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Coordinative Capabilities of Substituted Propane-1,3-diamine: Zinc(II) Halide Adducts of 2,2-Dimethylpropane-1,3-diamine

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Abstract

A series of compounds of formula Zn(dmpd)$_n$X$_2$·mH$_2$O (dmpd = 2,2-dimethylpropane-1,3-diamine, X = Cl, Br, I; n = 2, m = 0; n = 3, m = 1) has been prepared and studied by means of spectroscopic (IR and Raman) and structural investigations. The [Zn(dmpd)$_2$]I$_2$ (**I**) compound crystallizes in the tetragonal $P4_2/nmc$ space group, with two formula units in a cell of dimensions: $a = b = 8.417(2)$, $c = 12.726(2)$ Å. The structure consists of an ionic packing of iodide anions and of discrete [Zn(dmpd)$_2$]$^{2+}$ cations, where the Zn atoms are tetrahedrally coordinated to four nitrogen atoms of two chelating amine molecules.

The [Zn(dmpd)$_3$]Cl$_2$·H$_2$O (**II**) compound crystallizes in the triclinic space group $P\bar{1}$, with $Z = 2$ and cell of dimensions: $a = 9.021(2)$, $b = 12.087(3)$, $c = 13.785(3)$ Å, $\alpha = 59.01(2)$, $\beta = 70.35(2)$, $\gamma = 76.01(2)$°. The crystal consists of an ionic packing of discrete [Zn(dmpd)$_3$]$^{2+}$ cations and chloride anions plus two clathrate water molecules per unit cell. The Zn atom presents a trigonal bipyramidal geometry, being surrounded by four nitrogen atoms of two chelating dmpd molecules and one nitrogen of a monodentate dmpd ligand. The structures were solved by conventional Patterson and Fourier methods and refined by full matrix least-squares to R and R_w of 0.053 and 0.073, and 0.040 and 0.046 for **I** and **II** respectively. The Zn–N stretching vibrations are discussed and assigned in the light of the determined structures.

Introduction

Basicity and coordination capability toward metal ions of non-cyclic polyamines are widely studied. By combining the appropriate ligands and metal ions, it is possible to force the amine to act in an unusual manner, giving rise to compounds with peculiar structures.

Working with this goal in mind we have demonstrated, in previous papers [1, 2], the versatility of the propane-1,3-diamine, which acts as a chelating agent, but also as a bidentate bridge on two different metal ions, favouring the formation of unusual dimeric (1) and polymeric (2) structures. The greater versatility of propane-1,3-diamine with respect to ethylenediamine was expected on the basis of the lower stability of six-membered chelate rings, compared to five-membered ones, which favours other kinds of coordinative behaviors.

In this paper we report the preparation and the investigation, by means of IR and Raman spectroscopy and of single crystal X-ray diffraction of some halide Zn(II) adducts of 2,2-dimethylpropane-1,3-diamine (hereafter abbreviated as dmpd), having formula Zn(dmpd)$_n$X$_2$·mH$_2$O (X = Cl, Br, I; n = 2 and m = 0; n = 3 and m = 1). This amine, which so far was invariably found to chelate metal ions [3, 4], acts in the present case also as a monodentate ligand.

Experimental

Preparation of the Zn(dmpd)$_2$X$_2$ Complexes

By mixing methanolic solutions containing the zinc(II) halide salt (1 mM) and the amine (2.5–3 mM), white crystals separated after a few hours.

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$Zn(dmpd)_2Cl_2$: *Anal.* Found: C, 35.30; H, 8.21; N, 16.57. Calc. for $C_{10}H_{28}N_4ZnCl_2$: C, 35.24; H, 8.29; N, 16.45%.

$Zn(dmpd)_2Br_2$: *Anal.* Found: C, 27.89; H, 6.55; N, 13.04. Calc. for $C_{10}H_{28}N_4ZnBr_2$: C, 27.94; H, 6.57; N, 13.05%.

$Zn(dmpd)_2I_2$: *Anal.* Found: C, 23.00; H, 5.35; N, 10.69. Calc. for $C_{10}H_{28}N_4ZnI_2$: C, 22.92; H, 5.39; N, 10.70%.

