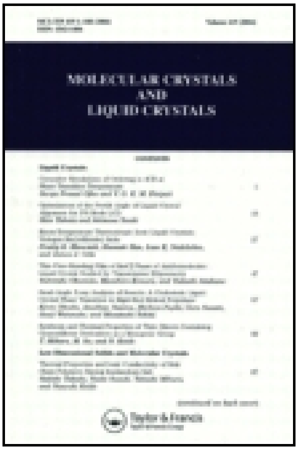

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Synthesis and Characterisation of Some new Lanthanide Hybride Conjugated Monomers

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Version of record first published: 18 Oct 2010

To cite this article: Ana Emandi*, Mirela Calinescu & Cornelia Nichita (2004): Synthesis and Characterisation of Some new Lanthanide Hybride Conjugated Monomers, Molecular Crystals and Liquid Crystals, 416:1, 31-38

To link to this article: http://dx.doi.org/10.1080/15421400490482123

Mol. Cryst. Liq. Cryst., Vol. 416, pp. 31/[287]–38/[294], 2004
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490482123

SYNTHESIS AND CHARACTERISATION OF SOME NEW LANTHANIDE HYBRIDE CONJUGATED MONOMERS

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The 1-substituted derivative of 3-methyl-5-pyrazolone, with benzothyazol was investigated in the system with some lanthanide cations: La^{3+}, Ce^{3+}, Pr^{3+}, Sm^{3+}, Gd^{3+}, Ho^{3+}, Eu^{3+}, Tb^{3+}, Er^{3+}. *The synthesis of these hybride compounds was found to be influenced by the proton affinity constants of the donors and those of the steric hindrance offered by the three chelate rings of the 1-(2′-benzthyazolyl)-3-methyl-5-pyrazolone (BTMP) around the metal cation to the approaching oxodonor as well as the preference of the lanthanide cations for the nitrogen atom as a donor.*

The structure of the products was proved by the elemental analysis, IR, UV-VIS spectra, molar conductance and molecular weight data and the thermogravimetrical study and all complexes correspond to a mononuclear monomers with the general formula.

$[Ln\ (BTMP)_3\ (H_2O)_2].H_2O$. *The synthesized compounds are expected to have luminiscent, antibacterial properties as a monomers or in a polymeric matrix.*

INTRODUCTION

In the last decay many papers have dealt with the new derivatives of the pyrazol-5-one system substituted at 1-position with different heterocyclic radicals [1–5]. These compounds exibit biologic activity [6–8] as well as

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This research was supported by the National Research Programme “MATNANTECH”.
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they were reported as the intermediar systems in the structure of azo-dyes and azo pigments [9–10].

These organic derivatives cover a large area of properties and we focused our interest into obtaining hybride compounds with a pyrazol-5-one derivative available to be a donor system for a metallic cation as an acceptor system. It is well known that in solution 1-(2′-benzthyazolyl)-3-methyl-5-pyrazolone (BTMP) there is in an tautomeric equilibrium between the keto and the enolic forms.

It has been studied the controlled synthesis and the behavior of the 1-(2′-benzthyazolyl)-3-methyl-5-pyrazolone (BTMP) as a ligand. The HYPER CHEM PRO 6 soft does not show a planar molecule both for the ketonic form (L) (Fig. 1) and for the enolic form HL (Fig. 2). In these tautomeric forms the planarity of the molecule is distroyed by the chair conformational isomer of benzenic ring of the 2-benzthyazolyl radical. In a basic or weak basic reaction medium this equilibrium is removed toward enolic tautomer and after the deprotonation the interaction with the metallic cation is established. In the enolic form according to the (Fig. 2) the sulfur atom is available to interact with the lanthanide cations. We suppose that the competition between sulfur and nitrogen atoms is won by the nitrogen atom because of the lanthanide cations have a strong preference for negatively charged donor groups which are also "hard" bases. With neutral ligands, the order of preference for donor atoms is O > N > S [11] and a planar molecule is possible for the organic ligand as a result of the existence of the four ortho condensed rings after the coordination process.

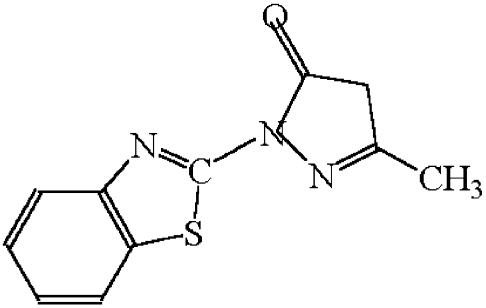

FIGURE 1 The conformational formula of BTMP in the keto tautomer.

