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Relation between Structures and Spectroscopic Properties of Group 2B Metal

[M(chelate)X₂] Complexes (X = Cl, Br, I). Crystal and Molecular Structure of

[H₂NCH₂(CH₃)₂CCH₂NH₂]MX₂ Complexes (M = Zn, X = Cl, Br; M = Cd, X = Br)

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The synthesis and structural and spectroscopic characterization of a series of d¹⁰ metal(II) compounds of the type [M(dmpd)X₂] (M = Zn(II), Cd(II), Hg(II); dmpd = 2,2-dimethylpropane-1,3-diamine; X = Cl, Br, I) are described. The different spectroscopic properties, which divide the complexes into two classes, are discussed and unambiguously assigned only on the basis of the knowledge of the crystal structure of compounds representative of each class. Therefore, the crystal structures of [Zn(dmpd)Cl₂] (I), [Zn(dmpd)Br₂] (II), and [Cd(dmpd)Br₂] (III) are determined from three-dimensional single-crystal X-ray data. The complexes are monoclinic, space groups *P*2₁/*m* for I and II and *P*2₁ for III, with two formula units in cells of the following dimensions: *a* = 6.014 (1) Å, *b* = 7.724 (1) Å, *c* = 10.483 (1) Å, and β = 91.32° for I; *a* = 6.234 (2) Å, *b* = 7.968 (2) Å, *c* = 10.628 (2) Å, and β = 91.81° for II; *a* = 11.288 (2) Å, *b* = 5.893 (1) Å, *c* = 7.622(1) Å, and β = 92.72° for III. The structures have been refined to *R* = 0.024, 0.036, and 0.025 for I, II, and III, respectively. The complexes I and II are isomorphous and isostructural. In these complexes the zinc atom is tetrahedrally surrounded by two halogen and two nitrogen atoms. The only difference between these complexes is the strength of hydrogen-bonding interactions. In the complex III the cadmium atom is octahedrally surrounded by four bromine atoms and two nitrogen atoms of a dmpd molecule. The octahedral moieties are linked in infinite chains by bromine bridges. In all the compounds the dmpd molecule acts as a chelating ligand, giving a six-membered chelate ring in a partially flattened chair conformation.

Introduction

The d¹⁰ metal(II)-halide adducts are rather interesting. They show a variety of coordination numbers and geometries, closely dependent on many factors, among which are interactions due to crystal-packing and hydrogen-bonding forces as well as metal ion and halide dimensions.² For these reasons, one must be very cautious in assigning the complex stereochemistry in the absence of structural data. Nevertheless, the majority of conclusions on the structures proposed are based largely on infrared evidence. We therefore undertook a systematic investigation of the structural and spectroscopic properties of a series of MX₂L (M = Zn(II), Cd(II), Hg(II); X = Cl, Br, I) complexes, where L is 2,2-dimethylpropane-1,3-diamine (hereafter abbreviated as dmpd).

Recently some complexes of dmpd with copper(II)³ and platinum(II)⁴ ions have been investigated. The crystal structures of [Cu(dmpd)₂(ClO₄)₂]³ and [Pt(dmpd)(malonate)]^{4a} show distorted-tetragonal-bipyramidal and square-planar metal coordination, respectively. In both cases, the ligand forms a six-membered chelate ring having a "flattened" chair conformation.

Further interest in the systems investigated here derives from a biological point of view, since it has been demonstrated that compounds with NH₂ groups of aliphatic amines show a significant antitumor activity as found for [Pt(dmpd)(malonate)].^{4a}

Experimental Section

All chemicals were reagent grade and used as received. 2,2-Dimethylpropane-1,3-diamine was kindly supplied by BASF.

Preparation of the Complexes. (i) [M(dmpd)X₂] (M = Zn, Cd, Hg; X = Cl, Br, I) Complexes. These complexes were obtained by mixing the MX₂ salt and dmpd in methanol with a metal to ligand 1:1 molar ratio. The compounds were recrystallized from methanol. Their deuterated analogues were prepared by recrystallization of the

compounds in tetradeuteriomethanol and deuterium oxide.

Zn(dmpd)Cl₂. Anal. Calcd for C₅H₁₄Cl₂N₂Zn: C, 25.16; H, 5.91; N, 11.75. Found: C, 25.01; H, 5.91; N, 11.47. Mp 264 °C.

Zn(dmpd)Br₂. Anal. Calcd for C₅H₁₄Br₂N₂Zn: C, 18.33; H, 4.31; N, 8.56. Found: C, 18.18; H, 4.38; N, 8.37. Mp 246 °C.

Zn(dmpd)I₂. Anal. Calcd for C₅H₁₄I₂N₂Zn: C, 14.24; H, 3.35; N, 6.65. Found: C, 14.34; H, 3.37; N, 6.37. Mp 274 °C.

Cd(dmpd)Cl₂. Anal. Calcd for C₅H₁₄CdCl₂N₂: C, 21.02; H, 4.94; N, 9.81. Found: C, 19.92; H, 4.88; N, 9.87. Mp >300 °C.

Cd(dmpd)Br₂. Anal. Calcd for C₅H₁₄Br₂CdN₂: C, 16.03; H, 3.77; N, 7.48. Found: C, 16.10; H, 3.75; N, 7.53. Mp 257 °C.

Cd(dmpd)I₂. Anal. Calcd for C₅H₁₄CdI₂N₂: C, 12.81; H, 3.01; N, 5.98. Found: C, 12.83; H, 2.98; N, 5.92. Mp 204 °C.

