

45. Synthesis, Characterization, and Crystal Structure of Complexes of Lanthanide Picrates with *N,N,N',N'*-Tetraphenyl-3,6-dioxaoctanediamide

by Shixia Liu^{a)}, Weisheng Liu^{a)}*, Minyu Tan^{a)}, Kaibei Yu^{b)}, and Ganzu Tan^{c)}

^{a)} Department of Chemistry, Lanzhou University, Lanzhou 730000, P. R. China

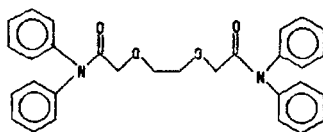
^{b)} Chengdu Center of Analysis and Measurement, Academia Sinica, Chengdu 610041, P. R. China

^{c)} Lanzhou Institute of Chemical Physics, Academia Sinica, Lanzhou 730000, P. R. China

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Lanthanide picrate complexes with the ligand *N,N,N',N'*-tetraphenyl-3,6-dioxaoctanediamide (tdd): [Ln(Pic)₃(tdd)] (Ln = La, Nd, Eu, Tb, Er) have been prepared in a nonaqueous medium and characterized by elemental analysis, conductivity measurements, IR, and ¹H-NMR spectra. The crystal structures of the complexes for Ln = Nd and Er were determined. The early lanthanide, Nd^{III}, crystallizes as the nona-coordinate complex [Nd(Pic)₃(tdd)] · 2 CH₃CN in the monoclinic space group *P*2₁/*n* with *a* = 11.384(2), *b* = 18.805(4), *c* = 27.526(5) Å, β = 99.41(1)°, *V* = 5832(2) Å³, and *D*_c = 1.58 g cm⁻³ for *Z* = 4. The structure was refined to *R* = 0.0505, based on 4772 observed reflections. The late lanthanide, Er^{III}, forms an octa-coordinate complex [Er(Pic)₃(tdd)]; crystals are triclinic, *P* $\bar{1}$, with *a* = 12.449(2), *b* = 17.065(2), *c* = 26.243(4) Å, α = 72.12(1), β = 87.86(1), γ = 84.60(1)°, *V* = 5282(1) Å³, and *D*_c = 1.68 g cm⁻³ for *Z* = 4. The structure was refined to *R* = 0.0469, based on 10666 observed reflections. The results reveal that tdd forms a ring-like structure with its four O-atoms, coordinating to the metal ions as multidentate ligand, together with one O-atom of the bidentate picrate. The structure of the complexes is greatly affected by the ionic radius due to participation of the picrates in coordination.

Introduction. – Acyclic polyethers offer many advantages over the use of crown ethers in the extraction and analysis (ion-selective electrodes) of the rare earths [1–4]. Ding *et al.* [3] have reported the extraction of lighter lanthanide ions using nitrobenzene solutions of five derivatives of glycol-*O,O'*-diacetamides, among which *N,N,N',N'*-tetraphenyl-3,6-dioxaoctanediamide (tdd) has the largest separation factor. Both the factor and distribution ratio of lighter lanthanide ions for tdd are larger than those for dicyclohexyl-18-crown-6 ether [5], if the picrate is used as accompanying ion. However, the solid complexes relating to the extraction have rarely been investigated, and no solid complexes of lanthanide picrates with tdd have been reported. To further research the mechanism of extraction and the effect of counter anion on structure and properties, and to investigate the selectivity/structure relationship, we report the synthesis, characterization, and structure of the complexes of lanthanide picrates with tdd.



N,N,N',N'-Tetraphenyl-3,6-dioxaoctanediamide

Results and Discussion. – Analytical data for the complexes conform to a 1:3:1 metal-to-picrate-to-tdd stoichiometry $\text{Ln}(\text{Pic})_3(\text{tdd})$ (see *Table 1*). All the complexes are soluble in DMSO, acetone, and MeCN, slightly soluble in MeOH and AcOEt, and sparingly soluble in benzene, Et_2O , and cyclohexane. The molar conductance values of the complexes in MeCN (*Table 1*) indicate the presence of a non-electrolyte [6].

