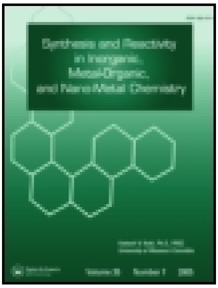

Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt19

Study of the Synthesis and Properties of the Ternary Complexes of Rare Earths with Mandelic Acid and 1,10-Phenanthroline

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To cite this article: Yan Ping Ren , Guo Lan Yan , Li Zhang , Kai Yu Yu , Liu Fang Wang & Ji Gui Wu (1996) Study of the Synthesis and Properties of the Ternary Complexes of Rare Earths with Mandelic Acid and 1,10-Phenanthroline, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 26:2, 293-303, DOI: 10.1080/00945719608004265

To link to this article: http://dx.doi.org/10.1080/00945719608004265

SYNTH. REACT. INORG. MET.-ORG. CHEM., 26(2), 293-303 (1996)

STUDY OF THE SYNTHESIS AND PROPERTIES OF THE TERNARY COMPLEXES OF RARE EARTHS WITH MANDELIC ACID AND 1,10-PHENANTHROLINE

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ABSTRACT

Fourteen ternary complexes of rare earths with mandelic acid (MAH) and 1,10-phenanthroline (phen) have been prepared in aqueous solution. The composition of the ternary complexes has been determined as $RE(MA)_3 \cdot phen \cdot nH_2O$ (RE = La, Ce, Pr, Nd, n = 0; RE = Sm, n = 1/2; RE = Eu, Gd, Dy-Lu, Y, n = 1) by elemental and chemical analyses. Their solubility in different solvents and molar conductances were measured. The structures and properties of the ternary complexes were investigated using IR, TGA, X-ray powder diffraction and UV. The bonding character of the complexes are also discussed.

INTRODUCTION

The ternary complexes of rare earths are receiving more and more attention nowadays. The formation of ternary complexes can obviously change the properties of the free ligands, increase the difference between rare earths and has broad applied prospects in seperation, analyses and measurement techniques of rare earths. For all of the above reasons, research on ternary complexes of rare earths has developed quite rapidly in recent years.

Studies of MAH and its complexes with some rare earths have been reported[1]. However, no paper concerning the study of the ternary complexes of rare earths with MAH and phen has been published. Therefore, in this paper, we wish to report the syntheses, characterization and proposed structures of rare earth complexes with MAH and phen.

RESULTS AND DISCUSSION

As seen in Table I, complexes of the type $RE(MA)_3 \cdot phen \cdot nH_2O$ (RE = La, Ce, Pr, Nd, n = 0; RE = Sm, n = 1/2; RE = Eu, Gd, Dy-Lu, Y, n = 1) have been prepared. All these complexes have the colour of their hydrated cations. These complexes are stable in air and soluble in dimethylsulfoxide (DMSO) and dimethylformamide (DMF), slightly soluble in water, and insoluble in methanol, ethanol, acetone and ether. The molar conductances of the complexes in DMSO solution vary from 16.32 to 24.09 S cm^2 mol^{-1}, indicating that they are non-electrolytes[2].

IR Spectra

The infrared spectra of the ternary complexes are fundamentally similar which reveals that they have the same general structure, but they differ from the free ligands MAH and phen. The absorption bands at 1061 and 1300 cm^{-1} in MAH, assigned to ν(C-O) and δ(OH) vibrations, respectively, shift towards lower wave numbers in all the complexes, which indicates that the hydroxyl groups coordinate with the rare earths through the OH oxygen. The characteristic ν(C=O) mode of the ligand carboxyl group (1721 cm^{-1}) disappeared upon complexation. However, the complexes displayed both symmetric and asymmetric

Table I. Analytical Data, Molar Conductances ($S\ cm^2\ mol^{-1}$), Melting Points (°C), and Decomposition Temperatures (°C) of the Complexes