Preparation of the $Zn(dmpd)_3X_2 \cdot H_2O$ (X = Cl, Br) Complexes

By mixing water solutions containing the zinc(II) halide salt (1 mM) and the amine (≅8–10 mM) and by slow evaporation of the solutions at room temperature, white crystals separated after a few days.

$Zn(dmpd)_3Cl_2 \cdot H_2O$: *Anal.* Found: C, 39.18; H, 9.66, N, 18.11. Calc. for $C_{15}H_{44}N_6OZnCl_2$: C, 39.07; H, 9.63; N, 18.24%.

$Zn(dmpd)_3Br_2 \cdot H_2O$: *Anal.* Found: C, 32.59; H, 8.76; N, 15.13 Calc. for $C_{15}H_{44}N_6OZnBr_2$: C, 32.76; H, 8.73, N, 15.29%.

Physical Measurements

Infrared spectra were recorded with a Perkin-Elmer 180 spectrophotometer on Nujol mulls on KBr pellets in the 4000–500 cm^{-1} range, 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 $Zn(dmpd)_2I_2$ (I) and $Zn(dmpd)_3Cl_2 \cdot H_2O$ (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 scan (ψ 0–360°, every 10°) on three reflections with χ values near to 90°, was applied to both data collections. The periodical monitoring of three reflections showed no evidence of crystal decay

TABLE 1. Crystal Data for $[Zn(dmpd)_2]I_2$ (I) and $[Zn(dmpd)_3]Cl_2 \cdot H_2O$ (II)

Compound	I	II
Formula	$C_{10}H_{28}I_2N_4Zn$	$C_{15}H_{44}Cl_2N_6OZn$
Formula weight (uma)	523.54	460.69
Crystal system	tetragonal	triclinic
a (Å)	8.417(2)	9.021(2)
b (Å)	8.417(2)	12.087(3)
c (Å)	12.726(2)	13.785(3)
α (°)		59.01(2)
β (°)		70.35(2)
γ (°)		76.01(2)
V (Å^3)	901.7	1209.1
Z, D_{calc} (g cm^{-3})	2, 1.93	2, 1.27
Space group	$P4_2/nmc$	$P\bar{1}$
$F(000)$	504	496
Radiation (graphite monochromated)	Mo Kα (λ = 0.71073)	
Diffractometer	Enraf-Nonius CAD4	
μ (Mo Kα) (cm^{-1})	47.75	12.82
2θ range (°)	6–48	6–42
Scan method	ω	ω
Scan interval	$0.8 + 0.347 tg\theta$	
Collected octants	$+h, +k, +l$	$\pm h, \pm k, +l$
No. data collected at room temperature	855	2560
No. data used ($I > 3\sigma(I)$)	602	1406
No. azimut reflections for absorption correction	3	3
Max. and min. transmission factors	1.00–0.84	1.00–0.88
Crystal size (mm)	0.25 × 0.25 × 0.20	0.25 × 0.10 × 0.10
R	0.053	0.040
R_w	0.073	0.046
GOF	2.943	1.273
No. variable parameters	30	137

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

for compound **I**, while compound **II** was unstable under the experimental conditions (18% of decay, linear correction applied).

The structures were solved by conventional Patterson and Fourier methods and refined by full-matrix least-squares. All the 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** the complex cation lies about a $\bar{4}2m$ position (in a Wyckoff notation) on which the Zn atom is located. The point symmetry causes the doubling of the tetrahedral N_4 moiety and of the carbon atoms directly bound to it, while the 'external', packing sensitive, C2 and C3 atoms are ordered on the *c* and *g* (in Wyckoff notation) positions, respectively. C1, differently from N, happens to be very close to its disordered mirror-symmetric equivalent and it was impossible to refine it with reliable anisotropic thermal parameters. Moreover the refined position of C1, as seen from the bonding parameters listed in Table 2, is quite uncertain.

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. See also 'Supplementary Material'.

