

Coordinative capability of propane-1,3-diamine: spectroscopic and structural properties of a complex of formula $[\text{Cd}(\text{pnH})_4\text{Cl}_2]\text{Cl}_4$

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Abstract

The compound $[\text{Cd}(\text{pnH})_4\text{Cl}_2]\text{Cl}_4$ (pn = propane-1,3-diamine) has been prepared and studied by means of spectroscopic (IR and Raman) and structural investigations. It crystallizes in the tetragonal $P4nc$ space group (No. 104), with two formula units in a cell of dimensions: $a = b = 11.972(4)$, $c = 9.129(4)$ Å. The structure consists of an ionic packing of chlorine anions and of discrete $[\text{Cd}(\text{pnH})_4\text{Cl}_2]^{4+}$ cations; the Cd atoms are octahedrally coordinated to four nitrogen atoms of four distinct monoprotonated diamines and to two chlorine atoms in *trans* position to each other, showing very loose Cd–Cl bonding interactions (2.680(3) and 2.884(2) Å). The protonated ends of the propane-1,3-diamines interact with the non-coordinated chlorine ions via hydrogen bonding. The Cd–N and Cd–X stretching vibrations are discussed and assigned in the light of the known structures.

Introduction

Among non-cyclic amines, ethylenediamines and propane-1,3-diamines show remarkable differences in the coordination capabilities toward metal ions. In fact, the less favourable entropy change in the formation of six-membered rings, with respect to five-membered ones, suggests the possibility for propane-1,3-diamine (pn) of alternative modes of coordinative behavior. This was demonstrated for propane-1,3-diamine and 2,2-dimethylpropane-1,3-diamine, which, acting both in chelating and 'extended' form toward metal ions, form discrete monomeric [1], dimeric [2] and polymeric [3] species, presenting very distinct structures.

The non-negligible basicity of the monoprotonated propane-1,3-diamine ($\text{p}K_b = 4.97$; $\text{p}K_b = 3.06$ for neutral propane-1,3-diamine) suggested that pnH^+ could act as monodentate, therefore, propane-1,3-diamine has been monoprotonated and reacted with cadmium(II) chloride. The isolated compound of unusual stoichiometry, $[\text{Cd}(\text{pnH})_4\text{Cl}_2]\text{Cl}_4$, has been investigated by means of spectroscopic (IR and Raman)

measurements and single crystal X-ray diffraction with the aim to ascertain the influence of the positive charge on the donor properties of the amino group and how much its coordinative behavior departs from that of donor primary amines.

Furthermore, this study, which is also of some biological interest for the important role of highly charged water-soluble species in biochemical reactions, gave us other basic information to depict a complete description of the coordinative behavior of propane-1,3-diamine.

Experimental

The complex $[\text{Cd}(\text{pnH})_4\text{Cl}_2]\text{Cl}_4$ was prepared by adding a methanolic metal halide salt solution (1 mM) to a methanolic propane-1,3-diamine (2 mM) and HCl (2 mM) solution. By slow evaporation of the solution at room-temperature white crystals precipitated.

$\text{Cd}(\text{1,3pnH})_4\text{Cl}_6$. *Anal.* Calc. for $\text{C}_{12}\text{H}_{44}\text{CdN}_8\text{Cl}_6$: C, 23.01; H, 7.09; N, 17.92. Found: C, 23.11; H, 7.12; N, 17.88%.

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Physical measurements

IR spectra were recorded with a Perkin-Elmer 180 spectrophotometer on Nujol mulls or KBr pellets in the 4000–500 cm^{-1} range (no differences were observed among spectra obtained by these two different methods), and on polythene, as support, in the 500–100 cm^{-1} range. Raman spectra were recorded on solid samples with a Coderg PHO spectrophotometer equipped with an argon laser. Nitrogen, carbon and hydrogen were analyzed with a Carlo Erba model 1106 elemental analyser.

