X-ray crystal structures of a series of $[M^{II}(SR)_4]^{2-}$ complexes ($M = Mn$, Fe, Co, Ni, Zn, Cd and Hg) with S_4 crystallographic symmetry

Amrita Silver, Stephen A. Koch* and Michelle Millar*
Department of Chemistry, State University of New York at Stony Brook, Stony Brook, NY 11794 (USA)

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Abstract

The X-ray crystal structures of an isomorphous and isostructural series of compounds, M(II) tetrathiolate complexes, $[Et_4N]_2[M(S\text{-}2\text{-}Ph\text{-}C_6H_4)_4]\cdot 2CH_3CN$ ($M = Mn$, Fe, Co, Ni, Zn, Cd, Hg) are determined. The compounds crystallize in the tetragonal space group $I\bar{4}c2$ (No. 120), which imposes S_4 crystallographic symmetry on the $[M(S\text{-}2\text{-}Ph\text{-}C_6H_4)_4]^{2-}$ anions. Each of the $[M(S\text{-}2\text{-}Ph\text{-}C_6H_4)_4]^{2-}$ anions have tetragonally compressed $[MS_4]$ cores. The structures of this series of complexes add to the structural analysis of conformational isomers of $[M(SAr)_4]^{2-/1-}$ complexes which are significant as models for [M(II)–(S-cys)$_4$] centers in proteins.

Introduction

Tetrahedral [M(S-cys)$_4$] centers occur as an important coordination mode in metalloproteins. The [M(S-cys)$_4$] unit exists as an Fe(II,III) center in rubredoxin [1] and as a Zn(II) center in alcohol dehydrogenase [2], aspartate transcarbamoylase [3] and in certain zinc-finger proteins [4]. In addition, new types of [M(S-cys)$_4$] centers have been created by the substitution of the metals in these proteins by such ions as Co^{II}, Ni^{II} and Cd^{II} [5–7]. Simple $[M(SR)_4]^{n-}$ ($n = 1, 2$) complexes have been extensively studied as structural and spectroscopic models for these biologically occurring [M(S-cys)$_4$] centers [8]. In particular, complexes of arylthiolates, $(ArS)^{1-}$, have played an important role in these investigations. For some time now, work in our laboratories has centered on the study of complexes of the 2,6-disubstituted derivatives of benzene thiolate as models for metal–cysteine centers in proteins [9–12]. We have recently expanded this work to include aromatic thiolate ligands that contain only one substituent in the *ortho* position. In the course of this study, we have discovered an isomorphous set of $[R_4N]_2[M^{II}(SAr)_4]$ metal complexes of 2-phenylbenzenethiolate, $[S\text{-}2\text{-}Ph\text{-}C_6H_4]^{1-}$.

Herein, we report the structure determinations of an isomorphous and isostructural series of complexes, $[Et_4N][M^{II}(S\text{-}2\text{-}Ph\text{-}C_6H_4)_4]$ with $M = Mn$, Fe, Co, Ni, Zn, Cd and Hg, which possess high crystallographic symmetry. The salts crystallize in a space group that requires the anions, $[M^{II}(SAr)_4]^{2-}$, to have rigorous S_4 point group symmetry. The crystal symmetry of the Fe^{II} complex and the diamagnetic and transparent Zn^{II} host complex has permitted detailed single crystal spectroscopic studies of the $[Fe^{II}(SR)_4]^{2-}$ complex as a model for the reduced form of rubredoxins [13]. Such studies have complemented the extensive spectroscopic studies performed on single crystals of the Fe^{III}–tetrathiolate complex, $[Fe^{III}(S\text{-}2,3,5,6\text{-}C_6H)_4]^{1-}$, which also possesses S_4 crystallographic symmetry [14]. The discussion of the structures of this series of complexes adds to previous analyses of possible conformational isomers of $[M(SAr)_4]^{2-/1-}$ anions [12, 15, 16].

