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Contribution from the Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan,
Department of Chemistry, Naruto University of Education, Naruto 772, Japan, Institute of Physical and Chemical Research,
Wako-shi, Saitama 351, Japan, and Institute of Protein Research, Osaka University, Suita, Osaka 565, Japan

X-ray Structures and Far-Infrared and Raman Spectra of Tetrahedral Thiophenolato and Selenophenolato Complexes of Zinc(II) and Cadmium(II)

Norikazu Ueyama,[1a] Takashi Sugawara,[1a] Kazuko Sasaki,[1a] Akira Nakamura,*[1a] Shinsuke Yamashita,[1b] Yasuo Wakatsuki,[1c] Hiroshi Yamazaki,[1c] and Noritake Yasuoka[1d]

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Single-crystal X-ray analysis of the tetrathiolato complexes $[NMe_4]_2[Zn(SPh)_4]$ (**1**) and $[NMe_4]_2[Cd(SPh)_4]$ (**2**) and the tetraselenolato complexes $[NMe_4]_2[Zn(SePh)_4]$ (**3**) and $[NMe_4]_2[Cd(SePh)_4]$ (**4**) revealed a C_2 structure distorted from D_{2d} for the $[M(X-Ph)_4]^{2-}$ (M = Zn(II), Cd(II); X = S, Se) unit. The crystal systems of **1**-**3** are monoclinic, with $a = 12.042$ (3) Å, $b = 14.366$ (1) Å, $c = 9.837$ (2) Å, and $Z = 2$, in space group $P2_1$, for $C_{32}H_{44}N_2S_4Zn$; $a = 12.053$ (2) Å, $b = 14.570$ (2) Å, $c = 9.827$ (5) Å, and $Z = 2$, in space group $P2_1$ for $C_{32}H_{44}N_2S_4Cd$; and $a = 12.089$ (7) Å, $b = 14.587$ (10) Å, $c = 9.950$ (7) Å, and $Z = 2$, in space group $P2_1$, for $C_{32}H_{44}N_2Se_4Zn$, respectively. **4** forms orthorhombic crystals, with $a = 20.157$ (15) Å, $b = 14.583$ (6) Å, $c = 12.214$ (8) Å, and $Z = 4$, in space group $P2_12_12_1$, for $C_{32}H_{44}N_2Se_4Zn$. The bond lengths of Zn-S, Cd-S, Zn-Se, and Cd-Se of these complexes are 2.357, 2.541, 2.469, and 2.649 Å, respectively. The Se-C bonds are slightly longer than the S-C bond, with the normal difference of large covalent radii. The Zn-Se and Cd-Se bonds have relatively less π-interaction. The far-infrared and Raman spectra of these complexes can be interpreted by the distorted T_d structures for the MX_4 core. An M-S stretching band (A) was found at 200 cm^{-1} for **1** (Zn-S) and 180 cm^{-1} for **2** (Cd-S), whereas the ($\nu + \delta$) vibration (B) of M-S-C was observed at 352 and 338 cm^{-1}, respectively. An M-Se stretching Raman band (A) was observed at 135 cm^{-1} for **3** (Zn-Se) and at 130 cm^{-1} for **4** (Cd-Se), which was confirmed by the polarized Raman spectra and the normal-coordinate analysis. The strong band assignable to M-Se-C ($\nu + \delta$) (B) was observed at 188 and 185 cm^{-1} for **3** and **4**, respectively.

Introduction

The structural characterization of metal-sulfur coordination in metalloproteins has mostly been carried out by using X-ray techniques. Horse liver alcohol dehydrogenase contains two Zn(II) sites, one of which has a tetrahedral $[Zn(Cys\text{-}S)_4]^{2-}$ site.[2] Aspartate carbamoyltransferase has a similar $[Zn(Cys\text{-}S)_4]^{2-}$ site,[3] as $Fe(Cys\text{-}S)_4$ sites in rubredoxin have been elucidated by an X-ray crystallographic study.[4] Many studies on metallothioneins, which contain multiple Zn or Cd atoms in the proteins, have been done by the analyses of the perturbed angular correlation of γ-rays for ^{111}Cd nuclei[5] and Co substitution of the proteins.[6] These analyses have suggested the possibility of the ZnS_4 core distorting from a tetrahedral structure, especially in alcohol dehydrogenase. A question has arisen whether the distortion is due to a conformational perturbation by peptide sequence or to the inherent properties of the ZnS_4 core. The substitution of the thiolate ligand with a selenolate ligand will provide one of the appropriate approaches for this purpose.

Involvement of selenocysteine residues in metalloproteins has been found in formate dehydrogenase[7] and glycine reductase.[8] The biological importance of Se ligands in Se-containing metalloproteins has not been clearly elucidated in both biological and coordination chemistries. The unique property of Se coordination thus requires further fundamental research.

In this paper, we compare the structures of $[NMe_4]_2[Zn(SePh)_4]$ and $[NMe_4]_2[Cd(SePh)_4]$ with those of $[NMe_4]_2[Zn(SPh)_4]$ and $[NMe_4]_2[Cd(SPh)_4]$ by using X-ray crystallography and Raman spectroscopy. Mononuclear Zn(II) or Cd(II) complexes containing four thiophenolate ligands have been characterized by Swenson et al.[9] and Dance.[10] They reported a distorted tetrahedral structure for the MS_4 core of $[PPh_4]_2[M(SPh)_4]$ (M = Zn(II), Cd(II)) and a D_{2d} symmetry for the $M(SPh)_4$ core by X-ray analyses. The observed distortion has been ascribed to be due to a conformationally preferable interaction between the phenyl ortho proton and the thiolato sulfur atom.

The Raman and the resonance Raman spectra of $[Co(SPh)_4]^{2-}$ were reported by Salama et al.[11] They assigned Co-S stretching bands at 215, 203, and 192 cm^{-1}. The assignments of Zn-S and Cd-S vibrations in Raman spectra are of considerable interest to us because the Raman and the resonance Raman spectroscopies of these metalloproteins may contribute to further characterization and identification of the active metal site structure. An orientation of M-S bonds in these biomolecules may thus be obtained by using a single crystal. Thus, single-crystal samples of tetracoordinated thiolato and selenolato complexes are important also for a Raman spectroscopic study.[12]

Experimental Section

Materials. Methanol, 2-propanol, *N,N*-dimethylformamide, Me_2SO-d_6, and tri-*n*-butylamine were purified by distillation. Tetramethylammonium chloride was purchased from Fluka Co. (Trimethylsilyl)selenophenol was prepared by the literature method.[13] The preparations of $[NMe_4]_2[Zn(SPh)_4]$ and $[NMe_4]_2[Cd(SPh)_4]$ were carried out by an extension of the method reported for the syntheses of $[NMe_4]_2[Co(SPh)_4]$.[9,10] $[NMe_4]_2[Zn(SPh)_4]$ (**1**) was recrystallized from methanol to give colorless needles. Anal. Calcd for $C_{32}H_{44}N_2S_4Zn$: C, 59.10; H, 6.82; N, 4.31. Found: C, 58.91; H, 6.78; N, 4.35. ^{1}H NMR (Me_2SO-d_6): NCH_3, 3.00 ppm; C_6H_5, 6.83 (*m*, *p*-H), 7.46 ppm (*o*-H). $[NMe_4]_2[Cd(SPh)_4]$ (**2**) was recrystallized from 2-propanol and obtained as colorless needles. Anal. Calcd for $C_{32}H_{44}N_2S_4Cd$: C, 55.11; H, 6.36;

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(1) (a) Department of Macromolecular Science, Faculty of Science, Osaka University. (b) Naruto University of Teacher Education. (c) The Institute of Physical and Chemical Research. (d) Institute of Protein Research, Osaka University.