TABLE 2. Bond Distances (Å) and Angles (°)

(a) $[Zn(dmpd)_2]I_2$			
Zn–N	2.041(7)	N–C(1)	1.509(9)
C(1)–C(2)	1.547(9)	C(2)–C(3)	1.531(9)
N–Zn–N′	97.6(4)	N–Zn–N″	115.7(2)
Zn–N–C(1)	105.2(5)	N–C(1)–C(2)	111.5(6)
C(1)–C(2)–C(1′)	115.2(6)	C(1)–C(2)–C(3′)	117.4(4)
C(1)–C(2)–C(3)	100.4(4)	C(3)–C(2)–C(3′)	106.7(7)
(b) $[Zn(dmpd)_3]Cl_2 \cdot H_2O$			
Zn–N(1A)	2.232(5)	N(1A)–C(1A)	1.458(8)
Zn–N(2A)	2.079(6)	N(2A)–C(3A)	1.456(9)
Zn–N(1B)	2.179(5)	C(1A)–C(2A)	1.552(9)
Zn–N(2B)	2.046(5)	C(2A)–C(3A)	1.527(9)
Zn–N(1C)	2.093(5)	C(2A)–C(4A)	1.504(10)
		C(2A)–C(5A)	1.533(10)
N(1B)–C(1B)	1.473(8)	N(1C)–C(1C)	1.491(8)
N(2B)–C(3B)	1.482(8)	N(2C)–C(3C)	1.454(9)
C(1B)–C(2B)	1.526(9)	C(1C)–C(2C)	1.536(9)
C(2B)–C(3B)	1.517(9)	C(2C)–C(3C)	1.522(10)
C(2B)–C(4B)	1.524(10)	C(2C)–C(4C)	1.531(10)
C(2B)–C(5B)	1.528(10)	C(2C)–C(5C)	1.525(10)
N(1A)–Zn–N(2A)	84.7(2)	N(1B)–Zn–N(2B)	91.3(2)
N(1A)–Zn–N(1B)	172.1(2)	N(1A)–Zn–N(2B)	96.6(2)
N(2A)–Zn–N(1B)	92.2(2)	N(2A)–Zn–N(2B)	111.7(2)
N(1A)–Zn–N(1C)	85.8(2)	N(2A)–Zn–N(1C)	137.5(2)
N(1B)–Zn–N(1C)	91.6(2)	N(2B)–Zn–N(1C)	110.6(2)
Zn–N(1A)–C(1A)	114.4(4)	Zn–N(1B)–C(1B)	115.7(4)
Zn–N(2A)–C(3A)	113.2(4)	Zn–N(2B)–C(3B)	117.2(4)
N(1A)–C(1A)–C(2A)	113.4(6)	N(1B)–C(1B)–C(2B)	115.2(6)
N(2A)–C(3A)–C(2A)	114.6(6)	N(2B)–C(3B)–C(2B)	116.1(5)
C(1A)–C(2A –C(3A)	111.4(6)	C(1B)–C(2B)–C(3B)	113.5(6)
C(1A)–C(2A)–C(4A)	108.5(6)	C(1B)–C(2B)–C(4B)	106.3(6)
C(1A)–C(2A)–C(5A)	109.2(6)	C(1B)–C(2B)–C(5B)	110.8(6)
C(3A)–C(2A)–C(4A)	112.1(6)	C(3B)–C(2B)–C(4B)	107.0(6)
C(3A)–C(2A)–C(5A)	106.6(6)	C(3B)–C(2B)–C(5B)	110.8(6)
C(4A)–C(2A)–C(5A)	109.0(6)	C(4B)–C(2B)–C(5B)	108.1(6)
Zn–N(1C)–C(1C)	112.9(4)	C(1C)–C(2C)–C(4C)	109.9(6)
N(1C)–C(1C)–C(2C)	116.4(6)	C(1C)–C(2C)–C(5C)	107.4(6)
C(1C)–C(2C)–C(3C)	112.7(6)	C(3C)–C(2C)–C(4C)	107.6(6)
C(2C)–C(3C)–N(2C)	117.4(6)	C(3C)–C(2C)–C(5C)	110.5(6)
C(4C)–C(2C)–C(5C)	108.7(6)		

