

Synthesis and Spectroscopy Studies of New Neodymium(III) Complexes with Cyanamide Derivatives as N-Donor Ligand

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Four new complexes $[\text{Nd}(\text{phen})_2(\text{pcyd})_3]$ (**1**), $[\text{Nd}(\text{phen})_2(2\text{-Clpcyd})_3]$ (**2**), $[\text{Nd}(\text{phen})_2(2,3,5\text{-Cl}_3\text{pcyd})_3]$ (**3**) and $[\text{Nd}(\text{phen})_2(2,3,4,5\text{-Cl}_4\text{pcyd})_3]$ (**4**) where pcyd = phenylcyanamide anion, 2-Clpcyd = (2-chlorophenyl)cyanamide anion, 2,3,5-Cl₃pcyd = (2,3,5-trichlorophenyl)cyanamide anion and 2,3,4,5-Cl₄pcyd = (2,3,4,5-tetrachlorophenyl)cyanamide anion, were prepared and characterized by IR, UV-Vis and ¹H NMR spectroscopy as well as elemental analysis. The ¹H NMR spectra of these complexes show broadening of ligand protons attributed to coordination of paramagnetic center.

Keywords: Lanthanide, Neodymium, Cyanamides, Coordination compounds

INTRODUCTION

Rare earth metal cations, Ln(III) are of great importance for their industrial [1], chemical [2], bio-chemical and medicinal applications [3] due to their specific spectroscopic and magnetic properties. The forbidden nature of the 4f-4f transition requires the use of antenna ligands which serve to facilitate energy transfer from the ligand-excited state stimulating metal-centered luminescence [4]. The search for strongly luminescent lanthanide complexes, which can be excited near UV spectral region, motivated us to synthesize lanthanide(III) complexes containing aromatic N-donor ligands [5-10]. They are increasingly used as highly efficient electroluminescent components for light-emitting diodes, luminescence probes for analytes, labels for proteins and amino acids, and for molecular recognition and chirality sensing of biological substrates [11].

Phenylcyanamide ligands (pcyd) are interesting and practically unexplored ligands from the synthetic and

magnetic points of view [12]. An extensive π conjugation between the cyanamide group and the phenyl ring provides an energetically favorable means by which a metal ion can couple into a conjugated organic π system [12-14]. Phenylcyanamide is an excellent species for doing research in molecular electronics field, such as molecular wires, diodes, switches, etc.

Here we report the synthesis of four new Nd(III) complexes with phenylcyanamide ligands: $[\text{Nd}(\text{phen})_2(\text{pcyd})_3]$ (**1**), $[\text{Nd}(\text{phen})_2(2\text{-Clpcyd})_3]$ (**2**), $[\text{Nd}(\text{phen})_2(2,3,5\text{-Cl}_3\text{pcyd})_3]$ (**3**), and $[\text{Nd}(\text{phen})_2(2,3,4,5\text{-Cl}_4\text{pcyd})_3]$ (**4**). Compounds (**1**)-(**4**) were characterized by IR, UV-Vis and ¹H NMR spectroscopy as well as elemental analysis. All compounds were paramagnetic and ¹H NMR spectra of (**1**)-(**4**) compounds show broadening of ligand protons attributed to coordination of paramagnetic center.

EXPERIMENTAL

$[\text{Nd}(\text{phen})_2\text{Cl}_3\text{OH}_2]$ [15,16], phenylcyanamide ligands and their thallium salts [17] were synthesized using literature

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methods. *Caution!* Thallium is extremely toxic.

All solvents were dried by refluxing for several days over Na and benzophenone under Ar and distilled immediately before use. All reagents and solvents used in this study were obtained from Merck and Aldrich Co.

UV-Vis spectra were recorded on an analytikjena SPECORD S100 spectro-meter with photodiode array detector. IR spectra were recorded as KBr disks on a Shimadzu IR instrument. NMR experiments were recorded at room temperature in CDCl₃ on a Bruker AV-500 spectrometer using an internal deuterated solvent lock.

