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Preparation of Zinc(II) and Cadmium(II) Complexes with (−)-Sparteine

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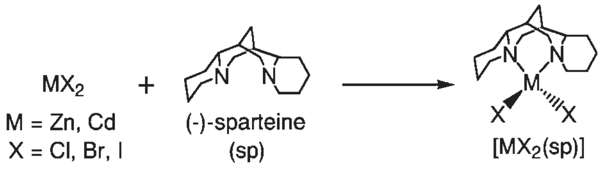
A systematic study on the effects of different metals and halogenide ions was carried out by using $[MX_2(sp)]$ (M = Zn and Cd; X = Cl, Br, and I; sp = (−)-sparteine). The complexes have been characterized by X-ray crystallography, and far-IR and Raman spectroscopy.

Zinc(II) and cadmium(II) complexes have recently been given a lot of attention in many fields such as inorganic, biological, and environmental chemistry. There are indeed many zinc(II) and cadmium(II) complexes but not so many systematic studies. We have been searching for zinc(II) and cadmium(II) complexes with "simple" supporting ligands for the purpose of applying data such as metal–ligand stretching frequencies and LMCT transition bands for physicochemical study.[1] In this paper, we describe MX_2N_2-type complexes with (−)-sparteine (referred to as sp). The ligand sp coordinates to metal ions in a didentate fashion. The lone pairs on nitrogen atoms in sp take an sp^3 conformation, and they face in a good direction for coordination to the metal ion. The complexes containing the sp ligand have been reported in many fields such as inorganic chemistry with zinc(II) ion,[2] bioinorganic chemistry,[3] and catalytic chemistry.[4] For zinc(II) and cadmium(II) complexes with the sp ligand, the crystal structures of $[ZnCl_2(sp)]$[3a] and $[ZnBr_2(sp)]$[2a] along with some properties of $[ZnX_2(sp)]$ (X = Cl and Br)[2b,3a,3c] have been reported already. However, there are no reports about the structures of cadmium(II) complexes. Moreover, there are no discussions of the relationships between their structures and properties. We discuss herein the crystal structures of $[ZnI_2(sp)]$ (**1**) and $[CdX_2(sp)]$ (X = Br (**3**) and I (**4**)), and metal–ligand stretching frequencies together with those of $[CdCl_2(sp)]$ (**2**) and the reported $[ZnCl_2(sp)]$[3a] and $[ZnBr_2(sp)]$.[2a]

The syntheses of all complexes were carried out by the reaction between zinc(II) or cadmium(II) halogenide compounds and excess sp as shown in the equation. The designed complexes were obtained easily and in good yield.



(1)

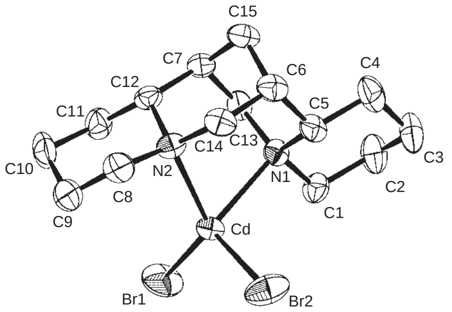


Fig. 1. Molecular structure of $[CdBr_2(sp)]$ (**3**) (ORTEP, 50% probability ellipsoids) with atomic numbering.

The representative crystal structure of **3** is shown in Fig. 1. Selected bond distances and angles for all complexes are given in Table 1. The central metal(II) ions in **1**, **3**, and **4** take a tetrahedral configuration the same as those in $[ZnX_2(sp)]$ (X = Cl[3a] and Br[2a]). The N–M–N angles are very compressed. The cadmium(II) complexes have a smaller angle (ca. 80°) compared with the zinc(II) complexes (ca. 88°). It can be explained by the difference of ionic radii of metal(II) ions. While the X–M–X angles are smaller from chloro to iodo in each metal(II) series, those of the cadmium(II) complexes are larger than those of the zinc(II) complexes. These X–M–X angles are larger than 109.5° for an ideal tetrahedral angle. The behavior in the metal(II) series indicates that the Cl–M–Cl angles have no space to extend for avoiding the steric hindrance of sp. Therefore, the X–M–X angles (X = Br and I) get smaller with increasing ionic radii. The bond distances of M–N and M–X are in the normal region. The M–N distances are also different in each metal series (averaged to 2.09 Å for zinc(II) series and to 2.32 Å for cadmium(II) series). However, the M–X distances get longer from chloro to iodo and from the zinc(II) complexes to the corresponding cadmium(II) complexes. It can be explained by the change of ionic radius of halogenide ions and metal(II) ions.