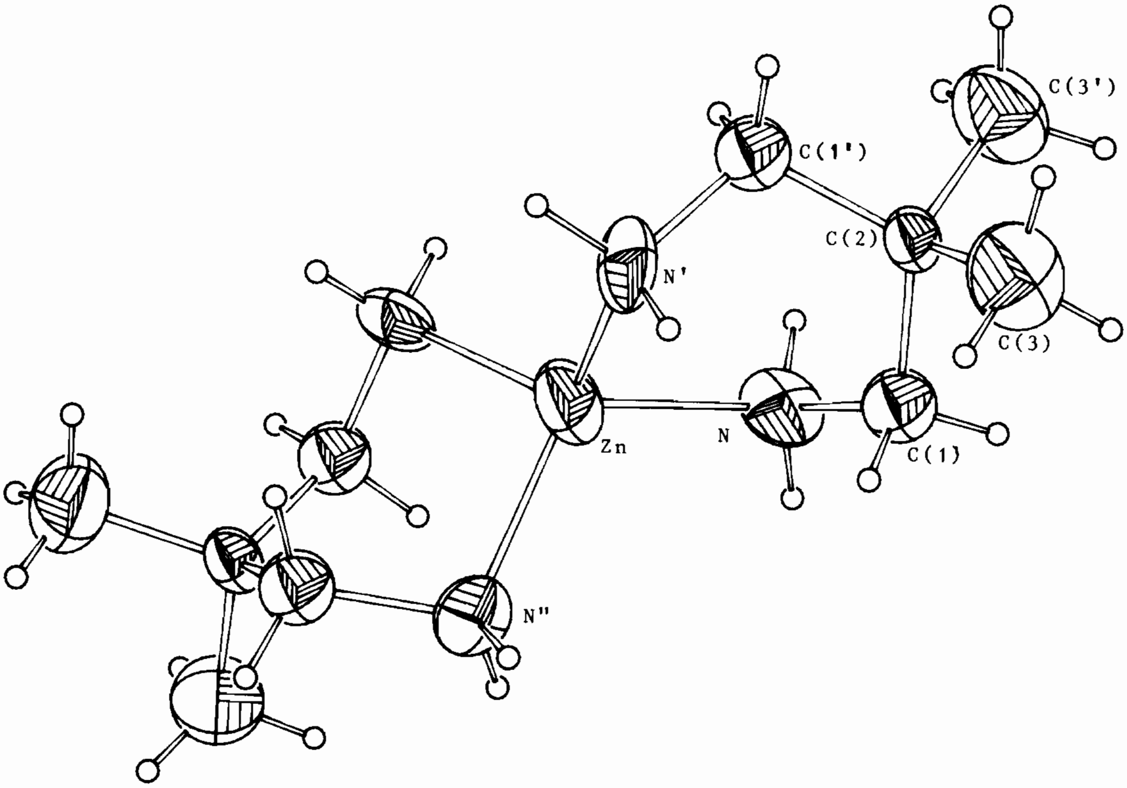


Fig. 1. ORTEP drawing of the $[Zn(dmpd)_2]^{2+}$ cation.

Results and Discussion

Description of the Structures

The structure of $Zn(dmpd)_2I_2$ consists of an ionic packing of discrete $[Zn(dmpd)_2]^{2+}$ cations and iodide anions with normal interionic distances. An ORTEP view of the cation is shown in Fig. 1. The Zn atom is tetrahedrally surrounded by four nitrogen atoms, originating from two chelating dmpd ligands. The actual point symmetry is lowered to D_{2d}, because of the presence of the chelating rings, requiring a bite-angle lower than the tetrahedral one. Its observed value (97.6(4)°) is larger than the corresponding angle in $Zn(dmpd)X_2$ (X = Cl 93.6(2)°, X = Br 93.0(2)°) [3]. The Zn–N interactions (2.041(7) Å) are not significantly larger than the ones found in $Zn(dmpd)X_2$ [3] (X = Cl 2.018(1), X = Br 2.024(4) Å) because of the high standard deviation in the present compound. The two symmetry equivalent metallo-cycles have a chair conformation.

In spite of the observed disorder, the distances within the dmpd ligands are reasonable, while the bond angles involving the C(1) atoms show significant deviations from the tetrahedral values.

The structure of $Zn(dmpd)_3Cl_2 \cdot H_2O$ consists of an ionic packing of discrete $[Zn(dmpd)_3]^{2+}$ cations (Fig. 2) and chloride anions, together with water molecules weakly bound both to Cl^- ions and to the 'free' NH_2 residual of the cations. Selected bond distances and angles are listed in Table 2.