X-ray structure determination

The refined cell constants and other relevant crystal data for $[\text{Cd}(\text{pnH})_4\text{Cl}_2]\text{Cl}_4$ are presented in Table 1, together with details of the intensity measurements. The intensity data were collected on an Enraf Nonius CAD4 diffractometer and corrected for Lorentz and

TABLE 1. Crystal data and intensity collection parameters

Compound	$[\text{Cd}(\text{pnH})_4\text{Cl}_2]\text{Cl}_4$
Formula	$\text{C}_{12}\text{H}_{44}\text{CdCl}_6\text{N}_8$
Formula weight (g mol^{-1})	625.66
Crystal system	tetragonal
$a = b$ (\AA)	11.972(4)
c (\AA)	9.129(4)
V (\AA^3)	1308.4(1)
Z , D_{calc} (g cm^{-3})	2, 1.59
Space group	$P4nc$ (No. 104)
$F(000)$	644
Radiation (graphite monochromated)	Mo $K\alpha$ ($\lambda = 0.71073 \text{ \AA}$)
Diffractometer	Enraf Nonius CAD4
μ (Mo $K\alpha$) (cm^{-1})	14.66
2θ range ($^\circ$)	6–50
Scan method	ω
Scan interval ($^\circ$)	$1.1 + 0.347 \tan\theta$
Prescan speed ($^\circ \text{ min}^{-1}$)	20
Prescan acceptance, $\sigma(I)/I$	0.6
Required, $\sigma(I)/I$	0.05
Max. time for 1 reflection measured (s)	60
Collected octants	$+h, +k, +l$
No. data collected at r.t.	1349
No. data used ($I > 3\sigma(I)$)	967
Crystal decay (%)	6
No. azimuth reflections for absorption correction	3
Max. and min. transmission factors	1.00–0.97
Crystal size (mm)	$0.20 \times 0.15 \times 0.12$
R^a	0.020
R_w^b	0.026
GOF^c	0.994
No. variable parameters	108
Max. peak in final difference Fourier ($\text{e}/\text{\AA}^3$)	0.44

^a $R = [\sum(F_o - k|F_c|)/F_o]$. ^b $R_w = \sqrt{[\sum w(F_o - k|F_c|)^2]/\sum w F_o^2}$.
^c $GOF = \sqrt{[\sum w(F_o - k|F_c|)^2]/(N_{\text{obs}} - N_{\text{var}})}$.

polarization effects. An empirical absorption correction, based on Ψ scans (Ψ 0–360 $^\circ$, every 10 $^\circ$) on three reflections with χ values near to 90 $^\circ$, was applied to the full data set. The periodical monitoring of three reference reflections showed that the title compound was slightly unstable under the experimental conditions, therefore the measured data were also corrected for decay (up to *c.* 6% on F_{obs} at the end of the data collection).

The structure was solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares. Individual weights were assigned as: $w = 4F_o/\sigma(F_o^2)$ where $\sigma(F_o^2) = [\sigma(I)^2 + (pI)^2]^{1/2}/LP$, LP being the Lorentz–polarization factor and p the ignorance factor, set equal to 0.030. All the non-hydrogen atoms were treated anisotropically while the hydrogen atoms, including those of the terminal ammonium groups, were refined using isotropic thermal parameters; an extinction coefficient was also included in the list of the refinable parameters and was found significantly different from zero. The handedness of the crystal was determined by refining both enantiomeric models ($R = 0.0204$ versus 0.0212, $R_w = 0.0260$ versus 0.0274 and $GOF = 0.994$ versus 1.044) and that refined with the best agreement indices was assumed.

All the computations were performed on a PDP 11/73 computer using the Enraf Nonius structure determination package (SDP) and the physical constants tabulated therein.

The final atomic coordinates are given in Table 2. Bond distances and angles are reported in Table 3. See also 'Supplementary material'.

Results and discussion

Description of the structure of $[\text{Cd}(\text{pnH})_4\text{Cl}_2]\text{Cl}_4$

The crystal structure of the title compound consists of an ionic packing of complex $[\text{Cd}(\text{pnH})_4\text{Cl}_2]^{4+}$ cations and isolated Cl^- anions, showing mutual interactions via hydrogen bonds (*vide infra*). Each $[\text{Cd}(\text{pnH})_4\text{Cl}_2]^{4+}$ unit is located on a crystallographic fourfold axis (a in Wyckoff notation) containing the metal and the chloride atoms, and possesses pseudo-octahedral geometry with the halides in *trans* positions and the four (symmetry related) pnH^+ ligands in the 'equatorial' plane. An ORTEP drawing of the complex is shown in Fig. 1.