Experimental

All manipulations were performed using Schlenk techniques. Each of the syntheses of $[Et_4N]_2[M(SR)_4]$ ($M = Mn$, Fe, Co, Ni, Zn, Cd, Hg) was conducted in an analogous manner.

$[Et_4N]_2[Fe(S\text{-}2\text{-}Ph\text{-}C_6H_4)_4]$

Lithium 2-phenylbenzenethiolate, $[Li(S\text{-}2\text{-}Ph\text{-}C_6H_4)]$, was generated in MeOH from the thiol (0.60 g, 3.2 mmol) and lithium (0.023 g, 3.3 mmol). The MeOH was removed, then $FeCl_2$ (0.070 g, 0.55 mmol) was added, followed by the addition of 30 ml of CH_3CN. After stirring for 3 h, the reaction mixture was filtered and the filtrate was added to $[Et_4N]Br$ (0.23 g, 1.1

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*Authors to whom correspondence should be addressed.

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mmol). Large crystals of product formed after 4 days at -20 °C.

X-ray crystallography

$[Et_4N]_2[M(S\text{-}2\text{-}Ph\text{-}C_6H_4)_4] \cdot 2CH_3CN$ (M = Mn, Fe, Co, Ni, Zn, Cd, Hg)

All the complexes were crystallized from hot CH_3CN solution. The common crystal morphology in each case was tetragonal plates. In several cases, crystals of suitable size were cut from larger crystals. All crystals were mounted and sealed in capillaries. The crystals were examined, unit cells were determined, and data were collected using a CAD4 diffractometer with Mo Kα radiation ($\lambda = 0.71069$ Å) at room temperatures. The air sensitive complexes (Mn, Fe, Co and Ni) and the Cd complex were encased in epoxy glue; the crystals showed no decay in the intensity of the standard reflections. In comparison, the Zn and Hg complexes showed a 20 to 30% decay in intensity. The compounds were isomorphous with tetragonal unit cells.

The equivalence of reflections established that the tetragonal cell has the symmetry of the Laue class 4/*mmm*. A set of unique data was collected with $+h$, $+k$, $+l$ with the restriction $k \geqslant h$. The systematic absences were consistent with the space groups $I4cm$ (No. 108), $I\bar{4}c2$ (No. 120) and $I4/mcm$ (No. 140). The unit cell volume indicated four molecules per unit cell. The value of Z and the possible symmetries for the molecules suggested the choice of $I\bar{4}c2$ (No. 120) which was confirmed by the successful structure solution and refinement. The metal ion is located in special position 4b which imposes S_4 symmetry on the $[M(SR)_4]^{2-}$ ions. The N atoms of the two cations occupy special position 8h; the cations have C_2 crystallographic symmetry. The CH_3CN, solvent of crystallization, lies on a crystallographic two-fold axis (special position 8e). The hydrogen atoms were calculated and used in the structure factor calculations but were not refined. An empirical correction for absorption was applied. Since the space group is acentric, each enantiomer was refined. The enantiomer with the lowest R values was chosen as the final model. The different enantiomers in $[Co(S\text{-}2Ph\text{-}C_6H_4)_4]^{2-}$ had R (R_w) of 0.0492 (0.0604) and 0.044 (0.053); $[Ni(S\text{-}2\text{-}Ph\text{-}C_6H_4)_4]^{2-}$, R (R_w) 0.0407 (0.0521) and 0.0506 (0.0639); $[Fe(S\text{-}2\text{-}Ph\text{-}C_6H_4)_4]^{2-}$, R (R_w) 0.0516 (0.0657) and 0.0475 (0.0615). Crystallographic information for the individual structures is given in Table 1. The atomic coordinates for $[Et_4N]_2[Ni(S\text{-}2\text{-}Ph\text{-}C_6H_4)_4] \cdot 2CH_3CN$ are given in Table 2; see also 'Supplementary material'.