The Zn atom is surrounded by five nitrogen atoms, deriving from three different dmpd ligands, two of which chelate the metal atom, while one is monodentate. The overall coordination geometry approaches an idealized trigonal bipyramidal symmetry, with the two chelate ligands occupying one axial and one equatorial position each. The remaining dmpd ligand coordinates the Zn atom in the remaining equatorial site and weakly interacts through the 'external' NH_2 group with the water molecule.

As already found in similar cases, the axial Zn–N distances show larger values than the equatorial ones ($Zn–N_{ax}$ average = 2.205, $Zn–N_{eq}$ average = 2.073 Å). Among the three equatorial Zn–N bond distances, the longest one appears to be the one belonging to the monodentate ligand (Zn–N(1C) = 2.093(5) Å). Moreover, the ZnN_5 coordination geometry shows slight distortion from the ideal *tbp* symmetry, with the two 'bite' angles of the chelate rings of 84.7(2) and 91.3(2)°. In the equatorial plane the distortion is even more sensible, the N(2A)–Zn–N(1C) angle being 137.5(2)°.

The C–N and C–C bond distances and angles in the organic ligands agree well with the standard literature values. However the two six-membered metallocycles, show different conformations: the A

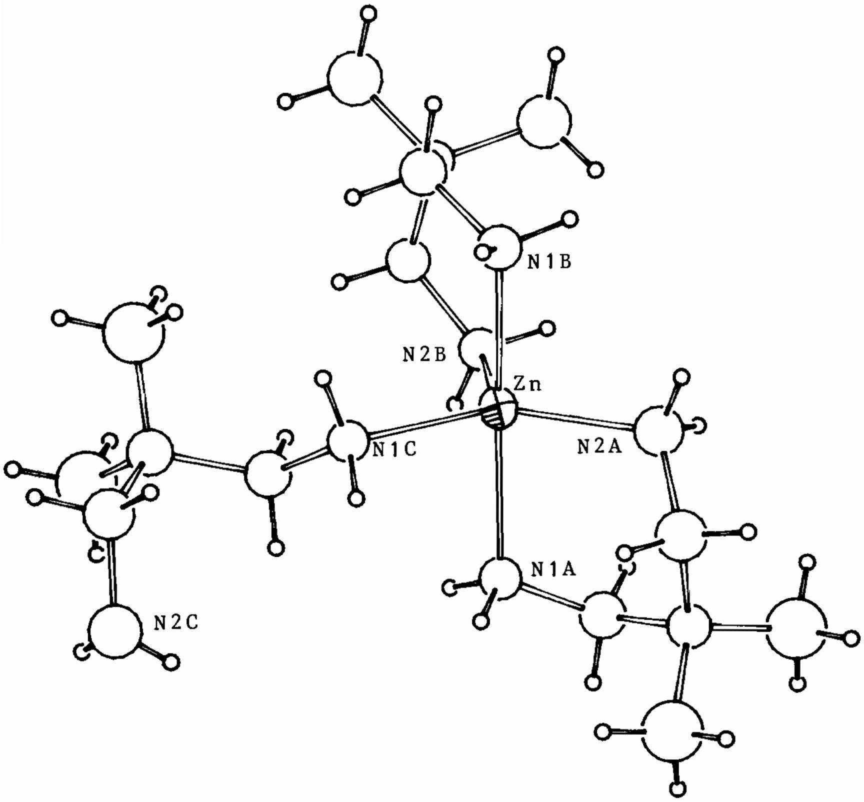


Fig. 2. ORTEP drawing of the $[Zn(dmpd)_3]^{2+}$ cation.

ring closely approaches a skew geometry, while the B ring is better described by a chair model. Although the refined positions of the hydrogen atoms of the water molecule are quite uncertain, the presence of a localized hydrogen bond with the non-coordinating amino group is evident; relevant bond distances for these interactions are N(2C)···OW = 2.79, N(2C)··· HW1 = 2.22, HW1–OW = 0.60 Å. A better defined hydrogen bond is the one formed by the OW, HW2 and Cl(1) atoms, with bond distances OW–HW2 = 1.17 and HW2···Cl(1) = 2.03 Å, the OW–HW2··· Cl(1) angle being 170°.