Synthesis of the Complexes

Synthesis of [Nd(phen)₂(pcyd)₃] (1). The excess amount of the ligand salt, Tl[pcyd] dissolved in boiling water, was cooled and then added to the aqueous solution of [Nd(phen)₂Cl₃.OH₂] (100 mg) and stirred for 3 h. The reaction mixture containing TlCl and the product was filtered and the precipitates were washed with hot water. In order to dissolve the product, dichloromethane (25 ml) was added to the resulting precipitates. The crude products and TlCl were then collected by filtration. The filtrate was concentrated to 5 ml by rotary evaporation, and dried in open air to give pale yellow powder. The product was dried in vacuum over P₄O₁₀ for several hours. Anal. Calcd. for NdC₄₅H₃₁N₁₀: C, 63.14; H, 3.65; N, 16.36%. Found: C, 63.03; H, 3.52; N, 16.15%. IR: ν (cm⁻¹) 2090 (NCN), UV-Vis (CH₂Cl₂): λ_{\max} , (nm) 231, 266, 488, 658. ¹H NMR (CDCl₃): δ_{H} , (ppm) 9.16, 8.28, 7.83, 7.66 (H, phen), 7.29, 7.14, 6.87 (H, pcyd).

Synthesis of [Nd(phen)₂(2-Clpcyd)₃] (2). This was prepared following the procedure used for [Nd(phen)₂(pcyd)₃] except that Tl[2-Clpcyd] ligand salt replaced Tl[pcyd]. Anal. Calcd. for NdC₄₅H₂₈N₁₀Cl₃: C, 56.34; H, 2.94; N, 14.60%. Found: C, 56.25; H, 2.74; N, 14.48%. IR: ν (cm⁻¹) 2110 (NCN), UV-Vis (CH₂Cl₂): λ_{\max} , (nm) 232, 265, 581, 583, 655. ¹H NMR (CDCl₃): δ_{H} , (ppm) 9.18, 8.26, 7.80, 7.67 (H, phen), 7.30, 7.22 (H, 2-Clpcyd).

Synthesis of [Nd(phen)₂(2,3,5-Cl₃pcyd)₃] (3). This was prepared using the procedure employed for [Nd(phen)₂(pcyd)₃] except that Tl[2,3,4-Cl₃pcyd] ligand salt replaced Tl[pcyd]. Anal. Calcd. for NdC₄₅H₂₂N₁₀Cl₉: C, 46.32; H, 1.88; N, 12.01%. Found: C, 46.17; H, 1.67; N, 11.84%. IR: ν (cm⁻¹) 2110 (NCN), UV-Vis (CH₂Cl₂): λ_{\max} , (nm) 233, 268,

587, 658, 748, 803. ¹H NMR (CDCl₃): δ_{H} , (ppm) 9.11, 8.22, 8.03, 7.71 (H, phen), 7.13, 6.71 (H, 2,3,5-Cl₃pcyd).

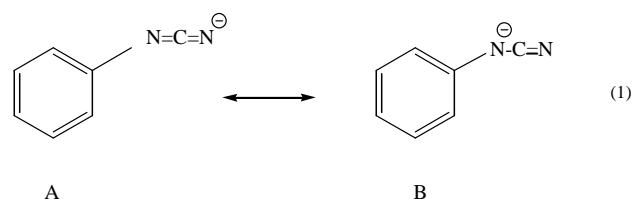
Synthesis of [Nd(phen)₂(2,3,4,5-Cl₄pcyd)₃] (4). This was prepared by the procedure used for [Nd(phen)₂(pcyd)₃] except that Tl[2,3,4,5-Cl₄pcyd] ligand salt replaced Tl[pcyd]. Anal. Calcd. for NdC₄₅H₁₉N₁₀Cl₁₂: C, 42.58; H, 1.51; N, 11.03%. Found: C, 42.43; H, 1.37; N, 10.95%. IR: ν (cm⁻¹) 2120 (NCN), UV-Vis (CH₂Cl₂): λ_{\max} , (nm) 233, 265, 654, 658.09. ¹H NMR (CDCl₃): δ_{H} , (ppm) 9.18, 8.32, 8.10, 7.75 (H, phen), 7.18 (H, 2,3,5-Cl₃pcyd).