Results

The reaction of simple metal salts with excess Li(SR) in CH_3CN provided the series of complexes, $[Et_4N]_2[M(S\text{-}2\text{-}Ph\text{-}C_6H_4)_4] \cdot 2CH_3CN$ (M = Mn, Fe, Co, Ni, Zn, Cd, Hg), which are isomorphous and isostructural. The crystallographic symmetry of the tetragonal unit cell with the $I\bar{4}c2$ (No. 120) space group imposes symmetry on both the cations and the anions. The $[NEt_4]^+$ cations have crystallographic C_2 point group symmetry as do the CH_3CN molecules of crystallization. The $[M(S\text{-}2\text{-}Ph\text{-}C_6H_4)_4]^{2-}$ anions have crystallographic S_4 point group symmetry and as a result the $[MS_4]$ cores have rigorous D_{2d} symmetry (Fig. 1). Relevant bond distances and angles for the series of complexes are given in Table 3. Each complex has a unique M–S bond distance. The reduction in symmetry of the $[MS_4]$ core from T_d to D_{2d} symmetry converts the six equivalent S–M–S tetrahedral angles (of 109.5°) into two sets of equivalent angles: the two S–M–S angles bisected by the S_4 axis (marked angle a in Fig. 2) and the four remaining S–M–S angles (marked angle b in Fig. 2). For each compound, the $[MS_4]$ core is distorted from T_d symmetry by a compression along the S_4 axis; the S–M–S angles bisected by the S_4 axis are greater than 109.5° and the four other S–M–S angles are less than the tetrahedral angle. The compression is the greatest for the Ni complex where the two angles are a = 116.56(8) and b = 106.05(4)° and the smallest for Fe where the angles are a = 113.43(8) and b = 107.53(8)°. Except for the nickel complex, the M–S bond distances in the series of $[Et_4N]_2[M(S\text{-}2\text{-}Ph\text{-}C_6H_4)_4]$ complexes are slightly shorter than the corresponding distances in the related isomorphous series of compounds, $[Ph_4P]_2[M^{II}(SPh)_4]$ [15].

Discussion

The details of the structures of the $[M^{II}(S\text{-}2\text{-}Ph\text{-}C_6H_4)_4]^{2-}$ anions can be understood in relationship to structural principles that have been previously discussed for $[M(SPh)_4]^{n-}$ complexes. The principles were described in detail by Coucouvanis *et al.* in the analysis of the structure of the isomorphous series, $[Ph_4P]_2[M^{II}(SPh)_4]$ (M = Mn, Fe, Co, Ni, Zn, Cd) [15] and extended by us in the analysis of the structure $[NEt_4][Fe^{III}(SPh)_4]$ [12, 16].

In most tetrahedral $[M(SPh)_4]^{2-/1-}$ complexes, the phenyl ring approaches coplanarity with its M–S–C plane*; this conformation (**I** in Fig. 3) allows the overlap

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*An exception to this situation is seen in $[Et_4N][Ga(SPh)_4]$ which has the 'mixed' combination of two coplanar M–SPh groups and two out-of-plane M–SPh groups. This discrepancy may result from the short Ga–S bond distances.

TABLE 1. Crystallographic parameters for $[Et_4N]_2[M(S\text{-}2\text{-}Ph\text{-}C_6H_4)_4]\cdot 2CH_3CN$

M	a (Å)	c (Å)	V (Å^3)	μ (cm^{-1})	$2\theta_{max}$	No. obs.	GOF	R (R_w)
Ni	15.860(7)	24.549(6)	6175(7)	4.90	64	1165	1.46	0.041 (0.052)
Co	15.814(5)	24.75(1)	6190(7)	4.64	64	1439	1.45	0.044 (0.053)
Zn	15.843(4)	24.755(6)	6214(5)	5.81	64	1379	1.48	0.041 (0.053)
Fe	15.844(5)	24.83(2)	6234(8)	4.23	64	1287	1.72	0.048 (0.062)
Mn	15.885(6)	25.05(2)	6323(8)	3.91	60	1070	1.58	0.045 (0.056)
Cd	15.876(9)	25.280(6)	6372(9)	5.12	64	1308	1.47	0.043 (0.053)
Hg	15.857(8)	25.29(1)	6359(9)	26.41	60	982	1.04	0.031 (0.036)

