Flexibility in Coordinative Behavior of Propane-1,3-diamine Toward Zn(II) and Cd(II) Halides: $M(1,3pn)_2X_2$ (M = Zn, Cd; X = Cl, Br, I)

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Abstract

A series of compounds of formula $M(1,3pn)_2X_2$ (M = Zn(II), Cd(II); 1,3pn = propane-1,3-diamine; X = Cl, Br, I) has been prepared; two of them (M = Zn, X = Cl) and (M = Cd, X = I) have been structurally characterized. The $Zn(1,3pn)_2Cl_2$ (**I**) compound crystallizes in the $P2_1/c$ space group, with eight formula units in a cell of dimensions: $a = 12.833(4)$, $b = 16.753(9)$, $c = 13.010(4)$ Å, $\beta = 118.88(3)°$. The $Cd(1,3pn)_2I_2$ (**II**) compound crystallizes in the $P2_1/n$ space group with four formula units in a cell of dimensions: $a = 12.406(3)$, $b = 8.655(2)$, $c = 14.372(4)$ Å, $\beta = 113.57(2)°$. The structures were solved with the heavy-atom method and refined by full matrix least-squares to R and R_w values of 0.029 and 0.038, 0.042 and 0.058 for **I** and **II** respectively. The asymmetric unit of **I** consists of a dimeric $[Zn(1,3pn)_2]_2^{4+}$ moiety, where both Zn ions are tetrahedrally coordinated to four nitrogen atoms belonging to one chelating and two bridging 1,3pn ligands. The dimeric moiety generates an infinite chain upon translation of one cell in the direction of the diagonal (1,0,1). The structure of **II** shows a polymeric arrangement of octahedral Cd atoms sharing both iodine atoms and 1,3pn ligands. The M–N stretching vibrations are discussed and assigned in the light of the known structures.

Introduction

A comparison of the stability of metal–amine complexes, in solution as a function of chelate ring-size, has revealed that those of propane-1,3-diamine (hereafter abbreviated as 1,3pn) have lower stability with respect to the ethylenediamine analogues, given the less favourable entropy change in the formation of six-membered rings [1, 2]. As a consequence, one can expect a greater coordinative versatility for propane-1,3-diamine than for ethylenediamine, suggesting for the 1,3pn ligand the possibility of acting also as monodentate or bidentate ligand, on two different metal centers.

To our knowledge propane-1,3-diamine was always found to form chelate ring [3–7], the only exception being represented by the copper(II) $Cu(1,3pn)_{2.5}(ClO_4)_2$ compound, in which the amine bridges two copper(II) ions, giving rise to a very distinct structure [8]. Therefore, in order to substantiate our expectations, propane-1,3-diamine has been reacted with Zn(II) and Cd(II) halides. The d^{10} metal(II) halide adducts can be considered ideal systems for our test, since they show a variety of coordination numbers and geometries, depending on many factors, among which are crystal-packing, hydrogen bonding, as well as metal ions and halide dimensions [9, 10]. In this paper we present the detailed structural and spectroscopic (IR and Raman) characterization of $M(1,3pn)_2X_2$ (M = Zn(II), Cd(II); X = Cl, Br, I) compounds.

Experimental

Preparation of the Complexes

All the complexes were prepared by adding a methanolic metal halide solution (1 mM) to a methanolic propane-1,3-diamine solution (2.5 mM). By standing several hours at room temperature white crystals precipitated.

$Zn(1,3pn)_2Cl_2$: *Anal.* Calc. for $C_6H_{20}ZnN_4Cl_2$: C, 25.31; H, 7.09; N, 19.70. Found: C, 25.41; H, 7.13; N, 19.86%.

$Zn(1,3pn)_2Br_2$: *Anal.* Calc. for $C_6H_{20}ZnN_4Br_2$: C, 19.28; H, 5.40; N, 15.01. Found: C, 19.39; H, 5.46; N, 14.99%.