The two coordinated Cl^- ions experience different intramolecular contacts with the neighboring pnH^+ ligands; therefore they are not stereochemically equivalent and show rather different metal-to-Cl bond lengths (Cd–Cl(1), 2.680(3) \AA ; Cd–Cl(2), 2.884(2) \AA). Previously reported Cd–Cl distances in octahedral

TABLE 2. Positional parameters and their e.s.d.s for $[\text{Cd}(\text{pnH})_4\text{Cl}_2]\text{Cl}_4^{\text{a}}$

Atom	x	y	z	B (Å ²)
Cd	0.000	0.000	0.000	1.695(4)
Cl(1)	0.000	0.000	0.2936(2)	2.52(2)
Cl(2)	0.000	0.000	0.3159(2)	2.32(2)
N(1)	-0.1802(2)	-0.0730(2)	0.0311(3)	2.06(5)
C(1)	-0.2548(3)	-0.0714(3)	-0.0958(4)	2.64(7)
C(2)	-0.3761(3)	-0.1035(3)	-0.0633(4)	2.58(7)
C(3)	-0.3880(2)	-0.2266(3)	-0.0281(4)	2.29(6)
N(2)	-0.5090(2)	-0.2571(2)	-0.0074(4)	2.41(5)
Cl(3)	-0.63721(7)	-0.17784(6)	-0.2934(1)	2.71(1)
H(1)	-0.160(3)	-0.144(3)	0.074(4)	3.8(9)*
H(2)	-0.204(3)	-0.037(3)	0.099(4)	2.6(8)*
H(3)	-0.231(3)	-0.120(3)	-0.165(4)	3.3(9)*
H(4)	-0.248(3)	-0.007(3)	-0.138(4)	3.0(9)*
H(5)	-0.429(3)	-0.090(3)	-0.154(3)	2.7(8)*
H(6)	-0.418(3)	-0.048(3)	0.017(6)	6(1)*
H(7)	-0.341(3)	-0.254(3)	0.061(4)	4(1)*
H(8)	-0.359(4)	-0.282(3)	-0.104(5)	5(1)*
H(9)	-0.516(3)	-0.332(4)	0.033(6)	5(1)*
H(10)	-0.556(3)	-0.205(3)	0.063(4)	5(1)*
H(11)	-0.548(3)	-0.250(3)	-0.088(4)	2.9(8)*

^aStarred atoms were refined isotropically; anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$.

CdCl_2N_4 complexes are as low as 2.468(1) Å for $\text{CdCl}_2(\text{C}_{12}\text{H}_{22}\text{N}_6)$ [4] and 2.501(1) for $\text{CdCl}_2(\text{C}_{16}\text{H}_{28}\text{N}_6)$ [5], while the μ_2 -bridging chlorine atoms of $[\text{CdCl}_2(\text{bpa})_2]$ (bpa = bis(3-aminopropyl)amine) [6] have Cd-Cl bond distances *c.* 2.66 Å. Therefore, the pseudooctahedral geometry around Cd(II) is better described as a heavily elongated square pyramidal coordination ($[\text{Cd}(\text{pnH})_4\text{Cl}]$), with the metal atom slightly shifted from the center of the metal-bonded nitrogen atoms of the four pnH^+ ligands toward Cl(1) (by about 0.28 Å), and a sixth very weak ligand (Cl(2)) in *trans*

position to Cl(1). The analysis of the shortest intermolecular contacts in proximity of the two weakly coordinated chlorine atoms shows a minimum distance of 3.17(5) Å for $\text{Cl}(2) \cdots \text{H}(11)$ and therefore excludes any 'external' influence of neighboring molecules or ions in the Cd-Cl bonding interactions. It is noteworthy that the amplitudes of the thermal parameters of the metal atom have a definite anisotropic distribution, with the ellipsoid elongated along the fourfold axis, while those of the (packing sensitive) chlorine atoms are much more spherical. Given that the shapes of the thermal ellipsoids of all the remaining lighter atoms, C and N included, are fairly reasonable and because the very good agreement indices *R* and *R_w* exclude the presence of broad or spurious data, we must conclude that some sort of soft vibrational mode of the Cd atom within the pseudooctahedral ligands' cage is present, thus confirming the weak interactions of Cd with the coordinated chlorine atoms.