Table 1. Analytical Data for the Complexes

Complex	Analysis [%] ^{a)}				Λ_m [s cm ² mol ⁻¹]
	C	H	N	Ln	
[La(Pic) ₃ (tdd)]	43.92 (44.22)	2.83 (2.63)	11.58 (11.82)	10.67 (10.65)	10.61
[Nd(Pic) ₃ (tdd)]	43.86 (44.04)	2.56 (2.62)	11.79 (11.77)	10.87 (11.01)	22.20
[Eu(Pic) ₃ (tdd)]	43.70 (43.78)	2.55 (2.60)	11.63 (11.70)	11.84 (11.54)	26.02
[Tb(Pic) ₃ (tdd)]	43.09 (43.55)	2.59 (2.59)	11.22 (11.64)	12.24 (12.00)	30.10
[Er(Pic) ₃ (tdd)]	43.02 (43.27)	2.55 (2.57)	11.38 (11.56)	12.74 (12.55)	27.30

^{a)} Calculated values in parentheses.

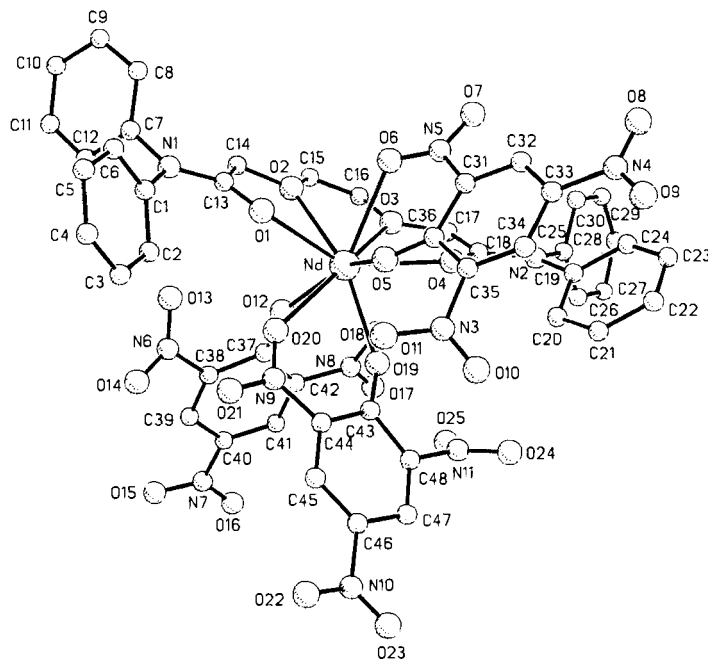
IR Spectra. The IR spectrum of the free tdd shows bands at 1685 and 1132 cm⁻¹ which may be assigned to $\nu(\text{C}=\text{O})$ and $\nu(\text{C}-\text{O})$, respectively. In the complexes, the two bands show shifts by *ca.* 70 and 40 cm⁻¹ towards lower wave numbers, thus indicating that all the C=O and ether O-atoms take part in coordination to the metal ions. The larger shift for $\nu(\text{C}=\text{O})$ in the spectra of the complexes suggests that the Ln–O(carbonyl) bond is stronger than the Ln–O(ether) one.

The OH out-of-plane bending vibration of the free Hpic at 1151 cm⁻¹ disappears in the spectra of the complexes [7], indicating that the H-atom of the OH group is replaced by Ln^{III}. The vibration $\nu(\text{C}-\text{O})$ at 1265 cm⁻¹ is shifted towards higher frequency by *ca.* 9 cm⁻¹ in the complexes. It suggests that the interaction between metal ion and picrate group is very weak. The free Hpic has $\nu_{\text{as}}(\text{NO}_2)$ and $\nu_{\text{s}}(\text{NO}_2)$ at 1555 and 1342 cm⁻¹, respectively, which split into two bands at *ca.* 1576, 1540 cm⁻¹, and *ca.* 1365, 1336 cm⁻¹, respectively, in the complexes. This indicates that some of the nitronyl O-atoms take part in coordination.

