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Structural and Spectroscopic Correlations in Cadmium(II) Halide Complexes of 2,2-Dimethylpropane-1,3-diamine

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Compounds of formula Cd(dmpd)$_2$X$_2$ (dmpd = 2,2-dimethylpropane-1,3-diamine; X = Cl, Br, I) were prepared and investigated by means of structural and spectroscopic (IR and Raman) measurements. The Cd(dmpd)$_2$I$_2$ compound crystallizes in the monoclinic $P2_1/c$ space group, with two formula units in a cell of dimensions a = 6.235 (5) Å, b = 18.462 (9) Å, c = 8.294 (5) Å, and β = 93.37 (6)°, with R = 0.039 and R_w = 0.044. The structure consists of discrete [Cd(dmpd)$_2$I$_2$] monomeric units, where the Cd atom is surrounded by four nitrogen atoms of two in-plane chelating dmpd molecules and by two iodine atoms asymmetrically coordinated in axial positions. The Cd(dmpd)$_2$Br$_2$ compound crystallizes in the triclinic $P\bar{1}$ space group, with Z = 3 and a cell of dimensions a = 12.713 (2) Å, b = 16.592 (2) Å, c = 6.281 (3) Å, α = 91.22 (2)°, β = 96.67 (2)°, and γ = 78.72 (3)°, with R = 0.031 and R_w = 0.036. The structure consists of 1:1 molecular packing of Cd(dmpd)$_2$Br$_2$ monomeric and [Cd(dmpd)$_2$Br$_2$]$_2$ dimeric units. In the monomer the Cd atom is octahedrally coordinated by four in-plane nitrogen atoms of two chelating dmpd molecules and by two bromine atoms in axial positions. The dimer consists of a pair of octahedrally coordinated Cd atoms, related by an inversion center, connected in a 12-membered metallacycle by two ambidentate dmpd molecules. The octahedral arrangement of each Cd atom in the dimer is completed by an in-plane chelating dmpd and by two bromine atoms, axially coordinated. The Cd(dmpd)$_2$Cl$_2$ compound is isomorphous with the bromine derivative, with unit cell dimensions a = 12.714 (3) Å, b = 16.228 (3) Å, c = 6.087 (5) Å, α = 91.61 (3)°, β = 96.02 (3)°, and γ = 77.76 (4)°. The CdN stretching vibrations are discussed and assigned in the light of the known structures.

Introduction

On the basis of a systematic investigation, we have previously demonstrated that propane-1,3-diamines posses a greater coordinative versatility than ethylenediamines and, in the presence of appropriate metal ions, give rise to compounds presenting very peculiar structures.[1-3] In this respect d^{10} metal ions seem very interesting and promising, because of the variety of coordination numbers and geometries closely dependent on metal ion and halide dimensions as well as on interactions due to crystal-packing and hydrogen-bonding forces.[4]

In particular, the chemical behavior of cadmium(II) halide materials recently received a great deal of attention, from both the theoretical and experimental points of view; their unique properties, related to their polymorphic behavior, impurity electronic configurations, and lattice locations, are key areas of interest in semiconductor physics.[5-7]

Therefore, we decided to combine cadmium(II) halides and 2,2-dimethylpropane-1,3-diamine, the most versatile among propanediamines,[2,3] with the aim to increase our knowledge on the coordinative behavior of this amine, to investigate the factors controlling the stereochemical nature of cadmium(II) halide materials, and to prepare new solid compounds as models for understanding the direct correlation between symmetry, vibronic instability, stereochemistry, and structural phase transition in condensed matter. In particular this paper deals with the structural and vibrational property correlations of Cd(dmpd)$_2$X$_2$ (dmpd = 2,2-dimethylpropane-1,3-diamine; X = Cl, Br, I) compounds.

Experimental Section

Preparation of the Complexes. All the complexes were prepared by adding a methanolic metal halide solution (1 mM) to a methanolic 2,2-dimethylpropane-1,3-diamine solution (2–2.5 mM). By standing several hours at room temperature, white crystals precipitated.

Cd(dmpd)$_2$Cl$_2$. Anal. Calc for $C_{10}H_{28}N_4CdCl_2$: C, 30.96, H, 7.28; N, 14.46. Found: C, 30.87; H, 7.32; N, 14.40.

Cd(dmpd)$_2$Br$_2$. Anal. Calc for $C_{10}H_{28}N_4CdBr_2$: C, 25.18; H, 5.92; N, 11.76. Found: C, 25.18; H, 5.96; N, 11.78.

Cd(dmpd)$_2$I$_2$. Anal. Calc for $C_{10}H_{28}N_4CdI_2$: C, 21.04; H, 4.95; N, 9.82. Found: C, 20.90; H, 4.88; N, 9.65.

Table I. Crystallographic Data

	compd	
	Cd(dmpd)$_2$I$_2$	Cd(dmpd)$_2$Br$_2$
formula	$C_{10}H_{28}CdI_2N_4$	$C_{30}H_{84}Br_6Cd_3N_{12}$
fw	570.6	1429.7
cryst system	monoclinic	triclinic
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	6.235 (5)	12.713 (2)
b, Å	18.462 (9)	16.592 (2)
c, Å	8.294 (5)	6.281 (3)
α, deg		91.22 (2)
β, deg	93.37 (6)	96.67 (2)
γ, deg		78.72 (2)
V, Å^3	953 (2)	1290.6 (9)
Z	2	1
D_{calc}, g cm^{-3}	2.02	1.84
radiation, Å	0.71073	0.71073
temp, K	297 ± 2	297 ± 2
linear abs coeff, cm^{-1}	44.00	58.56
R^a	0.039	0.031
$R_w{}^b$	0.044	0.036

[a] $R = \sum||F_o| - k|F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - k|F_c|)^2/\sum wF_o^2]^{1/2}$.