The four coordinated pnH^+ groups, showing a Cd-N(1) distance of 2.345(3) Å (the value of a 'standard' Cd-N (aliphatic amine) bond has been estimated from literature data at 2.33 + 0.05 Å [4]), are in a fairly elongated conformation, to avoid the overcrowding of atoms around the metal center which would arise from chain folding and to minimize the electrostatic interactions among the positively charged terminal $-\text{NH}_3^+$ groups of each protonated diamine. A similar 'extended' form of the propane-1,3-diamine has been found in the $[\text{Cd}(\text{pn})_2\text{Br}_2]_2$ dimer [7], where one of the two crystallographically independent pn molecules acts as ambidentate ligand, bridging two (otherwise non-interacting) cadmium ions; similarly, the monodentate pnH^+ ligand of the title compound can be formally envisaged as a neutral pn molecule connecting two different 'acidic' centers, one Cd^{2+} and one H^+ ion. Moreover, two fairly

TABLE 3. Bond distances (Å) and angles (°) for $[\text{Cd}(\text{pnH})_4\text{Cl}_2]\text{Cl}_4$

Cd-Cl(1)	2.680(3)	Cl(1)-Cd-N(1)	96.96(4)
Cd-Cl(2)	2.884(2)	Cl(2)-Cd-N(1)	83.04(4)
Cd-N(1)	2.345(3)	N(1)-Cd-N(1)'	89.16(4)
		N(1)-Cd-N(1)''	166.09(4)
N(1)-C(1)	1.464(5)	Cd-N(1)-C(1)	117.4(2)
C(1)-C(2)	1.531(5)	N(1)-C(1)-C(2)	115.0(3)
C(2)-C(3)	1.516(5)	C(1)-C(2)-C(3)	112.0(3)
C(3)-N(2)	1.505(5)	C(2)-C(3)-N(2)	110.6(3)
N(2) \cdots Cl(3)	3.173(5)	H(11) \cdots Cl(3)	2.33(5)
N(2) \cdots Cl(3)'	3.156(4)	H(10) \cdots Cl(3)'	2.13(6)
C-H (range)	0.91(5)-1.12(6)	N-H (range)	0.80(5)-1.05(6)

Primed and double primed atoms refer to the *y*, $-x$, *z* and $-x$, $-y$, *z* symmetry operations, respectively.

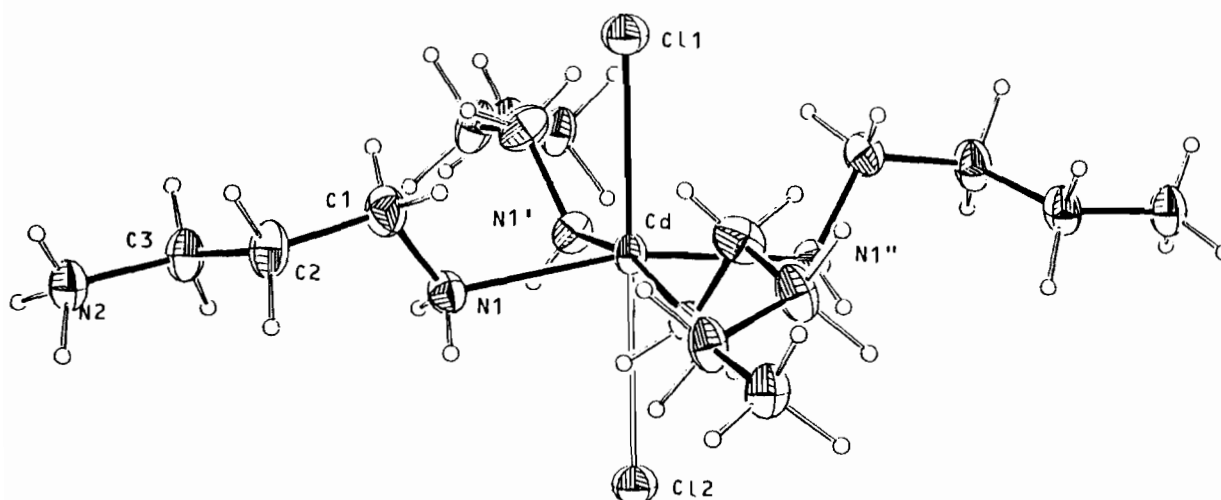


Fig. 1. ORTEP drawing of the $[\text{Cd}(\text{pnH})_4\text{Cl}_2]^{4+}$ cation with (partial) labelling scheme. Primed and double primed atoms refer to $y, -x, z$ and $-x, -y, z$ symmetry operation, respectively. Thermal ellipsoids of non-hydrogen atoms are drawn at 30% probability. Hydrogen atoms have been given, for sake of clarity, arbitrary radii.