Infrared and Raman Results

Spectral range 4000–500 cm^{-1}

Our purposes were to assign NH_2 and Zn–N frequencies and to correlate vibrational and structural results, in order to ascertain possible analogies. In a previous paper [3] the main differences among dmpd complexes with the same stoicheiometries and formulae $[M(dmpd)X_2$ (M = Zn, Cd, Hg; X = Cl, Br, I)] but different molecular structures, were found in the 3310–3240 cm^{-1} spectral ranges where the stretching and twisting NH_2 vibrations, respec-

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

Compound	NH_2 stretching	NH_2 scissoring
$[Zn(dmpd)_2]Cl_2$[b]	3440m, 3300sh, 3220m	1582s
$[Zn(dmpd)_2]Br_2$[c]	3240s, 3200s, 3120s	1575s
$[Zn(dmpd)_2]I_2$[c]	3240s, 3200s, 3120s	1590s
$[Zn(dmpd)_3]Cl_2 \cdot H_2O$[b]	3430m, 3340m, 3300sh, 3260m, 3210m, 3110s	1600s, 1590s
$[Zn(dmpd)_3]Br_2 \cdot H_2O$[c]	3480s, 3350sh, 3280s, 3220s, 3120s	1595s, 1575s

[a]Abbreviations: s = strong; m = medium; sh = shoulder. [b]In nujol. [c]In KBr pellets.

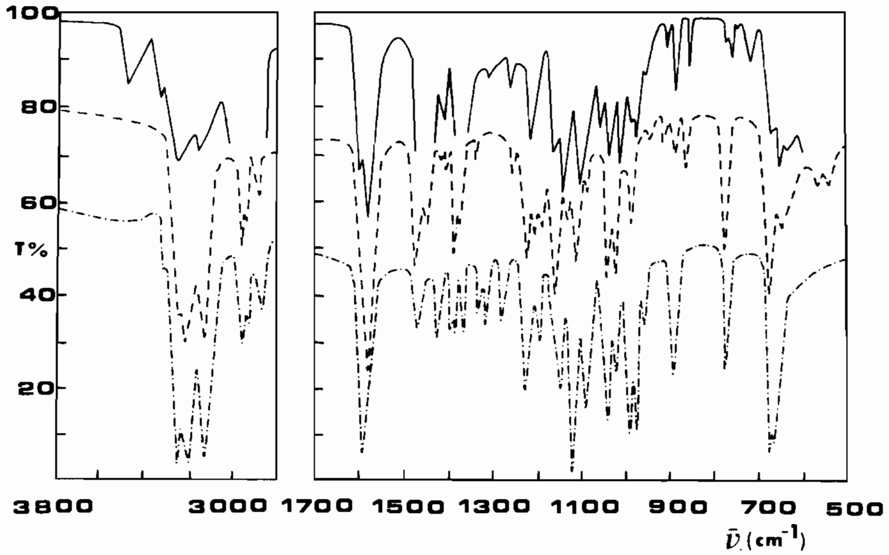


Fig. 3. Infrared spectra of $Zn(dmpd)_2Cl_2$ (in nujol mull) (——), $Zn(dmpd)_2Br_2$ (in KBr pellets) (– – –) and $Zn(dmpd)_2I_2$ (in KBr pellets) (– · –) compounds.

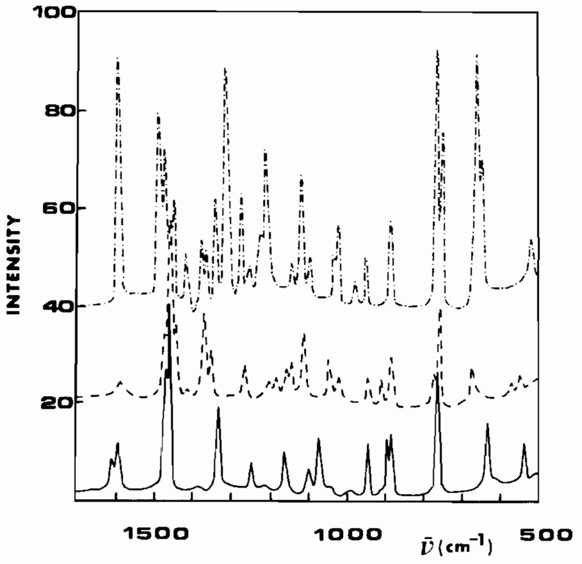


Fig. 4. Raman spectra of the $Zn(dmpd)_2Cl_2$ (——), $Zn(dmpd)_2Br_2$ (– – –) and $Zn(dmpd)_2I_2$ (– · –) compounds.