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 polyethylene, as support,

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Table II. Relevant Bond Distances (Å) and Angles (deg) for Cd(dmpd)$_2$I$_2$ (**1**)

Cd–I1	2.868 (3)	C2A–C4A	1.52 (4)
Cd–I2	3.451 (3)	C2A–C5A	1.56 (4)
Cd–N1A	2.40 (2)	C3A–N2A	1.50 (3)
Cd–N2A	2.28 (2)	N1B–C1B	1.55 (4)
Cd–N1B	2.31 (2)	C1B–C2B	1.49 (4)
Cd–N2B	2.33 (2)	C2B–C3B	1.57 (4)
N1A–C1A	1.49 (4)	C2B–C4B	1.56 (4)
C1A–C2A	1.53 (4)	C2B–C5B	1.53 (5)
C2A–C3A	1.57 (4)	C3B–N2B	1.57 (4)
I1–Cd–I2	178.2 (1)	C1A–C2A–C3A	115 (2)
I1–Cd–N1A	102.9 (5)	C1A–C2A–C4A	113 (3)
I1–Cd–N2A	101.2 (5)	C1A–C2A–C5A	103 (2)
I1–Cd–N1B	104.6 (5)	C3A–C2A–C4A	109 (2)
I1–Cd–N2B	98.3 (5)	C3A–C2A–C5A	106 (2)
I2–Cd–N1A	78.7 (5)	C4A–C2A–C5A	109 (3)
I2–Cd–N2A	78.1 (5)	C2A–C3A–N2A	112 (2)
I2–Cd–N1B	76.1 (5)	Cd–N1B–C1B	117 (2)
I2–Cd–N2B	80.2 (5)	Cd–N2B–C3B	116 (1)
N1A–Cd–N2A	81.4 (8)	N1B–C1B–C2B	109 (2)
N1A–Cd–N1B	92.6 (8)	C1B–C2B–C3B	112 (2)
N1A–Cd–N2B	158.7 (8)	C1B–C2B–C4B	115 (3)
N2A–Cd–N1B	154.2 (7)	C1B–C2B–C5B	105 (2)
N2A–Cd–N2B	96.8 (8)	C3B–C2B–C4B	112 (2)
N1B–Cd–N2B	79.8 (7)	C3B–C2B–C5B	99 (2)
Cd–N1A–C1A	116 (2)	C4B–C2B–C5B	113 (3)
Cd–N2A–C3A	119 (1)	C2B–C3B–N2B	113 (2)
N1A–C1A–C2A	116 (2)		

Table III. Relevant Bond Distances (Å) and Angles (deg) for Cd(dmpd)$_2$Br$_2$ (**2**)

Molecule **2a**			
Cd1–Br1	2.869 (1)	C1A–C2A	1.51 (1)
Cd1–N1A	2.324 (7)	C2A–C3A	1.54 (1)
Cd1–N2A	2.303 (7)	C2A–C4A	1.54 (1)
N1A–C1A	1.49 (1)	C2A–C5A	1.53 (1)
N2A–C3A	1.47 (1)		
Br1–Cd1–N1A	86.4 (2)	C1A–C2A–C3A	113.3 (7)
Br1–Cd1–N1A′	93.6 (2)	N2A–C3A–C2A	116.7 (7)
Br1–Cd1–N2A	90.8 (2)	Cd1–N2A–C3A	116.7 (5)
Br1–Cd1–N2A′	89.2 (2)	C1A–C2A–C4A	111.2 (7)
N1A–Cd1–N2A	87.1 (2)	C1A–C2A–C5A	106.1 (7)
N1A–Cd1–N2A′	92.9 (2)	C3A–C2A–C4A	111.0 (7)
Cd1–N1A–C1A	118.4 (5)	C3A–C2A–C5A	105.7 (7)
N1A–C1A–C2A	115.9 (7)	C4A–C2A–C5A	109.2 (7)
Molecule **2b**			
Cd2–Br2	2.803 (1)	C3B–N2B	1.47 (1)
Cd2–Br3	2.791 (1)	C2B–C4B	1.51 (1)
Cd2–N1B	2.385 (6)	C2B–C5B	1.52 (1)
Cd2–N2B′	2.363 (6)	N1C–C1C	1.47 (1)
Cd2–N1C	2.345 (6)	C1C–C2C	1.53 (1)
Cd2–N2C	2.347 (6)	C2C–C3C	1.52 (1)
N1B–C1B	1.47 (1)	C3C–N2C	1.46 (1)
C1B–C2B	1.55 (1)	C2C–C4C	1.54 (1)
C2B–C3B	1.53 (1)	C2C–C5C	1.50 (1)
Br2–Cd2–Br3	178.86 (4)	C2B–C3B–N2B	118.6 (7)
Br2–Cd2–N1B	95.4 (2)	C1B–C2B–C4B	107.2 (7)
Br2–Cd2–N2B′	93.3 (2)	C1B–C2B–C5B	111.0 (7)
Br2–Cd2–N1C	89.9 (2)	C3B–C2B–C4B	109.0 (7)
Br2–Cd2–N2C	88.3 (2)	C3B–C2B–C5B	110.5 (7)
Br3–Cd2–N1B	84.6 (2)	C4B–C2B–C5B	110.8 (7)
Br3–Cd2–N2B′	85.7 (2)	Cd2′–N2B–C3B	116.0 (5)
Br3–Cd2–N1C	90.1 (2)	Cd2–N1C–C1C	118.3 (5)
Br3–Cd2–N2C	92.9 (2)	N1C–C1C–C2C	115.6 (7)
N1B–Cd2–N2B′	94.6 (2)	C1C–C2C–C3C	113.0 (7)
N1B–Cd2–N1C	174.4 (2)	C2C–C3C–N2C	116.4 (7)
N1B–Cd2–N2C	92.3 (2)	C1C–C2C–C4C	106.3 (7)
N2B–Cd2–N1C	86.7 (2)	C1C–C2C–C5C	110.8 (7)
N2B–Cd2–N2C	172.8 (2)	C3C–C2C–C4C	106.5 (7)
N1C–Cd2–N2C	86.2 (2)	C3C–C2C–C5C	111.6 (7)
Cd2–N1B–C1B	122.2 (5)	C4C–C2C–C5C	108.3 (7)
N1B–C1B–C2B	117.6 (6)	Cd2–N2C–C3C	118.7 (5)
C1B–C2B–C3B	108.2 (6)		

