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Novel ligation of some rare earth metal supramolecular polymer complexes

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Summary

Novel seven, nine and ten-coordinated rare earth polymer complexes of N-Acryloyl-1-phenyl-2-thiourea (APT) of the composition $[Ln(NO_3)_3(APT)_2]_n$ (Ln = La, Sm, Tb, Pr and Nd) and $[Ln(NCS)_3(APT)_x]_n$ (where Ln = La or Pr at x = 2 and Ln = Nd, Sm and Tb at x = 3) have been prepared and characterized on the basis of their chemical analyses, magnetic measurements, conductance, visible and IR spectral data. The electronic spectra of Pr^{3+}, Nd^{3+} and Sm^{3+} show characteristic f-f transitions and the nephelauxetic effect (1-B) of these transitions has been evaluated. These data indicate the weak involvement of the 4f orbitals in complex formation. Composition and IR spectral data of the obtained polymeric complexes show that APT acts as a bidentate ligand. The structure and bonding of these high coordination number compounds were established and identified with the help of various physico-chemical studies. Conductance studies indicate a non-electrolytic behavior for these complexes. Their infrared spectra show that both the ligand and the nitrate group are bound to the metal ion in a bidentate fashion.

Introduction

Lanthanide polymeric metal complexes of acryloyl-1-phenyl-2-thiourea have not been reported in the literature. It was therefore thought of interest to investigate the rare earth metal polymeric complexes with this ligand. In our laboratories, the coordination behavior, chemical equilibria, thermal analysis and electron paramagnetic resonance of novel supramolecular d-block polymer complexes have been investigated in depth[1-8]. However, no structural or coordination studies have been reported for f-block supramolecular polymer complexes. A literature survey has revealed that no work appears to have been reported on the synthesis and characterization of the metal derivatives of the homopolymers. In view of the above, we were, therefore, intrigued by this notion to synthesize and characterize the novel homopolymer and their metal derivatives.

Due to the sensitivity of metal complexes towards physical, electrochemical and optical sensors, the integration of coordinative ligands into macromolecules has become an important approach for the preparation of novel functional polymers. Therefore, chelating compounds such as acryloyl-1-phenyl-2-thiourea are being utilized as suitable ligands[9]. They enable the formation of rigid coordination polymers. In order to obtain well-defined supramolecular polymer structures, maintained and controlled polymerization methods may be performed, using functionalized units as initiators [5-8]. The structural chemistry of the lanthanide elements has recently undergone considerable developments, where a wide variety of coordination numbers and geometries have been observed. This structural versatility arises from the lack of strong crystal effects for the large ionic radii of these metal ions, which change markedly with oxidation number, or atomic number of lanthanide[10]. In this paper we are reporting the synthesis and characterization of some lanthanide(III) complexes of the monomer derived from acryloyl chloride and 2-amino-1-phenylthiourea, *viz.* N-Acryloyl-1-phenylthiourea(APT)[8,11]. This ligand is expected to behave as bidentate since this will result in the formation of a stable polymeric complex[8,9,11].

Experimental

Experimental techniques were as described previously[1-9,11,13,14].

Material

Acryloyl chloride (Aldrich) was degassed, twice distilled on a vacuum line, stored over anhydrous Na_2SO_4 and kept below -18 ^oC in a tightly stoppered flask. 1-phenyl-2-aminothiourea (Merck) was used without further purification and 2,2$^-$-azobisisobutyronitrile (AIBN) (Eastman Kodak) was purified by crystallization from EtOH[12]. 2-Acrylamido-1-phenyl-2-thiourea monomer (APT) was prepared according to El-Sonbati *et al*[9,11] and Mubarak *et al*[2,5,7,8]. The infrared spectrum of the monomer shows the presence of an –NH absorption band in the 2950 – 3300 cm^{-1} region and its ^{1}HNMR spectrum shows characteristic bands at δ = 10.6 – 10.9 ppm due to NH groups.

Polymer synthesis

PAPT homopolymer was prepared by refluxing the monomer with (DMF) as solvent and 0.1 w/v AIBN as initiator for 6 h. The polymer was precipitated by pouring into distilled water.