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TABLE 1. Crystal Data for $Zn(1,3pn)_2Cl_2$ and $Cd(1,3pn)_2I_2$

Compound	$Zn(1,3pn)_2Cl_2$	$Cd(1,3pn)_2I_2$
Formula	$C_6H_{20}Cl_2N_4Zn$	$C_6H_{20}CdI_2N_4$
Formula weight (uma)	284.53	514.46
Crystal system	monoclinic	monoclinic
a (Å)	12.833(4)	12.406(3)
b (Å)	16.753(9)	8.655(2)
c (Å)	13.010(4)	14.372(4)
β (°)	118.88(3)	113.57(2)
V (Å^3)	2449.2	1414.4
Z, D_{calc} (g cm^{-3})	8, 1.54	4, 2.42
Space group	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)
$F(000)$	1184	952
Radiation (graphite monochr.)	Mo Kα (λ = 0.71073)	
Diffractometer	Enraf-Nonius	
μ(Mo Kα) (cm^{-1})	24.63	58.53
2θ range (°)	6–47	6–50
Scan method	ω	ω
Scan interval	0.9 + 0.347 tgθ	
Prescan speed (° min^{-1})	16	16
Prescan acceptance $\sigma(I)/I$	1	0.5
Required $\sigma(I)/I$	0.01	0.05
Max. time for 1 reflection measured (s)	40	40
Collected octants	$\pm h, +k, +l$	$\pm h, +k, +l$
No. data collected at room temperature	3618	2479
No. data used ($I > 3\sigma(I)$)	2580	1368
Crystal decay	50%	no
No. azimut reflections for absorption correction	3	3
Max. and min. transmission factors	1.00–0.71	1.00–0.92
Crystal size (mm)	0.25 × 0.20 × 0.05	0.32 × 0.25 × 0.18
Weighting fudge p factor	0.035	0.030
R	0.029	0.042
R_w	0.038	0.058
GOF	1.463	1.741
No. variable parameters	244	118
Max. peak in final ΔF map (Å^{-3})	0.33	1.8 (close to the I1 atom)

$w = 4F_o^2/\sigma(F_o^2)^2$ where $\sigma(F_o^2) = \sqrt{[\sigma(I)^2 + (pI)^2]}/\mathrm{LP}$. $R = [\Sigma(F_o - k|F_c|)^2/\Sigma F_o]$; $R_w = \sqrt{[\Sigma w(F_o - k|F_c|)^2/\Sigma w F_o^2]}$. $GOF = \sqrt{[\Sigma w(F_o - k|F_c|)^2/(N_{obs} - N_{var})}$.

$Zn(1,3pn)_2I_2$: *Anal.* Calc. for $C_6H_{20}ZnN_4I_2$: C, 15.41; H, 4.31; N, 11.99. Found: C, 15.44; H, 4.33; N, 12.22%.

$Cd(1,3pn)_2Cl_2$: *Anal.* Calc. for $C_6H_{20}CdN_4Cl_2$: C, 21.72; H, 6.08; N, 16.90. Found: C, 21.60; H, 6.18; N, 17.00%.

$Cd(1,3pn)_2Br_2$: *Anal.* Calc. for $C_6H_{20}CdN_4Br_2$: C, 17.13; H, 4.80; N, 13.33. Found: C, 17.21; H, 4.89; N, 13.29%.

$Cd(1,3pn)_2I_2$: *Anal.* Calc. for $C_6H_{20}CdN_4I_2$: C, 14.00; H, 3.92; N, 10.89. Found: C, 14.21; H, 3.93; N, 10.83%.

Physical Measurements

Infrared 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 Mod. 1106 elemental analyser.

X-ray Structure Determination

The refined cell constants and other relevant crystal data for $Zn(1,3pn)_2Cl_2$ (I) and $Cd(1,3pn)_2I_2$ (II) are presented in Table 1, together with details of intensity measurements. The intensity data were collected on an Enraf-Nonius CAD4 diffractometer and corrected for Lorentz and polarization effects. An empirical absorption correction, based on ψ scans (ψ 0–360°, every 10°) on three reflections with values near to 90°, was applied to both data collections. The periodical monitoring of three reference reflections showed compound **I** to be unstable under the experimental conditions, at the end of the data collection the reference intensities being almost halved; therefore the corresponding data set was corrected for decay.

The structures were solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares. All non-hydrogen atoms were treated anisotropically while the hydrogen atoms were located in their ideal positions (C–H = 0.95 Å) after each cycle of refinement. In compound **I** one of the two non-chelating 1,3pn is affected by a slight conformational ambiguity, the C(4) and C(5) atoms being disordered 70:30 on two different positions; the hydrogen atoms for that 1,3pn ligand have been considered only for the major conformer. All the computations were performed on a PDP 11/34 computer using the Enraf Nonius structure determination package (SDP) and the physical constants tabulated therein. The final values of the R and R_w conventional agreement indices and the fudge factor for the weighting scheme are reported in Table 1. Bond distances and angles are reported in Table 2 for both compounds. See also 'Supplementary Material'.

Results and Discussion

All the compounds are stable in air and soluble in polar organic solvents. Their spectroscopic properties demonstrate that there are some differences between Zn(II) and Cd(II) complexes. In order to clarify these differences one member of each type has been structurally characterized.

