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Lanthanum(III) complexes with phenylcyanamide ligands: Synthesis and crystal structure

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1. Introduction

In recent years, coordination chemistry of the rare earth elements has undergone remarkable growth, and a wide variety of geometries and coordination numbers have been observed. Low crystal effects of the 4f electronic configurations and the large ionic radii of these metal ions, which change considerably with atomic number or oxidation state of the lanthanides, lead to the structural versatility of these complexes [1].

Moreover, synthesis of lanthanide metal complexes has been a subject of rapid development in material and supramolecular chemistry due to their many structural motifs, high coordination numbers, and interesting magnetic, electronic, and spectroscopic properties [2]. Lanthanide (4f) complexes are extensively used in many applications [3] such as: chromophores for catalysts for organic syntheses in the field of organometallic chemistry [4], luminescent probes [5,6], NMR shift reagents [7], contrast agents for magnetic resonance imaging (MRI) [8], and artificial enzymatic "scissors" of DNA and RNA in the field of biochemistry [9]. Lanthanide ions are different in the optical properties from other luminescence materials because their absorbance and emission spectra have narrow wavelength ranges with high quantum yields [10,11].

1,10-Phenanthroline (phen) forms a variety of complexes with rare earth elements. One of the first complexes of this type was reported by Hart and Laming [12,13]. They proposed the formula of $[Ln(phen)_2Cl_3OH_2]$ and $[Ln(phen)_3(NCS)_3]$ for this complexes

ABSTRACT

Several novel mixed ligand lanthanum complexes with 1,10-phenantroline and phenylcyanamide derivatives with the formula of $[La(phen)_3Cl_3 OH_2]$ (1) and $[La(phen)_3L_3]$ (phen = 1,10-phenantroline; L = 2-clorophenylcyanamide (2), 2,5-dichlorophenylcyanamide (3), 2,4-dichlorophenycyanamide (4) and 2,4,5-trichorophenycyanamide (5)) are successfully synthesized in aqueous solution. The complexes are characterized by spectroscopic analysis such as infrared, ¹H NMR, UV–Vis spectroscopy as well as elemental analysis. The molecular structure of 3 is determined by single-crystal X-ray diffraction method. Three 2,5-Cl₂pcyd and three phenanthroline ligands are coordinated to the central La atom in monodentate and bidentate manner, respectively.

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but no crystal structure was reported [12,13]. Furthermore, Khan and Iftikhar reported a number of 1,10-phenanthroline complexes with typical stochiometry $[La(phen)_2(H_2O)xCl_3]\cdot xH_2O$ and studied their spectroscopic properties [14]. The crystal structures of more analogs of phenanthroline with lanthanides were reported by Lin-Pei Jin in 2003, Udai P. Singh in 2007, and other researchers [15–17].

The chemistry of phenylcyanamide attracts attention for the active role of its ligands in inorganic chemistry [18]. Material engineers are noticing the generation of novel electronic, magnetic and photonic devices. Extension of the π -electronic molecular structure is one of the most important and promising approaches to achieve high conductivity and strong effective magnetic coupling [19]. For this aim, several complexes of phenycyanamide ligands with some transition metals have been synthesized and the electronic properties of cyanamide group, especially its large π -conjugated system, have been investigated [19–27].

However, phenylcyanamide ligands were not used with rare earth elements until we used them as N-donor ligands for synthesis of new lanthanide complexes. We prepared novel complexes of Nd and Pr with 1,10-phenanthroline and phenylcyanamide as mixed ligands in our previous works [28,29]. Here we report the synthesis of new lanthanum complexes of phenanthroline and phenylcyanamide derivatives and investigate the crystal structure of [La(phen)₃(2,5-pcyd)₃]. To our knowledge, this is the first crystal structure of lanthanide complexes with cyanamide ligand.

2. Experimental

All reagents and solvents used in this work were purchased from Merck and Aldrich Chem. Co. Phenylcyanamide ligands and



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Fig. 1. ORTEP drawing of [La(phen)₃(2,5-Cl₂pcyd)₃].

their thallium salts were synthesized by the literature method [20]. *Caution:* Thallium is extremely toxic.

UV–Vis spectra were recorded on an Analytikjena SPECORD S-100 spectrometer with a photodiode array detector. IR spectra were recorded as KBr disks on a Shimatzu IR instrument. NMR experiments were recorded at room temperature in D₂O and CDCl₃ on a Bruker AV-500 spectrometer using an internal deuterated solvent lock.