Preparation of the polymer complexes

a) Preparation of $Ln(NO_3)_3(APT)_2$(Ln = La, Sm, Tb, Pr and Nd)

Solution of lanthanide nitrate (0.2 mol) and APT (0.6 mol) in DMF in presence of 0.1 w/v AIBN as initiator were mixed. The mixture was stirred under reflux for 3 h and the resulting polymer complexes were precipitated by pouring into a large excess of distilled water containing hydrochloric acid to remove the excess metal salt. The precipitate was filtered off, washed with water and dried in a vacuum oven at 40^{o}C for several days.

b) Preparation of $[Ln(APT)_x(NCS)_3]$ (Ln = La, Pr at x=2; Ln = Nd, Sm, or Tb at x=3)

A warm ethanolic solution (20 ml) of lanthanide nitrate hexahydrate (0.1 mmol) was added to a warm ethanolic solution (40 ml) of potassium thiocyanate (3.0 mmol). The solution was evaporated to half volume and left overnight for complete precipitation of potassium nitrate, which was removed by filtration. The filtrate was treated the same way with the ligand as in procedure (a). The colored precipitate was purified and dried as usual. The chemical analyses (See Table 1) correspond to the general formula [Ln$(NO_3)_3$$(APT)_2$] and [Ln$(NCS)_3$$(APT)_x$]. This formula is further supported by molar conductance and IR spectral data.

Results and Discussions

Elemental analysis

The polymer complexes under investigation were subjected to elemental analysis. These complexes showed high purity and the yields obtained were in the range between ~ 70-85% as seen in Table 1.

Table 1. Elemental analysis and magnetic data of the polymer complexes*.

Species Nos.[a]	Yield (%)	Found (Calc. %)					$\mu_{eff}^{.b}$ (BM)
		C	H	N	O	M	
$[La(NO_3)_3(APT)_2]_n$	85	32.6	2.7	13.3	8.7	18.9	dia.
(1)		(32.5)	(2.6)	(13.6)	(9.0)	(20.1)	
$[Sm(NO_3)_3(APT)_2]_n$	85	32.1	2.7	13.1	8.6	20.1	1.54
(2)		(32.0)	(2.8)	(13.4)	(8.9)	(20.4)	
$[Tb(NO_3)_3(APT)_2]_n$	80	31.7	2.6	13.3	8.5	21.0	1.65
(3)		(31.8)	(2.7)	(13.0)	(8.3)	(21.2)	
$[Pr(NO_3)_3(APT)_2]_n$	85	32.5	2.7	13.3	8.7	19.1	3.48
(4)		(32.6)	(2.8)	(13.5)	(9.0)	(18.8)	
$[Nd(NO_3)_3(APT)_2]_n$	82	32.3	2.7	13.2	8.6	19.4	4.46
(5)		(32.2)	(2.8)	(13.0)	(8.9)	(19.1)	
$[La(NCS)_3(APT)_2]_n$	70	33.1	2.8	13.5	22.1	19.2	dia.
(6)		(33.0)	(2.9)	(13.7)	(21.8)	(19.0)	
$[Pr(NCS)_3(APT)_2]_n$	72	33.0	2.8	13.5	22.0	19.4	3.46
(7)		(32.9)	(2.9)	(13.8)	(22.3)	(19.1)	
$[Nd(NCS)_3(APT)_3]_n$	72	38.5	3.2	13.5	20.5	15.4	3.51
(8)		(38.4)	(3.3)	(13.7)	(20.7)	(15.2)	
$[Sm(NCS)_3(APT)_3]_n$	70	38.2	3.2	13.4	20.4	16.0	1.64
(9)		(38.3)	(3.3)	(13.2)	(20.6)	(15.8)	
$[Tb(NCS)_3(APT)_3]_n$	73	37.9	3.2	13.3	20.2	16.7	9.84
(10)		(38.0)	(3.1)	(13.0)	(20.0)	16.9)	

* Microanalysis data as well as sulphur and metal estimations are in good agreement with the stoichiometry of the proposed complexes. [a]Insoluble in water and common organic solvents but soluble in hot coordinating solvents such as DMSO and DMF, colored, non-hygroscopic, air-stable at room temperature for long periods. [b]Per metal ion and measured at room temperature and uncorrected for diamagnetism. [c]dia. = diamagnetic.