Complexes	%RE	%C	%H	%N	%$C_6H_5CHOHCOO$	%phen	Molar conductances	Yield%	M.p.	Decomposition temperatures
$C_{36}H_{29}LaO_9N_2$	18.10	55.82	3.87	3.81	58.49	23.31				
$La(MA)_3\cdot phen$	(18.00)	(55.92)	(4.14)	(3.62)	(58.69)	(23.33)	16.32	91	229	277
$C_{36}H_{29}CeO_9N_2$	18.32	55.89	4.00	3.65	58.43	23.24				
$Ce(MA)_3\cdot phen$	(18.12)	(55.87)	(3.78)	(3.62)	(58.64)	(23.30)	16.40	90	226	265
$C_{36}H_{29}PrO_9N_2$	18.19	55.53	3.71	3.43	58.39	23.00				
$Pr(MA)_3\cdot phen$	(18.19)	(55.82)	(3.77)	(3.61)	(58.54)	(23.27)	16.41	91	222	262
$C_{36}H_{29}NdO_9N_2$	18.84	55.48	3.72	3.62	58.19	23.08				
$Nd(MA)_3\cdot phen$	(18.54)	(55.58)	(3.76)	(3.60)	(58.29)	(23.17)	16.39	91	218	255
$C_{36}H_{30}SmO_{9.5}N_2$	18.97	54.47	3.97	3.31	57.15	22.76				
$Sm(MA)_3\cdot phen\cdot 1/2H_2O$	(18.90)	(54.52)	(3.81)	(3.53)	(57.18)	(22.72)		88	196	242
$C_{36}H_{31}EuO_{10}N_2$	18.54	53.75	3.94	3.55	56.17	22.18				
$Eu(MA)_3\cdot phen\cdot H_2O$	(18.90)	(53.80)	(3.89)	(3.49)	(56.39)	(22.41)	23.67	86		215
$C_{36}H_{31}GdO_{10}N_2$	19.27				56.21	22.39				
$Gd(MA)_3\cdot phen\cdot H_2O$	(19.44)				(56.05)	(22.28)	23.81	85		280
$C_{36}H_{31}DyO_{10}N_2$	20.09				55.88	22.49				
$Dy(MA)_3\cdot phen\cdot H_2O$	(19.86)				(55.69)	(22.13)		84		305
$C_{36}H_{31}HoO_{10}N_2$	19.90				55.38	21.98				
$Ho(MA)_3\cdot phen\cdot H_2O$	(20.20)				(55.53)	(22.07)	23.59	85		300
$C_{36}H_{31}ErO_{10}N_2$	20.47				55.29	22.33				
$Er(MA)_3\cdot phen\cdot H_2O$	(20.42)				(55.37)	(22.00)		83		298
$C_{36}H_{31}TmO_{10}N_2$	20.36				55.08	21.73				
$Tm(MA)_3\cdot phen\cdot H_2O$	(20.59)				(55.26)	(21.96)		80		287
$C_{36}H_{31}YbO_{10}N_2$	20.69				54.85	21.77				
$Yb(MA)_3\cdot phen\cdot H_2O$	(20.98)				(54.98)	(21.85)		81		293
$C_{36}H_{31}LuO_{10}N_2$	21.05				54.76	21.82				
$Lu(MA)_3\cdot phen\cdot H_2O$	(21.17)				(54.85)	(21.80)		81		295
$C_{36}H_{31}YO_{10}N_2$	12.31	58.00	4.15	3.71	60.69	24.08				
$Y(MA)_3\cdot phen\cdot H_2O$	(12.01)	(58.38)	(4.22)	(3.78)	(60.98)	(24.23)	23.36	85		285