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Table I. Crystal and Refinement Data for $[NMe_4]_2[M(XPh)_4]$ (M = Zn, Cd; X = S, Se)

	$[NMe_4]_2[Zn(SPh)_4]$ (**1**)	$[NMe_4]_2[Cd(SPh)_4]$ (**2**)	$[NMe_4]_2[Zn(SePh)_4]$ (**3**)	$[NMe_4]_2[Cd(SePh)_4]$ (**4**)
formula	$C_{32}H_{44}N_2S_4Zn$	$C_{32}H_{44}N_2S_4Cd$	$C_{32}H_{44}N_2Se_4Zn$	$C_{32}H_{44}N_2Se_4Cd$
mol wt	650.34	697.36	837.94	884.96
color	colorless	light yellow	colorless	light yellow
cryst syst	monoclinic	monoclinic	monoclinic	orthorhombic
cryst shape	prism	prism	prism	prism
space group	$P2_1$	$P2_1$	$P2_1$	$P2_12_12_1$
a, Å	12.042 (3)	12.053 (2)	12.089 (7)	20.157 (15)
b, Å	14.366 (1)	14.570 (2)	14.587 (10)	14.583 (6)
c, Å	9.837 (2)	9.827 (5)	9.950 (7)	12.214 (8)
β, deg	90.80 (2)	90.89 (2)	90.84 (2)	
V, Å^3	1702 (0)	1725 (1)	1754 (2)	3590 (5)
Z	2	2	2	4
d_{calcd}, g/cm^3	1.269	1.343	1.587	1.637
radiation	Mo Kα	Mo Kα	Mo Kα	Mo Kα
μ, cm^{-1}	7.9	6.6	32.8	30.5
temp, °C	21 ± 2	21 [illegible] 2	21 ± 2	21 ± 2
scan speed, deg/min	4	4	4	4
2θ range, deg	0–55	0–55	0–60	0–50
octants	$+h,+k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$
no. of unique data	ca. 5000	ca. 5000	4139	3549
no. of used data ($I_o \geq 3\sigma(I)$)	3206	3570	2792	2168
R^a	0.053	0.039	0.048	0.046
$R_w{}^b$	0.059	0.045	0.063	0.053

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

Table II. Atom Coordinates and Estimated Standard Deviations for $[NMe_4]_2[M(SPh)_4]$ (M = Zn, Cd)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
Complex **1**									
Zn	0.2257 (1)	0.5000 (1)	0.2453 (1)	3.33	C32	0.2917 (8)	0.2821 (7)	0.1024 (9)	3.64
S1	0.4213 (2)	0.4987 (3)	0.2686 (3)	4.39	C33	0.3316 (9)	0.1922 (8)	0.0774 (11)	5.01
S2	0.1647 (3)	0.4164 (2)	0.4353 (3)	4.14	C34	0.2910 (9)	0.1413 (9)	0.9646 (11)	5.42
S3	0.1655 (3)	0.4372 (2)	0.0370 (3)	4.21	C35	0.2107 (11)	0.1827 (9)	−0.1190 (12)	6.55
S4	0.1370 (3)	0.6482 (2)	0.2343 (3)	4.01	C36	0.1716 (9)	0.2726 (8)	−0.0976 (11)	4.63
N10	0.4707 (7)	0.4199 (6)	0.7672 (8)	4.01	C41	0.2059 (8)	0.7168 (7)	0.1114 (9)	3.41
N20	0.0090 (7)	0.6410 (6)	0.7293 (8)	4.33	C42	0.2952 (8)	0.6845 (7)	0.0355 (10)	3.89
C11	0.4617 (8)	0.5885 (7)	0.3818 (9)	3.59	C43	0.3428 (9)	0.7411 (9)	−0.0671 (10)	5.04
C12	0.3836 (8)	0.6369 (7)	0.4614 (9)	4.59	C44	0.3044 (9)	0.8318 (8)	−0.0860 (10)	4.83
C13	0.4178 (9)	0.7087 (8)	0.5533 (10)	5.53	C45	0.2153 (9)	0.8645 (8)	−0.0068 (10)	4.75
C14	0.5304 (10)	0.7272 (9)	0.5721 (11)	6.27	C46	0.1658 (9)	0.8096 (8)	0.0912 (10)	4.58
C15	0.6073 (10)	0.6813 (9)	0.4953 (12)	6.72	C101	0.4642 (10)	0.4673 (8)	0.9018 (11)	6.01
C16	0.5774 (9)	0.6097 (8)	0.4014 (10)	4.85	C102	0.3676 (10)	0.4341 (10)	0.6824 (13)	7.44
C21	0.0195 (8)	0.4184 (7)	0.4367 (8)	3.25	C103	0.5649 (10)	0.4549 (11)	0.6886 (13)	8.24
C22	−0.0448 (8)	0.4658 (7)	0.3365 (8)	3.35	C104	0.4832 (12)	0.3148 (9)	0.8012 (13)	7.81
C23	−0.1603 (8)	0.4647 (7)	0.3424 (9)	3.68	C201	0.0223 (11)	0.7329 (9)	0.7957 (12)	7.01
C24	−0.2178 (9)	0.4157 (8)	0.4435 (10)	4.63	C202	0.1172 (13)	0.6057 (14)	0.6885 (18)	12.84
C25	−0.1547 (9)	0.3655 (8)	0.5409 (11)	4.87	C203	−0.0377 (16)	0.5750 (13)	0.8302 (18)	12.77
C26	−0.0350 (9)	0.3673 (8)	0.5389 (10)	4.23	C204	−0.0705 (13)	0.6474 (12)	0.6111 (14)	9.61
C31	0.2142 (8)	0.3230 (7)	0.0146 (9)	3.30					
Complex **2**									
Cd	0.2283 (1)	0.5000 (0)	0.2492 (1)	3.58	C32	0.2923 (7)	0.2818 (6)	0.0969 (8)	3.97
S1	0.4385 (2)	0.5036 (3)	0.2778 (3)	4.61	C33	0.3328 (8)	0.1923 (6)	0.0733 (11)	5.35
S2	0.1596 (2)	0.4103 (2)	0.4518 (3)	4.56	C34	0.2943 (9)	0.1404 (7)	0.9594 (11)	6.55
S3	0.1623 (2)	0.4314 (2)	0.0256 (3)	4.74	C35	0.2132 (10)	0.1797 (7)	−0.1254 (11)	6.90
S4	0.1300 (2)	0.6553 (2)	0.2323 (3)	4.31	C36	0.1720 (8)	0.2672 (7)	−0.1048 (10)	5.20
N10	0.4710 (6)	0.4242 (5)	0.7708 (7)	4.20	C41	0.2011 (7)	0.7211 (6)	0.1110 (8)	3.53
N20	0.0085 (6)	0.6439 (6)	0.7270 (8)	4.85	C42	0.2917 (7)	0.6895 (7)	0.0370 (9)	4.29
C11	0.4680 (7)	0.5947 (6)	0.3894 (8)	3.64	C43	0.3415 (8)	0.7436 (8)	−0.0635 (10)	5.50
C12	0.3874 (8)	0.6426 (7)	0.4626 (9)	4.72	C44	0.3040 (8)	0.8326 (7)	−0.0866 (9)	5.11
C13	0.4165 (9)	0.7137 (7)	0.5556 (9)	5.58	C45	0.2146 (8)	0.8669 (7)	−0.0121 (9)	5.25
C14	0.5265 (9)	0.7366 (8)	0.5777 (10)	6.24	C46	0.1637 (8)	0.8120 (6)	0.0865 (9)	4.60
C15	0.6078 (9)	0.6919 (8)	0.5051 (11)	6.46	C101	0.4626 (8)	0.4679 (7)	0.9075 (9)	5.76
C16	0.5835 (8)	0.6191 (7)	0.4112 (9)	5.12	C102	0.3688 (9)	0.4383 (10)	0.6881 (12)	8.06
C21	0.0144 (7)	0.4162 (6)	0.4459 (8)	3.44	C103	0.5672 (9)	0.4607 (9)	0.6943 (12)	8.40
C22	−0.0456 (6)	0.4640 (6)	0.3451 (8)	3.49	C104	0.4839 (13)	0.3206 (8)	0.7972 (13)	9.02
C23	−0.1609 (7)	0.4654 (6)	0.3440 (9)	4.25	C201	0.0172 (11)	0.7342 (8)	0.7921 (12)	7.95
C24	−0.2225 (8)	0.4182 (7)	0.4443 (9)	4.79	C202	0.1184 (12)	0.6119 (15)	0.6854 (20)	16.34
C25	−0.1613 (8)	0.3667 (7)	0.5441 (10)	5.26	C203	−0.0333 (17)	0.5773 (13)	0.8283 (19)	15.48
C26	−0.0438 (8)	0.3672 (7)	0.5457 (9)	4.82	C204	−0.0700 (13)	0.6455 (11)	0.6138 (14)	12.01
C31	0.2136 (7)	0.3194 (6)	0.0074 (8)	3.45					