Description of the Structures (Figs. 1 and 2)

Structure of Zn(1,3pn)$_2$Cl$_2$

The compound crystallizes in the $P2_1/c$ space group with $Z = 8$; the asymmetric unit contains, a dimeric $[Zn(1,3pn)_2]_2^{4+}$ moiety (and the related four chlorine anions) which generates an infinite chain upon translation in the direction of the diagonal (1,0, 1). The chlorine anions are not directly bound to the zinc atoms, but are deeply involved in an extended network of hydrogen bonds with the aminic hydrogen atoms of different chains, which is the glue that sticks the chains together. The polymeric nature in the solid state of the $[Zn(1,3pn)_2]$ species is due to the propane-1,3-diamine ligand which acts either as a chelating or bridging (on different metal atoms) ligand.

The two independent zinc atoms are tetrahedrally connected to four nitrogen atoms, belonging to one chelating and two bridging 1,3pn ligands. The presence of one chair-shaped six-membered metallocycle determines a slight distortion in the metal coordination; the Zn–N interactions, ranging from 1.992(2) to 2.030(2) Å, can consequently be classified, with respect to the metallocycle, in three different classes, *i.e.* those involving the nitrogen atoms of the chelating diamine Zn–N(c), those with the equatorial Zn–N(e) and those with the axially bonded propane-

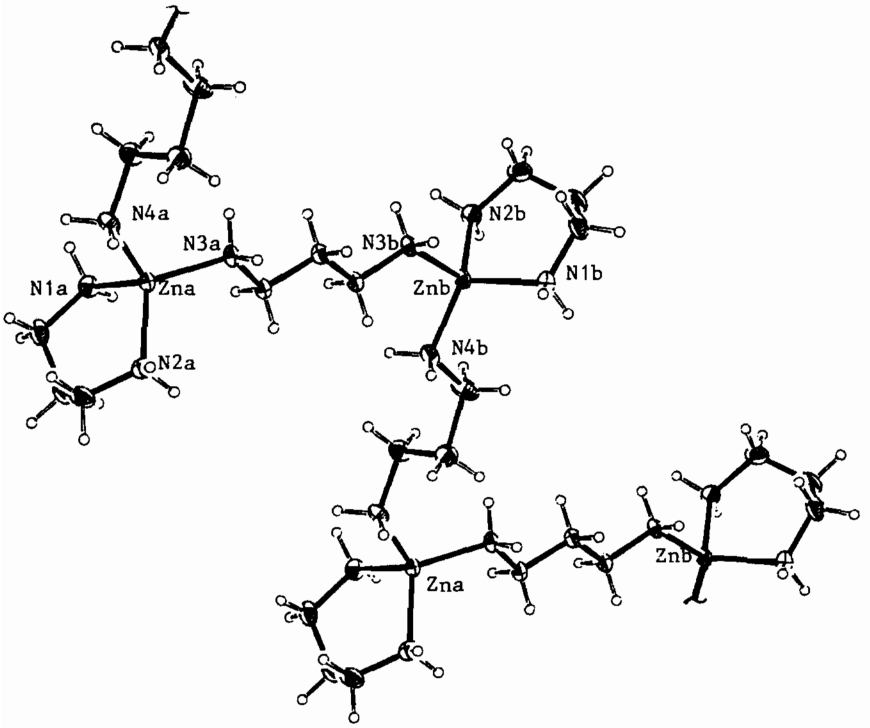

Fig. 1. ORTEP drawing of the repeating unit in the $Zn(1,3pn)_2X_2$ crystal (isolated anions are omitted for clarity).