strong hydrogen bonds between each pnH^+ ligand and two isolated Cl^- ions ($\text{N}(2)\cdots\text{Cl}(3)$, 3.173(5); $\text{N}(2)\cdots\text{Cl}(3)'$, 3.156(4); $\text{H}(11)\cdots\text{Cl}(3)$, 2.33; $\text{H}(10)\cdots\text{Cl}(3)'$, 2.13 Å) are present; a protonated ligand of similar formula and geometry, (dimethylammonio)propylamine (dmtnH^+), has also been found in the octahedral cadmium complex of the $[\text{Cd}_3(\text{dmtnH})(\text{CN})_7]\cdot\text{C}_6\text{H}_5\text{F}$ crystalline phase [8], and appears to form a hydrogen bond (with adjacent cyano groups) as well ($\text{N}_{\text{amine}}\cdots\text{N}_{\text{CN}} = 2.80(1)$ Å).

Spectroscopic results

Spectral range 4000–600 cm^{-1}

The IR spectrum of the title compound in the 4000–600 cm^{-1} range and the Raman spectrum in the 1700–600 cm^{-1} range (Figs. 2 and 3, respectively) present a large number of well-resolved bands, with respect to those observed in other zinc(II) and cadmium(II) 1,3pn complexes [3]. In particular in

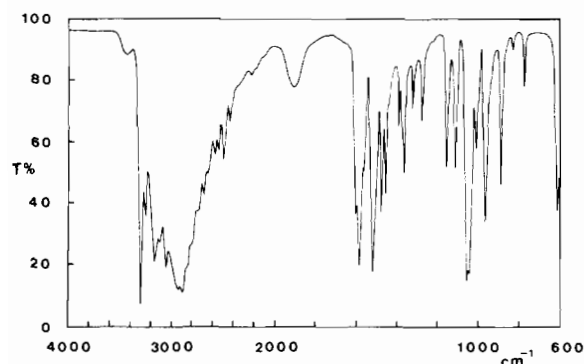


Fig. 2. IR spectrum of $[\text{Cd}(\text{pnH})_4\text{Cl}_2]\text{Cl}_4$ in KBr pellet.

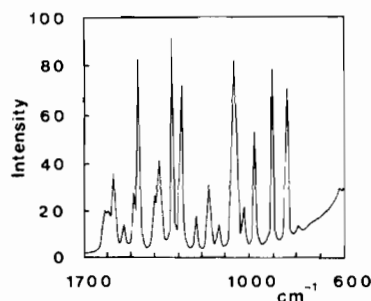


Fig. 3. Raman spectrum of solid sample of $[\text{Cd}(\text{pnH})_4\text{Cl}_2]\text{Cl}_4$.

TABLE 4. Main IR frequencies (cm^{-1}) of $[\text{Cd}(\text{pnH})_4\text{Cl}_2]\text{Cl}_4^a$

NH_2 stretching	NH_3^+ stretching	NH_2 scissoring	NH_3^+ scissoring
3290 vs	2900 s br	1605 sh	1570 sh
3250 m		1585 vs	1525 vs
3160 s			

^aAbbreviations: s = strong; m = medium; sh = shoulder; br = broad.

the present complex the NH_2 and NH_3^+ stretching and scissoring IR vibrations are well separated and easily assigned on the basis of the literature data [1, 3, 9, 10], as reported in Table 4. In the Raman spectra the scissoring vibrations of the NH_2 and NH_3^+ groups appear at 1600mb and 1565m, and 1525w cm^{-1} , respectively.

The shape and position of the NH_2 bands in the IR and Raman spectra of the cationic compound discussed in this paper, very similar to those observed in other previously studied zinc(II) and cadmium(II)

propane-1,3-diamine and 2,2-dimethylpropane-1,3-diamine complexes [1, 3, 9], are probably indicative of an apparent lack of influence of the positive site on the ligand properties of the donor atom. This point of view agrees with those of other cationic complexes [11, 12] and appears to be quite general for all such systems in which the donor atom L and the charged L^+ site are separated by a saturated organic skeleton.