Calculated values in parentheses

stretching vibrations of COO^- (1595-1616, 1363-1384 cm^{-1}), compared with 1590 [$\nu_{as}(COO^-)$], 1415 [$\nu_{s}(COO^-)$] cm^{-1} of sodium mandelate, $\nu_{as}(COO^-)$ of the complexes increased while $\nu_{s}(COO^-)$ decreased, that is $\Delta\nu$ [$\Delta\nu = \nu_{as}(COO^-) - \nu_{s}(COO^-)$] of the complexes is larger than $\Delta\nu$ of sodium mandelate which strongly suggests coordination of the ligand carboxyl group with the RE(Ⅲ) ions in a unidentate fashion[8]. By comparing the rare earth mandelates with the ternary complexes, it is easy to see that there appear three new absorption bands at 1637, 842 and 730 cm^{-1} which are assigned to ν(-N=C) (1637 cm^{-1}) and δ(C-H) (842, 730 cm^{-1}). The absorption bands δ(C-H) (852, 737 cm^{-1}) of phen and of the phen ring at 1558 cm^{-1} are red-shifted to 842, 730 cm^{-1} [δ(C-H)] and 1518 cm^{-1} (phen ring) after coordination, which proves that phen coordinates with RE(Ⅲ) ions through N. By comparison with the free ligands, the appearance of ν(RE-O) at 414-425 cm^{-1} and ν(RE-N) at 270-284 cm^{-1} in the complexes further proves coordination of the ligands with the RE(Ⅲ) ions[1,4]. It is also found that the ν(RE-O) wave numbers show a linear relationship with the ionic radii of the rare earth ions, which means that the strength of the bond of the rare earth ions with COO^- appears to increase as the rare earth radii decrease, that is, the covalent character of the RE-O bond appears to increase as the rare earth radii decrease[5]. The strong band of ν(OH) appears at 3000-3300 cm^{-1} in the IR spectra of some of the complexes and no characteristic band due to coordinated water is observed in the far-IR spectra of the complexes, which proves the existence of crystal water in these complexes and coincides with the results of thermal analyses. The important IR data of the ligands and their complexes are listed in Table Ⅱ.

On the basis of the above discussion, the mandelate ion is coordinated to the rare earth ions in a bidentate fashion through the oxygen atoms of carboxylate and the benzylic hydroxyl group; two nitrogen atoms of phen are also coordinated to the rare earth ions. The coordination

Table Ⅱ. Some Characteristic IR Data (cm^{-1}) of the Ligands and their Typical Complexes

Ligands			Ternary complexes								Assignment
MAH	Sodium mandelate	Phen	La	Ce	Pr	Nd	Eu	Gd	Ho	Y	
3395	3396										ν(OH)
1721											ν(C=O) carboxyl group
		1644	1637	1637	1637	1637	1637	1637	1637	1637	ν(-N=C)
	1590		1581	1596	1596	1595	1616	1600	1608	1629	$\nu_{as}(COO^-)$
		1518	1518	1518	1518	1518	1518	1518	1518	1518	phen ring
1448	1448		1448	1448	1448	1448	1448	1448	1446	1450	ν(C=C) benzene ring
	1415		1370	1370	1386	1371	1384	1384	1384	1363	$\nu_s(COO^-)$
1300	1286		1286	1286	1286	1286	1286	1286	1286	1286	ν(C-O), δ(OH)
1061	1047		1047	1047	1047	1047	1047	1047	1047	1047	
1223											
892											ν(C-O), δ(OH)
		852	842	842	842	842	842	842	842	842	δ(C-H) phen ring
		737	730	730	723	730	730	730	730	730	
695	695		695	695	695	695	695	695	695	695	(C-H) benzene ring
730	730		730	730	730	730	730	730	730	730	
			414	415	416	417	420	420	423	421	ν(RE-O)
			270	273	273	271	284	280	279	283	ν(RE-N)

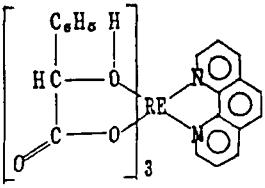

Fig. 1. The Proposed Structure of the Ternary Complexes

number of the ternary complexes is eight. The probable structure of the complexes is shown in Fig. 1.

X—Ray Powder Diffraction

Positions and intensities of the diffraction peaks were read from the recorder chart. X-ray results are shown in Table Ⅲ. As seen in Table Ⅲ, the X-ray powder diffraction analyses showed that the complexes were different from the two ligands. In agreement with thermal analyses, the X-ray diffraction data for powder samples indicate two different crystal structures for the complexes of the lighter rare earths (La, Ce, Pr, Nd, sm) and the heavier rare earths (Eu, Gd, Dy-Lu, Y).