TABLE 2. Relevant Bond Distances (Å) and Angles (°) for the Complexes

(a) $Zn(1,3pn)_2Cl_2$			
Zn(a)–N(1a)	2.011(2)	Zn(b)–N(1b)	2.007(2)
Zn(a)–N(2a)	2.015(3)	Zn(b)–N(2b)	2.009(2)
Zn(a)–N(3a)	1.992(2)	Zn(b)–N(3b)	2.030(2)
Zn(a)–N(4a)	2.027(2)	Zn(b)–N(4b)	2.004(2)
N(1a)–C(1a)	1.469(4)	N(1b)–C(1b)	1.472(4)
N(2a)–C(3a)	1.478(4)	N(2b)–C(3b)	1.469(4)
N(3a)–C(1)	1.481(4)	N(3b)–C(3)	1.485(3)
N(4a)–C(4)	1.539(5)	N(4b)–C(6)	1.466(4)
N(4a)–C(4′)	1.529(9)	C(1b)–C(2b)	1.517(6)
C(1a)–C(2a)	1.506(5)	C(2b)–C(3b)	1.498(5)
C(2a)–C(3a)	1.506(5)	C(2)–C(3)	1.502(4)
C(1)–C(2)	1.515(4)	C(4′)–C(5′)	1.611(13)
C(4)–C(5)	1.413(7)	C(5)–C(6)	1.563(6)
C(5′)–C(6)	1.658(9)		
N(1a)–Zn(a)–N(2a)	102.0(1)	N(1b)–Zn(b)–N(2b)	102.3(1)
N(1a)–Zn(a)–N(3a)	113.0(1)	N(1b)–Zn(b)–N(3b)	105.5(1)
N(1a)–Zn(a)–N(4a)	108.0(1)	N(1b)–Zn(b)–N(4b)	116.0(1)
N(2a)–Zn(a)–N(3a)	113.1(1)	N(2b)–Zn(b)–N(3b)	108.2(1)
N(2a)–Zn(a)–N(4a)	107.9(1)	N(2b)–Zn(b)–N(4b)	112.8(1)
N(3a)–Zn(a)–N(4a)	112.2(8)	N(3b)–Zn(b)–N(4b)	111.3(1)
Zn(a)–N(1a)–C(1a)	115.3(2)	Zn(b)–N(1b)–C(1b)	112.5(2)
Zn(a)–N(2a)–C(3a)	112.1(2)	Zn(b)–N(2b)–C(3b)	116.0(2)
Zn(a)–N(3a)–C(1)	119.7(2)	Zn(b)–N(3b)–C(3)	117.4(2)
Zn(a)–N(4a)–C(4)	125.4(2)	Zn(b)–N(4b)–C(6)	119.7(2)
Zn(a)–N(4a)–C(4′)	99.7(4)	N(3a)–C(1)–C(2)	109.9(2)
N(1b)–C(1b)–C(2b)	112.5(3)	C(1b)–C(2b)–C(3b)	116.8(3)
N(1a)–C(1a)–C(2a)	112.1(3)	C(1a)–C(2a)–C(3a)	116.3(3)
C(1)–C(2)–C(3)	115.4(2)	N(3b)–C(3)–C(2)	111.9(2)
N(2a)–C(3a)–C(2a)	112.6(3)	N(4a)–C(4)–C(5)	110.1(4)
N(2b)–C(3b)–C(2b)	112.2(3)	C(4)–C(5)–C(6)	109.8(4)
N(4a)–C(4′)–C(5′)	100.4(6)	N(4b)–C(6)–C(5)	120.0(3)
C(4′)–C(5′)–C(6)	100.3(6)	N(4b)–C(6)–C(5′)	88.5(4)
(b) $Cd(1,3pn)_2I_2$			
Cd–I(1)	3.109(1)	Cd–N(2a)	2.383(10)
Cd–I(1′)	3.053(1)	Cd–N(1b)	2.365(11)
Cd–N(1a)	2.341(10)	Cd–N(2b)	2.374(12)
N(1a)–C(1a)	1.488(17)	N(1b)–C(1b)	1.497(19)
C(1a)–C(2a)	1.499(17)	C(1b)–C(2b)	1.432(22)
C(2a)–C(3a)	1.486(17)	C(2b)–C(3b)	1.406(23)
C(3a)–N(2a)	1.518(14)	C(3b)–N(2b)	1.500(19)
I(1)–Cd–I(1′)	81.68(3)	I(1′)–Cd–N(1b)	93.5(3)
I(1)–Cd–N(1a)	88.0(3)	I(1′)–Cd–N(1a)	99.6(3)
I(1)–Cd–N(2a)	173.0(3)	I(1′)–Cd–N(2a)	91.6(2)
I(1)–Cd–N(1b)	93.6(3)	I(1′)–Cd–N(2b)	170.7(3)
I(1)–Cd–N(2b)	92.5(3)	N(2a)–Cd–N(1b)	88.8(4)
N(1a)–Cd–N(2a)	91.1(4)	N(2a)–Cd–N(2b)	94.3(4)
N(1a)–Cd–N(1b)	166.9(4)	N(1b)–Cd–N(2b)	79.6(4)
N(1a)–Cd–N(2b)	87.3(4)		

1,3-diamine Zn–N(a), with average values of 2.010, 1.998 and 2.028 Å respectively. In an analogous way the N–Zn–N angles can be classified as (N(c)–Zn–N(c) (av. 102.1°), N(a)–Zn–N(e) (av. 111.7°), N(a)–Zn–N(c) (av. 107.4°) and N(e)–Zn–N(c) (av. 113.7°). The axial ligand is therefore more loosely bound, but closer from an angular point of view to the metallocycle. A similar feature has been previously noted in the $Zn(dmpd)X_2$ (dmpd = 2,2-dimethylpropane-1,3-diamine; X = Cl, Br) molecules [11].