TABLE 2. Positional parameters for $[Et_4N]_2[Ni(S\text{-}2\text{-}Ph\text{-}C_6H_4)_4]\cdot 2CH_3CN$

Atom	x	y	z
Ni(1)	0	0	1/2
S(1)	0.1175(1)	0.0355(1)	0.45100(6)
N(1)	−0.3369(3)	0.1631	1/2
N(2)	0.3126(5)	0.3126	1/4
C(1)	0.0920(4)	0.1056(4)	0.3983(2)
C(2)	0.1494(3)	0.1252(4)	0.3557(2)
C(3)	0.1293(5)	0.1874(4)	0.3186(2)
C(4)	0.0522(5)	0.2299(5)	0.3204(3)
C(5)	−0.0037(5)	0.2090(5)	0.3600(3)
C(6)	0.0154(4)	0.1487(4)	0.3985(2)
C(7)	0.2303(4)	0.0794(4)	0.3468(2)
C(8)	0.2341(4)	−0.0075(5)	0.3459(3)
C(9)	0.3063(5)	−0.0505(5)	0.3319(3)
C(10)	0.3779(4)	−0.0079(7)	0.3197(3)
C(11)	0.3750(5)	0.0785(6)	0.3203(4)
C(12)	0.3035(4)	0.1219(5)	0.3339(3)
C(13)	−0.2498(5)	0.1510(6)	0.4767(4)
C(14)	−0.2210(6)	0.2182(8)	0.4377(4)
C(15)	−0.3485(6)	0.0988(5)	0.5457(4)
C(16)	−0.3495(6)	0.0090(6)	0.5278(4)
C(17)	0.3625(6)	0.3625	1/4
C(18)	0.4286(5)	0.4286	1/4

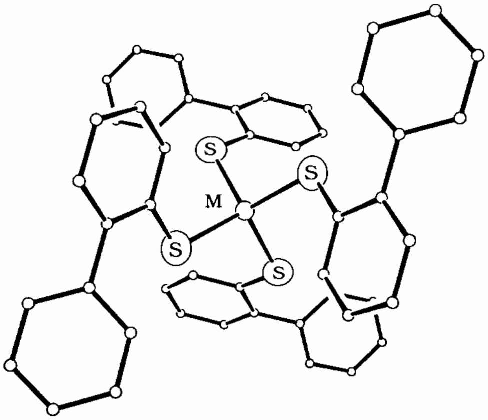

Fig. 1. ORTEP diagram of the anion $[Et_4N]_2[M(S\text{-}2\text{-}Ph\text{-}C_6H_4)_4]$ viewed down the S_4 axis.

of the 3pπ sulfur orbital with the aromatic ring. In contrast, in the structures of analogous complexes with 2,6-disubstituted benzenethiolate ligands the phenyl rings are orthogonal to the M–S–C plane (**II** in Fig. 3); the steric effect of the substituents taken together with the acute M–S–C angles (~90–120°) does not permit the in-plane conformation of the M–S–Ph groups [9–12]. In the present structures (with the 2-monosubstituted benzenethiolate ligand), the in-plane conformation of the M–S–Ar groups is observed (**I** in Fig. 3); the dihedral angles between the thiolate aromatic ring and the M–S–C planes are 14–16°. Since there is only a single bulky *ortho* substituent, the *ortho* hydrogen can be *syn* with respect to the metal while the *o*-phenyl substituent occupies an *anti* position.