¹H-NMR Spectra. The spectrum of tdd exhibits an unresolved *multiplet* at 7.37 ppm and two *singlets* at 4.01 and 3.57 ppm assigned to Ph, $-\text{C}(\text{O})\text{CH}_2-$, and $-\text{C}_2\text{H}_4-$ protons, respectively. Upon coordination, the proton signals move to lower field; the signals of the $-\text{C}(\text{O})\text{CH}_2-$ and $-\text{C}_2\text{H}_4-$ protons are shifted by 0.8 and 0.4 ppm, respectively, and those of the Ph protons by only 0.12 ppm. This is due to the inductive effect of Ln–O(tdd) bonds. The larger shift for $-\text{C}(\text{O})\text{CH}_2-$ protons than $-\text{C}_2\text{H}_4-$ ones indicates the Ln–O(C=O) bond to be stronger than the Ln–O(C–O–C) one.

The ¹H signal of OH group in the free Hpic disappears in the complexes, indicating that the H-atom of OH group is replaced by Ln^{III}. The benzene-ring protons of the free Hpic exhibit a *singlet* at 9.12 ppm. Upon coordination, the signal moves to higher field. Only one *singlet* is observed for the benzene-ring protons of the three coordinated picrate groups indicating fast exchange among the groups in solutions [8].

Crystal Structure of [Nd(Pic)₃(tdd)] · 2 MeCN. Fig. 1 shows the structure and the numbering scheme for the complex molecule. Selected bond distances and angles are given in *Table 2*.

Fig. 1. Molecular structure of $[Nd(Pic)_3(tdd)] \cdot 2 MeCN$ Table 2. Selected Bond Lengths [Å] and Angles [°] for $[Nd(Pic)_3(tdd)] \cdot 2 MeCN$ (e. s. d. in parentheses)

Nd–O(1)	2.453(4)	Nd–O(6)	2.668(5)
Nd–O(2)	2.608(4)	Nd–O(12)	2.277(7)
Nd–O(3)	2.580(5)	Nd–O(19)	2.375(5)
Nd–O(4)	2.457(3)	Nd–O(20)	2.623(5)
Nd–O(5)	2.380(4)		
Mean lengths			
Nd–O(C–O,Pic)	2.344	Nd–O(NO ₂ ,Pic)	2.646
Nd–O(C=O,tdd)	2.455	Nd–O(C–O–C,tdd)	2.594
O(1)–Nd–O(2)	61.0(1)	O(2)–Nd–O(3)	60.0(1)
O(3)–Nd–O(4)	59.6(1)	O(4)–Nd–O(5)	72.6(1)
O(1)–Nd–O(5)	81.5(1)		

The crystal structure is composed of $[Nd(Pic)_3(tdd)]$ and two MeCN molecules linked by weak *van der Waals* forces. The Nd^{III} ion is coordinated to nine O-atoms, four from tdd, and five from two bidentate and one unidentate picrates. The coordination polyhedron is a tricapped trigonal prism with O(2), O(4), O(20) being the capping atoms. The tdd molecule wraps around the metal ion with its O-atoms and forms a ring-like coordination structure together with the bidentate picrate (O(5)) situated at the open side of the tdd chain. The four O-atoms of tdd and O(5) are almost coplanar with a mean absolute deviation of 0.058 Å from the mean plane. The Nd-atom lies out of this plane by 0.86 Å. Two other picrates are located outside the mean plane. Each of three picrates is nearly planar.