Thermal Analyses

The thermographs of the complexes of the lighter rare earths (La, Ce, Pr, Nd, Sm) differ from those of the heavier rare earths (Eu, Gd, Dy-Lu, Y). The results of thermal analyses suggest that the ternary complexes of the lighter rare earths have characteristic melting points which decrease with increasing the atomic number. It means that the covalent character of the RE-O bond appears to increase as the atomic numbers increase. In other words, the combinative forces of rare earth ions with the oxygen of the carboxyl group strengthen with an increase of the atomic number which coincides with the results of the IR analyses. The decomposition of these complexes starts around

Table Ⅲ. Partial X-Ray Diffraction Data of the Ligands and Some of their Typical Complexes

MAH		Phen·H_2O		Pr(Ⅲ) complex		Nd(Ⅲ) complex		Eu(Ⅲ) complex		Er(Ⅲ) complex	
d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0
8.07	39.39	1.14	12.90	13.19	100	13.80	100	18.78	51.0	18.78	52.59
5.27	31.90	5.80	15.10	10.77	12.54	10.77	15.62	14.72	15.3	14.48	16.07
4.84	53.01	5.12	77.70	6.96	18.66	6.96	16.27	11.04	100	11.32	100
4.62	15.21	4.42	100	5.03	9.81	5.03	7.47	5.75	22.5	5.75	23.81
4.04	100	3.94	43.60	4.64	4.63	4.64	4.57				
3.50	21.60	3.81	11.20	3.48	5.42	3.48	5.90				
3.20	13.01	3.54	4.40	2.99	4.39	3.00	2.81				
2.69	20.79	3.36	11.70	2.32	4.47	2.32	3.68				
2.42	6.13	3.27	35.80								
2.19	4.42										

250-305°C and occurs through more than one stage. It is observed that a gadolinium break effect occurs in the beginning of the thermal decomposition. The complexes of Sm(Ⅲ) and the heavier rare earths(Ⅲ) have one endothermic peak in the DTA curve (around 90°C). The temperature corresponding to water loss indicates that the water molecules are crystal water, which has been confirmed by IR studies. Heating to about 600°C, the residue weights correspond to values calculated[1,6] for $RE_2(CO_3)_3$ (RE = La, Ce, Pr, Nd, Sm) and $RE_2O(CO_3)_2$ (RE = Eu, Gd, Dy-Lu, Y). The above results are in agreement with the structure in Fig. 1 for these complexes. Thermal analytical data are listed in Tables Ⅰ and Ⅳ.

Electronic Spectra

The electronic spectra of the ternary solid complexes $RE(MA)_3\cdot phen\cdot nH_2O$ (RE = Pr, Nd, n = 0; RE = Er, n = 1) have been determined. As

Table IV. Thermal Data of the Ligands and their Typical Complexes

Ligands and Complexes	Start of loss water Temperatures (℃)	% Water loss		% Weight loss (600℃)		Residue (600℃)
		Found	Calc.	Found	Calc.	
MAH				2.33		
Phen·H_2O	84	8.7	9.09	1.68		
La(MA)$_3$·phen				31.06	29.63	$La_2(CO_3)_3$
Nd(MA)$_3$·phen				29.89	30.12	$Nd_2(CO_3)_3$
Eu(MA)$_3$·phen H_2O	95	2.51	2.23	26.90	27.37	$Eu_2O(CO_3)_2$
Y(MA)$_3$·phen·H_2O	90	2.89	2.43	22.60	21.18	$Y_2O(CO_3)_3$

seen from Table V, by comparison with their hydrated cations, the absorption peaks of the complexes vary to some degree. The varying degrees are connected with the covalent character of the complexes. The measured spectral parameters[7], including Sinha's parameter (δ), the naphelauxetic ratio (β) and the bonding parameter ($b^{1/2}$) of solid Pr(MA)$_3$.phen, Nd(MA)$_3$.phen, Er(MA)$_3$.phen.H_2O and aqueous $PrCl_3$, $NdCl_3$, $ErCl_3$ solutions were used to indicate the nature of the bonding between metal and ligands. The β values were less than one. Positive values of δ and $b^{1/2}$ suggested the occurrence of some covalent character in the rare earth-ligand bond. The relatively small value of $b^{1/2}$ compared to the transition metal showed that the involvement of 4f orbitals is very small.