Table IV. Positional Parameters and Their Estimated Standard Deviations for Compound Cd(dmpd)$_2$I$_2$ (**1**)

atom	x/a	y/b	z/c	B_{eq},[a] Å^2
Cd	0.7098 (3)	0.0	0.7346 (3)	4.17 (4)
I1	0.4014 (3)	−0.0820 (1)	0.5402 (3)	4.54 (4)
I2	1.0931 (2)	0.0950 (1)	0.9654 (2)	4.28 (4)
N1A	0.571 (3)	0.121 (1)	0.713 (3)	4.7 (5)
N2A	0.925 (3)	0.043 (1)	0.543 (3)	4.5 (5)
C1A	0.525 (4)	0.149 (2)	0.547 (3)	4.7 (6)
C2A	0.719 (4)	0.156 (1)	0.444 (3)	4.5 (6)
C3A	0.824 (4)	0.082 (1)	0.398 (3)	4.3 (6)
C4A	0.891 (4)	0.206 (2)	0.516 (4)	6.0 (7)
C5A	0.623 (5)	0.189 (2)	0.283 (4)	8.0 (9)
N1B	0.604 (2)	−0.013 (1)	0.996 (2)	3.1 (4)
N2B	0.933 (3)	−0.095 (1)	0.823 (3)	4.3 (5)
C1B	0.534 (4)	−0.085 (1)	1.044 (3)	4.4 (6)
C2B	0.732 (4)	−0.135 (1)	1.070 (3)	4.1 (1)
C3B	0.823 (4)	−0.158 (2)	0.907 (3)	5.0 (6)
C4B	0.903 (5)	−0.106 (2)	1.186 (4)	6.3 (7)
C5B	0.640 (5)	−0.209 (2)	1.123 (4)	7.1 (9)

[a] $B_{eq} = {}^8/_3\pi^2[a^2a^{*2}U_{11} + b^2b^{*2}U_{22} + c^2c^{*2}U_{33} + 2aba^*b^*(\cos\gamma)U_{12} + 2aca^*c^*(\cos\beta)U_{13} + 2bcb^*c^*(\cos\alpha)U_{23}]$.

Table V. Positional Parameters and Their Estimated Standard Deviations for Compound Cd(dmpd)$_2$Br$_2$ (**2**)

atom	x/a	y/b	z/c	B_{eq},[a] Å^2
Cd1	0.0	0.0	0.0	3.07 (2)
Br1	−0.03278 (8)	0.11433 (6)	−0.3488 (2)	3.19 (2)
N1A	0.0998 (6)	0.0876 (4)	0.187 (1)	3.4 (2)
N2A	0.1594 (6)	−0.0678 (4)	−0.115 (1)	3.2 (2)
C1A	0.2136 (8)	0.0537 (6)	0.274 (2)	4.0 (2)
C2A	0.2856 (7)	0.0110 (5)	0.114 (1)	2.9 (2)
C3A	0.2575 (7)	−0.0716 (6)	0.036 (2)	3.6 (2)
C4A	0.2868 (8)	0.0677 (6)	−0.075 (2)	4.6 (2)
C5A	0.3989 (8)	−0.0102 (6)	0.235 (2)	4.7 (2)
Cd2	−0.22757 (5)	0.37952 (4)	0.4405 (1)	2.42 (1)
Br2	−0.31986 (8)	0.48259 (6)	0.7566 (2)	3.10 (2)
Br3	−0.13181 (8)	0.27621 (6)	0.1311 (2)	3.26 (2)
N1B	−0.1733 (5)	0.4857 (4)	0.255 (1)	2.5 (1)
N2B	0.0603 (5)	0.6583 (4)	0.345 (1)	2.5 (1)
C1B	−0.2045 (7)	0.5732 (5)	0.311 (1)	2.7 (2)
C2B	−0.1332 (6)	0.6326 (5)	0.247 (1)	2.5 (2)
C3B	−0.0217 (6)	0.6089 (5)	0.373 (1)	2.5 (2)
C4B	−0.1849 (8)	0.7180 (6)	0.311 (2)	4.5 (2)
C5B	−0.1243 (8)	0.6284 (6)	0.007 (2)	4.6 (2)
N1C	−0.2786 (5)	0.2673 (4)	0.593 (1)	2.8 (1)
N2C	−0.3982 (5)	0.4011 (4)	0.239 (1)	2.7 (1)
C1C	−0.3524 (7)	0.2232 (6)	0.461 (2)	3.6 (2)
C2C	−0.4599 (7)	0.2761 (5)	0.367 (1)	3.1 (2)
C3C	−0.4479 (7)	0.3302 (6)	0.183 (1)	3.3 (2)
C4C	−0.5310 (9)	0.2158 (7)	0.273 (2)	5.3 (3)
C5C	−0.5156 (7)	0.3254 (6)	0.539 (2)	3.8 (2)

[a] $B_{eq} = {}^8/_3\pi^2[a^2a^{*2}U_{11} + b^2b^{*2}U_{22} + c^2c^{*2}U_{33} + 2aba^*b^*(\cos\gamma)U_{12} + 2aca^*c^*(\cos\beta)U_{13} + 2bcb^*c^*(\cos\alpha)U_{23}]$.

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 analyzer.

X-ray Structure Determination. The refined cell constants and the most relevant crystal data for Cd(dmpd)$_2$I$_2$ (**1**) and Cd(dmpd)$_2$Br$_2$ (**2**) are presented in Table I. Crystal sizes were 0.30 × 0.18 × 0.05 mm for Cd(dmpd)$_2$I$_2$ and 0.25 × 0.10 × 0.10 mm for Cd(dmpd)$_2$Br$_2$. 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 χ values near 90°, was applied to both data sets. The structures were solved by conventional Patterson and Fourier methods and refined by full-matrix least squares. Heavy atoms (Cd, Br, I) were treated anisotropically, while the hydrogen atoms were located in their ideal positions (C–H = 0.95 Å, B = 6.0 and 5.0 Å^2 for **1** and **2**, respectively) after each cycle of refinement. 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 values of the R and R_w conventional agreement indices are reported in Table I. Bond distances and angles are reported in Tables II and III for compounds **1** and **2**, respectively. The final positional parameters are

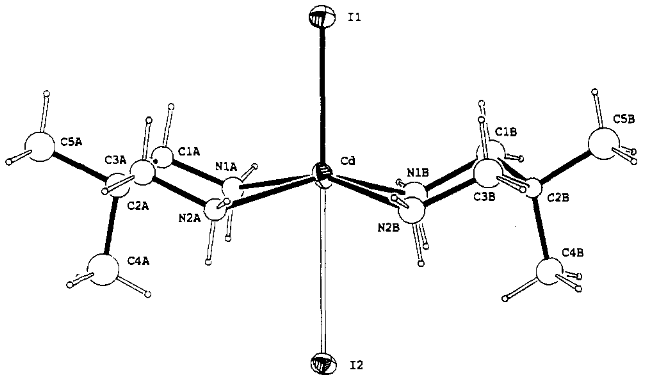

Figure 1. ORTEP drawing of the $Cd(dmpd)_2I_2$ complex, with partial labeling scheme. Thermal ellipsoids of non-hydrogen atoms are drawn at 30% probability, while, for sake of clarity, hydrogen atoms have been given arbitrary radii.