Far-IR spectra in the region of 600–150 cm^{-1} for all of the complexes showed some metal–ligand bands. The assignments are summarized in Table 1. The stretching frequencies for ν(M–N) are assigned by comparing isostructural zinc(II) and cadmium(II) complexes. The bands at ca. 461 and ca. 426 cm^{-1} in the spectra of zinc(II) series shift to ca. 455 and ca. 417 cm^{-1} in those of the cadmium(II) one, respectively. The assignments of ν(M–N) at ca. 460 and ca. 437 cm^{-1} for $[ZnX_2(sp)]$ (X = Cl and Br) have already been reported by Choi et al.[3c] In the same region, the zinc(II) and cadmium(II) complexes with not only didentate ligands such as ethylenediamine $[MX_2(en)]$ (M = Zn and Cd, X = Cl and Br),[5] 2,2-dimethylpropane-1,3-diamine $[MX_2(dmpd)]$ (M = Zn and Cd, X = Cl and Br),[6] but also with simple amine ligands[7] such as $[ZnX_2(NH_3)_2]$[8] (X = Cl, Br, and I), $[M(NH_3)_4]^{2+}$ (M = Zn[9] and Cd[10]) have been reported for ν(M–N). In addition, we have reported the ν(M–N) bands for zinc(II) and cadmium(II) complexes with a didentate ligand such as 1,4-dimethylhomopiperazine in the same region.[1a] The distinct shifts from zinc(II) to cadmium(II) complexes also support that their peaks relate to the bonds between metal(II) and the same coordination atom; that is to say, metal(II) ions are surrounded by the same coordination environment as each other. The assignments of

Table 1. Selected Bond Distances and Angles, Stretching Vibrations Corresponding to ν(M–N) and ν(M–X) of **1**–**4** and $[ZnX_2(sp)]$ (X = Cl and Br)

	$[ZnX_2(sp)]$			$[CdX_2(sp)]$		
	Cl[a)]	Br[a)]	I (**1**)	Cl (**2**)[b)]	Br (**3**)	I (**4**)
Bond distances/Å						
M–X1	2.220(1)	2.3571(8)	2.559(2)	—	2.5286(8)	2.698(2)
M–X2	2.226(1)	2.3753(8)	2.572(2)	—	2.5123(7)	2.715(2)
M–N1	2.081(3)	2.094(4)	2.078(6)	—	2.292(5)	2.345(4)
M–N2	2.081(3)	2.082(4)	2.100(7)	—	2.324(5)	2.311(8)
Bond angles/°						
X1–Zn–X2	116.12(5)	113.74(3)	111.93(6)	—	120.28(3)	118.86(6)
N1–Zn–N2	88.5(1)	88.5(2)	88.3(3)	—	80.4(2)	80.3(2)
Stretching vibrations/cm^{-1}						
ν(M–N) far-IR	461, 427	461, 426	460, 424	457, 417	456, 417	451, 416
(Raman)	(467, 426)	(462, 426)	(460, 423)	(462, 416)	(458, 417)	(457, 416)
ν(M–X) far-IR	331, 302	244, 218	204, 190	296, 279	218, 189	180, 159
(Raman)	(327, 297)	(244, 219)	(203, 191)	(294)	(218, 190)	(180, 160)

a) Crystal structures of $[ZnX_2(sp)]$ (X = Cl and Br) are also characterized by the same experimental conditions in this paper. b) The crystal structure of **2** was not available.

ν(M–X) are carried out by comparing with the same metal(II) series. The ν(M–X) band shifts from ν(M–Cl) to ν(M–I) toward lower energy as expected from the theory and our study.[1] The Raman spectra of all the complexes show good agreement with their far-IR spectra. The sp ligand has a good effect on the far-IR and Raman spectra as we expected in that the complexes containing "simple" ligands make their spectra very simple and easy to assignment.