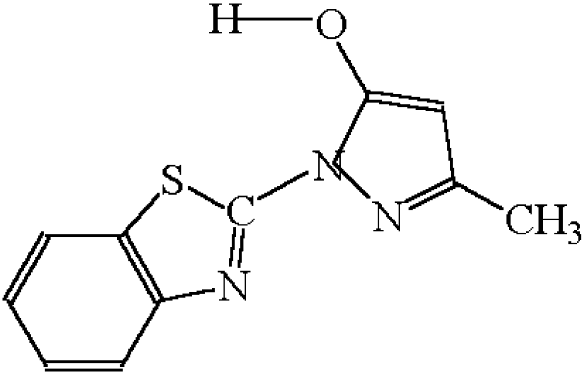

FIGURE 2 The conformational formula of BTMP in the enolic tautomer.

EXPERIMENTAL

Materials

$La(NO_3)_3 \cdot 6H_2O$, $CeCl_4$, $PrBr_3 \cdot 6H_2O$, $SmCl_3 \cdot 6H_2O$, $GdCl_3 \cdot 6H_2O$, $HoCl_3 \cdot 6H_2O$, Eu_2O_3, $TbCl_3 \cdot 6H_2O$, $Er_2(CO_3)_3$, EtOH, are purchased from MERK LTD, 1-(2′-benzthyazolyl)-3-methyl-5-pyrazolone (BTMP) was prepared in our laboratory by using the method presented elsewhere [12].

Measurement Techniques

Elementary analysis were obtained by a Carlo Erba 1108 apparatus. Metallic cations were determined by classical analytical methods.

Molecular weights were determined by GPC with polystyrene standards used for calibration and THF as eluent.

The IR spectra were obtained with a Perkin Elmer FT-IR spectrometer in the range 4000–200 cm^{-1}, in KBr pellets.

The UV-VIS spectra of all compounds were obtained by diffuse reflectance technique, dispersing the sample in MgO, with a JASCO V 570 spectrophotometer.

The thermal decomposition curves have been recorded by a derivatograph (MOM Budapest) in the temperature range of 20–1000°C. Heating rates were in the range of 2.8–10 K/ min.

Preparation of the Compounds

A suspension of (0.7728 g and 0.003 mols) ligand in 15 ml ethanol was adjusted from $pH = 4$ to $pH = 6$ for La^{3+}, Pr^{3+}, Ce^{4+}, Tb^{3+}, Er^{3+} and $pH = 5$ for Sm^{3+}, Gd^{3+}, Eu^{3+}, Ho^{3+} with diluted NH_4OH/water = 1/1(v/v). The ligand suspension was added drop by drop to an aqueous solution of Ln^{3+} equivalent to 0.009 mols of each salt. The mixture of reaction was stirring at around 1/2h at the room temperature than was filtered off and recrystallized from an ethanol/water = 1/1 (v/v) solution, dried at room temperature, with an yield ($\eta = 60$–65%). The complexes appeared as intense colored microcrystalline powders.

RESULTS AND DISCUSSION

The elemental analysis of the metal complex monomers and the moloecular weight (Table 1) indicated a ratio Ln/BTMP = 1/3 and correspond to a mononuclear coordination compounds. The molar conductance data (Table 1) exhibit a nonelectrolitic compounds in DMF solution. The thermogravimetrical study showed the presence of two coordinated water molecules and crystallized water one.

All complexes correspond to the general formula $[\mathrm{Ln}\ (\mathrm{BTMP})_3(\mathrm{H_2O})_2]\cdot \mathrm{H_2O}$.