2.1. X-ray determination

Colorless crystals of $[La(phen)_3(2,5-Cl_2pcyd)_3]$. CH₂Cl₂ (**3**) were grown by diethyl ether diffusion into a dichloromethane solution of the complex for several days. All measurements were made on a Bruker APEX DUO diffractometer with graphite monochromated Mo K α radiation. The data were collected at a temperature of -180.0 ± 0.1 °C to a maximum 2 θ value of 56.2° in a series of ϕ and ω scans in 0.50° oscillations with 15.0-s exposures. The crystal-to-detector distance was 70.00 mm. Of the 91864 reflections that were collected, 12879 were unique ($R_{int} = 0.060$); equivalent reflections were merged. Data were collected and integrated using the Bruker SAINT software package. The linear absorption coefficient, μ , for Mo K α radiation was 12.42 cm⁻¹. Data were corrected for absorption effects using the multi-scan technique (sADABS), with minimum and maximum transmission coefficients of 0.782 and 0.862, respectively.

The structure was solved by direct methods [30]. The material was crystallized with methylene chloride. Additionally, one ligand was disordered and was modeled in two orientations. The solvent molecule was only present with a relative population of 0.83. Finally, the material appeared to be very marginally twinned, with the two twin components related by a 180° rotation about the [-201] reciprocal lattice direction. All non-hydrogen atoms, except those of the minor disordered fragment, were refined anisotropically. All hydrogen atoms were placed in calculated positions but were not refined. A perspective view of complex **3** is shown in Fig. 1.

Table 1

The crystal data and experimental details of [La(phen)₃(2,5-Cl₂pcyd)₃]·CH₂Cl₂.

Empirical formula	C _{57.83} H _{34.65} N ₁₂ Cl _{7.65} La
Formula weight	1307.67
Crystal system	monoclinic
Dimension	$0.12\times0.25\times0.35~mm$
Space group	<i>C</i> 2/ <i>c</i> (#15)
a (Å)	19.459(2)
b (Å)	13.486(1)
<i>c</i> (Å)	41.464(4)
α (°)	90
β (°)	103.37(3)
γ (°)	90
V (Å ³)	10632(2)
Ζ	8
T (°C)	-180.0
D (gcm ³)	1.634
F(000)	5221.00
μ (cm ⁻¹)	12.42
Number of unique data	$12879 (R_{int} = 0.060)$
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.079; wR_2 = 0.171$
Final R indices(for all data)	$R_1 = 0.088; wR_2 = 0.174$
Goodness-of-fit (GOF)	1.31

 $R_{1} = \Sigma ||F_{o}| - |F_{c}|| / \Sigma |F_{o}|, wR_{2} = \sqrt{\Sigma} (w(F_{o}^{2} - F_{c}^{2})^{2}) / \Sigma w(F_{o}^{2}).$

Crystallographic data for $[La(phen)_3(2,5-Cl_2pcyd)_3]\cdot CH_2Cl_2$ are given in Table 1. Selected interaction distances and angles are given in Table 2.

2.2. Synthesis

2.2.1. Synthesis of $|La(phen)_3Cl_3 \cdot OH_2|$ (1)

 $[La(phen)_3Cl_3 \cdot OH_2]$ was synthesized by literature method [12] but the excess amount of 1,10-phen was used, as it was dissolved in the minimum amount of absolute ethanol and added drop wise to an ethanolic solution of LaCl_3 · 7H_2O (200 mg) while stirred and heated to 60 °C. The resulting solution was refluxed for 8 h in order

Table 2

1 ne	selected g	eometr	ic pai	amete	ers, band lengths
and	angles	(Å,	°)	of	[La(phen) ₃ (2,5-
Cl ₂ p	cyd) ₃]CH ₂	Cl ₂ .			

2.825(6)
2.782(5)
2.743(5)
2.749(5)
2.740(6)
2.546(6)
2.552(6)
2.532(6)
1.177(9)
1.291(9)
1.392(9)
1.176(9)
1.298(9)
1.377(9)
1.161(9)
1.296(9)
1.374(10)
175.1(8)
169.1(7)
137.1(5)
120.0(6)
150.4(5)
118.0(6)
162.7(5)
122.6(7)

to complete the reaction. The resulting white precipitate was filtered and washed several times by ethanol and dichloromethane. The product was dried in a vacuum over P_4O_{10} for several hours (Yield: 190 mg, 88%). *Anal*. Calc. for LaC₃₆H₂₆N₆Cl₃O: C, 53.77; H, 3.24; N, 10.45. Found: C, 53.14; H, 3.04; N, 10.06%. IR (KBr): $v(C=N) = 1421-1548 \text{ cm}^{-1}$; v(C-H) = 725-847, UV–Vis absorption (MeOH): 232, 266 nm. ¹H NMR (D₂O) ppm: 8.63, 7.77, 7.29, 7.06 (phen-H).