In this paper, we showed a systematic study of structures and physicochemical properties of $[MX_2(sp)]$ (M = Zn and Cd; X = Cl, Br, and I) containing sp as a "simple" ligand. From crystal structures, it was confirmed that sp forces a highly distorted tetrahedral configuration with MX_2N_2 coordination type. We carried out far-IR and Raman spectroscopy to assign metal–ligand stretching vibrations, which relate to direct information between metal and ligand for determining their metal surroundings.

Experimental

General. All manipulations were carried out under an argon atmosphere using standard Schlenk techniques. CH_2Cl_2 and heptane were carefully purified by refluxing/distilling under an argon atmosphere over P_2O_5 and sodium/benzophenone ketyl, respectively.[11] EtOH and MeOH were of commercially spectroscopic grade and stored in an argon atmosphere after bubbling argon gas prior to use. Other reagents were commercially available and used without further purification. IR (4000–400 cm^{-1}) and far-IR (600–100 cm^{-1}) spectra were recorded on KBr pellets and CsI pellets using a JASCO FT/IR-550 spectrometer, respectively. FT-Raman (600–100 cm^{-1}) spectra were recorded using a Perkin-Elmer Spectrum GX spectrophotometer. Elemental analyses (C, H, and N) were performed by the Research Facility Center for Science and Technology of the University of Tsukuba. $[ZnCl_2(sp)]$[3a] and $[ZnBr_2(sp)]$[2a] were synthesized by following each reference.

Preparations. $[ZnI_2(sp)]$ (1): An EtOH solution (10 cm^3) of sp (ca. 0.35 cm^3, 1.5 mmol) was added slowly to an EtOH solution (25 cm^3) of ZnI_2 (0.32 g, 1 mmol). While stirring for 2 h, a white powder was formed. The resultant white powder was collected by filtration and washed with EtOH. Colorless single crystals for X-ray analysis were obtained by recrystallization from a CH_2Cl_2/heptane mixed solution. Yield: 72% (0.40 g). Calcd for $C_{15}H_{26}I_2N_2Zn$: C, 32.54; H, 4.73; N, 5.06%. Found: C, 32.55; H, 4.70; N, 4.61%. Far-IR (CsI, cm^{-1}): 460m, 433w, 424m, 350w, 324w, 286w, 268w, 217m, 204s, 190s. IR (KBr, cm^{-1}): 3432m, 2933vs, 2858s, 1467m, 1443m, 1080m, 1035m, 723m. Raman shift (cm^{-1}): 460m, 433w, 423w, 347w, 323s, 282w, 268m, 218m, 203vs, 191s.

$[CdCl_2(sp)]$ (2): Preparation was carried out by the same method as for **1** with $CdCl_2$ (0.18 g, 1 mmol) and sp (ca. 0.35 cm^3, 1.5 mmol). Yield: 66% (0.28 g). Found: C, 41.50; H, 6.33; N, 6.29%. Calcd for $C_{15}H_{26}CdCl_2N_2 \cdot H_2O$: C, 41.34; H, 6.48; N, 6.43%. Far-IR (CsI, cm^{-1}): 457m, 434w, 417m, 350w, 309sh, 296s, 279s. IR (KBr, cm^{-1}): 3492m, 2940vs, 2857s, 2830s, 1472m, 1447s, 1302m, 1115s, 1041s, 721m, 610m. Raman shift (cm^{-1}): 462s, 435w, 416m, 351w, 312vs, 294vs.

$[CdBr_2(sp)]$ (3): Preparation was carried out by the same method as for **1** with $CdBr_2 \cdot 4H_2O$ (0.35 g, 1 mmol) and sp (ca. 0.35 cm^3, 1.5 mmol). Colorless single crystals for X-ray analysis were obtained by recrystallization from a CH_2Cl_2/heptane mixed solution. Yield: 90% (0.46 g). Calcd for $C_{15}H_{26}Br_2CdN_2$: C, 35.56; H, 5.17; N, 5.53%. Found: C, 35.32; H, 5.27; N, 5.25%. Far-IR (CsI, cm^{-1}): 456m, 431w, 417m, 349w, 312w, 218s, 189s. IR (KBr, cm^{-1}): 3447m, 2934vs, 2858s, 1470m, 1444m, 1039m, 876w. Raman shift (cm^{-1}): 458m, 431w, 417w, 347w, 311s, 218w, 190vs.