RESULTS AND DISCUSSION

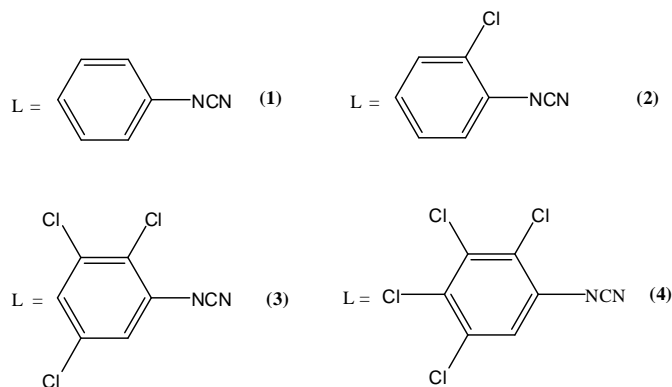
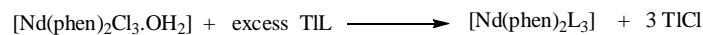
It is well-known that lanthanide ions have high affinity to hard donor atoms such as nitrogen and oxygen atoms [18-21]. Hart and Laming have synthesized lanthanide chloride phen complexes [15]. The results presented here show that neodymium(III) complex, [Nd(phen)₂Cl₃.OH₂], reacts with thallium phenylcyanamide salts to produce [Nd(phen)₂(pcyd)₃] (1), [Nd(phen)₂(2-Clpcyd)₃] (2), [Nd(phen)₂(2,3,5-Cl₃pcyd)₃] (3), [Nd(phen)₂(2,3,4,5-Cl₄pcyd)₃] (4) complexes (Scheme 1). These complexes were anhydrous, which is evident from their analytical and infrared studies. (1)-(4) complexes were soluble in dichloromethane. Their behavior in noncoordinating solvents, particularly dichloromethane and chloroform, are similar. (1)-(4) Complexes were obtained as stable pale yellow crystals in the presence of oxygen.

Infrared Spectra

IR spectroscopy is a proper tool for characterization of phenylcyanamide metal complexes. Interpretation of the IR spectrum requires an understanding of the effect of resonance on the cyanamide group. The protonated cyanamide group shows an infrared stretch with highly nitrile character. Upon deprotonation, two pairs of nonbonding electrons were delocalized in the three-atom π -system, generating two resonance forms:



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Scheme 1

Table 1. Infrared Absorption Frequencies (cm^{-1}) of Cyanamide Group

Complex	ν (NCN)	Tl salt	ν (NCN)	Free ligand	ν (NCN)
$[\text{Nd}(\text{phen})_2(\text{pcyd})_3]$	2090	Tl[pcyd]	2108	pcyd	2227
$[\text{Nd}(\text{phen})_2(2\text{-Clpcyd})_3]$	2110	Tl[2-Clpcyd]	2125	2-Clpcyd	2243
$[\text{Nd}(\text{phen})_2(2,3,5\text{-Cl}_3\text{pcyd})_3]$	2110	Tl[2,3,5-Cl ₃ pcyd]	2130	2,3,5-Cl ₃ pcyd	2245
$[\text{Nd}(\text{phen})_2(2,3,4,5\text{-Cl}_4\text{pcyd})_3]$	2120	Tl[2,3,4,5-Cl ₄ pcyd]	2135	2,3,4,5-Cl ₄ pcyd	2243

IR spectroscopy can differentiate nitrile versus amine coordination in both anionic and neutral form of phenylcyanamide. Neutral phenylcyanamide shows $\text{C}\equiv\text{N}$ in the range of $2225\text{-}2249 \text{ cm}^{-1}$, where coordination of anionic phenylcyanamide ligands seems to occur *via* nitrile nitrogen and produces a strong bond at a frequency lower than 2150 cm^{-1} [17]. The NCN infrared bands of the free ligands, their thallium salts and Neodymium(III) complexes are summarized in Table 1. The spectra of all compounds were relatively similar. The strong band observed at $2227\text{-}2243 \text{ cm}^{-1}$ in the spectra of the free ligands due to ν (NCN) shifted to lower frequencies upon complexation by $100\text{-}125 \text{ cm}^{-1}$. Infrared data for (1)-(4) were consistent with the presence of the resonance form B (Eq. 1) [12,17].