N, 4.02. Found: C, 55.09; H, 6.37; N, 4.12. ^1H NMR (Me_2SO-d_6): NCH_3, 3.00 ppm; C_6H_5, 6.77 (*m*-, *p*-H), 7.40 ppm (*o*-H).

Synthesis of $[NMe_4]_2[Zn(SePh)_4]$ (3). The complex was synthesized under argon atmosphere. (Trimethylsilyl)selenophenol (11.5 g, 0.05 mol), tetramethylammonium chloride (4.4 g, 0.04 mol), and tri-*n*-butylamine (11.6 mL, 0.04 mol) were mixed in 30 mL of methanol. To the solution was added $CdCl_2$ (1.3 g, 0.007 mol), in 50 mL of methanol, at room temperature. The colorless crystals obtained were collected by filtration, washed with cold methanol, and recrystallized from hot methanol. Anal. Calcd for $C_{32}H_{44}N_2Se_4Zn$: C, 45.87; H, 5.29; N, 3.34.

Table III. Atom Coordinates and Estimated Standard Deviations for $[NMe_4]_2[M(SePh)_4]$ (M = Zn, Cd)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
				Complex 3					
Zn	0.2754 (1)	0.0 (0)	0.2551 (2)	2.81	C32	0.2073 (11)	−0.1900 (9)	0.4674 (13)	3.06
Se1	0.0706 (1)	−0.0016 (1)	0.2345 (2)	3.53	C33	0.1593 (12)	0.2453 (14)	0.5662 (15)	4.75
Se2	0.3439 (2)	−0.0661 (1)	0.4682 (2)	3.46	C34	0.1957 (14)	0.3325 (11)	0.5870 (14)	4.59
Se3	0.3730 (2)	0.1484 (1)	0.2648 (2)	3.33	C35	0.2848 (14)	0.3673 (12)	0.5160 (14)	4.48
Se4	0.3331 (2)	−0.0881 (1)	0.0566 (2)	3.49	C36	0.3347 (12)	0.3118 (9)	0.4182 (13)	3.98
N10	0.4924 (9)	0.1454 (8)	0.7748 (10)	3.89	C41	0.4899 (9)	−0.0810 (9)	0.0559 (11)	3.00
N20	−0.0259 (9)	0.4192 (8)	0.2687 (10)	3.53	C42	0.5534 (10)	−0.0357 (8)	0.1536 (12)	4.00
C11	0.0338 (10)	0.0968 (8)	0.1100 (12)	3.16	C43	0.6652 (11)	−0.0363 (9)	0.1522 (12)	3.63
C12	−0.0733 (11)	0.1180 (10)	0.0872 (14)	4.25	C44	0.7246 (11)	−0.0821 (10)	0.0546 (15)	4.61
C13	−0.1018 (13)	0.1887 (13)	−0.0066 (20)	5.20	C45	0.6635 (13)	−0.1292 (12)	−0.0451 (16)	4.92
C14	−0.0222 (16)	0.2334 (10)	−0.0792 (17)	5.74	C46	0.5481 (13)	−0.1283 (11)	−0.0440 (12)	3.73
C15	0.0586 (14)	0.2102 (12)	−0.0570 (15)	5.34	C101	0.3837 (23)	0.1014 (26)	0.7984 (36)	9.08
C16	0.1176 (12)	0.1402 (10)	0.0338 (13)	4.33	C102	0.5375 (37)	0.0809 (26)	0.6752 (40)	11.66
C21	0.2858 (11)	−0.1836 (9)	0.4915 (12)	3.16	C103	0.5628 (24)	0.1520 (17)	0.8939 (23)	7.69
C22	0.3242 (12)	−0.2384 (10)	0.5975 (14)	3.80	C104	0.4781 (22)	0.2369 (16)	0.7138 (24)	7.15
C23	0.2856 (15)	−0.3220 (12)	0.6235 (19)	6.38	C201	−0.0069 (24)	0.3199 (16)	0.2900 (27)	8.18
C24	0.2038 (15)	−0.3591 (11)	0.5386 (22)	5.21	C202	−0.1297 (19)	0.4319 (23)	0.1934 (25)	8.06
C25	0.1656 (14)	−0.3103 (11)	0.4275 (19)	4.56	C203	−0.0346 (15)	0.4631 (13)	0.4044 (20)	6.03
C26	0.2078 (11)	−0.2212 (9)	0.4034 (15)	3.20	C204	0.0674 (21)	0.4619 (27)	0.1972 (26)	7.27
C31	0.2976 (10)	0.2224 (8)	0.3935 (12)	3.32					
				Complex 4					
Cd	0.1309 (1)	0.2577 (1)	−0.0020 (2)	3.86	C32	0.2874 (9)	0.5129 (14)	0.0797 (20)	4.51
Se1	0.0289 (2)	0.3502 (2)	0.0719 (2)	4.66	C33	0.2874 (12)	0.6055 (16)	0.0511 (23)	6.14
Se2	0.1346 (2)	0.0916 (2)	0.0873 (2)	4.56	C34	0.2473 (14)	0.6388 (16)	−0.0267 (25)	6.17
Se3	0.2462 (2)	0.3267 (2)	0.0588 (3)	5.30	C35	0.2012 (12)	0.5799 (14)	−0.0831 (28)	6.67
Se4	0.1122 (2)	0.2602 (2)	−0.2165 (2)	4.82	C36	0.2017 (11)	0.4906 (14)	−0.0533 (20)	5.58
N10	0.3671 (8)	0.1383 (10)	0.2537 (12)	4.64	C41	0.0467 (9)	0.1698 (13)	−0.2405 (15)	4.52
N20	0.3901 (9)	0.3827 (11)	−0.2300 (15)	5.82	C42	0.0351 (11)	0.1344 (15)	−0.3414 (15)	5.27
C11	0.0313 (9)	0.3406 (11)	0.2285 (14)	4.26	C43	−0.0148 (13)	0.0633 (15)	−0.3602 (18)	5.21
C12	0.0794 (9)	0.2919 (13)	0.2837 (16)	4.14	C44	−0.0502 (11)	0.0332 (16)	−0.2757 (18)	5.81
C13	0.0803 (11)	0.2911 (14)	0.3971 (18)	3.47	C45	−0.0397 (11)	0.0679 (16)	−0.1723 (18)	5.85
C14	0.0340 (12)	0.3361 (17)	0.4558 (17)	6.39	C46	0.0069 (10)	0.1349 (13)	−0.1548 (17)	5.18
C15	−0.0148 (11)	0.3849 (15)	0.4035 (20)	6.35	C101	0.3909 (14)	0.1496 (19)	0.1394 (17)	7.25
C16	−0.0172 (9)	0.3862 (14)	0.2917 (17)	4.55	C102	0.2944 (11)	0.1487 (19)	0.2611 (21)	7.00
C21	0.2116 (10)	0.0371 (12)	0.0276 (17)	5.01	C103	0.3867 (17)	0.0487 (18)	0.2986 (26)	7.56
C22	0.2492 (11)	0.0705 (13)	−0.0603 (18)	5.55	C104	0.4010 (15)	0.2071 (19)	0.3198 (22)	8.61
C23	0.3072 (11)	0.0293 (15)	−0.0990 (21)	5.20	C201	0.4357 (18)	0.3773 (19)	−0.3229 (25)	9.12
C24	0.3286 (12)	−0.0505 (17)	−0.0557 (21)	5.97	C202	0.3512 (14)	0.4696 (17)	−0.2266 (26)	8.24
C25	0.2924 (13)	−0.0863 (15)	0.0291 (20)	5.95	C203	0.3441 (17)	0.3042 (18)	−0.2348 (28)	9.72
C26	0.2337 (12)	−0.0480 (13)	0.0694 (18)	5.79	C204	0.4278 (16)	0.3731 (23)	−0.1317 (26)	9.45
C31	0.2443 (10)	0.4547 (12)	0.0241 (16)	4.76					