In most $[M(SPh)_4]^{n-}$ complexes, the coplanar [M–S–Aryl] group approximately bisects a face of the $[MS_4]$ tetrahedron. Coucouvanis *et al.* recognized that this interaction of the coplanar MSPh groups with the $[MS_4]$ core results in the overall distortion of the $[MS_4]$ tetrahedron in a systematic manner [15]. We later realized that if the individual MSPh groups have this arrangement with respect to the $[MS_4]$ core, then there are only two conformations possible for the entire $[M(SPh)_4]$ unit, both of which have high symmetry: a S_4 and a D_{2d} conformational isomer (Fig. 4) [12, 16].

The D_{2d} isomer is predicted to have a tetragonally elongated $[MS_4]$ core while the S_4 isomer is predicted to have a tetragonally compressed $[MS_4]$ core [12, 15, 16]. The D_{2d} isomer has been observed for $[Ph_4P]_2[M(SPh)_4]$ (M = Mn, Fe, Co, Ni, Zn, Cd) [15], $[Et_4N]_2[Ni(S\text{-}p\text{-}C_6H_4Cl)_4]$ [18] and $[Me_4N]_2[Hg(S\text{-}p\text{-}C_6H_4Cl)_4]$ [19]. In all the cases where the D_{2d} conformational isomer has been observed, the symmetry is only approximate; there is no example of an $[M(SAr)_4]^{2-}$ anion with crystallographically imposed D_{2d} symmetry. The S_4 conformational isomer has been observed for $[Et_4N]_2[Ni(SPh)_4]$ [20], $[Et_4N]_2[Fe(SPh)_4]$ [15], $[Et_4N][Fe(SPh)_4]$ [16], $[Me_4N]_2[M(SPh)_4]$ (M = Zn, Cd) and $[Me_4N]_2[M(SePh)_4]$ (M = Zn, Cd) [21]. In these examples of compounds possessing the S_4 isomer, the symmetry is only approximate. The S_4 symmetry is apparently difficult to discern, since it has gone un-

TABLE 3. Distances (Å) and angles (°) for $[Et_4N]_2[M(S\text{-}2\text{-}Ph\text{-}C_6H_4)_4]$

M	M–S	S–M–S′[a,b]	S–M–S″[c,d]	M–S–C	M–H[e]	H–S′[a]	H–S″[c]	H–S
Ni	2.288(2)	116.56(8)	106.05(4)	110.9(2)	2.85	3.16	3.04	2.83
Co	2.303(1)	114.95(7)	106.80(3)	111.5(2)	2.89	3.16	3.12	2.83
Fe	2.338(2)	113.43(8)	107.53(4)	111.6(2)	2.86	3.15	3.14	2.82
Zn	2.344(1)	115.90(7)	106.36(3)	109.5(2)	2.85	3.17	3.09	2.85
Mn	2.430(2)	115.7(1)	106.44(6)	109.6(2)	2.91	3.27	3.21	2.86
Cd	2.516(2)	115.6(1)	106.48(5)	107.9(3)	2.88	3.33	3.24	2.86
Hg	2.520(3)	115.5(1)	106.55(7)	108.2(4)	2.87	3.30	3.28	2.83

[a] S′ is related to S by C_2 rotation about the S_4 axis. [b] Angle bisected by S_4 axis; corresponds to angle a in Fig. 2. [c] S″ is related to S by a S_4 rotation. [d] Corresponds to angle b in Fig. 2. [e] Distance from metal to the *ortho* hydrogen.

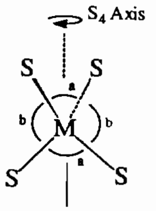

Fig. 2. Diagram showing the distortion of a $[MS_4]$ unit along the S_4 axis.