Hg(dmpd)Cl₂. Anal. Calcd for C₅H₁₄Cl₂HgN₂: C, 16.06; H, 3.78; N, 7.50. Found: C, 16.10; H, 3.85; N, 7.52. Mp 200 °C.

Hg(dmpd)Br₂. Anal. Calcd for C₅H₁₄Br₂HgN₂: C, 12.97; H, 3.05; N, 6.06. Found: C, 13.00; H, 3.07; N, 6.06. Mp 186 °C.

Hg(dmpd)I₂. Anal. Calcd for C₅H₁₄I₂HgN₂: C, 10.78; H, 2.54; N, 5.03. Found: C, 10.85; H, 2.53; N, 5.05. Mp 154 °C.

(ii) [MX₂]dmpdH₂ (M = Zn, X = Cl, Br; M = Cd, X = Br; M = Hg, X = I) Complexes. These complexes were obtained by adding 5 mmol of MX₂ to an aqueous solution of HX containing 5 mmol of dmpd. A precipitate was obtained that was then filtered and dried under vacuum.

[ZnCl₂]dmpdH₂. Anal. Calcd for C₅H₁₆Cl₄N₂Zn: C, 19.27; H, 5.18; N, 8.99. Found: C, 19.24; H, 5.25; N, 9.08. Mp 275 °C.

[ZnBr₂]dmpdH₂. Anal. Calcd for C₅H₁₆Br₄N₂Zn: C, 12.26; H, 3.29; N, 5.72. Found: C, 12.23; H, 3.25; N, 5.78. Mp 286 °C.

[CdBr₄]dmpdH₂. Anal. Calcd for C₅H₁₆Br₄CdN₂: C, 11.19; H, 3.01; N, 5.22. Found: C, 10.78; H, 3.01; N, 4.98. Mp 265 °C.

[HgI₄]dmpdH₂. Anal. Calcd for C₅H₁₆I₄HgN₂: C, 7.38; H, 1.98; N, 3.45. Found: C, 7.54; H, 2.21; N, 3.52. Mp 278 °C.

Physical Measurements. Infrared spectra were recorded on a Beckman 4250 spectrophotometer as Nujol mulls or KBr pellets in the 300–4000-cm⁻¹ range (no difference was observed among spectra obtained by these two different methods) and a Perkin-Elmer 180 spectrophotometer as Nujol mulls on polythene, as support, in the 100–500-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 elemental analyzer.

X-ray Data Collection, Structure Determination, and Refinement. The refined cell constants and other relevant crystal data for the three compounds [Zn(dmpd)Cl₂] (I), [Zn(dmpd)Br₂] (II), and [Cd(dmpd)Br₂] (III) are presented in Table I, together with details of intensity measurements. The intensity data for compounds I and III were collected on an Enraf-Nonius CAD-4 diffractometer, while the

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Table I. Details of Data Collection and Structures for the Three Compounds

	Zn(dmpd)Cl ₂ (I)	Zn(dmpd)Br ₂ (II)	Cd(dmpd)Br ₂ (III)
formula	C ₅ H ₁₄ Cl ₂ N ₂ Zn	C ₅ H ₁₄ Br ₂ N ₂ Zn	C ₅ H ₁₄ Br ₂ CdN ₂
mol wt	238.5	327.4	374.4
cryst syst	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>m</i> (No. 11)	<i>P</i> 2 ₁ / <i>m</i> (No. 11)	<i>P</i> 2 ₁ (No. 4)
<i>a</i> , Å	6.014 (1)	6.234 (2)	11.288 (2)
<i>b</i> , Å	7.724 (1)	7.968 (2)	5.893 (1)
<i>c</i> , Å	10.483 (1)	10.628 (2)	7.622 (1)
β , deg	91.32 (1)	91.81 (3)	92.72 (1)
<i>V</i> , Å ³	486.8	527.7	506.2
<i>Z</i>	2	2	2
ρ_{calcd} , g cm ⁻³	1.63	2.06	2.46
abs coeff	30.8	98.3	99.1
$\mu(\text{Mo K}\alpha)$, cm ⁻¹			
cryst size, mm	0.04 × 0.28 × 0.30	0.12 × 0.35 × 0.38	0.10 × 0.13 × 0.38
radiation (λ , Å)	Mo K α (0.71073)	Mo K α	Mo K α
scan type	ω scan	ω scan	ω scan
scan width, deg	1.2 + 0.347 tan θ	1.2	1.1 + 0.347 tan θ
max scan speed, deg/min	4.0	2.4	3.3
data collection range, deg	3 < θ < 26	3.5 < θ < 27	3 < θ < 26
part of the sphere	$\pm h, k, l$	$\pm h, k, l$	$\pm h, k, l$
no. of unique data	1027	1236	1077
no. of data used in the refinements	867 (<i>I</i> > 3 σ)	907 (<i>I</i> > 2.5 σ)	836 (<i>I</i> > 3 σ)
cryst decay	no decay	no decay	no decay
max and min transmission factors	1.00–0.67	0.25–0.05	1.00–0.73
weighting fudge factor	0.04	0.03	0.02
<i>R</i>	0.024	0.036	0.025
<i>R</i> _w	0.032	0.045	0.028

data of compound II were measured on the BASIC⁵ diffractometer. All the data were corrected for Lorentz and polarization effects. An empirical absorption correction was applied to data of compounds I and III by measuring the intensities of two reflections with χ near to 90° for different ψ values (ψ 0–360° every 10°). The data of compound II were corrected by using a local program based on the method of Busing and Levy.⁶

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. In compounds I and II hydrogen atoms were refined isotropically, while in compound III they were located in their ideal positions (C–H = 0.95 Å) after each cycle of refinement. For the noncentrosymmetric compound III both the possible structure enantiomers were refined, taking into account the anomalous scattering effects, with the final solution exhibiting very slightly lower values for the agreement indices.