2.2.2. Synthesis of [La(phen)₃(2-Clpcyd)₃] (2)

The excess amount of Tl[2-Clpcyd] ligand was dissolved in hot water, was cooled to 50 °C, was added to the aqueous solution of $[La(phen)_3Cl_3 \cdot OH_2]$ (100 mg), and was then stirred for 2 h at 50 °C. The reaction mixture that contained TlCl and product was filtered, and the precipitates were washed with hot water several times. The resulting yellow solid was re-crystallized by dissolving it in a minimum volume of dichloromethane and slowly adding diethyl ether to precipitate the product. The product was dried in a vacuum over P₄O₁₀ for several hours (Yield: 100 mg, 68%). *Anal.* Calc. for LaC₅₇H₃₆N₁₂Cl₃: C, 60.35; H, 3.18; N, 14.82. Found: C, 60.24; H, 3.08; N, 14.69%. IR (KBr): $v(NCN) = 2110 \text{ cm}^{-1}$, UV–Vis absorption (CH₂Cl₂): 232, 266 nm. ¹H NMR (CDCl₃) ppm: 9.19, 8.27, 7.81, 7.61 (phen-H); 6.85–7.12 (pcyd-H).

2.2.3. Synthesis of $[La(phen)_3(2,5-Cl_2pcyd)_3]$ (3)

This was prepared by the procedure used for La(phen)₃(2-Clpcyd)₃] except that the Tl[2,5-Cl₂pcyd] ligand replaced Tl[2-Clpcyd]. (Yield: 120 mg, 75%). *Anal.* Calc. for LaC₅₇H₃₃N₁₂Cl₆: C, 55.29; H, 2.67; N, 13.58. Found: C, 55.14; H, 2.53; N, 13.43%. IR (KBr): ν (NCN) = 2100 cm⁻¹, UV–Vis absorption spectrum (CH₂Cl₂): 239, 285 nm. ¹H NMR (CDCl₃) ppm: 9.37, 8.20, 7.69, 7.57 (phen-H); 6.92, 6.43, 6.18 (pcyd-H).

2.2.4. Synthesis of $[La(phen)_3(2,4-Cl_2pcyd)_3]$ (4)

This was prepared by the procedure used for $La(phen)_3(2-Clpcyd)_3]$ except that the Tl[2,4-Cl₂pcyd] ligand replaced Tl[2-Clpcyd] (Yield: 135 mg, 84%). *Anal.* Calc. for $LaC_{57}H_{33}N_{12}Cl_6$: C,

55.29; H, 2.67; N, 13.58. Found: C, 55.18; H, 2.49; N, 13.38%. IR (KBr): ν (NCN) = 2115 cm⁻¹, UV–Vis absorption spectrum (CH₂Cl₂): 234, 267 nm. ¹H NMR (CDCl₃) ppm: 9.45, 8.27, 7.80, 7.62 (phen-H); 7.31, 6.58–7.10 (pcyd-H).

2.2.5. Synthesis of [La(phen)₃(2,4,5-Cl₃pcyd)₃] (5)

This was prepared by the procedure used for La(phen)₃(2-Clpcyd)₃] except that the Tl[2,4,5-Cl₃pcyd] ligand replaced Tl[2-Clpcyd]. (Yield: 140 mg, 80%). *Anal.* Calc. for LaC₅₇H₃₀N₁₂Cl₉: C, 51.03; H, 2.38; N, 12.53. Found: C, 49.8; H, 2.23; N, 12.41%. IR (KBr): ν (NCN) = 2100 cm⁻¹, UV–Vis absorption spectrum (CH₂Cl₂): 234, 266 nm. ¹H NMR (CDCl₃) ppm: 9.25, 8.11, 7.58, 7.49 (phen-H); 6.84, 6.06 (pcyd-H).