Table IV. Selected Structural Parameters for $[NMe_4]_2[M(XPh)_4]$ (M = Zn, Cd; X = S, Se)

	$[Zn(SPh)_4]^{2-}$	$[Cd(SPh)_4]^{2-}$	$[Zn(SePh)_4]^{2-}$	$[Cd(SePh)_4]^{2-}$
		Bond Lengths (Å)		
M–X1	2.361 (3)	2.543 (2)	2.481 (2)	2.650 (3)
M–X2	2.345 (3)	2.533 (3)	2.461 (2)	2.657 (3)
M–X3	2.344 (3)	2.531 (3)	2.467 (2)	2.639 (3)
M–X4	2.378 (3)	2.556 (3)	2.466 (2)	2.648 (3)
mean	2.357	2.541	2.469	2.649
X1–C11	1.769 (9)	1.764 (8)	1.943 (11)	1.919 (17)
X2–C21	1.745 (9)	1.752 (8)	1.868 (13)	1.890 (20)
X3–C31	1.752 (9)	1.750 (8)	1.946 (12)	1.916 (19)
X4–C41	1.773 (9)	1.755 (8)	1.899 (13)	1.888 (18)
mean	1.760	1.755	1.907	1.903
		Angles (deg)		
M–X1–C11	108.2 (3)	106.4 (3)	105.3 (4)	105.4 (4)
M–X2–C21	108.6 (3)	106.8 (3)	110.1 (4)	104.4 (7)
M–X3–C31	111.7 (3)	110.6 (3)	106.8 (4)	106.4 (6)
M–X4–C41	108.6 (3)	107.5 (3)	105.6 (4)	104.0 (6)
mean	109.3	107.8	107.0	105.0
X1–M–X2	103.9 (1)	105.1 (1)	113.0 (1)	102.6 (1)
X1–M–X3	112.1 (1)	113.8 (1)	119.2 (1)	110.2 (1)
X1–M–X4	117.2 (1)	116.6 (1)	102.9 (1)	114.0 (1)
X2–M–X3	113.7 (1)	112.1 (1)	98.9 (1)	115.0 (1)
X2–M–X4	110.4 (1)	110.5 (1)	113.0 (1)	113.5 (1)
X3–M–X4	99.9 (1)	98.9 (1)	110.4 (1)	101.9 (1)

Found: C, 45.64; H, 5.31; N, 3.36. ^1H NMR (Me_2SO-d_6): NCH_3, 3.02 ppm; C_6H_5, 6.69 (*m*-, *p*-H), 7.53 ppm (*o*-H).

$[NMe_4]_2[CdSePh)_4]$ (4). The complex was synthesized by the same method described above. Colorless needles were obtained. Anal. Calcd for $C_{32}H_{44}N_2Se_4Cd$: C, 43.43; H, 5.01; N, 3.17. Found: C, 43.36; H, 5.14; N, 3.18. ^1H NMR (Me_2SO-d_6): NCH_3, 3.02 ppm; C_6H_5, 6.75 (*m*-, *p*-H), 7.58 (*o*-H) ppm.

Physical Measurements. Far-infrared spectra were recorded on a Jasco DS-402G spectrophotometer. Frequencies were calibrated with a polystyrene film. Nujol mulls were used for the solid-state spectra.

The Raman spectra were measured on a Jasco R-800 spectrophotometer equipped with a HTV-R649 photomultiplier. A single crystal placed in a capillary was irradiated with a 514-nm Ar laser excitation line. The frequency calibration of the spectrometer was carried out with indene as a standard.[14] The polarized Raman spectra were obtained with illumination of the two polarized excitation laser lines along the *b* and *c* axes of the crystals. The crystal was irradiated from the plane *c* (*y* direction) with a polarizing irradiation having an electric vector parallel to the *z* axis. Raman scattering in the *x* direction having a polarization in the *z* direction was recorded.

Crystallographic Data Collections and Structure Determinations. The X-ray diffraction measurements of the four complexes were performed by the following method. The crystals of **1–4**, sealed in glass capillaries under argon, were mounted on a Rigaku AFC-C-4 rotating anode automatic four-circle diffractometer for data collection at room temperature using graphite-monochromated Mo Kα radiation. No absorption correction was made, which might limit the accuracy of the present structure analyses. Crystal data concerning crystal characteristics and X-ray diffraction measurements are listed in Table I. Unit cell dimensions were refined with 25 reflections. Three standard reflections were chosen and monitored with every 100 reflections and did not show any significant change. The positions of the Zn or Cd and S or Se atoms were determined by direct methods (MULTAN 80). Subsequent Fourier syntheses

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[14] Hendra, P. J.; Loader, E. J. *Chem. Ind.* (*London*) **1968**, 718.