tively, appear [3, 5]. This permitted us to conclude that similarity in the spectra in the 4000–500 cm^{-1} spectral range is strongly suggestive of similarity in the molecular structure of the complexes. On this basis and by comparing infrared and Raman spectra of the compounds discussed in this paper, whose NH_2 stretching and scissoring vibrations (NH_2 twisting vibrations are unassignable being undistinguishable from C–N vibrations), in agreement with the literature data [3, 6–9] are reported in Table 3, we suggest the following conclusions: (i) for $Zn(dmpd)_3X_2 \cdot H_2O$ (X = Cl, Br) compounds, although some slightly spectroscopic differences exist, similar molecular structures can be reasonably suggested (Figs. 5 and 6); (ii) for $Zn(dmpd)_2X_2$ (X = Cl, Br, I) compounds it is not possible to infer similarity in the molecular structures because large spectroscopic differences are evident (Figs. 3 and 4).

Spectral range 500–100 cm^{-1}

In this spectral range differences among infrared and Raman spectra of $Zn(dmpd)_2X_2$ compounds are also observed, some bands which are common appearing in the characteristic spectral range of Zn–N vibrations [3, 6–11]. Therefore we can tentatively suggest a strict similarity at least in the first coordination sphere geometry of these complexes. Their infrared and Raman stretching frequencies, as reported in Table 4, are assigned on the basis of these considerations and agree with the predictable bands, three IR active and three Raman active (Table 5), calculated by considering a site symmetry D_{2d} and a factor group D_{4h}, as found in the $Zn(dmpd)_2I_2$ complex.

Table 4 also reports our tentative assignments of the Zn–N stretching vibrations for the $Zn(dmpd)_3X_2 \cdot H_2O$ complexes (X = Cl, Br). In the far IR of these complexes, starting from an idealized D_{3h} symmetry and considering a site symmetry C_1 and a factor group C_i five infrared and five Raman-active M–N stretching vibrations are expected (Table 6). These band assignments agree with the literature data [2, 3, 6–11].

Conclusions

In the present paper we have demonstrated that, in agreement with the variable coordinative capabil-

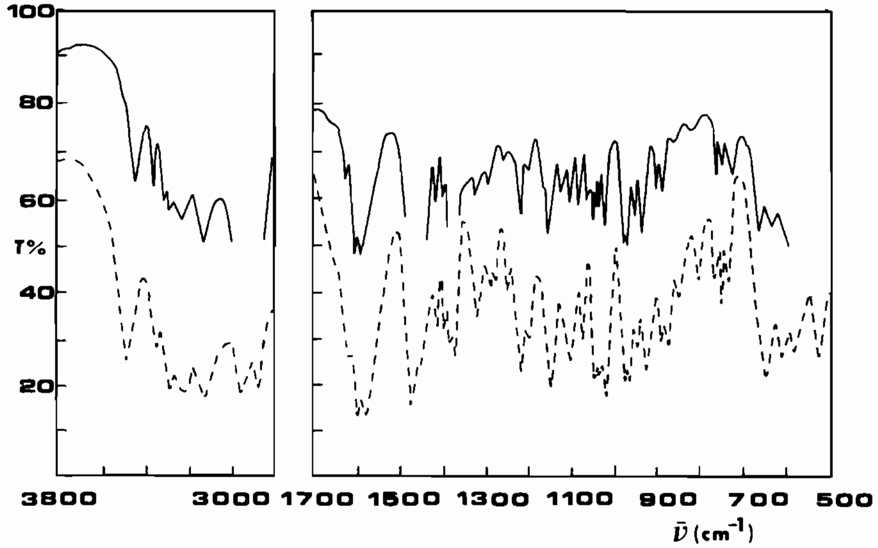


Fig. 5. Infrared spectra of $[Zn(dmpd)_3]Cl_2 \cdot H_2O$ (in nujol mull) (——) and $[Zn(dmpd)_3]Br_2 \cdot H_2O$ (in KBr pellets) (– – –).