3. Results and discussion

3.1. Synthesis and characterization of 1-5 complexes

The lanthanide ions are well-known for having a variety of coordination numbers which range from 3 to 12. Because of their large ionic radii and the ionic nature of the metal-ligand bonding, trivalent lanthanide ions usually form complexes of higher coordination numbers of typically 8 and 9 [31]. In this work, lanthanum(III) as a lanthanide ion, phenylcyanamide and phen as coordinated ligand were used to prepare various lanthanide complexes with different coordination sphere and coordination numbers. The reaction of aqueous solutions of lanthanum(III) complex [La(phen)₃Cl₃·OH₂] (1), with thallium phenylcyanamide salts led to the preparation of $[La(phen)_3(L)_3]$ (L = 2-Clpcvd (2), 2,5-Cl₂pcvd (3), 2,4-Cl₂pcvd (4), 2,4,5-Cl₃pcyd (5)) (Scheme 1). Analytical, infrared and crystallographic studies of these complexes have shown they are anhydrous. All of the complexes were air stable for extended periods. Complex (1) was soluble in polarized solvents such as water and methanol and insoluble in most organic solvents. Complexes (2-5) were soluble in dichloromethane and chloroform; slightly soluble in ethanol and methanol; insoluble in water and diethyl ether, and they indicated similar behavior in non-coordinating solvents, particularly dichloromethane and chloroform.

$$[La(phen)_3Cl_3.OH_2] + 3TlL \longrightarrow [La(phen)_3L_3] + 3TlCl$$



Scheme 1. The reaction of 1 with thallium phenylcyanamide salts.

 Table 3

 Infrared absorption frequencies (cm⁻¹) of cyanamide group.

Complex	v(NCN)	Tl salt	v(NCN)	Free ligand	v(NCN)
[La(phen) ₃ (2- Clpcyd) ₃]	2110	Tl[2-pcyd]	2090	2-Clpcyd	2235
[La(phen) ₃ (2,5- Cl ₂ pcyd) ₃]	2100	Tl[2,5- Cl ₂ pcyd]	2110	2,5- Cl ₂ pcyd	2235
[La(phen) ₃ (2,4- Cl ₂ pcyd) ₃]	2115	Tl[2,4- Cl ₂ pcyd]	2100	2,4- Cl ₂ pcyd	2230
[La(phen) ₃ (2,4,5- Cl ₃ pcyd) ₃]	2100	Tl[2,4,5- Cl₃pcyd]	2075	2,4,5- Cl ₃ pcyd	2230

The IR spectrum of free 1,10-phenanthroline underwent a modification when coordinated with a lanthanide. The strong CH outof-plane bending absorptions of phen at 849 cm⁻¹ and 732 cm⁻¹ were lowered to 847 cm⁻¹ and 725 cm⁻¹ in complex (**1**) so that the latter band became a doublet after complexation [12]. The v(C=C) and v(C=N) modes of phen appeared as intensive bands at 1421–1513 cm⁻¹ and 1584 cm⁻¹ compared to the free ligand values of 1418–1502 cm⁻¹ and 1558–1642 cm⁻¹, respectively [32]. These bands were shifted to higher wave numbers on complexation, which was due to the interaction between the lanthanum(III) ion and the nitrogen atoms of phen. The bands at 651 and 604 cm⁻¹ attributed to v(La-N) indicate the coordination of nitrogen to the central ion [33]. The broad peaks at 1637 cm⁻¹ and in the 3050–3330 cm⁻¹ region may be assigned to the bending and stretching vibrations of coordinated water [34].

Also, IR spectroscopy is a useful method for the characterization of phenylcyanamide metal complexes. The principal absorption frequencies and assignments [35] for all compounds are collected in Table 3. IR spectroscopy can diagnose nitrile versus amine coordination in both the anionic and natural forms of phenylcyanamide. In Neutral phenylcyanamide, the $C \equiv N$ band has been observed in the range of 2225–2249 cm⁻¹, whereas a strong band in the frequency lower than 2150 cm⁻¹ can be detected for N=C=N vibration if the coordination of anionic phenylcyanamide ligands to metal center occurs via nitrile nitrogen [20]. The IR spectra of (2-5) were relatively similar. The strong band observed at 2230-2235 cm⁻¹ in the spectra of the free ligands assigned to v(NCN)shifted to lower frequencies upon the complexation of Lanthanum by 130–135 cm⁻¹. The C=N stretching bands of phen in [La(phen)₃₋ Cl₃.OH₂] changed when the cyanamide ligands coordinated to the metal ion. The absorption bands at 1513, 1420 cm⁻¹ (C=N of phen) shifted to lower wave numbers upon complexation with cyanamide groups [28]. No vibrational mode was observed at the water stretching region, thus it is proposed that these complexes do not have any coordinated water in their coordination spheres.