Computations for structures I and III were performed on a PDP 11/34 computer using the Enraf-Nonius structure determination package (SDP), while for compound II local programs were used on a UNIVAC 1100/80 computer.

The final values of the *R* and *R*_w conventional agreement indices and the fudge factor for weighting are reported in Table I. The atomic scattering factors for compound II were taken from ref 7 for the non-hydrogen atoms and from ref 8 for hydrogen and were corrected for the real and imaginary parts of the anomalous scattering according to ref 9. The final difference Fourier maps were in all cases flat,

Table II.^a Selected Bond Distances (Å) and Angles (deg) within [Zn(dmpd)X₂] (X = Cl, Br)

	X = Cl	X = Br
Zn–X(1)	2.212 (1)	2.350 (1)
Zn–X(2)	2.290 (1)	2.418 (1)
Zn–N	2.018 (1)	2.024 (4)
N–C(1)	1.494 (4)	1.484 (6)
C(1)–C(2)	1.544 (4)	1.528 (7)
C(2)–C(3)	1.513 (7)	1.524 (12)
C(2)–C(4)	1.538 (7)	1.520 (11)
X(1)–Zn–X(2)	108.2 (1)	107.8 (1)
X(1)–Zn–N	122.0 (1)	122.5 (1)
X(2)–Zn–N	104.3 (1)	104.2 (1)
N–Zn–N ⁱ	93.6 (2)	93.0 (2)
Zn–N–C(1)	112.6 (2)	112.4 (3)
N–C(1)–C(2)	114.3 (3)	115.1 (5)
C(1)–C(2)–C(1) ⁱ	113.0 (4)	112.7 (5)
C(1)–C(2)–C(3)	111.3 (3)	111.4 (4)
C(1)–C(2)–C(4)	106.1 (3)	106.6 (4)
C(3)–C(2)–C(4)	108.9 (5)	107.7 (7)

^a Related position for i: $x, 1/2 - y, z$.

Table III.^a Selected Bonding Parameters within [Cd(dmpd)Br₂]

Distances (Å)			
Cd–Br(1)	2.925 (4)	N(1)–C(1)	1.44 (1)
Cd–Br(1) ⁱ	2.971 (4)	N(2)–C(2)	1.49 (1)
Cd–Br(1) ⁱⁱ	3.005 (1)	C(1)–C(3)	1.51 (1)
Cd–Br(2)	2.583 (1)	C(2)–C(3)	1.52 (1)
Cd–N(1)	2.295 (6)	C(3)–C(4)	1.55 (3)
Cd–N(2)	2.293 (6)	C(3)–C(5)	1.56 (1)
Angles (deg)			
Br(1)–Cd–Br(1) ⁱⁱ	91.8 (1)	Br(1)–Cd–Br(1) ⁱ	176.3 (1)
Br(1)–Cd–Br(2)	91.3 (1)	Br(1) ⁱⁱ –Cd–N(1)	164.8 (1)
Br(1)–Cd–N(1)	86.7 (6)	Br(2)–Cd–N(2)	162.3 (2)
Br(1)–Cd–N(2)	91.4 (6)	Cd–N(1)–C(1)	119.0 (6)
Br(1) ⁱ –Cd–Br(1) ⁱⁱ	90.9 (1)	Cd–N(2)–C(2)	118.6 (7)
Br(1) ⁱ –Cd–Br(2)	91.4 (1)	N(1)–C(1)–C(3)	119.8 (1)
Br(1) ⁱ –Cd–N(1)	90.0 (6)	N(2)–C(2)–C(3)	116.7 (10)
Br(1) ⁱ –Cd–N(2)	86.7 (6)	C(1)–C(3)–C(2)	112 (1)
Br(1) ⁱⁱ –Cd–Br(2)	86.6 (1)	C(1)–C(3)–C(4)	112 (1)
Br(1) ⁱⁱ –Cd–N(2)	75.9 (2)	C(1)–C(3)–C(5)	108 (1)
Br(2)–Cd–N(1)	108.6 (1)	C(2)–C(3)–C(4)	111 (1)
N(1)–Cd–N(2)	88.9 (2)	C(2)–C(3)–C(5)	106 (1)
		C(4)–C(3)–C(5)	108 (1)

^a Related positions: (i) $x, y - 1, z$; (ii) $-x, y - 1/2, -z$.

showing only random residual peaks not exceeding ca. 0.5 e/Å³. Bond distances and angles are reported in Table II for compounds I and II and in Table III for compound III. The final positional and thermal parameters and computed and observed structure factor moduli for the three compounds are given in the supplementary material.

Results and Discussion

All the compounds are stable in air and soluble in polar organic solvents. Their spectroscopic properties are such as to divide them into two classes: (A) [Zn(dmpd)X₂] (X = Br, I) and [M(dmpd)I₂] (M = Cd, Hg); (B) [M(dmpd)X₂] (M = Cd, Hg; X = Cl, Br). Furthermore, the Zn(dmpd)Cl₂ compound has spectroscopic properties different from either class. This different spectroscopic behavior was clarified by X-ray diffraction analysis of typical members of each class.