The average distance between the Nd-atom and the coordinated O-atoms is 2.491 Å, where the Nd–O(12) distance is the shortest probably due to the higher electron density on the oxygen anion of the picrate. The Nd–O(C=O) distance (mean 2.455 Å) are significantly shorter than the Nd–O(C–O–C) ones (mean 2.594 Å). This suggests that the Nd–O(C=O) bond is stronger than the Nd–O(C–O–C) one, in agreement with the IR spectral data.

Crystal Structure of [Er(Pic)₃(tdd)]. The crystal structure is composed of discrete molecular units linked by weak *van der Waals* forces. There are two independent [Er(Pic)₃(tdd)] monomers, designated [Er(1)(Pic)₃(tdd)] and [Er(2)(Pic)₃(tdd)], in an asymmetric unit, and environments around the two central atoms Er(1) and Er(2) are nearly identical except for subtle difference in their microsymmetry. In each of the [Er(Pic)₃(tdd)] monomers, the erbium ion is octa-coordinated by four O-atoms of tdd and four O-atoms of one bidentate and two unidentate picrates (*Fig. 2*). The coordination polyhedron is dodecahedral with O(1), O(19), O(5), O(6) forming the flattened tetrahedron. The tdd acts as a tetradentate ligand. It forms a ring-like coordination structure with its O-atoms and with one O-atom of the bidentate picrate (O(5) for Er(1) or O(30) for Er(2)) at the open side of the tdd chain. The five O-atoms of the ring are not quite coplanar; their mean shift from the least-squares plane is 0.27 Å. The Er-atom lies slightly below the plane by 0.29 Å. Two unidentate picrates are located above and below the plane, respectively.

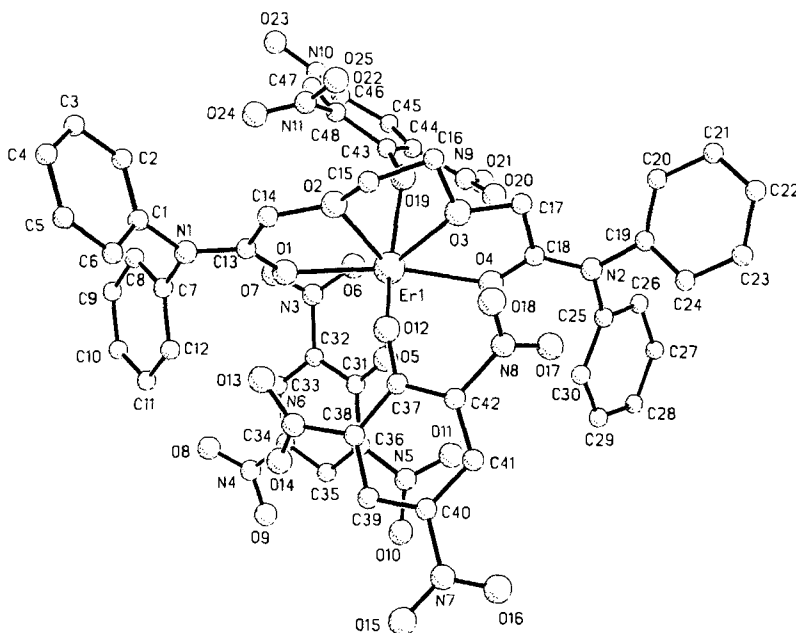


Fig. 2. Structure of [Er(1)(Pic)₃(tdd)]

The eight coordination bonds were divided into four classes based on their bond lengths (see *Table 3*). The average distance is 2.329 Å, and the average value of the four classes are in the order: Er–O(C=O,Pic[−]) (2.240 Å) < Er–O(C=O,tdd) (2.295 Å) < Er–O(C–O–C,tdd) (2.413 Å) < Er–O(NO₂,Pic[−]) (2.499 Å).