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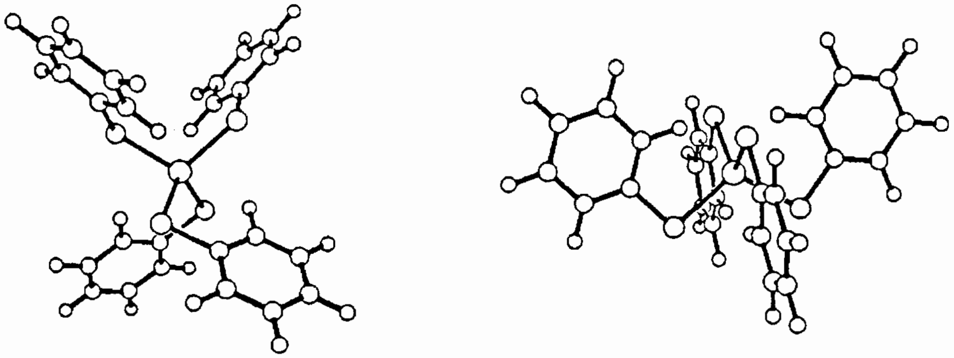
Fig. 3. Diagrams showing two conformations involving the orientation of aromatic ring with respect to the M–S–C plane.

recognized in the descriptions of several structures [15, 20, 21]. In agreement with the predictions [12, 16], all the D_{2d} structures have tetragonally elongated (along the S_4 axis) $[MS_4]$ cores and all the S_4 structures have $[MS_4]$ cores which are tetragonally compressed. A recent study of the EPR and magnetic susceptibility of $[Co(SPh)_4]^{2-}$ complexes has been interpreted to show that the orientation of the $[M(S\text{-}\alpha\text{-}C)_4]$ unit was more important than the distortions in the $[MS_4]$ core in determining the electronic structure of the metal complex [22]. However, the direct relationship between the conformation of the $[M(S\text{-}\alpha\text{-}C)_4]$ unit and the structure of the $[MS_4]$ core should not be overlooked.

The structures reported herein are the first $[M(SAr)_4]^{n-}$ structures (with the coplanar M–S–Ar conformation) that have high crystallographic symmetry imposed on the $[M(SAr)_4]^{n-}$ anion. In several other structures, the $[M(SAr)_4]^{n-}$ anion has C_2 crystallographic symmetry (and only approximate S_4 symmetry) [19, 21]. The $[M(S\text{-}2\text{-}Ph\text{-}C_6H_4)_4]^{2-}$ structures with the S_4 conformation have, as predicted, $[MS_4]$ cores which are distorted from T_d symmetry to D_{2d} symmetry by a compression along the S_4 axis. The extent of this compression varies only by a few degrees throughout the isomorphous series (Table 3).

It appears that the S_4 and the D_{2d} conformational isomers for the $[M(SAr)_4]^{2-}$ units must be close in energy. In several cases, the change in counter ion is enough to crystallize one conformational isomer or the other. There are now examples of both the S_4 and D_{2d} conformational isomers of $[M(SAr)_4]^{2-}$ complexes for Mn(II), Fe(II), Co(II) and Ni(II) as well as for the d^{10} metals (Zn, Cd and Hg). The electron configuration of the metal ion does not have a major influence upon the choice of the conformation of the $[M(SAr)_4]^{2-}$ unit. Crystal packing forces influence whether the D_{2d}



S_4 Isomer D_{2d} Isomer

Fig. 4. Diagrams of the two conformational isomers of $[M(SPh)_4]^{n-}$ compounds.

or the S_4 conformational isomer occurs in the crystalline state. However, it is important to emphasize that crystal packing forces between ions only have a secondary effect on the distortions in the [MS_4] cores which are primarily the result of the interactions of the arylthiolate ligands with the [MS_4] core.

