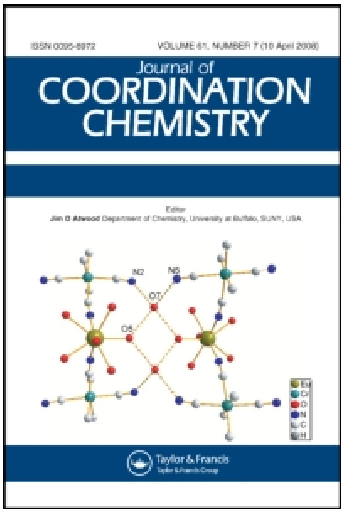

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SYNTHESIS AND CHARACTERIZATION OF COMPLEXES OF RARE EARTH PICRATES AND *RAC*-BIS(ETHYLSULFINYL)METHANE

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SYNTHESIS AND CHARACTERIZATION OF COMPLEXES OF RARE EARTH PICRATES AND *RAC*-BIS(ETHYLSULFINYL)METHANE

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The compound β-dissulfoxide bis(ethylsufinyl)methane (besm) was prepared by oxidation of bis(ethylthio)methane with hydrogen peroxide in acetic acid, and obtained as a mixture of its meso and d,l diastereomers. An analytical sample was obtained by recrystallization from chloroform-diethyl ether. The racemic-bis(ethylsulfinyl)methane was characterized and studied by CHS elemental analysis, high resolution mass spectrometry, infrared spectra, ^{1}H and ^{13}C NMR.

A series of compounds with composition RE(pic)$_3$2*rac*-besm [RE = La, Ce, Nd, Eu, Gd, Er, Tm, Yb, Lu and Y; pic = picrate and *rac*-besm = racemic-bis(ethylsulfinyl)methane] were synthesized and characterized by CHNS elemental analysis and rare earths complexometric titration with EDTA, conductance measurements, X-ray powder patterns, infrared spectra, visible absorption of the neodymium and emission spectra of the europium materials. The coordination polyhedron around the Eu^{3+} center is probably a dodecahedron with coordination number eight.

KEYWORDS: Complexes, rare earth, picrates, racemic-bis(ethylsulfinyl)methane

INTRODUCTION

Formation of complexes between lanthanides and sulfoxides has been studied recently in our laboratory. In particular, complexes containing picrate as an anion have aroused our interest, as, for example, several rare earth picrates with tetramethylene sulfoxide,[1,2] benzyl t-butyl sulfoxide[3] and dibenzyl sulfoxide.[4]

This work centers on preparation and characterization of the bis(ethylsulfinyl)-methane,[5] and its use in synthesis of several rare earth compounds containing the picrate ion. The complexes RE(pic)$_3$ · 2(rac-besm) were synthesized and characterized.

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EXPERIMENTAL

The β-dissulfoxide, bis(ethylsulfinyl)methane, prepared by oxidation of bis(ethylthio)methane with hydrogen peroxide in acetic acid, was obtained as a mixture of its d,l and meso diastereomers in a 46:54 ratio. Pure *rac*-besm was obtained by recrystallization from chloroform-diethyl ether, and was characterized by CHS elemental analysis, high resolution mass spectrometry, infrared spectroscopy and ^{1}H and ^{13}C NMR spectroscopy.

The hydrated metal picrates, $RE(pic)_3 \cdot nH_2O$, were prepared by reaction of an aqueous suspension of the respective basic carbonates with a stoichiometric amount of picric acid. The solutions were filtered, partially evaporated and allowed to stand to crystallize. The yellow needles thus obtained were separated and dried in air. The new materials were prepared by addition of a *rac*-besm's ethanolic solution to an ethanolic solution of the respective picrates, in a 2(*rac*-besm):1(salt) molar ratio.

The resulting solids were decanted, washed with diethyl ether, dried in air and in *vacuo* over anhydrous calcium chloride. All materials have elemental analysis and complexometric titration data consistent with the assigned formulae.

Conductivity measurements were carried out in acetonitrile and nitromethane solutions at 298 K, using home-made equipment consisting of a resistance box, a galvanometer and a Leeds and Northrup cell. X-ray powder patterns were determined on a Rigaku RU-200B instrument, using CuKα radiation. Infrared spectra were recorded on a Perkin Elmer FTIR-1750 spectrophotometer, using Nujol mulls and KBr pellets.

The absorption spectra of the neodymium compounds were obtained at room temperature and 77 K on a Zeiss DMR-10 spectrophotometer, using silicone mulls in a 0.5 mm optical path cell. The spectra in acetonitrile and nitromethane were determined using a 1.000 cm cell at 298 K. Refractive indexes were determined with an Abbe-type Bausch and Lomb refractometer.

Emission spectra of the europium compound at 298 and 77 K were recorded on a modified Hitachi Perkin-Elmer MPF-4 spectrofluorimeter.