$[CdI_2(sp)]$ (4): Preparation was carried out by the same method as for **1** with CdI_2 (0.37 g, 1 mmol) and sp (ca. 0.35 cm^3, 1.5 mmol). Colorless single crystals for X-ray analysis were obtained by recrystallization from a CH_2Cl_2/heptane mixed solution. Yield: 90% (0.54 g). Calcd for $C_{15}H_{26}CdI_2N_2$: C, 30.00; H, 4.36; N, 4.66%. Found: C, 30.00; H, 4.34; N, 4.21%. Far-IR (CsI, cm^{-1}): 451m, 431w, 416m, 347w, 312w, 277w, 260w, 180s, 159s. IR (KBr, cm^{-1}): 3460m, 2937vs, 2855s, 1468m, 1443m, 1039m, 876w. Raman shift (cm^{-1}): 457s, 430w, 416m, 346w, 311vs, 275w, 259m, 180w, 160w.

X-ray Crystallography. The diffraction data were measured on a Rigaku AFC 7S automated four-circle diffractometer with graphite-monochromated Mo Kα ($\lambda = 0.71069$ Å) radiation (50 kV, 30 mA). The structures were solved by direct-methods (heavy-atom Patterson methods[12] for **1** and **3**, and SIR92[13] for **4**) and successive different Fourier syntheses,[14] then refined by full-matrix least-squares methods by teXsan.[15] The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located on the calculated positions and refined isotropically. The absolute configuration was confirmed from the values of the Flack parameters.[16] Crystallographic data for **1**: $C_{15}H_{26}I_2N_2Zn$, fw = 553.57, colorless, prism, $0.45 \times 0.20 \times 0.20\,\text{mm}^3$, Triclinic, $P1$ (No. 1), $a = 7.973(3)$ Å, $b = 9.269(4)$ Å, $c = 7.681(3)$ Å, $\alpha = 111.482(9)°$, $\beta = 111.256(3)°$, $\gamma = 100.068(8)°$, $V = 460.2(3)$ Å^3, $Z = 1$, Temperature = 23 °C, $D_{\text{calcd}} = 1.997\,\text{g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 46.84\,\text{cm}^{-1}$, No. of unique reflections = 1761, No. of observed reflections = 1747 ($I > 3\sigma(I)$), $R = 0.032$, $R_w = 0.045$. **3**: $C_{15}H_{26}Br_2CdN_2$, fw = 506.60, colorless, plate, $0.44 \times 0.17 \times 0.07\,\text{mm}^3$, Triclinic, $P1$ (No. 1), $a = 7.804(2)$ Å, $b = 9.230(3)$ Å, $c = 7.608(2)$ Å, $\alpha = 111.62(2)°$, $\beta = 111.41(2)°$, $\gamma = 98.72(2)°$, $V = 447.7(3)$ Å^3, $Z = 1$, Temperature = 23 °C, $D_{\text{calcd}} = 1.879\,\text{g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 56.91\,\text{cm}^{-1}$, No. of unique reflections = 2054, No. of observed reflections = 1991 ($I > 2\sigma(I)$), $R = 0.026$, $R_w = 0.032$. **4**: $C_{15}H_{26}CdI_2N_2$, fw = 600.60, colorless, block, $0.25 \times 0.25 \times 0.15\,\text{mm}^3$, Triclinic, $P1$ (No. 1), $a = 7.852(7)$ Å, $b = 8.110(7)$ Å, $c = 9.332(8)$ Å, $\alpha = 111.216(5)°$, $\beta = 99.6980(6)°$, $\gamma = 111.485(8)°$, $V = 483.5(7)$ Å^3, $Z = 1$, Temperature = 23 °C, $D_{\text{calcd}} = 2.063\,\text{g cm}^{-3}$, $\mu(\text{Mo K}\alpha) = 43.19\,\text{cm}^{-1}$, No. of unique reflections = 1928, No. of observed reflections = 1915 ($I > 3\sigma(I)$), $R = 0.036$, $R_w = 0.044$. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, CCDC Nos. 265738–265740 for compounds **1**, **3**, and **4**. Copies of the data can be obtained free of charge by application to the Director CCDC, 12, Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.ac.uk or www: http://www.ccdc.cam.ac.uk/conts/retrieving.html).

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