Mixed-ligand complexes of lanthanide dialkyldithiocarbamates with 1,10-phenanthroline as precursors of lanthanide sulfides

Roman A. Ivanov,* Igor E. Korsakov, Natalya P. Kuzmina and Andrey R. Kaul

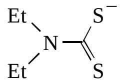
Department of Chemistry, M. V. Lomonosov Moscow State University, 119899 Moscow, Russian Federation.
E-mail: rivanov@inorg.chem.msu.ru

10.1070/MC2000v010n03ABEH001263

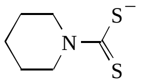
A simple method for the synthesis of the title complexes, which can be used as precursors of lanthanide sulfides, in aqueous solutions has been developed.

Lanthanide sulfides are of great interest in modern science and technology because of wide application of these compounds as ceramic and film materials.[1] The synthesis of lanthanide sulfides is a rather difficult task because pure metal lanthanides and hydrogen sulfide should be used.[2] Coordination compounds containing lanthanide–sulfur bonds can be promising precursors of lanthanide sulfides. The mixed-ligand complexes of lanthanide dialkyldithiocarbamates with 1,10-phenanthroline [Ln(dalkdtc)$_3$(phen)] were used as volatile precursors to obtain thin films of lanthanide sulfides.[3,4] However, the wide application of [Ln(dalkdtc)$_3$(phen)] is restricted by a complex synthetic procedure.[4–6] The well-known method of the synthesis involves the preparation of [Ln(dalkdtc)$_3$] complexes in anhydrous solvents followed by the formation of mixed-ligand complexes by mixing solutions containing 1,10-phenanthroline and [Ln(dalkdtc)$_3$]. The main difficulty in this method is due to the fact that [Ln(dalkdtc)$_3$] solutions exhibit extremely high sensitivity to hydrolysis, and the synthesis should be performed under strongly anhydrous conditions.

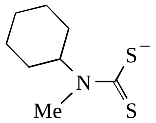
The prospects of [Ln(dalkdtc)$_3$(phen)] as precursors of lanthanide sulfides stimulated our interest in the development of a more suitable synthetic route to these coordination compounds. Here, we describe a new method for the synthesis of [Ln(dalkdtc)$_3$(phen)] in aqueous solutions and the use of the [Ln(dalkdtc)$_3$(phen)] complexes for the preparation of rare-earth metal sulfides. As examples, we used Eu and Er complexes with the following three dialkyldithiocarbamate ligands:



ddtc



pmdtc



mechdtc

(ddtc is diethyldithiocarbamate; pmdtc is pentamethylendithiocarbamate; and mechdtc is cyclohexylmethyldithiocarbamate).

This one-pot synthetic approach involves two consecutive reactions:† the interaction between $LnCl_3\cdot 6H_2O$ and phen·H_2O in an aqueous solution with the formation of [Ln(phen)aq]Cl_3 followed by the addition of an aqueous Na(dalkdtc)·H_2O solution to form coloured precipitates of [Ln(dalkdtc)$_3$(phen)]. The products obtained were dried in a vacuum at room temperature and characterised by elemental analysis and IR spectroscopy.† The new synthetic method was found to be successful for all dithiocarbamate ligands, and the product compositions were adequately described by the formulae [Ln(dalkdtc)$_3$(phen)]. Thus, the formation of [Ln(phen)aq]Cl_3 at the first stage of the synthesis allowed us, at the second stage, to obtain stable rare-earth metal dialkyldithiocarbamates in an aqueous solution.

Table 1 Thermal analysis data for Ln(dalkdtc)$_3$(phen).

Compound	T_s/°C (±5)	Δ*m* (%) (±5)	ΣΔ*m* (%) calc. for lanthanide sulfide formation
Eu(ddtc)$_3$(phen)	290	75	65
Er(ddtc)$_3$(phen)	280	70	62
Eu(pmdtc)$_3$(phen)	270	76	77
Er(pmdtc)$_3$(phen)	275	70	74
Eu(mechdtc)$_3$(phen)	250	74	79
Er(mechtc)$_3$(phen)	255	71	76

The behaviour of the [Ln(dalkdtc)$_3$(phen)] complexes on heating in a dry nitrogen flow was examined. The thermal stability of the complexes depends on the nature of ligands and decreases in the order ddtc > pmdtc > mechdtc (Table 1).‡ According to the TGA data, the thermal decomposition of [Ln(ddtc)$_3$(phen)] leads to the formation of lanthanide sulfides.