Molecular and Crystal Structures. (i) **Class A Complexes—Description of the Structures of the [Zn(dmpd)X₂] (X = Cl, Br) Complexes.** The two derivatives are isomorphous and isostructural (see Table I), with the molecule lying on a crystallographic mirror plane passing through X(1), X(2), Zn, C(2), C(3), and C(4) atoms. A view of the bromide derivative is reported in Figure 1. The zinc atom is tetrahedrally surrounded by two halogen and two nitrogen atoms; the dmpd

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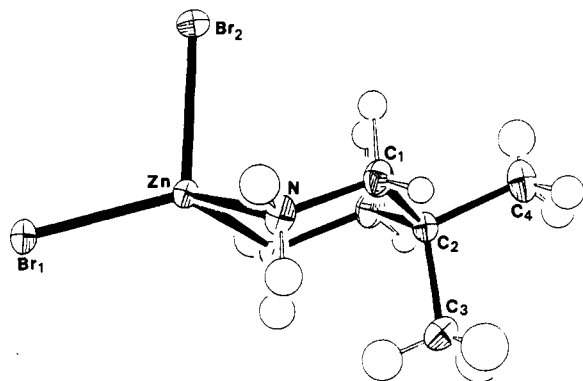


Figure 1. View of [Zn(dmpd)Br₂] representative also of the [Zn(dmpd)Cl₂] complex. The complex lies on a crystallographic mirror plane passing through the Br(1), Br(2), Zn, C(2), C(3), and C(4) atoms.

acts as a chelating ligand, giving a six-membered ring with a "chair" conformation where the "substituents" X(1) and C(4) are equatorial and X(2) and C(3) are axial. The Zn–N bond distances (2.018 (3) Å for X = Cl and 2.024 (4) Å for X = Br) are normal for this class of compounds (see ref 10 for a tabulation of Zn–N and Zn–Cl bond lengths) and are not significantly different in the two derivatives, just as all the other bonding parameters within the metallacycle. The zinc to chlorine distances, 2.212 (1) Å for Cl(1) and 2.290 (1) Å for Cl(2), are surprisingly different. A similar trend was found for the Zn–Br bond lengths (2.350 (1) and 2.418 (1) Å), although they are less dissimilar ($\Delta = 0.068$ vs. 0.078 Å). Another unexpected feature involves the inner angles of the coordination sphere of the zinc atom: both the molecules, in fact, display unusually small X–Zn–X angles (108.2 (1)°, X = Cl; 107.8 (1)°, X = Br) and exhibit a strong difference between the $X_{\text{axial}}\text{--Zn--N}$ (104.3 (1)°, X = Cl; 104.2 (1)°, X = Br) and the $X_{\text{equat}}\text{--Zn--N}$ angles (122.0 (1)°, X = Cl; 122.5 (1)°, X = Br). These angular values are consistent with a rotation of the halides about the axis that is normal to the X(1), Zn, X(2) plane (and passes through the Zn atom) in the same direction of ca. 21° for X(1) and ca 9° for X(2) from their idealized positions.

In the chloride derivative there is an intermolecular Cl(1)⋯Cl(2) contact of 3.93 Å, whereas such a contact should be 3.01 Å, if an "idealized" coordination geometry is assumed as suggested by the angular values normally found in the literature for similar complexes^{10,11} (Cl–Zn–Cl = 120°, Zn–Cl(1,2) = 2.23 Å, Cl(1)–Zn–N equal to Cl(2)–Zn–N). This fact, effective also for the bromide derivative, suggests that the packing forces are very probably responsible for the distortions present in these compounds. Besides normal van der Waals interactions, these packing forces also imply intermolecular hydrogen bonding between the halogens (X(2) more than X(1)) and the hydrogen atoms bound to nitrogen (Cl(2)⋯N = 3.31 Å, Br(2)⋯N = 3.43 Å). Consequently different strengths of the hydrogen bonds should be expected for the two isostructural derivatives.

(ii) Class B Complexes—Description of the Structure of the [Cd(dpmd)Br₂] Complex. The cadmium atom is octahedrally surrounded by four bromine atoms and two nitrogen atoms of a dpmd molecule. A view of the coordination sphere is shown in Figure 2. These octahedral moieties are linked in infinite chains by bromine bridges as shown in Figure 3. The Br(1) atom is involved in three interactions with metal atoms, which are much larger (mean 2.967 Å) than the single contact Cd–Br(2) of 2.583 (1) Å, a situation present also in [Cd-

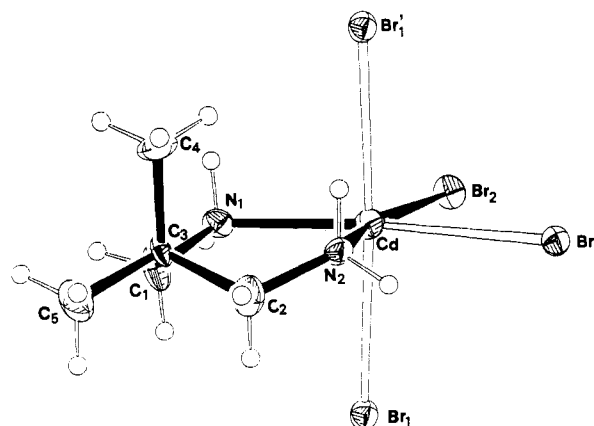


Figure 2. Coordination about the metal atom in the [Cd(dmpd)Br₂] complex.