The data of elemental analysis indicate that the stoichiometric ratio for the reaction of monomer with various LnX_3 is 1 : 2 and 1 : 3 (Ln : monomer). The polymer complexes do not contain any water of coordination or hydration indicating that the coordination sites in these complexes are all occupied by donor centers from the ligand groups SO. The reaction between LnX_3 and ligand can be represented as follows:

$$\begin{aligned} LnX_3 + nAPT &\rightarrow [Ln(NO_3)_3(APT)_2]_n \\ &\rightarrow [Ln(NCS)_3(APT)_2]_n \\ &\rightarrow [Ln(NCS)_3(APT)_3]_n \end{aligned}$$

These data suggest that three nitrato and/isothiocyanato ions are within the coordination sphere.

Structural investigation of homopolymer by ^{1}H-NMR, IR and UV-Vis spectra

N-Acryloyl-1-phenyl-2-thiourea (APT) was prepared by the amidation reaction of acryloyl chloride with 1-phenyl-2-aminothiourea in presence of pyridine and hydroquinone under reflux in benzene[9,11]. The monomer was then polymerized by radical polymerization initiated by 2,2ˋ-azobisisobutyronitrile (AIBN). The homopolymer has been characterized by various techniques[1-9]. Both IR and ^{1}HNMR spectroscopies were used to characterize the APT homopolymer. The recorded IR spectrum of the homopolymer and assignments of characteristic bands are based on published data[3-9].

^{1}H-NMR spectrum of uncomplex

The ^{1}HNMR spectrum of APT homopolymer exhibited the expected peaks δ (DMSO-d_6) 10.4–10.8 (2H, 2NH) and ~ 2.88 (2H, CH_2) protons, which are downfield from TMS. The first signal disappeared on adding D_2O, while the other signals were still observed. The ^{1}HNMR spectrum of APT monomer showed the expected peaks and pattern of the vinylic group (CH_2=CH), *i.e.* δ (DMSO-d_6) 6.36 (dd, J = 17, 11 Hz) for the vinyl CH proton and δ 5.21 ppm (AM part of AMX system dd, J = 17, 1Hz, and dd, J 11, 1Hz) for the vinyl CH_2 protons, respectively. These peaks disappeared on polymerization while a triplet at δ 1.98 (t, J = 7 Hz) and a doublet at δ 1.86 ppm (d, J = 7Hz) appeared. This indicates that the polymerization of APT monomer occurs on the vinyl group. It is worth noting that the rest of the protons spectra of the monomer and polymer remain almost without change.

Spectrum of uncomplex

The spectrum of homopolymer in DMF registered bands at 38460, 34480 and 32760 cm^{-1} which can be assigned to the n → π and π → π* transitions, respectively, of the thiocarbonyl group. These transitions occur at wavelength longer than for the carbonyl group due to ionization of sulphur lone pair being lower than that of its oxygen congener. The C=S group stabilizes the π* level and destabilizes the n level compared to the C=O group.

The IR spectra and mode of bonding in polymer complexes

The mode of bonding of the metal ion to the monomer ligand is easily investigated by studying the IR spectra of the complexes in comparison with those of the ligand. On comparing the IR spectra of the Ln-APT polymer complexes obtained as KBr discs with those of the ligand (Table 2), the following features are observed:

Table 2. Infrared band assignments (cm^{-1}) for homopolymer and its polymer complexes*.

Species	CS	CO	M-O	M-S
PAPT	1240, 765	1660	-	-
(1)	1220, 750	1640, 1605	390	230
(2)	1225, 755	1600	390	225
(3)	1225, 755	1615, 1603	380	223
(4)	1230, 645	1630, 1605	385	220
(5)	1220, 635	1625, 1610	388	218
(6)	1225, 740	1640, 1608	389	222
(7)	1230, 750	1630	390	224
(8)	1223, 755	1625, 1605	393	218
(9)	1228, 745	1635, 1610	345	220
(10)	1230, 740	1620, 1608	385	225

*For the structures, see Table1.