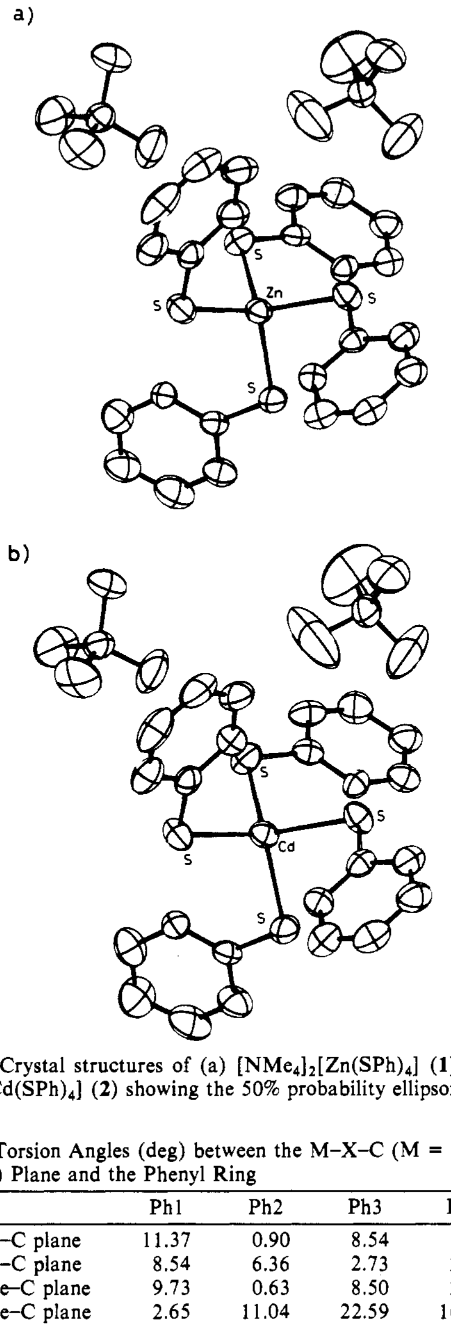

Figure 1. Crystal structures of (a) $[NMe_4]_2[Zn(SPh)_4]$ (**1**) and (b) $[NMe_4]_2[Cd(SPh)_4]$ (**2**) showing the 50% probability ellipsoids.

Table V. Torsion Angles (deg) between the M-X-C (M = Zn, Cd; X = S, Se) Plane and the Phenyl Ring

	Ph1	Ph2	Ph3	Ph4
Zn-S-C plane	11.37	0.90	8.54	1.13
Cd-S-C plane	8.54	6.36	2.73	2.96
Zn-Se-C plane	9.73	0.63	8.50	2.03
Cd-Se-C plane	2.65	11.04	22.59	16.33

based on the phases of Zn or Cd and S or Se atoms determined the positions of the remaining nonhydrogen atoms. The final refinement was carried out using full-matrix least-squares techniques with non-hydrogen atoms except for hydrogens on the phenyl rings. The refined anisotropic thermal parameters result in convergence at $R = 0.039$–0.053. Atom scattering factors were taken from ref 15. The absolute configurations of (Zn-S), (Cd-S), (Zn-S), and (Zn-Se) were determined from five reflections with large Bijvoet differences.

The atomic coordinates of the non-hydrogen atoms and the estimated standard deviations for the four complexes are given in Tables II and III.

Results and Discussion

Structures of $[NMe_4]_2[Zn(SPh)_4]$, $[NMe_4]_2[Zn(SePh)_4]$, $[NMe_4]_2[Cd(SPh)_4]$, and $[NMe_4]_2[Cd(SePh)_4]$. **1**–**3** crystallized in space group $P2_1$ of the monoclinic system with two formula units per unit cell, and **4** belongs to the orthorhombic system in $P2_12_12_1$ with four units per unit cell. **1**–**3** have a significantly distorted T_d structure of the MX_4 (M = Zn(II); Cd(II); X = S, Se) core, whereas **4** shows a slight distortion. The crystal data are collected in Table I. The bond lengths of Zn-S and Cd-S are 2.357 and 2.541 Å, respectively. Table IV lists selected structural parameters of the four complexes. Swenson et al. have reported the crystal structure ($Pbc2_1$, $Z = 4$) of $[Ph_4P]_2[M(SPh)_4]$ (M = Zn, Cd), which has a cation different from those of **1** and **2**.[9] The distortion of the MS_4 cores of **1** and **2** is almost same as that of $[Ph_4P]_2[M(SPh)_4]$. The S-Zn-S angles of $[Ph_4P]_2[Zn(SPh)_4]$ were reported to be 96.7–121.1°,[9] but the angles of **1** are 99.9–117.2°. The S-Cd-S angles of $[Ph_4P]_2[Cd(SPh)_4]$ have been reported to be 98.7–120.0°, whereas **2** has bond angles of 98.9–116.6°. This distortion of the MS_4 core is independent of the packing forces since adoption of the different cations results in formation of different space groups. Coucouvanis et al. have discussed that the distortion of FeS_4 core in $[Ph_4P]_2[Fe(SPh)_4]$ is caused by the intramolecular interaction between sulfur and an ortho proton of the thiophenolato group.[16] A large distorted tetrahedral structure has been observed for $[NEt_4]_2[Ni(S\text{-}p\text{-}C_6H_4Cl)_4]$ by Rosenfield et al.[17] They suggested that the distortion occurs to reduce steric interaction between the ortho hydrogen atom of the phenyl group and Ni or S atoms.

The MX_4 cores of **1**–**3** have similar distorted structures with X-M-X angles in the range 99–119°, but **4** shows only a slight distortion with angles of 102–115°. The presence of an intramolecular interaction among sulfur, the metal ion, and the phenyl ring is supported by the distortion of the MS_4 core, especially an interaction between phenyl ortho proton and S or Se as proposed for $[PPh_4]_2[Fe(SPh)_4]$ by Coucouvanis et al.[16] A weak hydrogen bond between them has been considered to be involved with the lone pair of the sulfur ligating atoms. Although the increased ionicity of Se trends to be more preferable for the interaction, **3** and **4** exhibit less distorted MSe_4 cores. A small distortion of the MSe_4 core of **4** is explicable with less interaction between the phenyl ortho proton and Se by the elongation of the Se-C bond. However, steric congestion should also be considered for the structure of **1**–**3**.

A C_2 symmetry was found for the structure of $M(SC)_4$ cores of **1** and **2** as shown in Figure 1 and is different from the D_{2d} symmetry reported by Swenson et al. for their related complexes having a different cation.[9] The difference in the crystal structures between the C_2 structure of **1** or **2** and the D_{2d} structures of $[PPh_4]_2[M(SPh)_4]$ is caused by a packing force effect. Table V lists the X-C torsion angle between M-X-C (M = Zn, Cd; X = S, Se) plane and the phenyl ring for the four complexes. It is noteworthy that **4** has relatively large X-C torsion angles with rotated phenyl rings probably due to the packing force effect, since ~0° for the X-C torsion angle is expected by the π-interaction between S pπ and phenyl π orbitals. The packing force effect probably includes a phenyl-phenyl interaction between thiophenolato ligands and $[PPh_4]^+$.