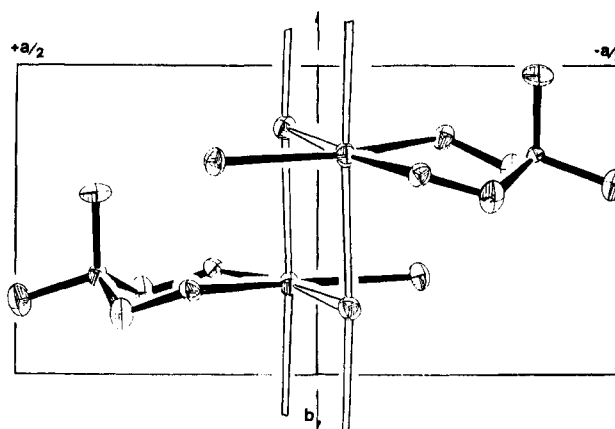


Figure 3. Projection of the structure of [Cd(dmpd)Br₂] in the *ab* plane showing the polymeric nature of the complex. The chain grows about the screw axis. Hydrogen atoms are omitted for clarity.

(tn)Cl₂] (tn = 1,3-diaminopropane).¹² The dmpd ligand forms a six-membered chelate ring with a "chair" conformation flattened at the CdN₂ end. This flattening is evidenced by a decrease of the dihedral angle (D_1)¹³ between the NMN and NCCN planes, decreasing from 60°, in the ideal chair, to 20.7° in this compound, and by an increase in the M–N–C angles (mean 119°) with respect to the ideal value 109.5°. Similar flattenings are observed in many square-planar and octahedral diamine complexes, for instance, in [Cd(tn)Cl₂] (Cd–N–C = 120.3 (4) and 119.8 (4)°),¹² [Cr(tn)₃]³⁺ (Cr–N–C (mean) = 120.7°, D_1 (mean) = 28.5°),¹³ and [Pt(dmpd)X] (X = malonate) (Pd–N–C = 121.0 (3)°, D_1 = 2.4°),¹⁴ while the chelate ring in tetrahedral complexes seems to be less flattened. In the [Zn(dmpd)X₂] complexes, for instance, D_1 and the Zn–N–C angles are 45.8 and 112.6 (2)° when X = Cl and 45.5 and 112.4 (3)° when X = Br; analogously in the [M(BSN)I₂] complexes (BSN = 1,3-bis(methylamino)-2,2-dimethylpropane, M = Zn, Cd) the M–N–C angle mean values are 110.9° when M = Zn and 111.8° when M = Cd.¹⁴

Nonbonding contacts involving the halogen atoms, including the possible hydrogen bond contacts, are reported in the supplementary material for the three compounds. It is relevant to note that the shortest nonbonding Br⋯N contact in [CdBr₂(dmpd)] is 3.31 Å vs. a value of 3.34 Å found in [ZnBr₂(dmpd)].

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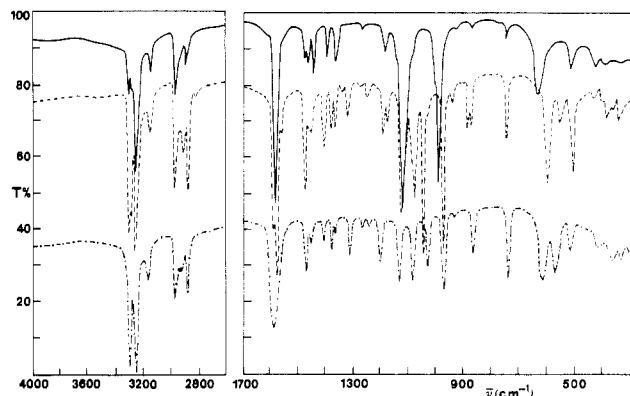


Figure 4. Infrared spectra of [Zn(dmpd)Br₂] (—), [Cd(dmpd)Br₂] (---), and [Zn(dmpd)Cl₂] (· · ·) in KBr pellets.

Table IV. Infrared Frequencies (cm⁻¹)^a

compd	NH ₂ str	NH ₂ sciss	NH ₂ twist + CN str
Zn(dmpd)Cl ₂	3295 s, 3240 s	1585 s	1145 m, 1100 m, 1040 m
Zn(dmpd)Br ₂	3300 m, 3250 s	1590 vs 1130 vs, 997 vs	
Zn(dmpd)I ₂	3290 m, 3245 s	1588 vs 1125 vs, 1015 sh, 995 vs	
Cd(dmpd)I ₂	3300 m, 3250 s	1580 vs 1087 vs, 1000 vs, 990 vs	
Hg(dmpd)I ₂	3310 m, 3250 s	1582 vs 1050 m, 995 vs, 985 vs	
Cd(dmpd)Cl ₂	3285 s, 3280 sh, 3245 vs	1580 vs 1128 m, 1080 m, 1050 s, 1000 m, 978 vs	
Cd(dmpd)Br ₂	3290 s, 3280 sh, 3240 vs	1585 vs 1125 m, 1080 m, 1050 vs, 975 vs	
Hg(dmpd)Cl ₂	3290 s, 3240 vs	1575 vs 1115 m, 1050 vs, 981 vs	
Hg(dmpd)Br ₂	3300 s, 3250 vs	1580 vs 1115 m, 1055 vs, 985 vs	

^a Abbreviations: s = strong; m = medium; vs = very strong; sh = shoulder.

Spectroscopic Results. The assignment of IR and Raman ligand bands are based on the literature data reported both for the [MX₂(dmpd)] complexes (M = Pd, Pt; X = Cl)⁴ and for the ethylenediamine complexes. The spectra of our complexes, although more complicated, present many features in common with these. Comparison with the spectra of the deuterated analogues of our complexes strongly confirms our assignments.