RESULTS AND DISCUSSION

The *rac*-besm ligand was synthesized and characterized.[5] Table 1 contains a summary of the elemental analysis[6,7] and high resolution mass spectrometry results. Table 2 contains the IR spectra, ^{1}H and ^{13}C NMR data.

Table 1 Summary of the elemental analysis* and high resolution mass spectrometry** results for *rac*-besm

*THEOR (%)	CALC.	EXP.
C	35.67	35.56
H	7.19	7.13
S	38.11	37.80
**FORMULA	CALC.	EXP.
$C_5H_{12}S_2O_2$	168.0279g/mol	168.0277g/mol

Table 2 Infrared (cm^{-1}), NMR (ppm) ^1H and ^{13}C data for *rac*-besm

VIBRATIONS	BANDS (cm^{-1})	GROUPS	SPECIES	δ(ppm)
vasCH$_3$	2965 vs	$-CH_2CH_3$	3H, t, J = 7.4	1.44/1.40/1.36
vsCH$_3$	2936 m	$-C\mathit{H}_2CH_3$	2H,m	2.82–3.13
vsCH$_3$	2911 m	$-S(O)C\mathit{H}_2S(O)-$	2H, s	3.91
vasSO	1043 vs	$-CH_2\mathit{C}H_3$	1C	6.36
vsSO	1020 vs	$-\mathit{C}H_2CH_3$	1C	47.76
ωCH	970 vs	$-S(O)\mathit{C}H_2S(O)-$	1C	70.99
γCH	780 s	—	—	—
vasCS	700 s	—	—	—
vsCS	646 w	—	—	—

Table 3 Elemental analysis and complexometric titration data (%) for RE(pic)$_3$·2(*rac*-besm)

	RE		C		H		N		S	
RE	calc	exp	calc	exp	calc	exp	calc	exp	calc	exp
La	11.98	12.01	29.00	29.35	2.61	2.86	10.87	11.46	11.06	10.98
Ce	12.07	11.96	28.97	28.92	2.61	2.69	10.86	10.87	11.05	11.20
Nd	12.38	12.38	28.87	29.04	2.59	2.71	10.82	11.06	11.01	—
Eu	12.96	12.92	28.68	28.79	2.58	2.61	10.75	10.87	10.94	—
Gd	13.35	13.40	28.55	28.48	2.57	2.57	10.70	10.94	10.89	—
Tb	13.47	13.52	28.51	28.64	2.56	2.62	10.68	11.17	10.87	11.03
Er	14.08	14.05	28.31	28.61	2.54	2.60	10.61	10.57	10.79	10.31
Tm	14.20	14.14	28.27	28.40	2.54	2.54	10.59	10.39	10.78	10.87
Lu	14.63	14.51	28.12	28.43	2.53	2.68	10.54	10.50	10.72	—
Y	8.01	8.18	30.30	30.48	2.72	2.88	11.36	11.51	11.56	—

The materials reported have the general formula RE(pic)$_3$·2(rac-besm). Table 3 contains the elemental analysis[6,7] and complexometric titration[8] data.

The compounds behave as nonelectrolytes[9] in acetonitrile and in nitromethane (Λ_m between 13.4 and 37.2 $\Omega^{-1}cm^2mol^{-1}$), suggesting that the picrates are coordinated to the metal centers.

The La, Nd, Eu, Gd and Tb compounds are crystalline; the others are poorly crystalline. The La, Nd and Eu compounds form an isomorphous series, as shown by their identical X-ray powder patterns.[10]

Infrared Spectroscopy

The IR spectra of all compounds show the expected absorptions.[1,2,11–13] The vSO mode, which in free *rac*-besm occurs at 1020 and 1043 cm^{-1}, is found at *ca.* 973, 1020 and 1036 cm^{-1} in the complexes. This frequency lowering (970 cm^{-1}) suggests coordination of the sulfinyl group to the rare earth ion through the oxygen atom and/or ωCH. The stretching modes of the nitro group of the picrate ligands, $v_{as}NO_2$ (≈1574, ≈1544) and v_3NO_2 (≈1364, ≈1338, ≈1322 cm^{-1}) resemble those of free picric acid in which one of the ortho-NO$_2$ groups is asymmetric, being hydrogen bonded to the phenolic -OH. A similar situation exists in the picrate complexes as the phenoxy oxygen and one oxygen atom of an ortho -NO$_2$ group possibly form a six-membered ring with the metal center.[1,11] Table 4 contains the IR data.