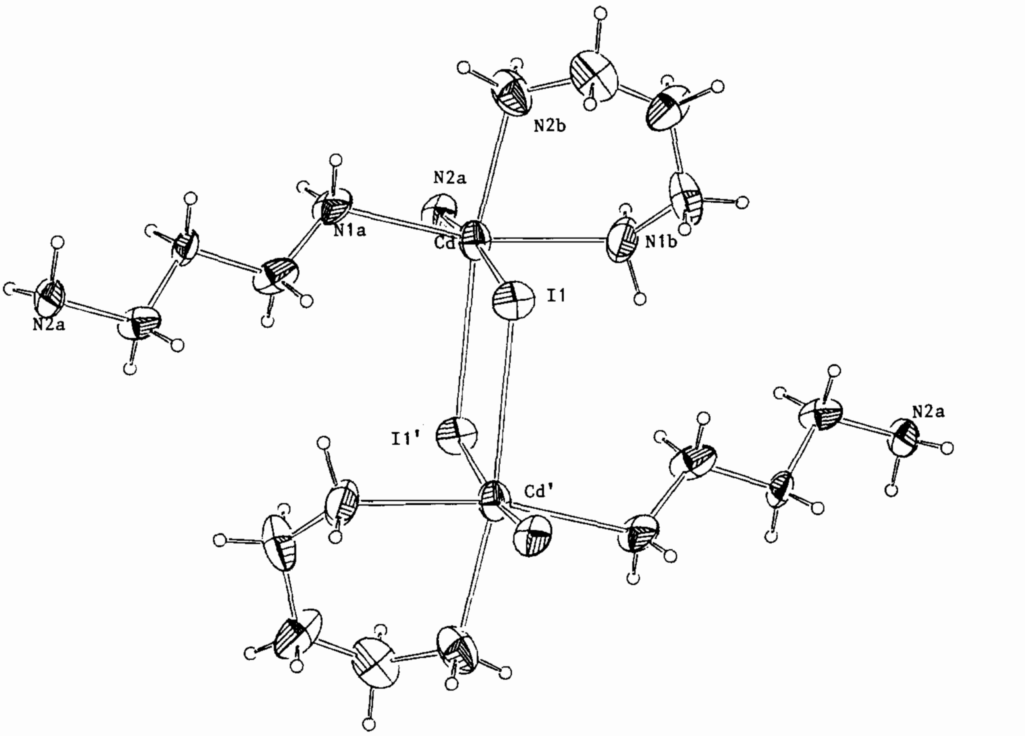

Fig. 2. ORTEP drawing of the repeating unit in the Cd(1,3pn)$_2$I$_2$ crystal (isolated anions are omitted for clarity).

Structure of Cd(1,3pn)$_2$I$_2$

The compound crystallizes in the $P2_1/n$ space group as a layer structure, the layers being approximately orthogonal to the (–1,0,1) direction. The asymmetric unit consists of one octahedral complex of cadmium, generating the layers, plus one isolated iodide ion involved in some loose interactions with the aminic hydrogen atoms. Of the two independent propane-1,3-diamine ligands, one chelates on Cd with a six-membered ring in a chair conformation and N(1b)–Cd–N(2b) bond angle of 79.6(4)°, while the second is coordinated to two different (symmetry related) Cd atoms through N(1a) and N(2a) atoms. In addition, a four-membered Cd–I–Cd–I ring is formed by the presence of a crystallographic inversion center, thus completing the octahedral coordination, which is slightly distorted along the I(1)–Cd–N(2a) axis; in fact the I(1)–Cd distance (3.109(1) Å) is significantly longer than the I(1′)–Cd one (3.053(1) Å) and the Cd–N(2a) distance shows the highest Cd–N value (average 2.366 Å, range 2.341–2.383 Å). A significant stretching of all Cd–N distances is however present, when compared to the values reported for Cd(1,3pn)Cl$_2$ (Cd–N av. 2.290 Å) [7] and Cd(dmpd)Br$_2$ (Cd–N av. 2.294 Å) [11], where there are only two nitrogen atoms (and four halides) in the coordination sphere. Furthermore, none of the angles of mutually *trans* ligands on Cd is close to 180°; the major discrepancy is observed for the N(1a)–Cd–N(1b) angle (166.9(4)°), probably due to the repulsion effective between the chains of these nitrogen atoms, being in the ‘axial’ position, and the heavy atoms of the ‘equatorial’ four-membered rings.