4000–500-cm⁻¹ Spectral Range. The main differences among the infrared spectra of the class A and B complexes are in regard to the NH₂ stretching and twisting vibrations (Figure 4). These bands, assigned on the basis of data reported in the literature^{4,15–22} and by comparison with the spectra of the corresponding NH₂-deuterated complexes, are collected in Table IV. In particular the NH₂ twisting and CN stretching vibrations are reported together, since for some compounds they are not well distinguishable, appearing at very similar frequency values. The Raman bands are not reported, as the differences in the Raman spectra between class A and B compounds are less evident, as exemplified in Figure 5.

The differences in the spectroscopic properties of the class A and B compounds should be ascribed to their structural differences such as the "flattening" of the chair conformation of the ligand and the hydrogen-bonding interactions between halides and the NH₂ groups. Both these factors are greater

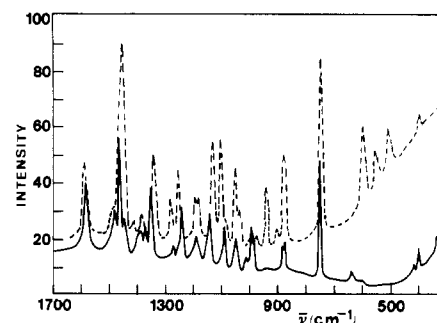


Figure 5. Raman spectra of solid [Zn(dmpd)Br₂] (—) and [Cd(dmpd)Br₂] (---).

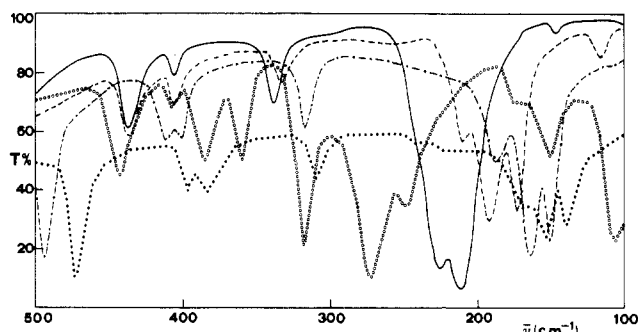


Figure 6. Infrared spectra (Nujol mulls) of [Zn(dmpd)Br₂] (—), [Zn(dmpd)I₂] (---), [Cd(dmpd)I₂] (· · ·), [Hg(dmpd)I₂] (— · —), and [Zn(dmpd)Cl₂] (○).

Table V. Metal-Halogen Stretching Frequencies (cm⁻¹) for Pseudotetrahedral Complexes with C_{2v} Symmetry Restricted to the Skeleton N₂MX₂^a

compd	ν _{as}		ν _s	
	IR	R	IR	R
Zn(dmpd)Cl ₂	276 vs		320 s	310 ms
Zn(dmpd)Br ₂	226 sh		213 vs	210 vs
Zn(dmpd)I ₂	192 s	193 w	173 s	173 ms
Cd(dmpd)I ₂	165 vs	167 w	150 s	147 vs
Hg(dmpd)I ₂	154 s	160 w	140 s	137 vs

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

in class B than in class A complexes. The infrared spectra of the two class A complexes [Zn(dmpd)Cl₂] and [Zn(dmpd)Br₂] show different patterns (Figure 4). The unexpected spectral differences in two isostructural derivatives may be associated with the different strengths of hydrogen-bonding interactions as found in the structures.

The presence of stronger halogen...NH₂ interactions in [ZnCl₂(dmpd)] vs. [ZnBr₂(dmpd)] give rise to a situation for the aminic groups that has some resemblance to that in [CdBr₂(dmpd)] and may be responsible for a certain similarity of the IR spectra of their NH₂ groups. This above all depends on the fact that the vibrations of these groups, involving very small masses, may occur independently of the vibrations of the remaining part of the molecule and therefore do not represent the coordination geometry of the dmpd molecule in the complex.

500–100-cm⁻¹ Spectral Range. The differences among the far-IR spectra of the class A and B compounds are related to the different geometries around the metal ion. In [Zn(dmpd)Cl₂] and [Zn(dmpd)Br₂] (representative of class A complexes), the metal ion is involved in a distorted-tetrahedral N₂ZnX₂ skeleton with an idealized C_{2v} symmetry.

For these complexes both the symmetric and antisymmetric MX₂ and MN₂ stretching vibrations are infrared and Raman active. All the class A complexes present two well-resolved

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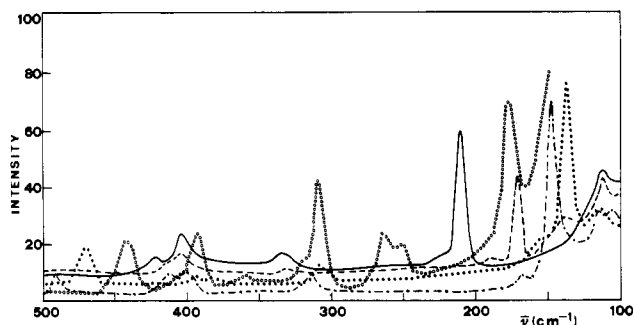


Figure 7. Raman spectra of solid [Zn(dmpd)Br₂] (—), [Zn(dmpd)I₂] (---), [Cd(dmpd)I₂] (-·-·-), [Hg(dmpd)I₂] (···), and [Zn(dmpd)Cl₂] (○).