1- The infrared spectra of all the polymer complexes show a considerable shift to lower frequency in the carbonyl (N-Acrylamido) absorption $\Delta \boldsymbol{V}$(C=O) by 25 – 35 cm^{-1}, indicating a decrease in the stretching force constant of C=O as a consequence of coordination through the oxygen atom of the ligand. It is well known[2,8,9,13,14] that as a result of coordination through the carbonyl oxygen the double bond character between the carbon and the oxygen is reduced. The decrease in the bond character causes a bathgochromic shift in the carbonyl stretching frequency. The CO stretching frequency occurs at 1660 cm^{-1} in the ligand[2,8,11] and has been observed at 1640 – 1610 cm^{-1} in all of the complexes. This exceptionally high shift to lower frequency of the carbonyl frequency may be attributed to the greater flow of electrons from the carbonyl group to the trivalent lanthanide atom due to greater delocalization of the positive charge on the sulphur atom.

2- Another important band occurring at 765 cm^{-1} assigned to the v(CS) mode[9,11]. In the spectra of all the polymer complexes, this band is shifted to lower frequency and appears at 750 – 740 cm^{-1} indicating the involvement of the S-atom of the thione group of the thiourea in coordination[14];

3- In the lanthanide(III) nitrate polymer complexes the occurrence of two strong absorptions at ~1475 and ~1290 cm^{-1} are assigned respectively to the $\boldsymbol{V}_4$ and $\boldsymbol{V}_1$ vibrations of the coordinated C_{2V} nitrate group[13,15]. The magnitudes of $\boldsymbol{V}_4 - \boldsymbol{V}_1$ are in the range 180–190 cm^{-1} in all cases indicating that the nitrate group is coordinated in a bidentate fashion (Table 3).

Table 3. IR spectral data of nitrato polymer complexes*.

compound	V_4 (NO_3)	V_1 (NO_3)	V_2 (NO_3)
(1)	1480	1295	1025
(2)	1475	1295	1025
(3)	1470	1290	1020
(4)	1480	1290	1025
(5)	1480	1290	1025

*For the structures, see Table 1.

4. Bailey *et al*[16] and Burmeister[17] suggested that the region near or above 2100 cm^{-1} for SCN is due to S-bonding, whereas below this region belongs to N-bonding. The C-S stretching frequency ($\boldsymbol{V}_2$) was assigned at 860 – 780 cm^{-1} for M-NCS and at 720 – 690 cm^{-1} for the M-SCN group. The NCS frequency ($\boldsymbol{V}_3$) is also different for the two isomers; it is at 490 – 450 cm^{-1} for the M-NCS and at 440 – 400 cm^{-1} for the M-SCN group. Bridging thiocyanate usually gives higher coordination number stretching frequencies than a terminal-NCS group. In the present $[Ln(NCS)_3.nAPT]_n$ polymer complexes the IR absorption frequencies of the C-N stretching ($\boldsymbol{V}_1$) occur in the 2035 – 2030 cm^{-1}, 840 – 830 cm^{-1} and 480 – 470 cm^{-1} regions, respectively. These frequencies are associated with terminal N-bonded isothiocyanate ions[17](Table 4).

Table 4. IR spectral data of thiocyanato polymer complexes*.

compound	V(CN) of NCS	V (CS) of NCS	V (NCS) of NCS	V (Ln-N) (thiocyanate)
(6)	2120	790	470	295
(7)	2110	795	465	290
(8)	2105	780	460	280
(9)	2103	785	470	275
(10)	2108	787	475	280

*For the structures, see Table 1.

5. On the basis of the above discussions, it is possible to conclude that the ligand (APT) is attached to the metal ion at bi-coordination sites involving thioketosulphur and carbonyl oxygen atoms. Similar type of ligands have been reported to act as bidentate ligands with metal ions by Mubarak *et al.*[2,5,7,8], El-Sonbati *et al.*[1,4,6,11] and others[3].