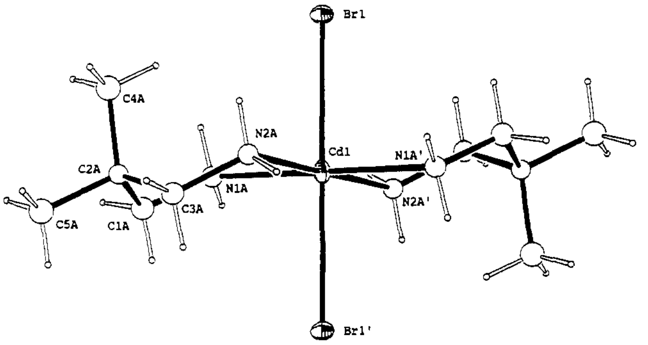

Figure 2. ORTEP drawing of the $Cd(dmpd)_2Br_2$ monomer (**2a**). Primed atoms are generated by the ($-x$, $-y$, $-z$) symmetry operation.

collected in Tables IV and V, while tables of complete crystal data, of final thermal parameters, and of computed and observed structure factor moduli for both compounds are given in the supplementary material.

Results and Discussion

All the compounds are stable in air and strongly soluble in organic polar solvents. Their spectroscopic properties demonstrate that there are some differences among the chloride and bromide complexes and the iodide derivative. In order to clarify these differences unambiguously, the bromide and the iodide complexes were structurally characterized.

The lattice parameter determination of a single crystal of $Cd(dmpd)_2Cl_2$ gave unit cell dimensions of a = 12.714 (3) Å, b = 16.228 (3) Å, c = 6.087 (5) Å, α = 91.61 (3)°, β = 96.02 (3)°, and γ = 77.76 (4)°, which make its crystal structure isomorphous with that of the bromine derivative. Reasonably, also the most relevant molecular and conformational parameters are similar, except for the small influence of the limited covalent radius of Cl vs Br; therefore, a complete analysis of the chlorine derivative was not performed.

Description of the Structures. Structure of $Cd(dmpd)_2I_2$. The structure of the $Cd(dmpd)_2I_2$ compound consists of a molecular packing of monomeric units with normal van der Waals contacts. The Cd atom is surrounded by two chelating dmpd ligands and two iodine atoms (Figure 1), which have markedly different Cd–I bond lengths (Cd–I1 = 2.868 (3), Cd–I2 = 3.451 (3) Å). The inner coordination sphere may be considered as formed from one (apical) iodine and four (basal) nitrogen atoms in a square pyramidal arrangement, of C_{2v} idealized symmetry, with the C_2 axis passing through I1 and Cd. The loosely interacting I(2) atom, however, completes the coordination in a quasi-octahedral manner (I1–Cd···I2 = 178.2 (1)°). The asymmetric coordination of the two iodine atoms is also reflected in the relative arrangement of the dmpd ligands, both being tilted away from I1, with the I1–Cd–N angles significantly larger than 90° (average value 101.7°) and the trans N–Cd–N angles averaging 156.4°. The endocyclic N–Cd–N (bite) angles are significantly smaller than the exocyclic N–Cd–N angles (average 80.6 and 94.7°, respectively).

Table VI. Relevant Infrared Frequencies (cm^{-1})[a]

compd	NH_2 stretching	NH_2 scissoring
$Cd(dmpd)_2Cl_2$	3360 w, 3320 m, 3300 m, 3240 sh, 3220 vs, 3160 w, 3130 w	1588 sh, 1572 vs
$Cd(dmpd)_2Br_2$	3360 w, 3320 s, 3270 m, 3220 vs, 3150 s	1605 sh, 1588 vs
$Cd(dmpd)_2I_2$	3315 vs, 3260 s, 3230 vs, 3140 m	1578 vs

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

Structure of $Cd(dmpd)_2Br_2$. The structure of the $Cd(dmpd)_2Br_2$ compound consists of a 1:1 molecular packing of $Cd(dmpd)_2Br_2$ monomers (**2a**) and $[Cd(dmpd)_2Br_2]_2$ dimers (**2b**); both molecules lie on crystallographic inversion centers, and no abnormal intermolecular interactions are present.

Molecule **2a** (Figure 2) is an octahedral complex of Cd(II) with two bromine atoms trans to each other and two chelated dmpd rings. The complex has idealized C_{2h} symmetry with the 2-fold axis bisecting the two N–Cd–N angles not belonging to the same metallacycles. The presence of the crystallographically imposed inversion center makes the Cd–Br bond lengths perforce symmetric (Cd1–Br1 = 2.869 (1) Å) but allows the tilting of the Br1–Cd1–Br1′ axis slightly out from the normal to the CdN_4 plane (Br1–Cd1–N1A = 86.4 (2)° vs Br1–Cd1–N1A′ = 93.6 (2)°). The endocyclic and exocyclic N–Cd–N angles are 87.1 (2) and 92.9 (2)°, respectively.