Spectroscopic Results

Spectral range 4000–500 cm^{-1}

The infrared and Raman spectra of the zinc(II) compounds are all very similar. Thus, together with that reported in our previous work [11], they can be considered isomorphous and isostructural. Figure 3 exemplifies the infrared and Raman spectra of this class of compounds.

Similar conclusions can also be drawn for the cadmium(II) compounds by comparing their infrared and Raman spectra (Figs. 4 and 5). Some small differences in the spectra of the chloride complex with respect to the others can only reflect slight differences in the crystal packing due to the different hydrogen bonding capabilities of the halides.

The sharp differences of the spectroscopic behavior among zinc(II) and cadmium(II) compounds (compare Figs. 3–5 and the stretching and scissoring NH$_2$ vibrations, assigned on the basis of literature data for similar amine compounds [11, 12], reported in Table 3) agree with the different structural arrangements reported above. The high number of bands in the infrared and Raman spectra of the zinc(II) and

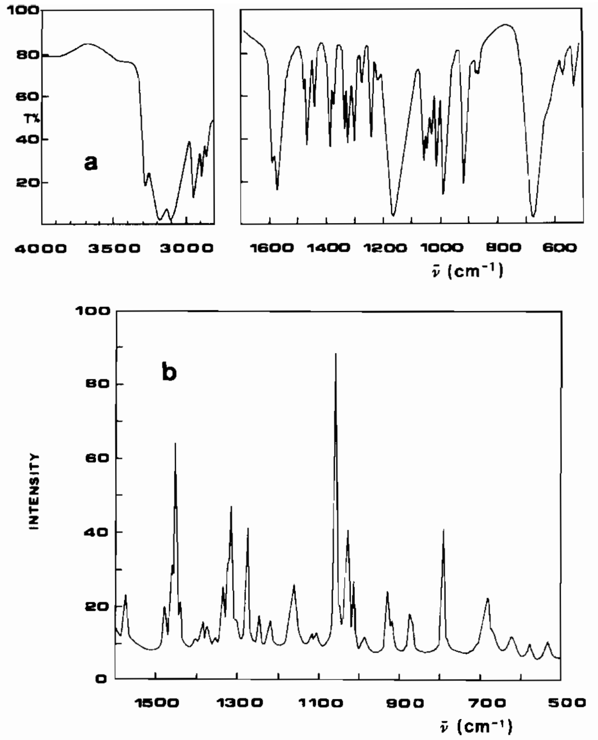

Fig. 3. Exemplified infrared (a) and Raman (b) spectra of the Zn(1,3pn)$_2$X$_2$ compounds.

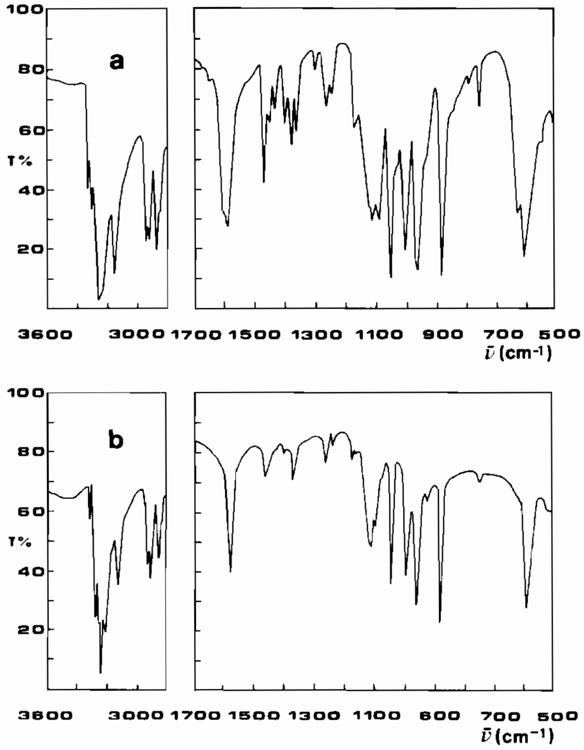

Fig. 4. Comparison of the infrared spectra of the Cd(1,3pn)$_2$-Cl$_2$ (a) and Cd(1,3pn)$_2$I$_2$ (b) compounds.