Magnetic moment

The magnetic moments of the rare earth polymer complexes, recorded in Table 1, show little deviation from the Van values[18] indicating thereby that 4f-electrons do not participate in bond formation in these polymeric chelates. The magnetic moments of these polymer complexes are within the range predicted and observed in the compounds of the lanthanide ions[19].

Measurements in the visible region

A Comparison of the spectrum of the aqueous solutions of $Ln(NCS)_3$ with their corresponding polymer complexes of APT (in DMF) has been investigated. The data are summarized in Table 5.

These data clearly indicate that the energy of f-f transitions in the polymers complexes is red-shift due to nephelauxetic effect. This red-shift is usually marked as an evidence of a higher degree of covalency than existing in the aqua complexes[20,21]. In all of the polymer complexes a marked enhancement in the intensity of the bands has been observed. The nephelauxetic effect (which is regarded as a measure of covalency) for the rare earth polymer complexes has been determined. From the β-values the

Table 5. Electronic Spectral data (cm^{-1}) and Related Bonding Parameters of Lanthanide(III) Isothiocyanate Polymer Complexes* of APT.

Complexes	Ln(NCS) Electronic Spec. bands	Complex Electronic Spec. bands	Energy Levels	$(1 - \beta)$	(β)	$b^{1/2}$	δ%	ŋ
(7)	22390	22245	$^3H_4 \rightarrow {}^3P_2$	0.007	0.993	0.041	0.673	0.007
	21225	21045	$\rightarrow {}^3P_1$	0.009	0.991	0.045	0.854	0.004
	20805	20618	$\rightarrow {}^3P_0$	0.009	0.991	0.046	0.872	0.004
	16895	16715	$\rightarrow {}^1D_2$	0.010	0.989	0.052	0.076	0.005
(8)	19395	19210	$^4I_{9/2} \rightarrow {}^2G_{5/2}, {}^3G_{7/2}$	0.010	0.990	0.098	0.960	0.005
	17395	17205	$\rightarrow {}^4G_{5/2}, {}^3G_{7/2}$	0.011	0.988	0.105	1.113	0.006
	13395	13245	$\rightarrow {}^2S_{3/2}, {}^4F_{7/2}$	0.012	0.989	0.107	1.163	0.006
	12495	12225	$\rightarrow {}^4F_{5/2}, {}^4H_{9/2}$	0.023	0.977	0.150	2.303	0.012
(9)	24900	24723	$^4H_{5/2} \rightarrow {}^4F_{9/2}$	0.007	0.993	0.084	0.705	0.004
	24000	23795	$\rightarrow {}^6P_{5/2}$	0.007	0.993	0.081	0.655	0.004
	21600	21445	$\rightarrow {}^4I_{3/2}$	0.007	0.993	0.073	0.534	0.005

*For the structures, see Table 1.

covalency factor ($b^{1/2}$), Sinha parameter (δ%) (metal-ligand covalency in %) and the covalency angular overlap parameter (n) have been calculated using the expressions[22].

$$b^{1/2} = [(1 - \beta)^{1/2}]\ ,\ d(\%) = [(1 - \beta)/\beta] \times 100 \text{ and } ŋ = (1 - \beta^{1/2})/\beta^{1/2}$$

The positive values of $(1 - \beta)$ and δ % in these coordination compounds indicate that the bonding between the metal and the ligand is covalent compared with the bonding between the metal and an aqua ion. The values of covalence factor and the angular overlap parameter were found to be positive indicating covalent bonding.

Conclusions

From the study presented it is concluded that in the polymeric complexes (1) – (10) APT behave as a bidentate neutral ligand through CO and CS atoms. Furthermore, for a given equatorial ligand μ_{eff}. the relation SCN > NO_3 cannot be so easily explained. It has been found that the NH groups were not involved in chelation for all the prepared polymeric complexes. The results have shown that for all the polymeric complexes, the electrolytic conductivity data indicate that these polymeric complexes in DMF behave as non-electrolytes. Thus, all of the NO_3^- and NCS^- ions are present in the coordination sphere. Whereas the IR data reveal the bi/mono dentate nature of NO_3^- and APT/NCS^- in the polymeric complexes and hence, a coordination number of ten/nine has been suggested for the entire lanthanide ion in the polymeric complexes.

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