Based on these data we have formulated the following chemical synthesis reactions of our coordinative compounds:

TABLE 1 The Elemental Analysis, the Molar Conductance Data, the Molecular Weights, the Colour and the Formula of the Lanthanide Complexes

Complex	Elemental analysis data				Molecular weight	λ Ω^{-1}cm^{2}mol^{-1} in DMF 10^{-3} M	Colour
	C%	H%	N%	Ln%			
1. $[\mathrm{La\ (BTMP)_3(OH)_2](H_2O)}$	(44.85)*	(3.39)	(14.27)	(15.73)	(882.9)	25.32	Brown-reddish
	44.80	3.30	14.25	15.70	880		
2. $[\mathrm{Ce(BTMP)_3(OH)_2](H_2O)}$	(44.79)	(3.39)	(13.91)	(15.84)	(884.1)	28.15	brown
	44.70	3.31	13.89	15.12	882		
3. $[\mathrm{Pr(BTMP)_3(OH)_2](H_2O)}$	(44.75)	(3.39)	(14.23)	(15.92)	(884.9)	24.95	brown
	44.72	4.00	14.97	15.71	881		
4. $[\mathrm{Sm(BTMP)_3(OH)_2](H_2O)}$	(44.27)	(3.35)	(14.08)	(16.81)	(894.36)	24.99	Reddish-brown
	44.64	3.87	14.10	16.22	894		
5. $[\mathrm{Gd(BTMP)_3(OH)_2](H_2O)}$	(43.93)	(3.32)	(13.98)	(17.63)	(901.25)	35.11	pink
	43.44	3.92	13.55	17.85	900		
6. $[\mathrm{Ho(BTMP)_3(OH)_2](H_2O)}$	(43.56)	(3.30)	(13.86)	(18.14)	(908.93)	31.45	Brown-pinkish
	44.96	3.15	13.92	18.02	910		
7. $[\mathrm{Eu(BTMP)_3(OH)_2](H_2O)}$	(44.19)	(3.34)	(14.06)	(16.96)	(895.96)	27.41	Brown-yellow
	44.01	3.30	14.00	16.21	890		
8. $[\mathrm{Tb(BTMP)_3(OH)_2](H_2O)}$	(43.85)	(3.32)	(13.95)	(17.60)	(902.92)	29.06	Brown-reddish
	43.68	3.22	13.87	16.45	900		
9. $[\mathrm{Er(BTMP)_3(OH)_2](H_2O)}$	(43.45)	(3.29)	(13.82)	(18.35)	(911.26)	31.15	brown
	43.22	3.12	13.78	18.30	910		

*(Calculated) Experimental.

$Ln(X)_3 + 3NH_4OH + 3LH \rightarrow [Ln\,(BTMP)_3(H_2O)_2].H_2O + 3\,NH_4X + H_2O$
where LH = BTMP.

The IR spectra of the metal complexes monomers (Table 2) are rather complex but a comparison of the spectra with some previous works [13–15] has enable to assign the most characteristic bands.

The free ligand 1-(2′-benzthyazolyl)-3-methyl-5-pyrazolone (BTMP) exhibits an intense and characteristic band at $1634\,cm^{-1}$ assigned to $\nu(C=O)$ pyrazolonic and a band at $1523\,cm^{-1}$ assigned to $[\nu(C=O) + \nu(C=N)]$ skeleton. The position of the last band is affected by the complexation process and it is shifted with $20–30\,cm^{-1}$ toward lower frequency. The band of $\nu(C=O)$ pyrazolonic disappears in the complexes and it is replaced by a new intense band at $1015\,cm^{-1}$ assigned to $\nu C{-}O$ enolic coordinated.

The IR spectra show the new bands in the region $625–425\,cm^{-1}$ that were assigned according to the literature data to $\nu(M{-}O) = 425–430\,cm^{-1}$ and $\nu(M{-}N) = 600–625\,cm^{-1}$ respectively. All complexes exhibit a new very strong band near $3450\,cm^{-1}$ which was assigned to ν_{OH} of the crystallized water molecules within the complexes.

The thermogram of these complexes [16] exhibit a small exothermic peak at 90°C owing to their hygroscopic nature. The thermic decomposition show four stages for $[Gd(BTMP)_3(OH)_2].2H_2O$:

- (35–100°C) the loss in the weight is 1 mg that means ~2.63% and corresponds to the crystallized water molecules.
- (100–200°C) the loss in the weight is 2 mg that means ~5.26% and corresponds to the coordinated water molecules that leave the system at ~190°C in an endothermic process.