The structures of **3** and **4** have C_2 geometries for $[M(SePh)_4]^{2-}$ cores, which are illustrated in Figure 2. The averages of the Zn-Se and Cd-Se lengths are 2.469 and 2.649 Å, respectively. The differences between the Zn-S and Zn-Se lengths or between the Cd-S and Cd-Se lengths are approximately 0.1 Å, which is consistent with the difference in the covalent radii of S (1.02 Å) and Se (1.17 Å). However, the Se-C lengths of **3** and **4** are longer by 0.14 Å than the S-C lengths of the corresponding complexes. The results indicate that the Zn-S bond has a relatively covalent character since the π-interaction between S pπ and the phenyl ring is incorporated into the Zn-S bonding. Such covalent character has been discussed in the case of the other metal complexes having thiolate ligands such as blue copper proteins.[18] Then the S-C distance of **1** becomes slightly longer with a decrease in the S-C bond strength when compared with **2**. Actually, S-C

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(15) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, p 99.

(16) Coucouvanis, D.; Swenson, D.; Baenzinger, C.; Murphy, C.; Holah, D. G.; Sfarnas, N.; Simopoulos, A.; Kostikas, A. *J. Am. Chem. Soc.* **1981**, *103*, 3350.

(17) Rosenfeld, S. G.; Armstrong, W. H.; Mascharak, P. K. *Inorg. Chem.* **1986**, *25*, 3014.

(18) Penfield, K. W.; Gay, R. R.; Himmelwright, R. S.; Eickman, N. C.; Norris, V. A.; Freeman, H. C.; Solomon, E. I. *J. Am. Chem. Soc.* **1981**, *103*, 4382.

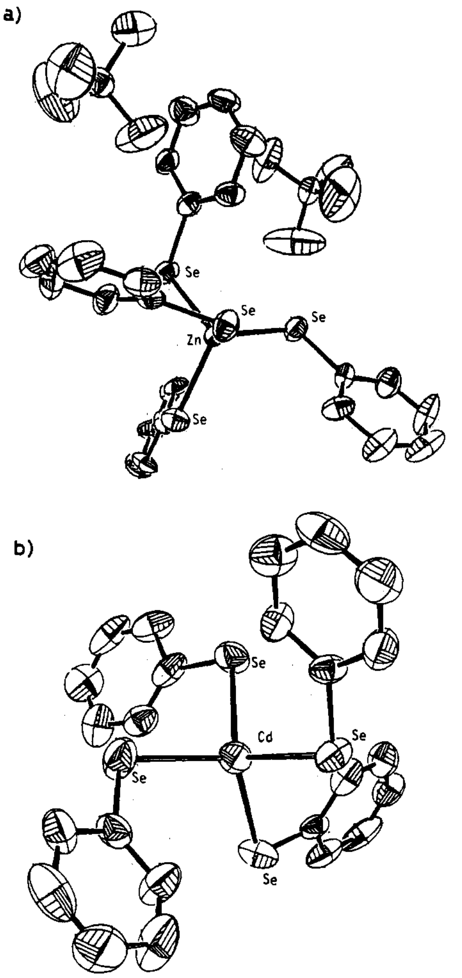

Figure 2. Crystal structures of (a) $[NMe_4]_2[Zn(SePh)_4]$ (**3**) and (b) $[NMe_4]_2[Cd(SePh)_4]$ (**4**) showing the 50% probability ellipsoids.

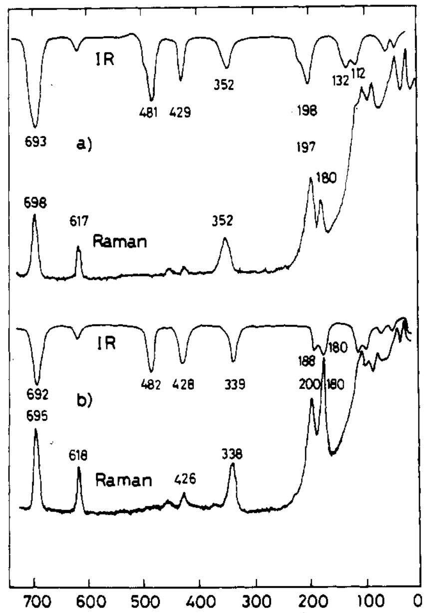

Figure 3. Far-infrared and resonance Raman spectra (800–60 cm^{-1} region) of $[NMe_4]_2[Zn(SPh)_4]$ (**1**) and $[NMe_4]_2[Cd(SPh)_4]$ (**2**) in the solid state.

is 1.80 (1) Å for Ph-S-S-Ph.[19] **1** has a larger Zn–S–C angle (109.3°) than the Zn–Se–C angle (106.9°) in **3**. The Cd–S–C angle (107.5°) is also larger than the Cd–Se–C angle (105.0°). The small M–X–C (M = Zn(II), Cd(II); X = S, Se) angles are interpreted to reflect the increase of the ionic M–X character, which is accompanied by a longer M–X bond. This trend is due to the slightly higher polarity of the M–Se bond. Thus, the weakness of Se–C bonding parallels the smaller M–Se–C angles. In the case of strongly covalent M–S bonds, the M–S–C bond angle with a strong covalent M–S band has been reported to be

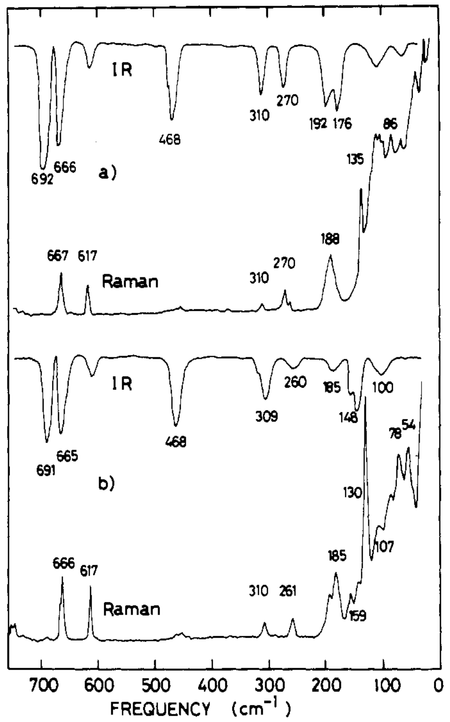

Figure 4. Far-infrared and resonance Raman spectra (800–60 cm^{-1} region) of $[NMe_4]_2[Zn(SePh)_4]$ (**3**) and $[NMe_4]_2[Cd(SePh)_4]$ (**4**) in the solid state.