The intensive and broad band of water stretching mode at

1635 cm^{-1} in IR spectrum of $[\text{Nd}(\text{phen})_2\text{Cl}_3 \cdot \text{OH}_2]$ was absent in IR spectra of (1)-(4) complexes. The $\text{C}=\text{N}$ stretching bands of phen in $[\text{Nd}(\text{phen})_2\text{Cl}_3 \cdot \text{OH}_2]$ underwent a modification when cyanamide ligands coordinated to the metal. The absorption bands at $1514, 1421 \text{ cm}^{-1}$ ($\text{C}=\text{N}$ of phen) shifted to lower waves upon complexation with cyanamide groups [12,22].

Electronic Spectra

The absorption spectra of the solution of neodymium complex were measured in dichloromethane. As an example, UV-Vis spectrum of $[\text{Nd}(\text{phen})_2(\text{pcyd})_3]$ is shown in Fig. 1.

The bands that appear below 300 nm are assigned to charge-transfer and $\pi \rightarrow \pi^*$ transitions of phen and phenylcyanamide ligands. The f-f transitions occur at

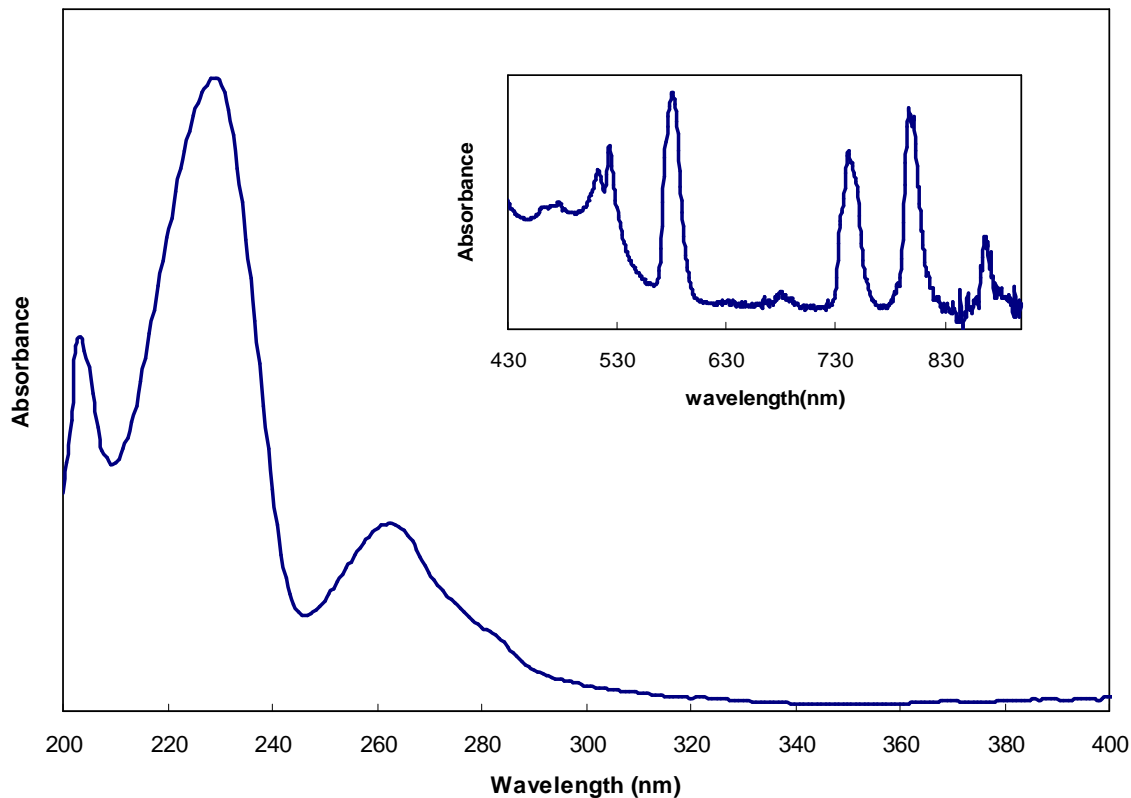


Fig. 1. Uv-vis spectrum of $[\text{Nd}(\text{phen})_2(\text{pcyd})_3]$ in dichloromethane solution. Inset, f-f transitions (430-900 nm).

wavelengths 430-900 nm and with lower intensity. The absorption bands of neodymium(III) in the visible and near infrared region appear due to transitions from the ground levels of $^4I_{9/2}$, to the excited J-levels of the 4f configuration [5,15].