Table 3. Selected Bond Lengths [Å] and Angles [°] for [Er(Pic)₃(tdd)] (e. s. d. in parentheses)

Er(1)–O(1)	2.307(4)	Er(2)–O(26)	2.291(4)
Er(1)–O(2)	2.423(4)	Er(2)–O(27)	2.397(4)
Er(1)–O(3)	2.420(5)	Er(2)–O(28)	2.412(5)
Er(1)–O(4)	2.299(4)	Er(2)–O(29)	2.284(4)
Er(1)–O(5)	2.241(6)	Er(2)–O(30)	2.255(6)
Er(1)–O(6)	2.510(6)	Er(2)–O(31)	2.488(7)
Er(1)–O(12)	2.232(5)	Er(2)–O(37)	2.213(5)
Er(1)–O(19)	2.235(5)	Er(2)–O(44)	2.263(5)
Mean lengths			
Er(1)–O(C=O,tdd)	2.303	Er(2)–O(C=O,tdd)	2.288
Er(1)–O(C–O–C,tdd)	2.422	Er(2)–O(C–O–C,tdd)	2.404
Er(1)–O(C–O,Pic)	2.236	Er(2)–O(C–O,Pic)	2.244
Er(1)–O(NO ₂ ,Pic)	2.510	Er(2)–O(NO ₂ ,Pic)	2.488
O(1)–Er(1)–O(2)	65.3(2)	O(26)–Er(2)–O(27)	66.0(2)
O(1)–Er(1)–O(5)	84.2(2)	O(26)–Er(2)–O(30)	85.2(2)
O(2)–Er(1)–O(3)	65.6(1)	O(27)–Er(2)–O(28)	65.9(1)
O(3)–Er(1)–O(4)	65.5(2)	O(28)–Er(2)–O(29)	65.9(1)
O(4)–Er(1)–O(5)	80.6(2)	O(29)–Er(2)–O(30)	81.5(2)

Conclusion. – The structures of the Nd and Er complexes differ in crystal system, space group, or composition. The coordination number, configuration and ‘ring-like’ structure are different for the two central ions. It is possible that these differences in the structures reflect a coordination selectivity of tdd for different rare earth ions and affect the separation of the ions by tdd.

In the Nd complex, the Nd ion with a larger ionic radius lies out of the ring formed by the tdd ligand, while in the Er complex, the Er ion with a smaller ionic radius enters the cavity of the ligand. These coordination structures are similar to those of macrocyclic compound [1].

The perimeter of the ring composed of O(1), O(2), O(3), O(4), O(5) (13.691 Å) in the Nd complex is almost equal to that (13.718 Å) in the Er complex. This indicates that the ring-like form of the open-chain crown ethers also shows a fixed cavity size. Thus, the ligand tdd can strongly coordinate those metal cations whose ionic radii best match the radius of the cavity formed by the polyether chain. This is a main reason that the open-chain crown ethers have coordination selectivity to rare earth ions.

Moreover, there are two bidentate picrates and one unidentate picrate in the Nd complex, but one bidentate picrate and two unidentate picrates in the Er complex. Thus, the coordination numbers are 9 and 8 in the Nd and Er complexes, respectively. As the ions become smaller they are less able to support the higher coordination numbers or the sterically more bulky picrate. In addition, the complexes have excellent liposolubility; therefore, it is possible that the coordination selectivity and extractability can be improved to some extent by adding Hpic to the extraction system.

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Experimental Part

General. The lanthanide picrates [9] and tdd [10] were prepared following literature methods. All other chemicals were of reagent-grade and used without further purification. The metal ion was determined by EDTA titration using xylenol-orange as an indicator; C, N, and H were determined using a *Carlo Erba 1106* elemental analyser. IR Spectra: *Nicolet 170SX FT-IR* instrument using KBr discs in the 220–4000-cm⁻¹ region. Conductivity measurements: *DDS-11A* type conductivity bridge using 10⁻³ mol dm⁻³ solns. in MeCN at 25°. ¹H-NMR Spectra: *FT-80A* spectrometer in CD₃COCD₃ solns. with TMS as a internal standard.