Fig. 2. The UV–Vis absorption spectra of a dichloromethane solution of (a) 2,4- Cl_2pcyd (b) phen, and (c) [La(phen)_3(2,4- $Cl_2pcyd)_3$].

|--|

Η	NMR	data	for	(1-5)	complexes	(in	ppm)).
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Complex	H of p	hen ^a	H of pcyd ^b		
	2	3	4	5	
[La(phen) ₃ Cl ₃ ·OH ₂]	8.63	7.06	7.77	7.29	-
[La(phen) ₃ (2-Clpcyd) ₃]	9.19	7.61	8.27	7.81	6.85-7.12
[La(phen) ₃ (2,5-Cl ₂ pcyd) ₃]	9.37	7.57	8.20	7.69	6.92, 6.43, 6.18
[La(phen) ₃ (2,4-Cl ₂ pcyd) ₃]	9.45	7.62	8.27	7.80	6.58-7.10, 7.31
[La(phen) ₃ (2,4,5-Cl ₃ pcyd) ₃]	9.25	7.49	8.11	7.58	6.84, 6.06
Phen(D ₂ O)	8.90	7.60	8.23	7.65	-
Phen(CDCl ₃)	9.19	7.63	8.24	7.83	-





The absorption spectra of complex (1) and its cyanamide derivatives were obtained in the methanol and dichloromethane solvents, respectively. The UV-Visible spectrum of (4) is shown in Fig. 2 as example. The absorption observed at 200-300 nm attribute to ligand centered charge transfer included $\pi \rightarrow \pi^*$ transitions of phenanthroline and benzene chromophore of phenylcyanamide ligands. In spite of other cyanamide complexes with transition metals such as [Ru(NH₃)₅(2,3-Cl₂Hpcyd)]²⁺ [20], [(bpy)₂Cu((4-Cl)pcyd)][PF₆] [21], cis-[Co(bpy)₂(2,4-Me₂pcyd)₂]PF₆ [23], that show intensive LMCT and MLCT bands in visible region, there were no observable transitions in this region for the prepared complexes. The effect of coordination of the metal center on the phenanthroline transitions was the stabilization of the π^* orbitals and the partial shifting of its absorptions to lower energies, but the phenyl cyanamide ligand transitions showed unusual blue shifts after complexation. These complexes did not display f-f transition bands because the lanthanum(III) ion did not have any electrons in its f orbitals.

All resonances in the ¹H NMR spectra of the (**1–5**) complexes were assigned on the basis of their intensities, line width and chemical shifts at room temperature. The NMR spectrum of complex (**1**) consisted of four relatively broad resonances. The phen signals of D₂O solution of complex (**1**) were found to shift to minor higher fields compared with free phen [36] which is in opposition with the reported characteristics of similar La complexes [14,36]. The NMR signals of phen protons in (**2–5**) appeared as four signals in the range of 7.49–9.47 ppm. The signals of H₂ and H₄ protons of phen have shifted to down field but the signals of H₃ and H₅ of phen have shifted to up field and all of the signals have slightly broadened compared with the free ligand.

The proton chemical shifts of pcyd ligands mostly occurred in the 6–7 ppm range [27]. The protons of pcyd ligand of complex (**2**) were obtained as one broad signal at 6.85–7.12 ppm. The NMR signals of pcyd protons in (**3**) showed three signals, two doublets at 6.92 ppm and at 6.43 ppm respectively for H_4 and H_3 with ${}^{3}J_{H3,H4}$ = 8 Hz and one broad singlet for H₆ proton at 6.18 ppm. Complex (**4**) showed one broad signal at 6.58–7.10 ppm and one singlet at 7.31 ppm assigned to the H₃ proton. Also, pcyd protons in (**5**) showed two broad singlets at 6.84 and 6.06 for H₃ and H₆ protons, respectively. The ¹H NMR data of all species are shown in Table 4. For example, Fig. 3 shows the ¹H NMR spectra of (**3**) and (**5**) in CDCl₃ at room temperature.

