex **2** gave high selectivity coefficients for Cl^- anion: $pK_{Cl,Br} = -1.19 \gg pK_{Cl,I} = -2.71 > pK_{Cl,ClO4} = -2.94$. Copper bis(β-diketonate) was also examined under the same conditions, but its selectivity and sensitivity were extremely low: $pK_{Cl,Br} = -0.24 \leqslant pK_{Cl,I} = -0.21 \gg pK_{Cl,ClO4} = -2.88$. It is probable that the highly coordinated complexation with lanthanide receptor plays essential roles in the anion-selective electrode systems. These results successfully demonstrated that lanthanide tris(β-diketonate) receptors are of practical importance for anion visualization in rapid screening and also for ion-selective electrode determination in the aqueous systems.

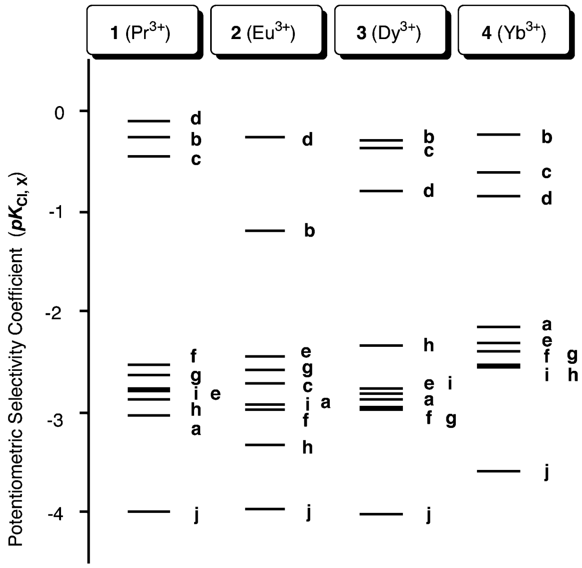

Fig. 2 Potentiometric selectivity coefficients toward Cl^- anion of ion-selective electrodes based on lanthanide tris(β-diketonates) **1–4**. a = F^-, b = Br^-, c = I^-, d = SCN^-, e = OH^-, f = HCO_3^-, g = $CH_3CO_2^-$, h = NO_3^-, i = ClO_4^-, j = SO_4^{2-}.

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13 Excitation at 294 nm; [**2**] = 8.75×10^{-6} M; [each anion] = 2.63×10^{-5} M; in CH_3CN; slit width, 5.0 nm for excitation and emission. The addition of Cl^- anion rarely changed the form of the europium luminescence.

14 NO_3^- and HSO_4^- anions also formed the highly coordinated complexes and enhanced the luminescence intensity.

15 UV lamp for TLC detection was used for excitation of complex **2**. Concentrations: see ref. 13.

16 Typical membrane composition: **2**, 5.1 mg; $NaBPh_4$, 1.0 mg; PVC, 112.4 mg; dioctyl phathalate, 180.0 mg. The nature of plasticizer greatly influenced electrode performance. Dioctyl phathalate exhibited higher performance than bis(2-ethylhexyl)sebacate, dioctyl adipate, dibutyl phathalate or tri-n-butyl phosphate: linear range, 1.0×10^{-1}–5.0×10^{-5} M; detection limit, 1.07×10^{-5} M.