^1H NMR Spectra

All resonances in the ^1H NMR spectrum of the (1)-(4) complexes were spread out well and assigned to the bases of their intensities, line width and chemical shifts at room temperature. The ^1H NMR spectra of these species were similar to each other (Table 2). Figure 2 shows, for example, the spectrum of $[\text{Nd}(\text{phen})_2(\text{pcyd})_3]$ in CDCl_3 at 25 °C in the range of 6.7-9.4 ppm.

The proton chemical shifts of pcyd ligands mostly occurred in the 6-7 ppm range [23]. The NMR signals of pcyd protons in **1** appeared as three broad signals at 7.29, 7.14, 6.87

ppm. Also, pcyd protons in **2**, **3** show two broad signals at 7.30, 7.22 and 7.13, 6.71 ppm, respectively. Only one broad signal was observed for pcyd protons in **4** at 7.18 ppm.

The NMR signals of phen protons in **1-4** appeared as four broad signals in the range of 7.66-9.14 ppm. The signals of coordinated phen were found to shift slightly to lower fields and broad signals compared with free ligand [5].

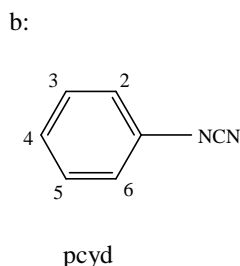
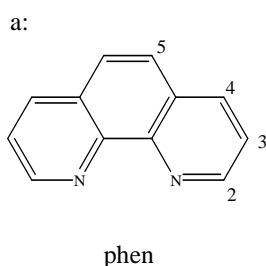
^1H NMR data for free ligands, and some diamagnetic complexes containing pcyd ligands [24-25], have been reported in Table 2. As can be observed, the NMR signals of coordinated pcyd and phen protons in **1-4** were observed to shift slightly to broad signals compared with free ligands, suggesting that the ligands were coordinated to the paramagnetic center. Therefore, this complex, like other triply positive charged lanthanide complexes, is paramagnetic due to the presence of 4f-electrons, which are effectively shielded by $5s^2$ and $5p^2$ electrons [15].

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Table 2. ¹H NMR Data for Free Ligands and some Complexes Containing Phenylcyanamide

complex	H of pcyd ^b	H of phen ^a				Ref.
		2	3	4	5	
[Rh(tpy)(bpy)(pcyd)](PF ₆) ₂	6.30(t), 6.41(d), 6.97(t)					[24]
[Rh(tpy)(bpy)(2-Clpcyd)](PF ₆) ₂	6.33(d), 6.48(t), 6.98(t), 7.05(d)					[24]
[Ru(bipy) ₂ (2,3-Cl ₂ pcyd) ₂]	6.28(d), 6.70(m)					[25]
[Ru(bipy) ₂ (2,4,5-Cl ₃ pcyd) ₂]	6.15(s), 7.35(s)					[25]
[Ru(bipy) ₂ (2,4,5,6-Cl ₄ pcyd) ₂]	6.17(s)					[25]
Hpcyd	7.02-7.07(m), 7.28-7.33(m), 7.64 (br)					This work
2-ClHpcyd	6.54(br), 7.05(m), 7.31(m), 7.35(m)					This work
2,3,5-Cl ₃ Hpcyd	6.65(s), 7.32(s)					This work
2,3,4,5-Cl ₄ Hpcyd	6.75(s)					This work
phen	-	9.19	7.63	8.24	7.83	[5]
[Nd(phen) ₂ (pcyd) ₃]	7.29(br), 7.14(br), 6.87(br)	9.16	8.28	7.83	7.66	This work
[Nd(phen) ₂ (2-Clpcyd) ₃]	7.30(br), 7.22(br)	9.18	8.26	7.80	7.67	This work
[Nd(phen) ₂ (2,3,5-Cl ₃ pcyd) ₃]	7.13(br), 6.71(br)	9.11	8.22	8.03	7.71	This work
[Nd(phen) ₂ (2,3,4,5-Cl ₄ pcyd) ₃]	7.18(br)	9.18	8.32	8.10	7.75	This work

Abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; br, broad.