Spectral range 500–100 cm^{-1}

The far-IR and Raman spectra of the compound are listed and assigned in Table 5 and depicted in Fig. 4. As reported in the structural section the cadmium atom, surrounded by four coplanar nitrogen atoms and two axially coordinated chlorine atoms, presents a square-bipyramidal geometry. In order to do a correct assignment of the metal–nitrogen and metal–chlorine stretching frequencies the theoretically expected bands are calculated by considering both the site symmetry (C_4) and factor group (C_{4v}) effects

On the basis of the C_4 site symmetry of the cadmium atom two $\nu(Cd-Cl)$ vibrations, IR and Raman active ($2A_1(IR, R)$), and four $\nu(Cd-N)$, two IR and three Raman active ($A_1(IR, R) + B_2(R) + E_1(IR, R)$), with two coincidences among IR and Raman frequencies, can be theoretically predicted, while considering the

TABLE 5. $\nu(Cd-Cl)$ and $\nu(Cd-N)$ stretching frequencies of $[Cd(pnH)_4Cl_2]Cl_4^a$

$\nu(Cd-Cl)$		$\nu(Cd-N)$	
IR	Raman	IR	Raman
250 sh	244 w	401 s	410 vw
200 s	210 w		380 vw
		320 sh	318 w
		298 s	290 vw

^aAbbreviations: s=strong; w=weak; vw=very weak; sh=shoulder.

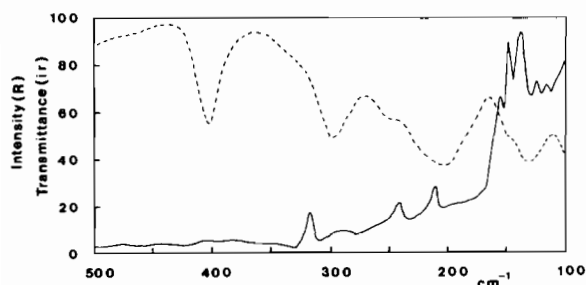


Fig. 4. Far vibrational spectra of $[Cd(pnH)_4Cl_2]Cl_4$: (---) Raman spectrum of solid sample; (—) IR spectrum of nujol mull sample.

C_{4v} factor group and the presence of two cadmium atoms in the unit cell the number of theoretically foreseen $Cd-Cl$ and $Cd-N$ stretching bands increase. In particular for $\nu(Cd-Cl)$ the number of noticeable bands exactly agrees with those suggested on the basis of only site symmetry considerations, since of the four theoretical expected bands ($2A_1(IR, R) + 2A_2(\text{inactive})$) only two are IR and Raman active. For $\nu(Cd-N)$ five Raman active and three IR active bands ($A_1(IR, R) + A_2(\text{inactive}) + B_1(R) + B_2(R) + 2E_1(IR, R)$ (three coincidences among IR and Raman frequencies values are present)) are instead expected.

By examining the spectral data of the present compound (Fig. 4) it seem possible to identify in the IR spectrum two peaks and one shoulder and in the Raman spectrum two weak and two very weak bands, three of which are coincident with the IR frequencies, reasonably assignable to $\nu(Cd-N)$ (see Table 5), agreeing very well with the literature data [1, 3, 9].

Table 5 also reports our IR and Raman assignments of the cadmium–chlorine bands, which strictly agree with those reported in the literature [13, 14].

Conclusions

The cationic complexes of cadmium(II) ion have until now received very little attention with respect to other metal ions such as cobalt(II), nickel(II), copper(II) and zinc(II), which in the presence of chlorine atoms generally form trigonally distorted tetrahedral monomeric inner complex species of general formula $M(L_N^+)Cl_3$ [12, 15, 16] and highly charged species only in the presence of less coordinating counteranions, such as NO_3^- and ClO_4^- [17].

The complex discussed in this paper demonstrates the capability of the cadmium(II) ion to form a species presenting a very distinct and unpredictable structure.

The coordinative ability of the amine, which acts as monodentate in an extended form, seems to be unaffected by the presence of a positive site on the ligand.

Supplementary material

Lists of the refined anisotropic thermal parameters and of the computed and observed structure factor moduli are available from the authors on request.

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