Molecule **2b** (Figure 3) consists of a pair of octahedral Cd(II) complexes, related by an inversion center, connected in a 12-membered metallacycle by two ambidentate dmpd ligands. On each metal center the octahedral coordination is completed by two bromine atoms (trans to each other) and a chelating dmpd ligand. The Br2–Cd2–Br3 moiety is almost linear (Br2–Cd2–Br3 = 178.86 (4)°), displays similar Cd–Br interactions (Cd2–Br2 = 2.803 (1) Å, Cd2–Br3 = 2.791 (1) Å), and is slightly bent with respect to the CdN_4 plane. A comparison of the Cd–N interactions within the 12-membered and the 6-membered metallacycle shows longer Cd–N distances (average 2.374 vs 2.345 Å) and a larger N–Cd–N angle (94.6 (2) vs 86.2 (2)°) for the former. The 6-membered metallacycles have the usual chair conformation, while the 12-membered one has a "superchair" conformation with the 12 atoms equally (6 and 6) distributed on two stacked planes (connected by two N–C bonds; see Figure 3).

Comparative Analysis of the Three Structures. Gollogly and Hawkins[8] have extensively studied the metal–diamine complexes

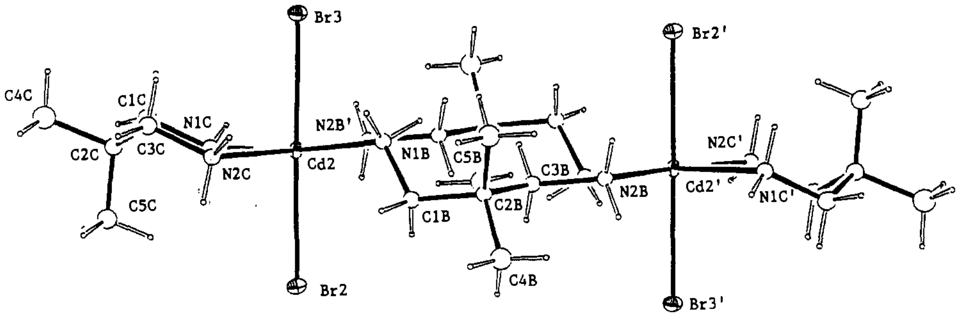

Figure 3. ORTEP drawing of the $[Cd(dmpd)_2Br_2]_2$ dimer (**2b**). Primed atoms are generated by the ($-x$, $0.5 - y$, $0.5 - z$) symmetry operation.

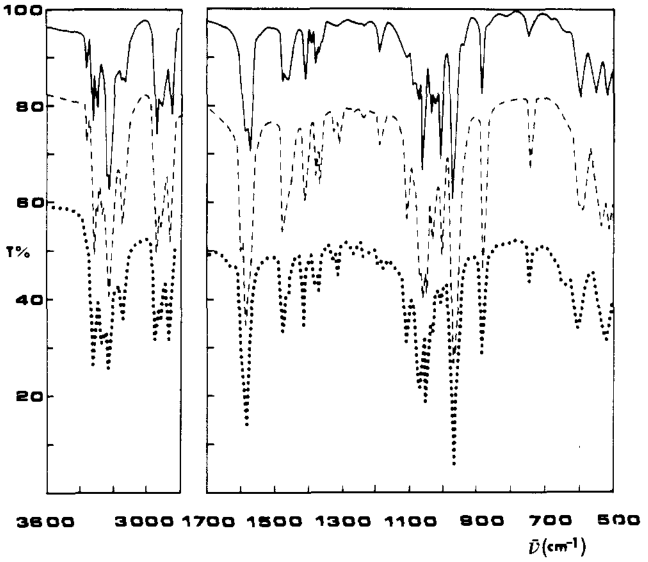

Figure 4. Infrared spectra of $Cd(dmpd)_2Cl_2$ (—), $Cd(dmpd)_2Br_2$ (- - -), and $Cd(dmpd)_2I_2$ (···).

using the molecular mechanics approach. In the analysis of *trans*-Co(1,3-propanediamine)$_2L_2$ derivatives they found that the most stable conformers, of C_{2h} and C_{2v} symmetry, respectively, have the chair conformation for the metallacycles, boat and skew-boat metallacycles being avoided because of unfavorable interactions with the axial ligands. In our case, which is only roughly similar (because of the two geminal methyl groups and the larger cadmium covalent radius with respect to the cobalt), we found that the iodine derivative has the C_{2v} conformation and the bromide (molecule **2a**) has the C_{2h} conformation. The C_{2h} conformer displays moderately long, symmetric Cd–Br interactions and flattened metallacycles (the dihedral angle between NCdN and NCCN is 29.8°), while the C_{2v} one has one short and one long Cd–I interaction, nearly approximating pentacoordination (the larger the X ligand, the smaller the coordination number), and more "regular" metallacycles (the dihedral angles between the NCdN and NCCN planes are 41.7 and 44.6° for the two independent rings). In both species the "axial" halogen atoms (X) interact with the axial ring substituents: the shortest X···H(C) interactions are repulsive in nature and are responsible for the flattening of the six-membered metallacycles in molecules **2a** and **2b** and for the asymmetrization of the I–Cd–I moiety in **1**; on the contrary, the intramolecular X···H(N) interactions, even if, on average, shorter than the X···H(C) ones (I···H(N) ranging from 3.09 to 3.22 Å in **1**, Br···H(N) from 3.12 to 3.28 Å in **2a** and from 3.17 to 3.34 Å in **2b**), are attractive (because of their polar nature) as evidenced by the presence of even shorter intermolecular X···H(N) interactions (the shortest I···H(N) is 2.83 Å in **1**, while the corresponding Br···H(N) is 2.53 Å in **2a**) and by the systematic bending of the X–Cd–X moieties toward the axial aminic hydrogen atoms in all three molecules.

Spectroscopic Results. Spectroscopic measurements were made with the aim of correctly assign the stretching and bending NH_2 and the stretching Cd–N and Cd–X (X = Cl, Br, I) vibrations and finding correlations among the vibrational spectra and the crystal and the molecular structures of the title compounds.

Spectral Range 4000–500 cm^{-1}. The IR spectra in the range of 4000–500 cm^{-1} and the Raman spectra in the range 1700–500 cm^{-1} are illustrated in Figures 4 and 5. Among the high number of bands of the spectra, only the stretching and scissoring NH_2 vibrations can be unambiguously assigned (see Table VI) by comparing our spectra with those of the $M(dmpd)X_2$ (M = Zn, Cd)[1,9] and $[Zn(dmpd)_n]X_2$ (n = 2, 3)[3] compounds.