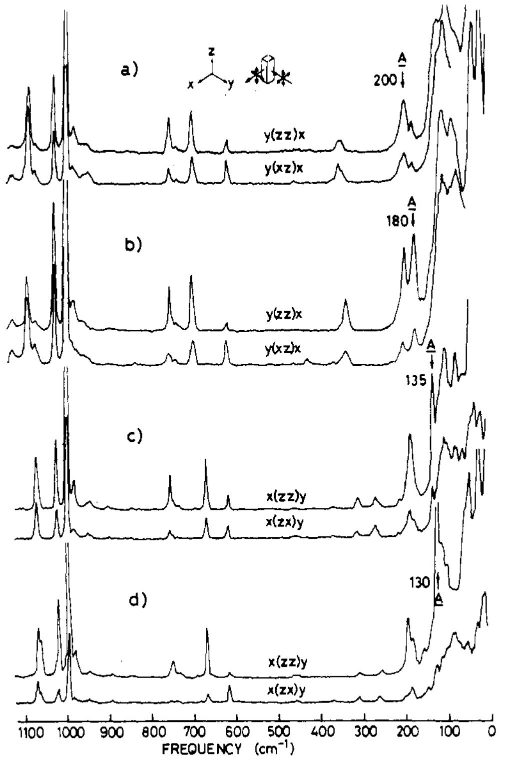

Figure 5. Polarized resonance Raman spectra of single-crystal $[NMe_4]_2[M(XPh)_4]$ (M = Zn(II), Cd(II); X = S, Se) at ambient temperature: (a) **1**; (b) **2**; (c) **3**; (d) **4**.

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[19] Llabres, P. G.; Dupont, O. D. L. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *B28*, 2438.

Table VI. Far-Infrared and Raman Frequencies (cm^{-1}) of $[NMe_4]_2[Zn(SPh)_4]$, $[NMe_4]_2[Cd(SPh)_4]$, $[NMe_4]_2[Zn(SePh)_4]$, and $[NMe_4]_2[Cd(SePh)_4]$[a]

1		2		3		4	
IR	Raman	IR	Raman	IR	Raman	IR	Raman
	1082 m		1082 m		1069 m		1072 m
	1022 w		1022 m		1024 m		1022 m
	994 s		995 s		996 s		996 s
	980 w		980 w		983 w		983 w
	945 w		945 w		945 w		946 w
	751 m		750 w		755 w		751 w
693 s	698 m	692 s	695 w	692 s		691 s	
				666 s	667 m	665 s	666 m
615 m	617 m	616 m	618 m	616 m	617 m	616 m	617 m
481 s		482 s					
				468 s		468 s	
					455 w		
429 m		428 s	426 w				
352 m	352 m						
		339 m	338 m				
				310 m	310 w	309 m	310 w
	200 w			270 m	270 m	260 m	261 m
198 m	197 s	188 w	200 m	192 m	188 s		197 w
	180 w	180 m	180 s	176 m		185 w	185 s
						148 m	146 w
132 m					135 s		130 s
112 w	103 w	114 m	108 w	106 m	106 w	100 w	107 w
	80 w	99 w	91 w		86 w		86 w
			71 w				71 w
					65 w		
	40 w		39 w		38 w		54 w
	24 w		24 w		23 w		17 w

[a] Key: s, m, and w refer to strong, medium, and weak, respectively.

Table VII. Far-Infrared and Raman Frequencies (cm^{-1}) of $[NMe_4]_2[Zn(SPh)_4]$, $[NMe_4]_2[Cd(SPh)_4]$, $[NMe_4]_2[Zn(SePh)_4]$, and $[NMe_4]_2[Cd(SePh)_4]$[a]

	1		2		3		4	
assignts	IR	Raman	IR	Raman	IR	Raman	IR	Raman
ν(X–C)	693 s	698 m	692 s	695 m	666 s	667 m	665 s	666 m
ν(M–X) + δ(M–X–C)	352 m	352 m	339 m	338 m	192 m	188 s	185 w	185 s
ν(M–X)	198 m	200 w	180 m	180 s		135 s		130 s

[a] Key: s, m, and w refer to strong, medium, and weak, respectively.

about 109°, as observed for the Co–S–C, Ni–S–C, of Mn–S–C angles in $[M'(SPh)_4]^{2-}$ (M′ = Co(II), Ni(II), Mn(II)).[9] However, the formation constant of $[Cd(SPh)_4]^{2-}$ in a methanol solution has been reported to be smaller than that of $[Cd(SePh)_4]^{2-}$.[20] The large formation constant may correspond to the stronger Cd–Se bond. Further investigation is required to rigorously correlate the M–S–C angle to the M–S bond strength.

Infrared and Raman Spectra. $[NMe_4]_2[Zn(SPh)_4]$ (**1**) and $[NMe_4]_2[Cd(SPh)_4]$ (**2**) in the solid state show similar IR and Raman bands in the region 2000–700 cm^{-1}, while $[NMe_4]_2[Zn(SePh)_4]$ (**3**) and $[NMe_4]_2[Cd(SePh)_4]$ (**4**) have an analogous pattern of Raman bands. Therefore, two strong bands at 1570 and 994–996 cm^{-1} are assignable to the modes associated with the phenyl ring, which are observed at 1570 and 997 cm^{-1} for PhSSPh or PhSeSePh and at 1532 and 999 cm^{-1} for PhSH (liquid). Figures 3 and 4 shows the far-infrared and the resonance Raman spectra of the four complexes in the region 800–60 cm^{-1}. Selected frequencies of the four complexes are listed in Table VI. The characteristic bands for the thiophenolato complexes (**1** and **2**) were found at 1082 and 695–698 cm^{-1} (692–693 cm^{-1} in the IR spectra), whereas the corresponding bands for the selenophenolato complexes (**3** and **4**) were observed at 1069–1072 and 666–667 cm^{-1} (665–667 cm^{-1} in the IR spectra). The respective former bands are assignable to the mode of phenyl ring coupled with S–C or Se–C and the respective latter bands are due to S–C or Se–C. Two steady bands at 751 and 617–618 cm^{-1} observed for all four complexes are due to the conjugated C=C bands of the phenyl ring.

3 and **4** exhibit two strong Raman bands at 188 and 135 cm^{-1} and at 185 and 130 cm^{-1}, respectively. These bands are associated with the vibrations of M–Se bonds. These assignments were confirmed by the measurement of polarized Raman spectra using $x(yz)y$, $x(yx)y$, $x(zx)y$, and $x(zz)y$ conditions. A typical polarized resonance Raman spectra of **1**–**4** in a single crystal is shown in Figure 5. Raman bands with the higher peak height irradiated under $x(zz)y$ are assigned to a ν(M–X) (A) stretching vibration in the C_2 structure. A strong Raman line at 200 cm^{-1} for **1**, at 180 cm^{-1} for **2**, at 135 cm^{-1} for **3**, or at 130 cm^{-1} for **4**, was observed in $x(zz)y$. These bands are IR inactive as shown in Table VI. **1**–**3** have a similar crystalline packing state while the Bravais primitive cell contains two molecules. The weak polarized Raman band for A in **1** is probably ascribed to the splitting of degenerating frequencies by a distortion of the ZnS_4 core from T_d rather than by intermolecular interactions in the crystalline state. The strong band at 188 cm^{-1} for **3** or at 185 cm^{-1} for **4** is associated with the (ν + δ) mode of M–Se (M = Zn(II), Cd(II)). Table VII lists the assignment of the observed bands concerned with M–X. The small difference of the A stretching bands for **3** and **4** indicates that the mass effect of Cd(II) is compensated with the long Cd–Se bond.