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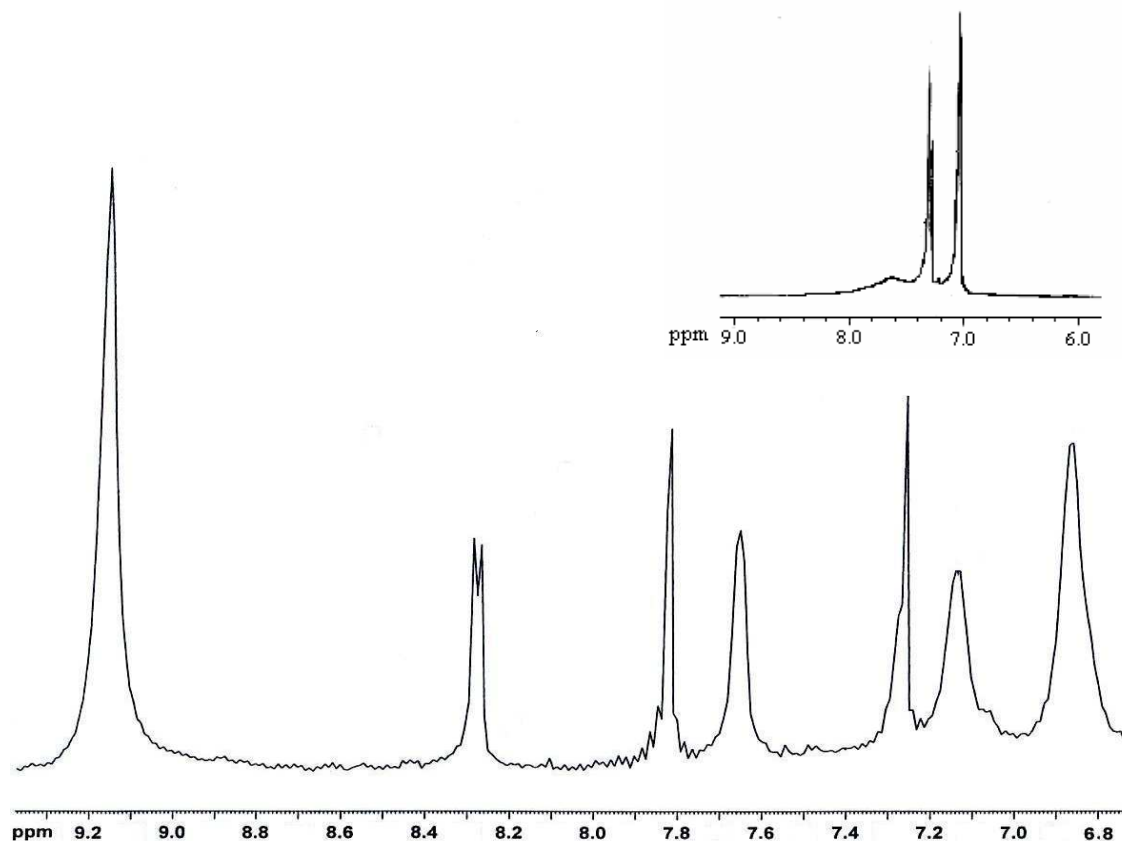


Fig. 2. 500 MHz ^1H NMR spectrum $[\text{Nd}(\text{phen})_2(\text{pcyd})_3]$ in chloroform-d at RT in the range of 6.7-9.4 ppm. Inset, ^1H NMR spectrum Hpcyd in chloroform-d in the range of 6.0-9.0 ppm.

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