Previously,[4] it was found that the [Ln(ddtc)$_3$(phen)] prepared by the known method can be evaporated at 250–300 °C and 0.01 Torr. The [Ln(ddtc)$_3$(phen)] complexes prepared by the developed method demonstrated the same ability to evaporation.§ For [Ln(pmdtc)$_3$(phen)], only 80–85% of the starting sample was evaporated at 240–280 °C because of considerable thermal degradation at this temperature. In the case of the [Ln(mechdtc)$_3$(phen)] complex, the evaporation was not observed. The powders of lanthanide sulfides were found in the evaporation boat after heating to 450 °C. The data obtained at a low pressure correlate with the difference in the thermal stability of complexes found by thermal analysis in nitrogen.

The low thermal stability of [Ln(dalkdtc)$_3$(phen)] forms the basis of the preparation of lanthanide sulfides by thermal decomposition of these complexes. This method can be implemented either at an atmospheric pressure in nitrogen or at a reduced pressure depending on the nature of dithiocarbamate ligands. These modes were applied to the most available diethyldithiocarbamate complex with 1,10-phenanthroline and the thermally unstable [Ln(mechdtc)$_3$(phen)] complex, respectively.

The samples of [Ln(ddtc)$_3$(phen)] were slowly decomposed in a flow of dry oxygen-free nitrogen in the temperature range 200–400 °C for 3 h and then annealed at a higher temperature. Fine crystals of lanthanide sulfides were obtained at 1000–

---

† *Synthesis of* Ln(dalkdtc)$_3$(phen): a solution of 1,10-phenanthroline (1 mmol) in boiling water (20 ml) was added to an aqueous solution of $LnCl_3$ (1 mmol, 10 ml) with intense stirring; next, aqueous solution of Na(dalkdtc) (3 mmol, 20 ml) was added dropwise to the [Ln(phen)aq]Cl_3 solution, and coloured crystals were collected and dried in a vacuum at room temperature. Yield ~90%. IR (Nujol and hexachlorobutadiene mulls, ν/cm^{-1}): 1000–1020 (ν_{C-S}); 1480–1490 (ν_{C-N}); 2980–2990 (ν_{C-H}); 1600, 1620, 1630, 850, 750 (phen vibration frequencies).

Eu(ddtc)$_3$(phen). Found (%): C, 42.0; H, 5.2; N, 9.2; Eu, 19.7. Calc. for $C_{27}H_{38}N_5S_6Eu$ (%): C, 41.7; H, 4.9; N, 9.0; Eu, 19.6.

Er(ddtc)$_3$(phen). Found (%): C, 41.1; H, 4.3; N, 9.0; Er, 21.9. Calc. for $C_{27}H_{38}N_5S_6Er$ (%): C, 41.1; H, 4.8; N, 8.9; Er, 21.1.

Eu(pmdtc)$_3$(phen). Found (%): C, 44.8; H, 5.1; N, 8.9; Eu, 20.5. Calc. for $C_{30}H_{38}N_5S_6Eu$ (%): C, 44.3; H, 4.7; N, 8.6; Eu, 21.1.

Er(pmdtc)$_3$(phen). Found (%): C, 43.6; H, 4.4; N, 8.5; Er, 17.8. Calc. for $C_{30}H_{38}N_5S_6Er$ (%): C, 43.5; H, 4.6; N, 8.5; Er, 18.3.

Eu(mechtc)$_3$(phen). Found (%): C, 48.8; H, 5.0; N, 7.7; Eu, 19.3. Calc. for $C_{36}H_{50}N_5S_6Eu$ (%): C, 48.2; H, 5.6; N, 7.8; Eu, 19.5.