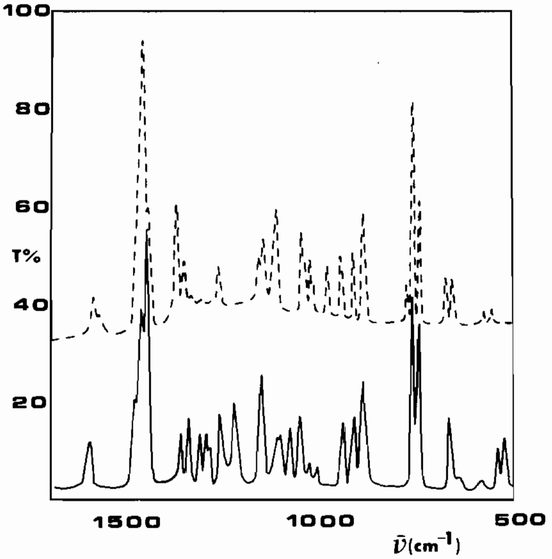


Fig. 6. Raman spectra of $[Zn(dmpd)_3]Cl_2 \cdot H_2O$ (——) and $[Zn(dmpd)_3]Br_2 \cdot H_2O$ (– – –).

TABLE 4. ν(Zn–N) Stretching Frequencies (cm^{-1})[a]

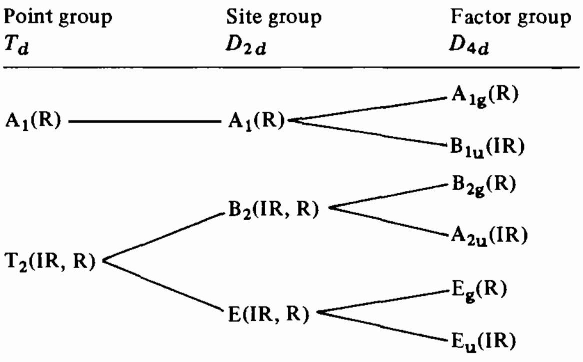
Compound		ν(Zn–N)
$[Zn(dmpd)_2]Cl_2$	IR	428m, 406s, 344s
	R	440m, 400w, 348w
$[Zn(dmpd)_2]Br_2$	IR	438m, 400s, 350m
	R	414m, 407m, 350m
$[Zn(dmpd)_2]I_2$	IR	414s, 398s, 352w
	R	443vs, 413s, 354w
$[Zn(dmpd)_3]Cl_2 \cdot H_2O$	IR	426sh, 406s, 400sh, 364w, 344m
	R	428m, 400s, 390s, 355m, 345sh
$[Zn(dmpd)_3]Br_2 \cdot H_2O$	IR	437m, 406sh, 398s, 362m, 340m
	R	440m, 410s, 400s, 355m, 340m

(continued)

TABLE 4. *(continued)*

[a]Abbreviations: s = strong; m = medium; w = weak; sh = shoulder; v = very; IR = infrared; R = Raman.

TABLE 5. Correlation Diagram and Selection Rules of the Zn–N Stretching Vibrations of the Compound $[Zn(dmpd)_2]Cl_2$



[a]Abbreviations: IR = infrared; R = Raman.

ity of propane-1,3-diamine [1, 2], 2,2-dimethylpropane-1,3-diamine can also give rise to very distinct structures.

Generally diamines, if not chelating, are expected to bridge different metal ions forming dimeric or polymeric structures [1, 2]. The crystal structure of 2 shows, however, an unpredicted coordination

TABLE 6. Correlation Diagram and Selection Rules of the Zn–N Stretching Vibration of Compounds $[Zn(dmpd)_3]X_2 \cdot H_2O$

Point group	Site group	Factor group
D_{3h}	C_1	C_i

$$\begin{tikzcd}
2A_1'(R) \arrow[dr] & & 5A_g(R) \arrow[dl] \\
A_2''(IR) \arrow[r] & 5A(IR, R) & \\
E'(IR, R) \arrow[ur] & & 5A_u(IR) \arrow[ul]
\end{tikzcd}$$

[a]Abbreviations: IR = infrared; R = Raman.

behavior of a dmpd ligand, which has one of its binding sites devoted to hydrogen bonding.

Supplementary Material

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

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