Synthesis and Structural Characterization of Monomeric Zinc(II), Cadmium(II), and Mercury(II) Arenethiolates with a Chelating Oxazoline Ligand

G. Mugesh,[a] Harkesh B. Singh,*[a] and Ray J. Butcher[b]

Keywords: Metal thiolates / Helical chirality / Spontaneous resolution / Disulfide / Intramolecular coordination

The synthesis and characterization of homoleptic zinc(II), cadmium(II), and mercury(II) thiolates derived from 4,4-dimethyl-2-phenyloxazoline (**1**) are described. The disulfide [Ox_2S_2 (**3**), Ox = 2-(4,4-dimethyl-2-oxazolinyl)phenyl] is prepared by the oxidation of lithium arenethiolate OxS^-Li^+ (**2**), and structurally characterized. The disulfide **3** is chiral and enantiomerically pure in the solid state. The thiolate derivatives, $M[S(Ox)]_2$ [M = Zn (**4**), or Cd (**5**)], are prepared in good yield by the metathesis reactions of MCl_2 with lithium arenethiolate **2**. The mercury complex **6** is synthesized by treating **3** with elemental mercury. The complexes are quite stable and highly soluble in common nonpolar organic solvents. X-ray diffraction results show that the zinc thiolate **4** and cadmium thiolate **5** are monomeric in the solid state. The geometry around the metal ion in these two complexes is found to be distorted tetrahedral. The zinc complex is chiral and has crystallized in two different crystalline modifications. The single crystal structures have been determined for both the crystalline modifications, a monoclinic modification (**4a**) and an orthorhombic one (**4b**). The crystal structure of **4a** shows that the complex is "helically" chiral and enantiomerically pure whereas the crystal structure of **4b** shows the modification to be racemic. The spontaneous splitting of the racemates, which is responsible for the isolation of optically active compound, indicates that there should be some solubility differences between the racemates and pure enantiomers. ^1H- and ^{13}C-NMR measurements indicate that the complex **4** retains its "helical" structure in solution.

Introduction

There is considerable general interest in the bonding and unusual structures adopted by chalcogenolate complexes of the Group 12 elements.[1] Besides their importance as single-source stoichiometric precursors to Group 12−16 semiconductors,[2] the metal-chalcogen chemistry of these elements has yielded many surprising results with respect to structural features, method of preparation, and degree of aggregation.[3]

As part of our work on intramolecularly coordinated organochalcogens,[4] we have recently isolated some stable monomeric mercury selenolates using *ortho*-chelating [(dimethylamino)benzyl]- and [(dimethylamino)ethyl]ferrocenyl ligands[5] and well-characterized examples of zinc, cadmium and mercury selenolato complexes by using a more rigid 4,4-dimethyl-2-phenyloxazoline substrate.[6] Interestingly, the zinc selenolato complex derived from 4,4-dimethyl-2-phenyloxazoline was found to be chiral at room temperature and the cadmium selenolate showed chirality at low temperatures. Although the corresponding tellurolate complexes of zinc and cadmium showed chirality at low temperatures, the complexes could not be crystallized due to their instability in solution.[7] In order to investigate the effect of the chalcogen atom on the chirality in Group 12 chalcogenolates, we extended our approach to the thiolate chemistry since the high affinity of zinc ions towards thiolates and the very marked preference for ZnN_2S_2 coordination may allow the isolation of "helically" chiral metal complexes.

In this paper, we describe the use of a phenyloxazoline-derived ligand to prepare monomeric Group 12 metal thiolates including a novel "helically" chiral zinc thiolate **4** and its spontaneous resolution. Structurally characterized "mono-helical" complexes of zinc are very rare[8] and this is the first example, to the best of our knowledge, where the two optically active forms have been spontaneously resolved in a four-coordinate zinc thiolate complex. We also describe the synthesis and structure of a novel chiral disulfide stabilized by intramolecular S···N interactions. In addition, the thermal behavior of the zinc, cadmium, and mercury thiolates provided some insight into their utility as CVD precursors.

Results and Discussion

Monomeric Thiolates

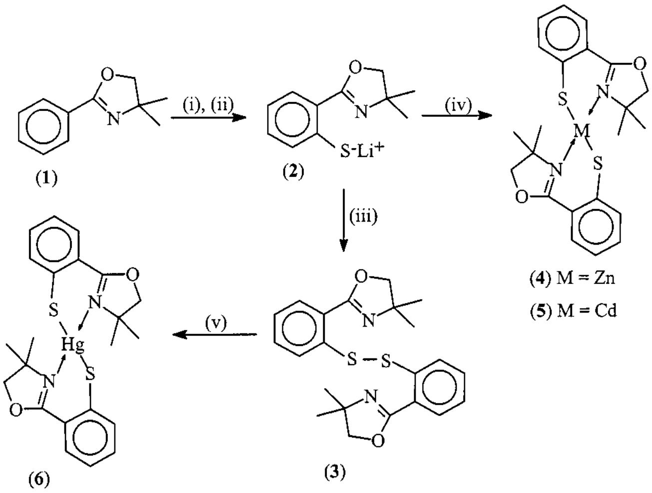
Synthesis of the thiolate complexes was approached by the metathesis reaction of the lithium arenethiolate with the corresponding MCl_2 in ether according to our recently reported method for the synthesis of metal selenolates (Scheme 1).[6] The 2:1 molar reactions of **2** and anhydrous MCl_2 (M = Zn, Cd) in ether afforded the desired products in moderate yields. Attempts to synthesize the mercury thi-