Preparation of the Complexes. A soln. of 0.1 mmol tdd in 15 cm³ of anh. EtOH was added dropwise to a soln. of 0.1 mmol lanthanide picrates in 20 cm³ of anh. EtOH. The mixture was stirred at r.t. for 4 h. The precipitated solid complex was filtered, washed with anh. EtOH and dried *in vacuo* over P₄O₁₀ for 48 h. All the complexes are yellow powders. Yield 85–90%. Crystals suitable for single-crystal X-ray studies were obtained by slow evaporation of an MeCN soln. of the complexes for Ln = Nd and Er. These crystals were found to have stoichiometry [Nd(Pic)₃(tdd)] · 2 MeCN and [Er(Pic)₃(tdd)], respectively.

X-Ray Diffraction Studies. The two data sets were collected at r.t. on an *R3M/E* four-circle diffractometer using graphite-monochromatized MoK_α radiation (λ = 0.71073 Å). The unit-cell parameters were determined by least-squares refinement of 24–25 accurately centred reflections in the range 6° < 2θ < 25°. The data sets were corrected for *Lorentz* and polarization effects, absorption correction for the Nd complex but not for the Er complex. A summary of crystal data, intensity measurement, and structure refinement is given in *Table 4*. Crystallographic data (No. CCDC-10/37) were deposited with the *Cambridge Crystallographic Data Centre*, Cambridge, England.

 Table 4. *Crystal Data*

Complex	[Nd(Pic) ₃ (tdd)] · 2 MeCN	[Er(Pic) ₃ (tdd)]
Formula	C ₅₂ H ₄₀ N ₁₃ O ₂₅ Nd	C ₄₈ H ₃₄ N ₁₁ O ₂₅ Er
Crystal size [mm]	0.20 × 0.50 × 0.80	0.24 × 0.50 × 0.50
Formula weight	1391.2	1332.2
Temp. [K]	293(1)	294(1)
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> $\bar{1}$
<i>a</i> [Å]	11.384(2)	12.449(2)
<i>b</i> [Å]	18.805(4)	17.065(2)
<i>c</i> [Å]	27.526(5)	26.243(4)
α [°]		72.12(1)
β [°]	99.41(1)	87.86(1)
γ [°]		84.60(1)
<i>V</i> [Å ³]	5832(2)	5282(1)
<i>Z</i>	4	4
<i>D_c</i> [g cm ⁻³]	1.58	1.68
μ (MoK _α) [cm ⁻¹]	9.82	17.39
<i>F</i> (000)	2812	2668
2θ _{max} [°]	44	43
No. of measured refl.	8085	13179
No. of unique refl.	7919	12913
No. of observed refl. ^{a)}	4772	10666
Variables	820	1367
<i>g</i>	0.00008	0.00015
<i>S</i>	0.994	1.438
<i>R</i> = Σ(<i>F_o</i> - <i>F_c</i>)/Σ <i>F_o</i>	0.0505	0.0469
<i>R_w</i> = Σ(<i>w</i> ^{1/2} <i>F_o</i> - <i>F_c</i>)/Σ <i>w</i> ^{1/2} <i>F_o</i>	0.0411	0.0437
Δρ (max;min) [e Å ⁻³]	0.49; -0.46	1.12; -1.66

^{a)} [*I* > 3σ(*I*)].

The crystal structures were solved by the *Patterson* method and subsequent difference *Fourier* techniques and refined by block-matrix least-squares procedures based on *F*. Non-H-atoms were refined with anisotropic thermal parameters; H-atoms were placed in calculated positions (C–H, 0.96 Å). In the final refinement the weighting scheme $w = [\sigma^2(F) + gF^2]^{-1} \{1 - \exp[-5(\sin\theta/\lambda)^2]\}$ was used. All calculations were performed with the SHELXTL program system [11]. Scattering factors for neutral atoms from [12].

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