Table 4 IR data (cm^{-1}) for RE(pic)$_3$·2*rac*-besm

ATRIB. RE	vasNO$_2$	v$_s$NO$_2$	v$_{as}$SO	v$_s$SO	vSO and/or ωCH	vCN and/or γCH	vCS
Eu	1574 vs 1543 vs	1364 vs 1338 vs 1321 vs	1035 s	1020 s	973 m	790 m	706 s
Gd	1575 s 1544 s	1364 s 1338 s 1322 s	1036 m	1021 m	974 w	790 w	706 m
TB	1574 s 1544 vs	1364 vs 1338 vs 1322 vs	1037 m	1021 s	974 w	790 m	706 m
Lu	1578 m 1543 s	1366 s 1331 s —	—	1019 w	972* w	789 w	—
Y	1578 s 1542 vs	1365 vs — 1329 vs	—	1025 s	972* w	789 m	—

*spectra in KBr pellets.

VISIBLE ABSORPTION SPECTROSCOPY

For the Nd complex, a spectrophotometric study was performed. The absorptions arising from the hypersensitive $^2G_{7/2}$, $^4G_{5/2} \leftarrow {}^4I_{9/2}$ transition of neodymium, at 298 and at 77 K, are shown in Figure 1.

The nephelauxetic parameter ($\beta = 0.988$), covalent factor ($b^{1/2} = 0.0762$) and Sinha's parameter[14,15] ($\delta = 1.17$) obtained from the spectrum at room temperature are indicative of essentially electrostatic bonds between the metallic ion and the oxygen donors[15] (Figure 1a). The number of bands in the spectra at 77 K (Figure 1b)

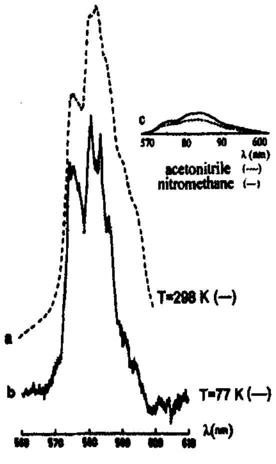

Figure 1 Absorptions arising from the hypersensitive $^2G_{7/2}$, $^4G_{5/2} \leftarrow {}^4I_{9/2}$ transition of solid Nd(pic)$_3$·2*rac*-besm: a(----) at 298 K, b (—) at 77 K and c in solutions in acetonitrile (----) and in nitromethane (—) at 298 K.

and at 298 K (Figures 1a) suggest that the Nd^{3+} ion does not occupy a cubic site in the crystal lattice.

Figure 1c shows the spectra in acetonitrile and nitromethane solutions at 298 K, arising from the hypersensitive $^2G_{7/2}, {}^4G_{5/2} \leftarrow {}^4I_{9/2}$ transition of the neodymium ion. These spectra are very similar and have similar oscillator strengths[15,16] ($P_{acet} = 56.4 \times 10^{-6}$ and $P_{nit} = 64.3 \times 10^{-6}$), but differ from the solid spectrum, indicating some interaction with the solvents.

Fluorescence Studies

For $Eu(pic)_3 \cdot 2$*rac*-besm, intense visible (red) fluorescence is observed with excitation at 445 nm. The transitions from the europium ion $^5D_0$ level to the ^7F_J manifold are very useful in suggesting the site symmetry of the central ion. In Figures 2a and b, the presence of the very weak band due to the $^5D_0{}^7F_0$ transition, consistent with an A_1 [DE(−), DM(−)] species, is interpreted in terms of a distortion from D_{nd} towards C_{nv} symmetry.[17] The $^5D_0{}^7F_1$ transitions, whose $^7F_1$ level splits into three components, is consistent with E [DE(+), DM(+)] and A_2[DE(−), DM(+)] species. The $^5D_0 \rightarrow {}^7F_2$ transition, whose $^7F_2$ level splits into four components, is consistent with E[DE(+), DM(+)], B_2 [DE(+), DM(−)], B_1 and A_1. The last two transitions are totally forbidden and their presence is interpreted in terms of a distortion. The $^5D_0 \rightarrow {}^7F_2$ transition is more intense than that of $^5D_0 \rightarrow {}^7F_1$ indicating the absence of an inversion center. All these data suggest that the $Eu(O)_8$ chromophore has D_{2d} symmetry distorted toward C_{nv}.[17-19]

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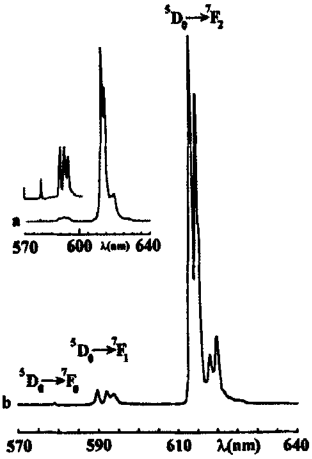

Figure 2 Fluorescence spectra of the solid $Eu(pic)_3 \cdot 2$*rac*-besm: a (at 298 K) and b (at 77 K).

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