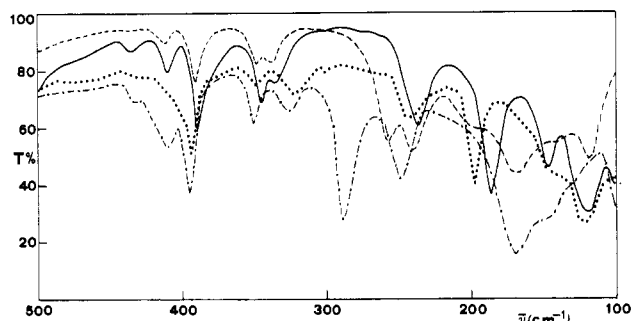


Figure 8. Infrared spectra (Nujol mulls) of [Cd(dmpd)Br₂] (—), [Cd(dmpd)Cl₂] (---), [Hg(dmpd)Cl₂] (-·-·-), and [Hg(dmpd)Br₂] (···).

far-infrared bands attributable to the metal-halogen stretching vibrations (Figure 6 and Table V). For some of these complexes the corresponding Raman spectra show only one strong band, which is assigned to the symmetric MX₂ stretching vibration, as this mode is expected to present a higher Raman intensity than the antisymmetric one (Figure 7 and Table V). The positions of the bands, which are sensitive to the mass of the halogens, perfectly agree with the literature data for other tetrahedral MX₂L₂ complexes having C_{2v} symmetry.²³⁻²⁹ Then the far-IR spectra of the [M(dmpd)X₂] complexes, where M = Zn, X = Cl, Br, I, and M = Cd, Hg, X = I, namely, all the class A complexes, which are very similar, to one another, confirm that these complexes must have the same molecular structure. To explain the far-IR spectrum of the polymeric [Cd(dmpd)Br₂] complex, which represents the class B complexes, we used as a model the N₂CdBr₄ skeleton formed by the two nitrogen atom ligands, one terminal bromine atom, and three bridging bromine atoms shared among three metal atoms. In fact, in Figure 2 it is possible to individuate a symmetry plane passing through the N(1), N(2), Br(1), and Br(2) atoms. Then for an idealized C_s symmetry four IR- and Raman-active metal-halogen stretching vibrations and one cadmium-terminal bromine ($\nu(\text{Cd}-\text{Br})_t$) and three cadmium-bridging bromine ($\nu(\text{Cd}-\text{Br})_b$) stretching modes are expected. In particular, according to the literature data³⁰⁻³² the three $\nu(\text{Cd}-\text{Br})_b$ vibrations may be expected at frequency values

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Table VI. Metal-Halogen Stretching Frequencies (cm⁻¹)^a for Pseudooctahedral Complexes with Idealized C_s Symmetry Restricted to the N₂MX₄ Skeleton

compd	$\nu(\text{MX})_t$		$\nu(\text{MX})_b$	
	IR	R	IR	R
Cd(dmpd)Cl ₂	257 ms	250 sh 230 vs, br	170 ms, br	
Cd(dmpd)Br ₂	186 s	175 m	146 m	142 vs
Hg(dmpd)Cl ₂	288 s	280 ms	168 s, br	
Hg(dmpd)Br ₂	199 s	190 vs	121 s, br	

^a t and b denote terminal and bridging $\nu(\text{MX})$ stretching modes, respectively. Abbreviations: s = strong; m = medium; sh = shoulder; br = broad; IR = infrared; R = Raman.

Table VII. $\nu(\text{M}-\text{N})$ Stretching Frequencies (cm⁻¹)

compd	$\nu(\text{M}-\text{N})$	
Zn(dmpd)Cl ₂	IR	444 m, 386 ^a m, 362 ^a m
	R	442 m, 393 m, 361 w
Zn(dmpd)Br ₂	IR	437 m, 338 m
	R	425 w, 335 w
Zn(dmpd)I ₂	IR	437 m, 334 mw
	R	420 w, 330 w
Cd(dmpd)I ₂	IR	411 ^a m, 401 m, 316 m
	R	413 ^a m, 400 ^a m, 315 m
Hg(dmpd)I ₂	IR	398 m, 381 ^a m, 310 m
	R	395 w, 382 w, 310 m
Cd(dmpd)Cl ₂	IR	390 ms, 349 mw, 338 mw
	R	440 w, 390 m, 350 w
Cd(dmpd)Br ₂	IR	435 w, 390 ms, 345 m, 336 mw
	R	435 w, 384 m, 343 w
Hg(dmpd)Cl ₂	IR	434 w, 399 ms, 351 m
	R	410 ^a m, 350 w
Hg(dmpd)Br ₂	IR	434 sh, 394 ms, 349 w
	R	400 m, 345 w

^a The band has been considered because it is very much stronger than the corresponding band of the [dmpdH₂]²⁺ dication. Abbreviations: m = medium; w = weak; sh = shoulder; ms = medium strong; mw = medium weak; IR = infrared; R = Raman.

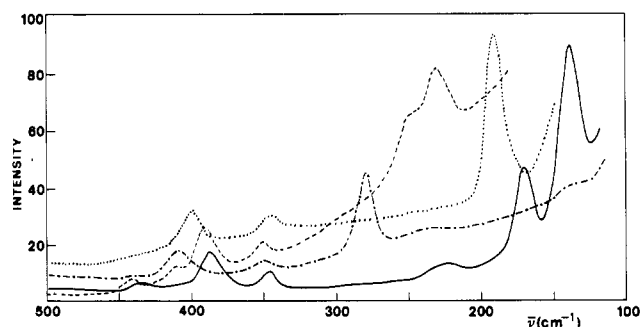


Figure 9. Raman spectra of solid [Cd(dmpd)Br₂] (—), [Cd(dmpd)Cl₂] (---), [Hg(dmpd)Cl₂] (-·-·-), and [Hg(dmpd)Br₂] (···).

lower than 180 cm⁻¹, while $\nu(\text{Cd}-\text{Br})_t$ should be observed in the 180-200-cm⁻¹ spectral range. If an idealized C_s symmetry is also assumed for [Cd(dmpd)Cl₂], three $\nu(\text{Cd}-\text{Cl})_b$ bands are expected at frequencies lower than 200 cm⁻¹³⁰⁻³³ and $\nu(\text{Cd}-\text{Cl})_t$ is expected at about 280 cm⁻¹.^{32,33}

As the far-IR spectra of the [Hg(dmpd)X₂] complexes (X = Cl, Br) are very similar to those of the cadmium analogues (Figures 8 and 9 and Table VI), we may also suggest that all the class B complexes should have the same molecular structures.