It is of interest to compare the structures of [Fe^{II}(S-2-Ph-C_6H_4)$_4$]$^{2-}$ and [Fe^{III}(S-2,3,5,6-Me_4C_6H)$_4$]$^{1-}$, since each [Fe(SR)$_4$]$^{1-/2-}$ anion possesses crystallographic S_4 symmetry. Both complexes have been the subject of extensive single crystal spectroscopic studies by the Solomon group [13, 14]. In each case, the [FeS_4] cores are distorted in a nearly identical manner by a compression along the S_4 axis. In [Fe(S-2-Ph-C_6H_4)$_4$]$^{2-}$, the two S–Fe–S angles which are bisected by the S_4 axis are a = 113.4° while the remaining four angles are b = 107.5°. Whereas in [Fe^{III}(S-2,3,5,6-Me_4C_6H)$_4$]$^{1-}$, the two S–Fe–S angles bisected by the S_4 axis are a = 114.4° while the remaining four angles are b = 107.08 °. The Fe–S–C angles are larger in [Fe^{II}(S-2-Ph-C_6H_4)$_4$]$^{2-}$ (111.6°) than they are in [Fe^{III}(S-2,3,5,6-Me_4C_6H)$_4$]$^{1-}$ (102°). It is the orientation of the α-C atoms that determines the orientation of the sulfur valence orbitals with respect to the [FeS_4] core. The dihedral angle between the S–Fe–S plane (which is bisected by the S_4 axis) and the Fe–S–C plane is 47.6° in [Fe(S-2-Ph-C_6H_4)$_4$]$^{2-}$ and 90° in [Fe(S-2,3,5,6-Me_4C_6H)$_4$]$^{1-}$.

The structure of the nickel complex, [Ni(S-2-Ph-C_6H_4)$_4$]$^{2-}$, deserves special comment. There has been much discussion on the stereochemical preference of NiS_4 compounds for either tetrahedral or square-planar coordination geometry. It has been suggested that the preferred coordination geometry for [NiS_4] complexes should be square planar [23, 24]. The fact that [Ni(SAr)$_4$]$^{2-}$ complexes are tetrahedral rather than square planar has been rationalized to result from steric factors involving the benzenethiolate ligands [18]. However, there are no structural features in either the D_{2d} or S_4 geometries of the [Ni(SAr)$_4$]$^{2-}$ anions that are not present in the other tetrahedral [M(SAr)$_4$]$^{2-}$ complexes. In both the [Ph_4P]$_2$[M(SPh)$_4$] and the [Et_4N]$_2$[M(S-2-Ph-C_6H_4)$_4$] series, the Ni structures have the greatest tetragonal distortions of the [MS_4] cores; this likely results from the fact that the Ni–S bonds are the shortest in the series of structures. Experimental observations of many examples of complexes with the tetrahedral [NiS_4] geometry as well as examples of the square planar [NiS_4] geometry indicate that there is not a strong preference for either coordination geometry [15, 18, 20, 25–30].

We note that the structure of [Cd(SC_6H_4-o-$SiMe_3$)$_4$]$^{2-}$ recently reported by Zubieta and co-workers, shows a new conformation for [M(SAr)$_4$]$^{n-}$ complexes [31]. Herein, we add to the structural analysis. Although the anion has crystallographic C_2 symmetry, its geometry closely approaches S_4 symmetry. The coplanar [Cd–S–Aryl] groups are oriented with respect to the [MS_4] cores in a manner not previously observed. The Cd–S–Ar planes are oriented along an S–S edge of the [MS_4] tetrahedron. As a result, the o-H of the [Cd–S–Ar] unit closely interacts with only one sulfur. This conformation isomer can be converted to the previously discussed S_4 isomer by rotation of the [SAr] groups about the Cd–S bonds by 180°. The structural analysis predicts a tetragonally elongated [MS_4] tetrahedron for this new S_4 isomer which is in agreement with the observed structure. Interaction between the thiolate ligands would absolutely prevent the occurrence of a D_{2d} isomer in this new conformational system.

Supplementary material

Listings of crystallographic parameters, atomic coordinates, thermal parameters, bond distances and angles (48 pages) and observed and calculated structure factors (65 pages) for [Et_4N]$_2$[M(S-2-Ph-C_6H_4)$_4$]·2CH_3CN (M = Mn, Fe, Co, Ni, Zn, Cd, Hg) are available from the authors on request.

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