TABLE 2 The IR(cm^{-1}) Spectra of the Hybride Lanthanide Complexes

Assignments	BTMP	1	2	3	4	5	6	7	8	9
ν(C=O) pyrazolonic	1634	–	–	–	–	–	–	–	–	–
ν(C=N) + ν(C=O)	1523	1515	1521	1520	1521	1521	1521	1521	1521	1521
	1361	–	–	–	–	–	–	–	–	–
δH_2O coord.	–	506	506	506	552	506	551	551	506	551
		585	554	583	572	580	571	572	581	571
ν C−O−M enolic coord.	–	1382	1380	1381	1380	1380	1380	1381	1382	1382
ν C−O enolic	–	1015	1012	1015	1015	1010	1011	1011	1012	1012
ν(Ln−O)	–	430	400	400	430	430	430	435	432	433
ν(Ln−N)	–	620	620	620	620	625	620	619	625	625

The numbers (1–9) indicated in the columns correspond to the coordinative complexes according with the (Table 1).

- (200–520°C) the loss is 20.99 mg that means ~55.26% of the total weight corresponding to the organic part.
- (520–700°C) the loss is ~3 mg(~7.89%), and at 635°C is present Gd_2O_3.

UV-VIS spectra of all hybride compounds correspond to the cation Ln^{+3} spectra because of the f-f transition are not affected by the neighbors but in the coordinative compounds all bans are shifted comparable with the spectra in the aqueous solutions and the bands of the region 16000–20000 cm^{-1} are very sensitive to the geometry around the metallic cation and they were assigned according with the literature data [17–19].

[Pr (BTMP)$_3$ (H$_2$O)$_2$].H$_2$O. 16900 cm^{-1} for $^3H_4\rightarrow{}^1D_2$ (in Pr^{3+}(aq) 16980 cm^{-1}), 20200 cm^{-1} for $^3H_4\rightarrow{}^3P_0$ (in Pr^{3+}(aq) 20700 cm^{-1}), 20850 cm^{-1} for $^3H_4\rightarrow{}^1I_6$ (in Pr^{3+}(aq) 21500 cm^{-1}), The banda at 33300 cm^{-1} corresponds to the transition $4f^{\,n}\rightarrow 4f^{n-1}$.

[Sm (BTMP)$_3$ (H$_2$O)$_2$].H$_2$O. 17450 cm^{-1} for $^6H_{7/2}\rightarrow{}^4G_{5/2}$ (in Sm^{3+} (aq) 17880 cm^{-1}), 18340 cm^{-1} for $^6H_{7/2}\rightarrow{}^4F_{3/2}$ (in Sm^{3+}(aq) 18880 cm^{-1}), 20400 cm^{-1} for $^6H_{7/2}\rightarrow{}^4G_{7/2}$(in Sm^{3+} (aq) 19950 cm^{-1}).

[Gd (BTMP)$_3$ (H$_2$O)$_2$].H$_2$O. The bands in the region 32000–33000 cm^{-1} were assigned according with Sidall and Stewart [8] to the following transitions:

31250 cm^{-1} for $^8S_{7/2}\rightarrow{}^6P_{7/2,}$ 32258 cm^{-1} for $^8S_{7/2}\rightarrow{}^6P_{5/2}$, 32894 cm^{-1} for $^8S_{7/2}\rightarrow{}^6P_{3/2}$, The transitions at $^6I({}^6I_{7/2}, {}^6I_{9/2,}{}^6I_{17/2,}{}^6I_{11/2}, {}^6I_{13/2,}{}^6I_{15/2})$ appear in the range 36000–37000 cm^{-1}. A very intense band at 36340 cm^{-1} corresponds to the transition $^8S_{7/2}\rightarrow{}^6I_{9/2.}$ And the band at 45454 cm^{-1} corresponds to the transition $^8S_{7/2}\rightarrow{}^6D({}^6D_{9/2,\ 1/2,\ 7/2,\ 3/2,\ 5/2})$.

[Ho (BTMP)$_3$ (H$_2$O)$_2$].H$_2$O. 11111 cm^{-1} for $^4I_{15/2}\rightarrow{}^5I_5$, 16260 cm^{-1} for $^4I_{15/2}\rightarrow{}^5F_5$, 17094 cm^{-1} for $^4I_{15/2}\rightarrow{}^5S_2$, 18018 cm^{-1} for $^4I_{15/2}\rightarrow{}^5F_4$, 19607 cm^{-1} for $^4I_{15/2}\rightarrow{}^5F_3$, 20000 cm^{-1} for $^4I_{15/2}\rightarrow{}^5F_2$, 21052 cm^{-1} for $^4I_{15/2}\rightarrow{}^3K_8$, 23255 cm^{-1} for $^4I_{15/2}\rightarrow{}^5G_6$, 25000 cm^{-1} for $^4I_{15/2}\rightarrow{}^5G_4$, 25974 cm^{-1} for $^4I_{15/2}\rightarrow{}^3K_7$, 28169 cm^{-1} for $^4I_{15/2}\rightarrow{}^3G_6$, 28985 cm^{-1} for $^4I_{15/2}\rightarrow{}^3D_3$, 35714 cm^{-1} for $^4I_{15/2}\rightarrow({}^3H_{4,}{}^5D_{4,}{}^1G_4)$, $^5G_6$ si $^3G_6$ (23255 si 28169 cm^{-1}) are hypersensitive transitions.