EXPERIMENTAL

General

The chemicals used included rare earth oxides (99.99 %, Yaolong Chemical Works, Shanghai, China) which were transformed into carbonates, $RE_2(CO_3)_3$, MAH (CP grade) and phen·H_2O (AR grade). The rare earth content in all complexes was determined by thermally decomposing the samples at 800℃. The residue was then dissolved in 1:1 hydrochloric acid and the solution thus obtained was titrated with EDTA and xylenol orange as indicator. The contents of carbon, hydrogen and nitrogen were determined on a Carlo Erba 1106 elemental analyser. The contents of $C_6H_5CHOHCOO^-$ and phen were obtained by literature methods[8,9]. The IR spectra were recorded on a Nicolet-170X FT-IR spectrophotometer using KBr discs in the range 4000-200 cm^{-1}. TGA analyses were carried out with a Du Pont 1090 thermal analyser. X-Ray powder diffraction patterns were obtained using nickel filtered copper X-rays and a XD-3A X-ray recording diffractometer. Electronic spectra were obtained on a Shimadzu UV-240 spectrophotometer. Molar conductance measurements

Table V. Electronic Spectral Parameters of Pr(Ⅲ), Nd(Ⅲ), Er(Ⅲ) Ternary Solid Complexes

Solid complexes	ν complex (cm^{-1})	ν aquated (cm^{-1})	Assignment	Covalent parameters
Pr(MA)$_3$·phen	16835	16975	$^3H_4 \rightarrow {}^1D_2$	β = 0.9990
	20747	20768	$\rightarrow {}^3P_0$	δ = 0.10
	21368	21349	$\rightarrow {}^3P_1$	$b^{1/2}$ = 0.022
	22624	22532	$\rightarrow {}^1I_6$	
Nd(MA)$_3$·phen	17212	17397	$^4I_{9/2} \rightarrow {}^4G_{5/2}, {}^2G_{7/2}$	β = 0.9989
	19120	19182	$\rightarrow {}^4G_{7/2}$	δ = 0.11
	19608	19512	$\rightarrow {}^4G_{9/2}$	$b^{1/2}$ = 0.023
	21053	21039	$\rightarrow {}^2G_{9/2}$	
	21739	21720	$\rightarrow {}^4G_{1/2}$	
	23419	23402	$\rightarrow {}^1P_{11/2}$	
Er(MA)$_3$·phen·H$_2$O	19450	18470	$^4I_{15/2} \rightarrow {}^4S_{3/2}$	β = 0.9982
	19120	19149	$\rightarrow {}^2H_{11/2}$	δ = 0.18
	20634	20559	$\rightarrow {}^4F_{7/2}$	$b^{1/2}$ = 0.03
	22222	22241	$\rightarrow {}^4F_{5/2}$	
	24670	24679	$\rightarrow {}^2H_{9/2}$	

were made with a DDS-11A molar conductometer with DMSO as the solvent at 25℃. All other chemicals used were of analytical grade.

Synthesis of the Ternary Complexes

RE$_2$(CO$_3$)$_3$ (1 mmol) was added to a solution of MAH (6 mmol) in water (50 mL). After stirring and heating for 1 h and keeping the temperature below 80℃, a solution of phen (2 mmol) in ethanol (10 mL) was added with stirring to the mixture. The mixture was then stirred and refluxed for about 1 h and then concentrated. After cooling to room temperature, the resulting precipitate was collected by filtration, washed with absolute ethanol and ether three times, respectively, and dried in a vacuum desiccator to constant weight.

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Received: 27 February 1995
Accepted: 28 August 1995
Referee I: T. C. Strekas
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