In previous papers[1-3] we have observed that dmpd complexes of identical stoichiometry but different molecular structure always present some significant differences in the vibrational spectra in the 4000–500-cm^{-1} spectral range. From this point of view the compounds examined in this work seem to present a unique behavior since, in spite of the different molecular structures of the bromide (and chloride as well; vide infra) compound and the iodide one, they show very similar IR spectra in the 4000–500-cm^{-1} spectral range (Figure 4), with only some negligible differences in the NH_2 stretching vibrations. On the contrary, the Raman spectra are consistent with the structural differences of the three derivatives, since in the 1700–500-cm^{-1} spectral range the spectra of $Cd(dmpd)_2Cl_2$ and $Cd(dmpd)_2Br_2$ are very similar to one another but significantly different from that of the iodide one.

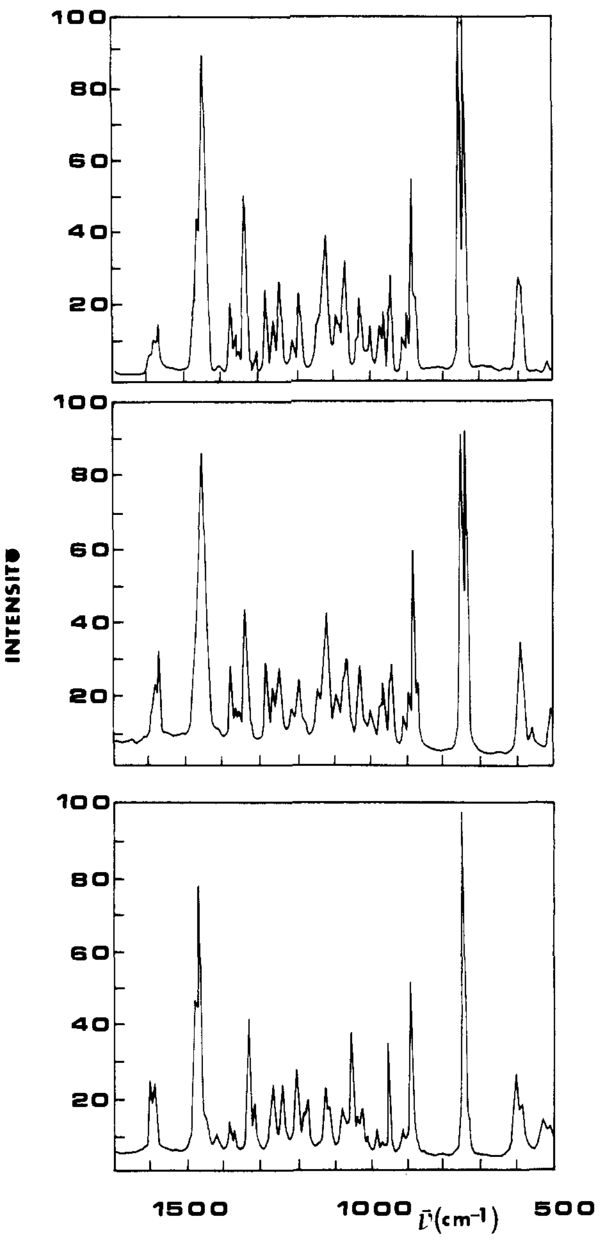

Figure 5. Raman spectra of $Cd(dmpd)_2Cl_2$ (top), $Cd(dmpd)_2Br_2$ (middle), and $Cd(dmpd)_2I_2$ (bottom).

The strict similarity of the spectra of $Cd(dmpd)_2Cl_2$ and $Cd(dmpd)_2Br_2$ in the full 4000–500-cm^{-1} spectral range suggests to us that, although a single-crystal structure determination of the Cl derivative was not performed, the two compounds are isostructural, if not isomorphous.

Spectral Range 500–100 cm^{-1}. The IR and Raman spectra of all the compounds in the (Cd–N) stretching vibration region present similar trends. The calculation of the theoretical (Cd–N) stretching vibrations of $Cd(dmpd)_2X_2$ (X = Cl, Br) were based on the following considerations: C_i is the factor group and the site symmetry of both monomeric and dimeric species, in the

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(8) Gollogly, J. R.; Hawkins, C. J. *Inorg. Chem.* **1972**, *11*, 156.
(9) Appleton, T. G.; Hall, J. R. *Inorg. Chem.* **1970**, *9*, 1800.

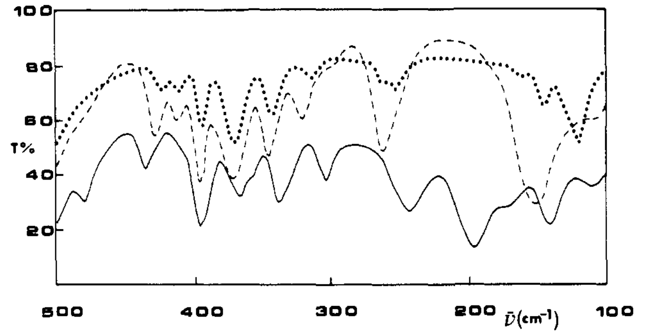

Figure 6. Far-infrared spectra of $Cd(dmpd)_2Cl_2$ (—), $Cd(dmpd)_2Br_2$ (- - -), and $Cd(dmpd)_2I_2$ (···).

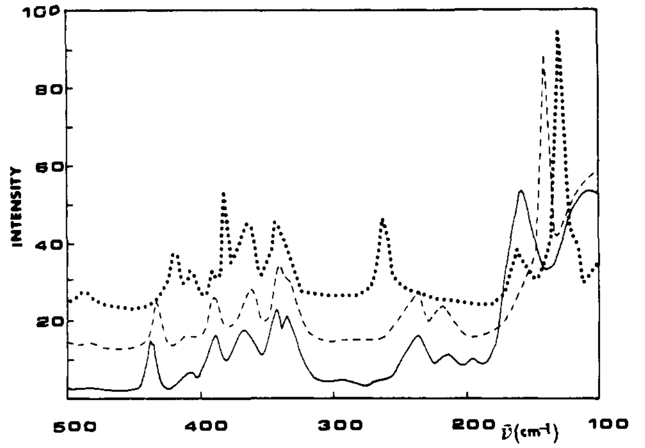

Figure 7. Raman spectra of $Cd(dmpd)_2Cl_2$ (—), $Cd(dmpd)_2Br_2$ (- - -), and $Cd(dmpd)_2I_2$ (···).