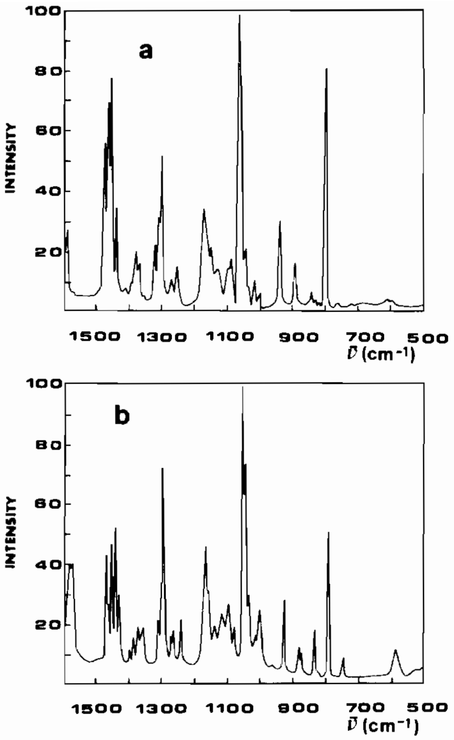

Fig. 5. Comparison of the Raman spectra of the Cd(1,3pn)$_2$-Cl$_2$ (a) and Cd(1,3pn)$_2$I$_2$ (b) compounds.

cadmium(II) complexes which makes the band assignments difficult, also derives from the presence of the amines in both chair and elongated conformations.

Spectral range 500--100 cm^{-1}

Owing to the structural differences between zinc-(II) and cadmium(II) complexes they are considered separately. Our assignments of M–N stretching vibrations, reported in Table 4, are however based on some common considerations, such as (i) zinc(II) compounds are isostructural; (ii) the IR or likewise Raman spectra, of zinc(II) complexes must present the same number of bands (see Figs. 6 and 7); (iii) idem as points (i) and (ii) for cadmium(II) compounds; (iv) comparison with ν(M–N) vibrations reported in the literature [11, 12].

As reported above, the zinc atom is tetrahedrally coordinated to four nitrogen atoms. On the basis of the C_1 site symmetry, four ν(Zn–N) vibrations, infrared and Raman active, can be theoretically expected, while by considering the C_{2h} factor group and the presence of eight zinc atoms in the cell, (classified in two sets of four zinc atoms each) the number of theoretically predicted Zn–N stretching bands greatly increases. Since the number of experimental ν(Zn–N) bands found in the spectra is not too high we suggest, for our solid-state complexes at room temperature, a site symmetry static effect prevailing on a factor group dynamic effect.

TABLE 3. Infrared Frequencies (cm^{-1})[a]

Compound	NH_2 stretching	NH_2 scissoring
$[Zn(1,3pn)_2]Cl_2$	3280sh, 3190vs, 3105vs	1585sh, 1572vs
$[Zn(1,3pn)_2]Br_2$	3270sh, 3170vs, 3100vs	1585sh, 1570vs
$[Zn(1,3pn)_2]I_2$	3262sh, 3170vs, 3100vs	1570sh, 1562vs
$Cd(1,3pn)_2Cl_2$	3330sh, 3300sh, 3250vs, 3230sh, 3150s	1605sh, 1590s
$Cd(1,3pn)_2Br_2$	3330w, 3300m, 3250vs, 3230sh, 3145m	1600sh, 1582s
$Cd(1,3pn)_2I_2$	3330w, 3280s, 3240vs, 3215sh, 3130m	1575s

[a] Abbreviations: s = strong; m = medium; w = weak; vs = very strong; sh = shoulder.

TABLE 4. $\nu(M-N)$ Stretching Frequencies (cm^{-1})[a]

Compound		$\nu(M-N)$
$[Zn(1,3pn)_2]Cl_2$	IR	488m, 452w, 435w, 349w
	R	490w, 459w, 437m, 352m
$[Zn(1,3pn)_2]Br_2$	IR	483ms, 442w, 430w, 344w
	R	486w, 432m, 350m
$[Zn(1,3pn)_2]I_2$	IR	480ms, 437w, 426w, 343w
	R	484w, 427m, 347m
$Cd(1,3pn)_2Cl_2$	IR	465s, 356m, 332m
	R	464w, 355w, 343m, 327mw
$Cd(1,3pn)_2Br_2$	IR	456s, 356w, 332m
	R	458w, 353w, 345m, 328mw
$Cd(1,3pn)_2I_2$	IR	451s, 350sh, 333m
	R	453w, 352sh, 342m, 333w

[a] Abbreviations: s = strong; m = medium; w = weak; mw = medium weak; sh = shoulder.