3.2. Crystal structure of [La(phen)₃(2,5-Cl₂pcyd)₃]·CH₂Cl₂

 $[La(phen)_3(2,5-Cl_2pcyd)_3]\cdot CH_2Cl_2$ was crystallized in the monoclinic system with the C2/c space group. As shown in Fig. 1, this complex is mononuclear. Lanthanum atom was coordinated through six nitrogen atoms from three phenanthroline ligands and three nitrogen atoms from three 2,5-Cl₂pcyd which resulted in nine coordination numbers of the metal center. The average La–N cyanamide bond (2.543(6) Å) was significantly shorter than that of La–N phen bonds (2.771(6) Å). The average La–N phen bond distance (2.771 Å) was slightly longer than the average La–N phen bond distances in different lanthanum phenanthroline complexes. For example average La–N phen bond was (2.753(4)) Å for [La(phen)₃(NCS)₃] [36], (2.716(4) Å) for [La(DMPA)₃phen]₂ [37], (2.746(6) Å) for {[La₂(IA)₃(phen)₂]·2H₂O]_n [38], and (2.734(7) Å) for [La₂(APA)₆(phen)₂(H₂O)₂](ClO₄)₆(phen)₄·2H₂O [39]. Moreover La–N band distances were longer than those in [Pr(phen)₂Cl₃·OH₂] (2.665 Å) [28]. This is in accord with the anticipated "lanthanide contraction" when progressing from lanthanum to praseodymium [36].







Scheme 2. Resonance structures of phenylcyanamide anionic ligand.

The phenylcyanamide anionic ligands had a resonance stabilized three-atom π -system, from which two pairs of non-bonding electrons can be delocalized (Scheme 2). In resonance structure I, the terminal nitrogen of cyanamide group will coordinate to the metal center via the nitrile lone pair, which results in an ideal bond angle of 180°. Resonance structure II will produce the ideal bond angle of 120°. However, if the structure results in both I and II resonance states, the bond angle will be between two extremes. Electropositive metal ions and metal ions with strong π -acceptor character favor the resonance structure I. In these cases, the bond angle will be close to 180°, to maximize interaction with the electron pairs on the nitrogens [21].

The coordination configuration of cyanamide ligands strongly depended on the nature and oxidation state of the metal atoms [21]. As mentioned above, the coordination of the anionic cyanamide group to a strongly polarizing metal ion should increase the contribution of resonance structure II, but strong π -acceptor metal ions prefer bond angles of 180°. In this regard, Ru(III), a strong π acceptor, had been shown to coordinate to 2.3-Cl₂pcvd- with a bond angle 171°, while Cu(II) had far weaker π - acceptor properties with Cu(II)-cyanamide bond angles between 141° and 165°, and Fe(III) had weaker π -acceptor properties with Fe(III)-cyanamide band angles between 143.9° and 168.53° in different complexes [21,40,41]. Here, the bonds between the anionic cyanamide groups and La(III) were relatively nonlinear, with angles of 162.7(5)°, 137(5)° and 150.4(5)° for C(51)–N(11)–La, C(37)–N(7)–La and C(44)–N(9)–La, respectively. These data indicated the weak π acceptor property of La(III) ion.

In reference to the Cambridge Structural Database, the C(37)–N(7), C(44)–N(9) and C(51)–N(11) bond lengths were much longer than that of a CN triple bond [42]. These observations were in agreement with IR data: these data showed one strong absorption band at 2100 cm⁻¹ that was close to the absorption band of N=C=N bond, as previously reported by other researchers [20].

NCN was almost linear, with an angle of $N(9)-C(44)-N(10) = 175.1(8)^{\circ}$. These angles were $171.7(8)^{\circ}$ and $169.7(7)^{\circ}$ for N(7)-C(37)-N(8) and N(11)-C(51)-N(12), respectively, with a linear bond between the anionic cyanamide group and La(III).

Free anionic cyanamide ligands were anticipated to be planar, if there were not any steric effects. This was easily explained by the strong interaction of the cyanamide group with the phenyl ring [22]. This interaction was apparently maintained upon coordination to La(III), and the torsion angles C(37)-N(8)-C(38)-C(43), $7.9(11)^\circ$, C(44)-N(10)-C(45)-C(50), $4.2(10)^\circ$ and C(51)-N(12)-C(52)-C(57), $0.7(13)^\circ$, showed that the phenyl rings were approximately planar with cyanamide to optimize the interaction between the phenyl rings and cyanamide groups. By considering these torsion angles, we suggest that the coupling of the cyanamide groups with the phenyl ring in $[La(phen)_3(2,5-Cl_2pcyd)_3]$ is noticeably high and is compatible with other cyanamide complexes such as [Fe^{III}(OEP)(pcyd)] [41] and [Fe^{III}(OEP)(2,4-Me₂pcyd)] [43].

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