Bravais cell ($Z^B = 1$). Consequently the number of calculated (Cd–N) stretching vibrations is the same if we consider either the crystal field effect alone (static effect, site symmetry) or the dynamic coupling effect (factor group analysis). In fact, in both cases, four IR-active (A_u type) and four Raman-active (A_g type) (Cd–N) stretching vibrations for the dimeric species and two IR-active (Au type) and two Raman-active (A_g type) (Cd–N) stretching vibrations for the monomeric species are calculated.

An identical number and type of IR- and Raman-active (Cd–N) stretching vibrations are also calculated on the basis of an approximation which takes into consideration a half-dimeric molecule with the C_1 site symmetry of the Cd atom. Subsequently, the (Cd–N) stretching vibrations of the dimeric molecule can be calculated through the correlation between C_1 and C_i groups and considering that in the Bravais cell two half-dimeric molecules are present ($Z^B = 2$).

The IR and Raman spectra of the chloride and bromide compounds are illustrated in Figures 6 and 7. As reported in Table VI, four bands are observed in the expected ν(Cd–N) spectral range,[1,3] in agreement with the above reported prediction. Furthermore, it appears evident that the ν(Cd–N) stretching vibrations of the monomer are screened or coincident with those of the dimeric molecule.

For the $Cd(dmpd)_2I_2$ compound on the basis of the site symmetry C_1, four IR- and Raman-active ν(Cd–N) frequency vibrations are calculated, whereas taking into account the factor group C_2, eight IR- and Raman-active (Cd–N) stretching vibrations (4A + 4B) are expected. Since the experimental IR and Raman spectra of this compound (Figures 6 and 7), very similar to those of the above discussed $Cd(dmpd)_2X_2$ (X = Cl, Br) compounds, do not present a sufficient number of bands to support the factor group participation, we suggest that in $Cd(dmpd)_2I_2$ the site symmetry effect may be the prevailing one.

This effect could also be present in the spectra of the $Cd(dmpd)_2X_2$ (X = Cl, Br) compounds especially in the case of the dimeric molecule, even if the site symmetry effect alone should never be evident because the symmetry group C_i is valid both for site symmetry and factor group. But, if the hypothesis is accepted that the bridging ligand molecules are unable to transmit vibrational coupling, then the dimeric molecule too might be analyzed within the site symmetry frame, as being formed by two half-molecules of C_1 symmetry (the expected frequencies still number only four in the IR and Raman region but are now coincident). Within this assumption the iodine compound and the dimeric species of the chloride and bromide compounds from the vibrational point of view could be all referable to an octahedral *trans*-CdN_4X_2 molecule with C_1 symmetry. The monomeric species of the chloride and bromide compounds are the sole exceptions. In any case the number of the predicted (Cd–N) vibrations for the monomeric species in C_i site symmetry is lower than that calculated for the half-molecule of the dimeric species with C_1 symmetry.

Table VII. Cd–N Stretching Frequencies (cm^{-1})[a]

compd	type	ν(Cd–N)			
$Cd(dmpd)_2Cl_2$	IR	435 mw	395 m	367 m	337 m
	R	437 m	390 m	368 m	345 m
$Cd(dmpd)_2Br_2$	IR	427 m	395 m	372 m	345 m
	R	432 m	390 m	362 m	340 m
$Cd(dmpd)_2I_2$	IR	422 w	393 m	370 m	342 m
	R	422 m	390 w	365 m	345 m

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

In conclusion, it seems very reasonable that the IR and Raman spectra of all the present compounds should be very similar in the ν(Cd–N) region. Since the experimental results agree with the aforementioned hypothesis, we consider it well-founded to explain the vibrations appearing in the 500–100-cm^{-1} spectral range on the basis of the site symmetry of the Cd atom alone, neglecting the vibrational coupling arising from the ligand molecules bridging two metal ions and from the factor group.

In particular, as reported in Table VII, the band observed at 384 cm^{-1} in the Raman spectrum of the $Cd(dmpd)_2I_2$ compound is not assigned to any ν(Cd–N) owing to its anomalously high intensity, higher than those assigned to the other ν(Cd–N) vibrations. Analogously, the IR shoulders and bands appearing at about 150 cm^{-1} and in the 300–320-cm^{-1} range are not considered, being also present in the IR spectrum of the dication $(dmpdH_2)^{2+}$.

In the spectra of our compounds, bands are missing in the 280–150-cm^{-1} spectral region, in which terminal ν(Cd–X) stretches are expected[1] (Figures 6 and 7). For the chloride and bromide compounds we calculated one IR (A_u) and one Raman (A_g) active vibration for the monomeric species in C_i symmetry and two IR (A_u) and two Raman (A_g) active vibrations for the dimeric species. In the last case, the number of expected bands is lowered from 4 to 2, both IR and Raman active, by referring (with all the consequences of this type of approximation) to a half-dimeric molecule with C_1 site symmetry.

For the iodide compound in C_1 site symmetry two IR- and Raman-active bands are calculated.

In the spectra reported in Figures 6 and 7, we observe a lower number of bands than those expected. In fact in the IR and Raman spectra of the bromide and iodide compounds we find only one band, which, on the basis of the literature frequency values,[1,10–12] can reasonably be assigned to the (Cd–X) stretching vibrations at 150 (IR) and 141 (Raman) cm^{-1} for the bromide and at 120 (IR) and 130 (Raman) cm^{-1} for the iodide compound.

An unambiguous assignment of the ν(Cd–Cl) band in the spectrum of the $Cd(dmpd)_2Cl_2$ compound is difficult. Although in the IR and Raman spectra bands appear at 194 and 160 cm^{-1}, respectively, the IR band at 240 cm^{-1}, which is not paralleled in the Raman spectrum, should however be preferred, finding consistency in the ν(Cd–X)/ν(Cd–Cl) (X = Br, I) ratio method, which

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(10) (a) Goldstein, M.; Hughes, R. *Inorg. Chim. Acta* **1979**, *37*, 71. (b) Ibid. **1980**, *40*, 229.

(11) Goel, R. G.; Ogini, W. O. *Inorg. Chem.* **1977**, *16*, 1968.