Er(mechtc)$_3$(phen). Found (%): C, 47.2; H, 5.7; N, 8.1; Er, 16.9. Calc. for $C_{36}H_{50}N_5S_6Er$ (%): C, 47.4; H, 5.5; N, 7.7; Er, 17.0.

‡ Thermogravimetric analysis was performed on an OD-102 derivatograph in a nitrogen atmosphere at a heating rate of 5 °C min^{-1}.

§ Isothermal vacuum sublimation experiments were performed in glass tubes at a pressure of 0.01 Torr using 100 mg samples.

1100 °C. In the case of [Ln(mechdtc)$_3$(phen)], lanthanide sulfides were obtained on heating at 500 °C for 2 h at a low pressure. The formation of crystalline EuS and Er_2S_3 was confirmed by X-ray diffraction analysis¶ (Figure 1).

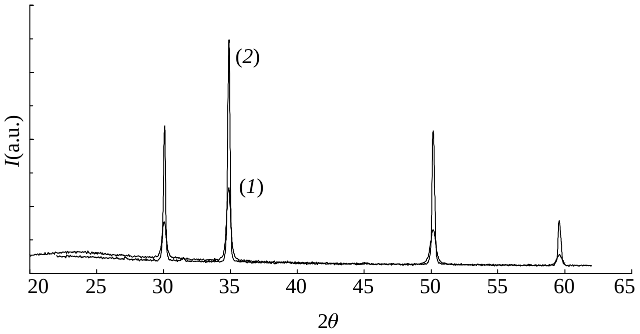


Figure 1 X-ray diffraction patterns of (*1*) EuS obtained by the thermolysis of [Eu(ddtc)$_3$(phen)] at 1100 °C in a nitrogen flow and (*2*) a reference sample of EuS powder.

Note that the crystallinity of sulfides prepared from [Ln(mechdtc)$_3$(phen)] at a low pressure was slightly worse than that of the samples obtained at a higher temperature in a nitrogen flow. Thus, the temperature conditions of lanthanide sulfide formation at a low pressure should be optimised.

In summary, we developed a new very simple method for the synthesis of mixed-ligand dialkyldithiocarbamate complexes of lanthanides with 1,10-phenanthroline and demonstrated that these complexes can be used as precursors of lanthanide sulfides.

This work was supported by the programmes ‘Universities of Russia’ and ‘Basic Research in Chemical Technologies’ and by INTAS (grant no. 96-2359).

References

1 P. Maestro and D. Huguenin, *J. Alloys Compd*., 1995, **225**, 520.

2 *Gmelin Handbook of Inorgan. Chem*., 8th Edn., Springer, Berlin, 1984, 61B67, p. 105.

3 V. I. Bessergenev, E. N. Ivanova, Ya. A. Kovalevskaya and S. V. Larionov, *Spring Meeting of Electrochem. Soc*., Los Angeles, 1996, p. 105.

4 N. P. Kuzmina, R. A. Ivanov, S. E. Paramonov and L. I. Martynenko, *Electrochem. Soc. Proceed. 14th Intern. Conf. on CVD and EUROCVD*, ed. M. Allendorf, Electrochemical Society, Inc., Pennington, 1997, p. 872.

5 *Comprehensive Coordination Chemistry*, ed. V. C. Willkinson, Pergamon Press, Oxford, 1986, p. 92.

6 N. I. Gorshkov, G. V. Sidorenko and D. N. Suglobov, *Radiokhimiya*, 1994, **36**, 154 [*Radiochem*. (*Engl. Transl*.), 1994, **36**, 167].

Received: 18th January 2000; Com. 00/1589

¶ X-ray diffraction data for EuS obtained using [Eu(ddtc)$_3$(phen)] as a precursor: $a = 17.0$ (0.1), $b = 4.00$ (0.04) and $c = 10.11$ (0.03) Å, $\beta =$ $= 99.4$ (0.4)°; CCDC no. 21-324: $a = 17.404$, $b = 3.978$ and $c = 10.092$ Å, $\beta = 98.67°$.