Our infrared and Raman assignments are reported in Table VI. The assignments of the mercury-halogen bands strictly agree with those reported for similar complexes.^{24,29,34,35} It

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Table VIII

M	X		
	Cl	Br	I
Zn	A	A	A
Cd	B	B	A
Hg	B	B	A

is worth noting that for all class B compounds we found only one broad band for the metal-bridging halogen stretching vibrations instead of three, since probably the three expected frequencies have accidentally very similar values.

In the far-IR spectra of all our complexes, on the basis of their idealized symmetries two IR- and Raman-active M-N stretching vibrations are expected. In assigning these bands, which must occur in the same spectral range as those found in ethylenediamine and 1,3-propanediamine complexes (300-500 cm^{-1}),^{16,17,19,20,22,36,37} one must proceed cautiously, as other vibrations may appear in the same positions. The differences in both infrared and Raman spectra of class A and B compounds could derive either from their structural differences or from different mixing of the M-N vibration with other vibrations. The latter assumption seems to be confirmed by an unusually large difference found between the asymmetric and symmetric M-N stretching frequencies. The bands reported in Table VII for the probable (M-N) stretching frequencies are assigned by comparing the spectra of the complexes with those of a series of $[\text{MX}_4(\text{dmpdH}_2)]$ complexes,³⁸

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in which M-N bands are absent. Furthermore, the assignment of these bands also takes into account that differences in metal or halogen masses influence the M-N band position.

Conclusion

According to infrared, Raman, and X-ray analysis we classified the complexes of the group 2B metals of general formula $[\text{M}(\text{dmpd})\text{X}_2]$ into two classes. Results are reported in Table VIII. Class A contains tetrahedral complexes and class B octahedral. In both classes the dmpd forms a six-membered chelate ring, which shows a "chair" conformation more (group B) or less (group A) flattened. Indeed the ratio between the metal and the halogen radii decides the complex geometry. When the halogen size is increased and/or the metal size is decreased, the tetrahedral coordination is preferred because of the difficulty of accommodating four rather than two large halogen atoms around a small metal center.

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Registry No. I, 85336-89-6; II, 85336-90-9; III, 85354-82-1; $\text{Zn}(\text{dmpd})\text{I}_2$, 85336-91-0; $\text{Cd}(\text{dmpd})\text{Cl}_2$, 85336-99-8; $\text{Cd}(\text{dmpd})\text{I}_2$, 85336-92-1; $\text{Hg}(\text{dmpd})\text{Cl}_2$, 85337-01-5; $\text{Hg}(\text{dmpd})\text{Br}_2$, 85337-03-7; $\text{Hg}(\text{dmpd})\text{I}_2$, 85336-93-2; $[\text{ZnCl}_4][\text{dmpdH}_2]$, 85336-94-3; $[\text{ZnBr}_4][\text{dmpdH}_2]$, 85336-95-4; $[\text{CdBr}_4][\text{dmpdH}_2]$, 85336-96-5; $[\text{HgI}_4][\text{dmpdH}_2]$, 85336-97-6.

Supplementary Material Available: Tables of positional and thermal parameters, computed and observed structure factor moduli, non-bonding contacts involving halogen atoms, and IR and Raman stretching frequencies and two figures of IR and Raman spectra of $[\text{MX}_4]^{2-}$ complexes (24 pages). Ordering information is given on any current masthead page.

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Role of the Tosyl Group in the Coordination Ability of N-Protected Amino Acids. 3. Ternary Complexes of Copper(II) with N-Tosylglycine and Aromatic Amines. Crystal and Molecular Structure of Bis(N-tosylglycinato)bis(N-methylimidazole)copper(II)

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Some compounds of the type $\text{Cu}(\text{TsglyH})_2\text{X}_2$ (TsglyH = N-tosylglycinate anion; X = imidazole, N-methylimidazole, and pyridine) have been prepared and characterized by means of magnetic moments and ESR, electronic, and infrared spectra. For one of them, bis(N-tosylglycinato)bis(N-methylimidazole)copper(II), the crystal structure has also been determined. The crystals are monoclinic ($P2_1/n$) with cell dimensions $a = 13.733$ (3) Å, $b = 8.766$ (2) Å, $c = 13.641$ (3) Å, $\beta = 105.97$ (5)°, and $Z = 2$. The structure has been determined from diffractometric data by Patterson and Fourier methods and refined by full-matrix least squares to an R value of 0.052. The complex has square-planar coordination via two centrosymmetric carboxylic oxygens and two imidazole nitrogens. Two weak interactions (2.758 Å) with two carboxylic oxygens complete the coordination to a strongly distorted tetragonal bipyramid. Packing is determined by N-H(amide)⋯O(carboxylate) hydrogen bonds and by van der Waals contacts. Electronic, infrared, and ESR spectra are consistent with this type of structure for all the complexes.

Introduction

In our previous investigation on the copper(II) ion-N-tosylglycinate system in the solid state and in aqueous solution,²

it was suggested that the ligand presents the properties of both the L- α -amino acids³ and their N-acetyl or N-benzoyl deriv-

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