(12) Moggi, G.; Bart, J. C. J.; Cariati, F.; Psaro, R. *Inorg. Chim. Acta* **1980**, *43*, 87.

has been demonstrated to be very effective in Cd–X band assignments.[1]

Conclusions

The coordinative versatility of propane-1,3-diamines toward metal ions has been demonstrated on the observation that the propane-1,3-diamine complexes in solution, owing to the less favorable entropy change in the formation of six-membered rings,[13] present lower stability than the ethylenediamine analogues. Our systematic investigations have demonstrated that, by using appropriate metal ions, it is possible to force the propane-1,3-diamines to act in unusual ways, giving rise to compounds which present uncommon and unpredictable structures.

In fact, propane-1,3-diamine and 2,2-dimethylpropane-1,3-diamine, in the presence of Cu(II), Zn(II), and Cd(II) ions, have been found to act both as chelating and as bridging (toward two metal ions) ligands, giving rise to dimeric and/or polymeric species.[2,14] This ability of propanediamines to act as bridging ambidentate ligands can play an important role in the design of ferromagnetic-like polymetallic systems.

A greater coordinative flexibility of 2,2-dimethylpropane-1,3-diamine than that of propane-1,3-diamine may be suggested by the complexity of its compounds, whose crystalline phases, as shown in this paper, can simultaneously contain monomeric and dimeric units, and by its further unique ability to act in the extended form also as monodentate ligand,[3] with the uncoordinated amino group stabilized by hydrogen bonding interactions with a water molecule of crystallization. Moreover, the apparently simple (dmpd)MX_2 (M = Zn, Cd; X = Cl, Br, I) compounds, in which the amine invariably acts as chelating agent, present some interesting features, since, the metal ion environment closely depending and on the metal ion and halogen dimensions, discrete monomeric or one-dimensional polymeric species are formed.

Acknowledgment. We are grateful to the Italian Consiglio Nazionale delle Ricerche (CNR) for financial support and to the "Centro CNR di Studio sulla Sintesi e la Struttura dei Composti dei Metalli di Transizione nei Bassi Stati di Ossidazione" for the use of the Coderg PHO spectrophotometer.

Registry No. 1, 139167-79-6; Cd$(dmpd)_2Cl_2$ (monomer)/Cd$(dmpd)_2Cl_2$ (dimer), 139167-77-4; Cd$(dmpd)_2Br_2$ (monomer)/Cd$(dmpd)_2Br_2$ (dimer), 139167-78-5.

Supplementary Material Available: Detailed listings of crystallographic parameters (Table S1), fractional coordinates of hydrogen atoms (Tables S2 and S3), anisotropic thermal factors (Tables S4 and S5), and "best" molecular planes formed by selected groups of atoms (Tables S6 and S7) (6 pages); listings of observed and calculated structure factor moduli (Tables S8 and S9) (19 pages). Ordering information is given on any current masthead page.

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Resolutions Involving Metal Complexation. Optical Resolution and Photochemical Rearrangement of (±)-(2-Mercaptoethyl)methylphenylphosphine

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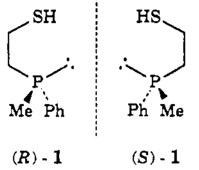
The asymmetric bidentate (±)-(2-mercaptoethyl)methylphenylphosphine has been resolved by the fractionial crystallization of a pair of diastereomeric thiolato-*S*-bridged dipalladium(II) complexes containing the deprotonated form of the ligand and ortho-metalated (*R*)-(1-(dimethylamino)ethyl)naphthalene. In order to recover the resolved ligand from the less soluble diastereomer of the dipalladium complex, the terminal palladium resolving unit was displaced with ethane-1,2-diamine, and the residual (thiolato)palladium(II) complex was treated with benzyl bromide; this gave a bromopalladium(II) complex containing (*S*)-(2-(benzylthio)ethyl)methylphenylphosphine bound through phosphorus only. The crystal and molecular structure of the bromopalladium complex has been determined. Crystal data: orthorhombic, $P2_12_12_1$, $a = 8.774$ (1) Å, $b = 17.908$ (3) Å, $c = 18.412$ (4) Å, $Z = 4$, and $R = 0.042$. The geometry around the palladium is distorted square-planar with the tertiary phosphine-*P* stereocenter of *S* absolute configuration trans to the tertiary amine-*N* of the resolving ligand of *R* absolute configuration. Optically pure (*R*)-(2-(benzylthio)ethyl)methylphenylphosphine, $[\alpha]_D$ −27.8° (*c* 1.6, dichloromethane), was displaced from the bromopalladium complex with (R^*,R^*)-(±)-1,2-phenylenebis(methylphenylphosphine) and was, in turn, converted by sodium in ammonia into a separable mixture of optically pure (*R*)-(2-mercaptoethyl)methylphenylphosphine, $[\alpha]_D$ −17.0° (*c* 3.0, dichloromethane), and optically pure (*R*)-ethylmethylphenylphosphine, $[\alpha]_D$ −7.3° (*c* 2.4, toluene). The (*R*)-(mercaptoethyl)phosphine rearranges in light with retention of configuration at phosphorus into optically pure (*S*)-ethylmethylphenylphosphine sulfide, $[\alpha]_D$ −21.6° (*c* 2.0, methanol), by an intermolecular radical chain mechanism.

Introduction

Deprotonated 2-mercaptoethyl-substituted arsines and phosphines are powerful chelating agents for a variety of transition metal ions,[1-4] giving complexes containing highly nucleophilic thiolato-*S* atoms that can be readily alkylated. Thus, with appropriate choice of ligand and alkylating agent, a *cis*-P_2S_2 macrocycle was synthesized on nickel(II),[1,4] and on palladium(II), *trans*-As_2S_2 macrocycles were prepared in diastereomerically homogeneous and optically pure forms.[5] In this paper, we describe the optical resolution of (±)-(2-mercaptoethyl)methylphenylphosphine (**1**), a model ligand for the metal-template synthesis of *trans*-P_2S_2 macrocycles.[6] The resolution procedure for the phosphine–thiol, which involves the fractional crystallization of a pair of thiolato-*S*-bridged dipalladium(II) complexes containing



(*R*)-1 (*S*)-1

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