[Eu (BTMP)$_3$ (H$_2$O)$_2$].H$_2$O. Eu(III) has many terms $^5G_7$, $^5L_{7,8,9,10}$ and also $^7F_0\rightarrow{}^5D_3$, $^5G_3$ and $^5G_5$ forbidden and may be noted that the transition to $^5L_6$ at 25400 cm^{-1} is the strongest absorbtion band in the whole region from 6000–40000 cm^{-1}. The observed transitions are the following: 20500 cm^{-1} $^7F_0\rightarrow{}^5D_4$, 25400cm^{-1} $^7F_0\rightarrow{}^5L_6$, 26700cm^{-1} $^7F_0\rightarrow{}^5G_6$, 31500 cm^{-1} $^7F_0\rightarrow{}^5H_6$.

[Tb (BTMP)$_3$(H$_2$O)$_2$].H$_2$O. 20500 cm^{-1} $^7F_6 \rightarrow ^5D_4$, 26300 cm^{-1} $^7F_6 \rightarrow ^5D_3$, 26500 cm^{-1} $^7F_6 \rightarrow ^5G_6$, 27100 cm^{-1} $^7F_6 \rightarrow ^5L_{10}$, 27800 cm^{-1} $^7F_6 \rightarrow ^5G_5$.

[Er (BTMP)$_3$ (H$_2$O)$_2$].H$_2$O. 15300 cm^{-1} $^4I_{15/2} \rightarrow ^4F_{9/2}$, 18400 cm^{-1} $^4I_{15/2} \rightarrow ^4S_{3/2}$, 19200 cm^{-1} $^4I_{15/2} \rightarrow ^2H_{11/2}$, 20500 cm^{-1} $^4I_{15/2} \rightarrow ^4F_{7/2}$, 22200 cm^{-1} $^4I_{15/2} \rightarrow ^4F_{5/2}$, 22600 cm^{-1} $^4I_{15/2} \rightarrow ^4F_{3/2}$, 24600 cm^{-1} $^4I_{15/2} \rightarrow ^2G_{9/2}$, 26400 cm^{-1} $^4I_{15/2} \rightarrow ^4G_{11/2}$.

All bands correspond to an eight coordination number and a square antiprysmatic geometry (C$_2$).

CONCLUSION

In this paper we have reported the synthesis and the characterisation of a new series of the nine coordinative compounds of the lanthanide cations with a 1-derivative of pyrazol-5-one that possesses many possibilities to bind the metallic cations. It can be observed that it might behave as a neutral and a tetradentate ligand with the chromophores (ON) and (SN) in the keto form and as a monobasic and a tetradentate ligand with the chromophores (OS) and (NN) in the enolic form. The experimental results showed a special behaviour of the 1-(2′-benzthyazolyl)-3-methyl-5-pyrazolone (BTMP) as a monobasic and a bidentate with the chromophore (ON) in the presence of the Ln^{3+} cations. This behaviour does not correspond to the presence in a weak basic medium of the deprotonated enolic form of the 1-(2′-benzthyazolyl)-3-methyl-5-pyrazolone (BTMP) in a ratio of 90% with the chromophore (OS). We supposed that the binding site (ON) is owing to the strong preference of the lanthanide cations for negatively charged donor groups which are also “hard” bases like the deprotonated enolic form of the ligand and the order of preference for neutral donor atoms $O > N > S$ that forced the twisting of the benzothyazole ring in the enolic form of the 1-(2′-benzthyazolyl)-3-methyl-5-pyrazolone (BTMP). The twisting energy is probabily balanced by the bond energy $Ln \leftarrow N > Ln \leftarrow S$. The synthesized coordinative compounds as a colored microcrystalline powders are very stabile at the room temperature, the normal pressure and in a dry medium and belong to a π-delocalized coordinative compounds and could exhibite potential fluorescent properties.

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