In the Cd complexes, the metal atom presents a slightly distorted octahedral coordination. On the basis of a C_1 site symmetry four $\nu(Cd-N)$ vibrations, infrared and Raman active, are expected, as found in zinc(II) complexes, while by considering the dimeric structural unity and the C_i site symmetry eight Cd–N stretching vibrations ($2A_g + 2B_g + 2A_u + 2B_u$) can be theoretically predicted, of which four are IR and four are Raman active. Furthermore considering the C_{2h} factor group and the presence of four cadmium atoms in the unit cell sixteen $\nu(Cd-N)$ vibrations are expected of which eight are IR and eight are Raman active. The number of experimental $\nu(Cd-N)$ bands rules out the effect of the C_{2h} symmetry but does not allow an unambiguous choice between the C_1 or C_i site symmetries. In any case our assignments of the most probable Cd–N stretching vibrations for the cadmium(II) compounds are reported in Table 4.

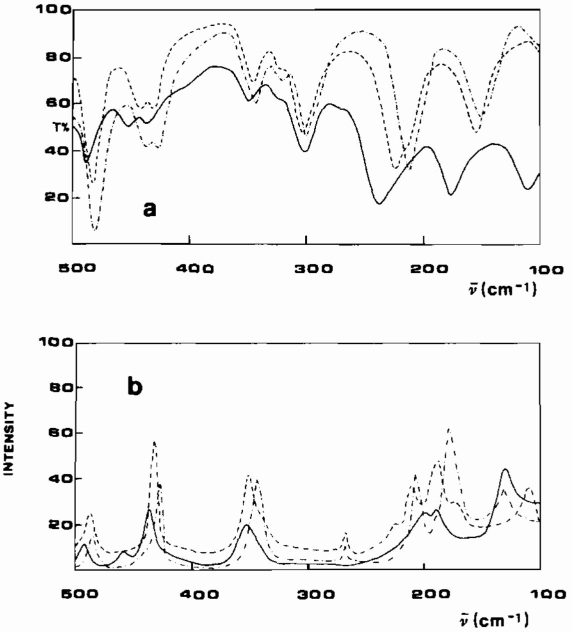

Fig. 6. Far-infrared (a) and Raman (b) spectra of the $Zn(1,3pn)_2X_2$ compounds.

Furthermore from the analysis of the infrared and Raman spectra of the cadmium(II) complexes we were unable to propose sure assignments of Cd–X (X = Cl, Br, I) stretching vibrations, even if this has been easily done in similar cases [11].

Conclusions

In this paper the coordinative flexibility of propane-1,3-diamine is well demonstrated. By using appropriate metal ions it is possible to force the amine to act in an unusual way, giving rise to compounds which present uncommon and unpredictable structures. This capability of 1,3pn with respect to

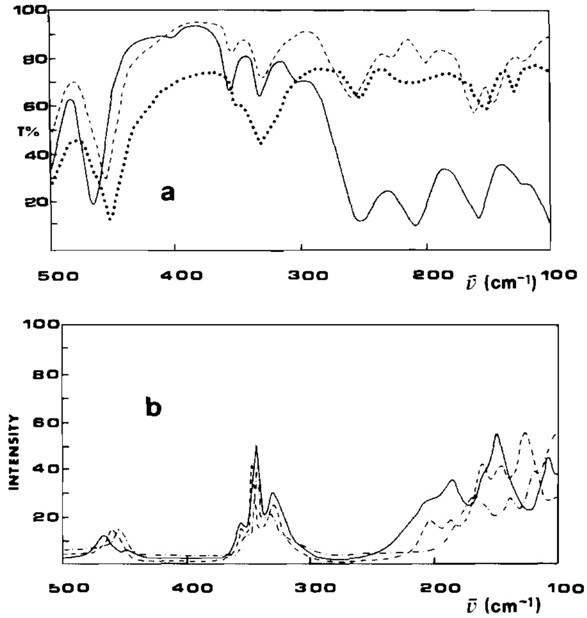

Fig. 7. Far-infrared (a) and Raman (b) spectra of the Cd-$(1,3pn)_2X_2$ compounds.

ethylenediamine is favoured by the lower stability of six-membered chelate rings compared to five-membered ones.

The ability of 1,3pn to act as a bridging ligand can make it very important in the design of ferromagnetic-like polymetallic systems.

The present results further suggest that caution should be taken in assignment of the stereochemistry in the absence of structural data.

Supplementary Material

The final positional and thermal parameters and computed and observed structure factor moduli for both compounds are available from the authors on request.

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