In conclusion, the Raman bands associated with M–S vibrations were found at 352 and 197 cm^{-1} for **1** and at 338 and 180 cm^{-1} for **2**. The strong Raman bands at 197 and 180 cm^{-1} are assignable to Zn–S and Cd–S stretching bands (A), respectively. Actually, the Zn–S and Cd–S Raman bands were been reported to occur at 273 and 193 cm^{-1} and at 245 and 180 cm^{-1} for bis(monothioacetylacetonato)zinc(II) and -cadmium(II), respec-

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(20) Carson, G. K.; Dean, P. A. W. *Inorg. Chim. Acta* **1982**, *66*, 37.

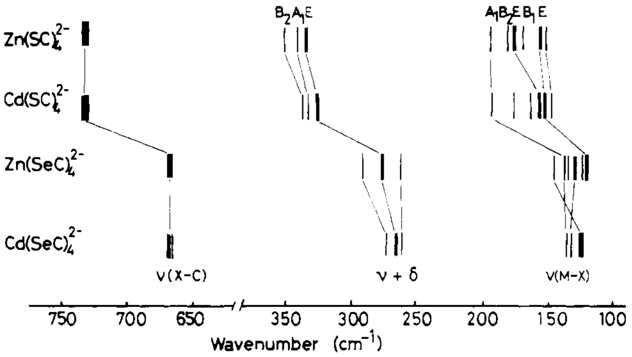

Figure 6. Calculated vibrational frequencies of ideal D_{2d} $[M(X{-}C{=})_4]^{2-}$ (M = Zn(II), Cd(II), X = S, Se). The following parameters were employed for the normal-coordinate analysis. Bond lengths: Zn–S = 2.36 Å, Cd–S = 2.54 Å, Zn–Se = 2.47 Å, Cd–Se = 2.65 Å, S–C = 1.76 Å, Se–C = 1.90 Å. Bond angles: Zn–S–C = 109.35°, Cd–S–C = 107.59°, Zn–Se–C = 106.95°, Cd–Se–C = 105.03°. Force constants:[23-25] K_Y(M–X) = 0.60 mdyn/Å, K_Y(X–C) = 2.75 mdyn/Å, H_θ(X–M–X) = 0.31 mdyn Å/rad^2, H_θ(X–C) = 1.39 mdyn Å/rad^2, F_R(M–X,M–X) = 0.14 mdyn/Å, F_R(M–X,X–C) = 0.17 mdyn/Å, $F_{R\theta}$(M–X,X–M–X) = 0.128 mdyn/rad, $F_{R\theta}$(M–X,M–X–C) = 0.128 mdyn/rad, $F_{R\theta}$(X–C,M–X–C) = 0.128 mdyn/rad, T(M–X,X–C) = 0.1 mdyn Å/rad.

tively.[21] Haberkorn et al. reported the Cd–S Raman bands at 197 and 160 cm^{-1} for $[Cd_{10}(SCH_2CH_2OH)_{16}][ClO_4]$ and at 190 and 168 cm^{-1} for $Cd(SCH_2CH_2OH)_2$.[22]

Normal-Coordinate Analysis. For the assignment of the vibrational frequencies of these four complexes, the normal coordinate analysis was carried out by using the lattice Vibration Program.[23] For a simple calculation of the frequencies in the region 800–100 cm^{-1}, a point carbon atom was employed, in stead of the phenyl group, as $[M(XC{=})_4]^{2-}$ (M = Zn, Cd, X = S, Se) in the calculation because of the convenient analysis of M–S frequencies in the 800–100-cm^{-1} region. The coordinate parameters obtained by the X-ray analysis were used. The force constants were obtained by fitting the observed values in the reference with the literature values for the related compounds.[23-25] The same force constants (Figure 6) were utilized for the normal-coordinate analysis to compare the M–X bond character. A D_{2d} structure was adopted as an ideal geometry because it has the highest symmetry for the $[M(XPh)_4]^{2-}$ structure. Figure 6 shows the calculated vibrational frequencies if ideal D_{2d} $[M(X{-}C{=})_4]^{2-}$. The Raman band in **1** and **2** (695–698 cm^{-1}) or **3** and **4** (666–667 cm^{-1}) is assigned to ν(X–S). An M–Se stretching vibration (A_1) of **3** and **4** also shifts to lower frequency (120-cm^{-1} shift). The vibrational frequencies for the four complexes with C_2 point symmetries were calculated by using the coordinates obtained by the X-ray analysis and compared with the above results for the D_{2d} structure. The calculated M–X stretching frequencies are in good agreement with the observed bands and support the assignment in Table VII. Thus, no significant difference in M–X stretching bands (A_1 and A) between D_{2d} and C_2 was found. Therefore, the M–X stretching band (A) is not suitable as a monitor for the distortion from D_{2d} to C_2. For the vibrational frequencies of phenyl ring, two bands at 750 and 618 cm^{-1} for **1–4** were assigned.

In the cases of native proteins, a distorted ZnS_4 core in pseudo-C_2 symmetry has been found for the $[Zn(cys\text{-}S)_4]^{2-}$ core of horse liver alcohol dehydrogenase.[2,26] The less distorted ZnS_4 core in pseudo-D_{2d} symmetry has been reported for aspartate carbamoyltransferase.[3,26] Likewise, rubredoxin has a pseudo-D_{2d} structure around the active site, $[Fe(cys\text{-}S)_4]^-$.[4] These alternative structures are probably fixed with different peptide conformations due to the characteristic amino acid fragments such as Cys-X-Y-Cys for aspartate carbamoyltransferase and rebredoxin, and Cys-X-Y-Cys-A-B-Cys for horse liver alcohol dehydrogenase.

In conclusion, distinguishable distorted-tetrahedral structures were found for the MX_4 cores of **1–3** and only a slight distortion was found for **4**. The X-ray analyses of **1–4** indicate C_2 geometries for $[M(XPh)_4]^{2-}$. M–X stretching bands (A) for **1–4** were assigned by the polarized Raman spectral method and the normal-coordinate analysis.

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Registry No. **1**, 76915-22-5; **2**, 82677-50-7; **3**, 112247-25-3; **4**, 112247-26-4; (trimethylsilyl)selenophenol, 33861-17-5.

Supplementary Material Available: Listings of complete atomic parameters and anisotropic thermal parameters for **1–4** (10 pages); listings of observed and calculated structure factors for **1–4** (44 pages). Ordering information is given on any current masthead page.

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Notes

Contribution from the Department of Chemistry,
University of Louisville, Louisville, Kentucky 40292

Reactions at a Dimolybdenum(V) Sulfur Bridge. Alkyne Additions

Ana C. Lizano and Mark E. Noble*

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Addition reactions of metal sulfide, hydrosulfide, disulfide, and higher polysulfide complexes with alkenes and alkynes have recently revealed a variety of product types. Some products are characterized as arising from formal S,S-addition to unsaturated substrates and contain 1,2-alkanedithiolate and 1,2-alkenedithiolate ligands.[1-16] M,S-addition (M = metal) to alkynes has been shown to give alkene disulfide complexes wherein the ligand is bound to the metal via carbon and sulfur.[15-18] Formal S,H-addition to

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