---

[a] Department of Chemistry, Indian Institute of Technology,
Powai, Bombay 400076, India
Fax: (internat.) + 91-22/578-3480,
E-mail: chhbsia@chem.iitb.ernet.in
[b] Department of Chemistry, Howard University,
Washington, D.C. 20059, USA

1434−1948/99/0808−1229 $ 17.50+.50/0

olate by the reaction of **2** with $HgCl_2$ were unsuccessful. The 2:1 molar reactions of **2** and anhydrous $HgCl_2$ afforded the corresponding disulfide **3** resulting, presumably, due to the oxidation of **2** with $HgCl_2$. Recently, we have shown that pure monomeric mercury selenolate complexes could be obtained in two further steps, whereby the lithium areneselenolate was oxidized to the diselenide (which was air-stable and readily purified), followed by the oxidative addition of mercury.[5,6] Therefore, we have approached the synthesis of **6** by the reaction of **3** with elemental mercury. In contrast to the synthesis of corresponding diselenide[4f] and ditelluride,[7] the synthesis of disulfide by aerial oxidation of the lithium arenethiolate **2** was found to be difficult due to higher stability of the arenethiol produced by the addition of the lithium arenethiolate to water, and, therefore, vigorous oxidation was required to convert the thiol to disulfide. The reaction of **3** with elemental mercury then afforded, after several days of stirring at room temperature, **6** in 60% yield.



Scheme 1. Synthesis of M^{II} complexes; reagent and conditions: (i) *n*BuLi, hexane, room temp., 1 h; (ii) S powder, ether, 0°C, 2 h; (iii) O_2, H_2O; (iv) anhydrous MCl_2, 0°C, 1 h, and room temp., 18 h; (v) elemental mercury, methanol, room temp., 5 d

The significant feature of the chemistry of the entire class of complexes **4−6** is their excellent solubility in both nonpolar and slightly polar solvents at room temperature which is generally not a feature of metal chalcogenolate chemistry. They are, however, almost insoluble in highly polar solvents like DMSO and methanol.

Complex **4**, obtained as a yellow solid, shows some interesting features. The complex affords two types of crystals; yellow needle-shaped (**4a**, enantiomerically pure) and white plates (**4b**, racemic) crystals due to spontaneous crystallization of the enantiomers (vide infra). The complex **4** shows very good solubility in ether but the solubility is reduced for the enantiomers in the same solvent. The differences observed between **4a** and **4b** may also be ascribed to the different speed of crystallization. The crystals of **4a** were obtained from a mixture of chloroform/hexane within a day whereas the crystals of **4b** were separated from the solution after five days.

NMR-Spectroscopic Studies

In order to investigate the solution behavior of **3** and the complexes **4−6**, we have studied the ^1H- and ^{13}C-NMR spectra in $CDCl_3$. Although the crystal structure shows that **3** is chiral (vide infra), the room-temperature NMR (^1H, ^{13}C) spectra are not indicative of chirality. A sharp singlet for the methylene protons and another sharp singlet for the methyl protons observed in the ^1H-NMR spectrum of **3** at room temperature infer that the nonbonded S···N interactions are weak in the solution. The room-temperature ^1H-NMR spectrum of **4** contains a well-resolved AB doublet of doublets for the methylene protons and two sharp singlets for the methyl protons (Figure 1). The AB pattern for the methylene protons implies that the strong coordination of the "hard" imine nitrogen atom with the "hard" zinc(II) ion removes the erstwhile enantiotopic nature of these protons. The protons become diasteriotopic resulting in chirality of the complex. We[6] and others[8b,9] have noted a similar AB spin behavior of methylene protons in other complexes and have used it as a diagnostic probe of chirality. The inequivalence of the methylene group protons and two methyl group protons even at 55°C indicates a strong coordination of the nitrogen atom to the metal center and retention of the "helicity" even at higher temperatures. The spectra of both the crystalline modifications [yellow needles (**4a**) and white square plates (**4b**)] are identical.

The room-temperature ^1H-NMR spectrum of **5** consists of a sharp singlet for the methylene protons and another sharp singlet for the methyl protons. At −60°C, the methyl protons give rise to two singlets, however, the signal for the methylene protons is observed as a broad singlet (Figure 2). This is in contrast to the spectra of the corresponding cadmium selenolate[6] and cadmium tellurolate[7] where an AB doublet of doublets for the methylene protons was observed at −60°C. This indicates that the complex is probably not rigid even at −60°C. For complex **6**, the signals for the methylene and methyl protons are observed as sharp singlets. Since the exchange between "helical" and "nonhelical" arrangements is very fast, the splitting of the signals due to chirality could not be detected even at −60 °C. At this temperature only a slight broadening of the signals was observed.

From the current results and their comparison with those of corresponding selenolates[6] and tellurolates,[7] it is observed that the chemical shift values in all the complexes lie almost in the same region and there is no drastic change in the chemical shift values by changing the metal atom or changing the chalcogen atom. However, the signals due to the methyl and methylene protons are shifted upfield compared with the corresponding dichalcogenides probably due to the d^{10} configuration of the metal ions.

The ^{13}C-NMR spectra of the complexes are not very informative. The chemical shift values for the methyl and methylene carbon atoms are very close to the values observed for the disulfide. However, the ^{13}C-NMR spectrum of complex **4** gives some information about the chirality of the complex. Two signals at δ = 26.99 and 28.28 observed

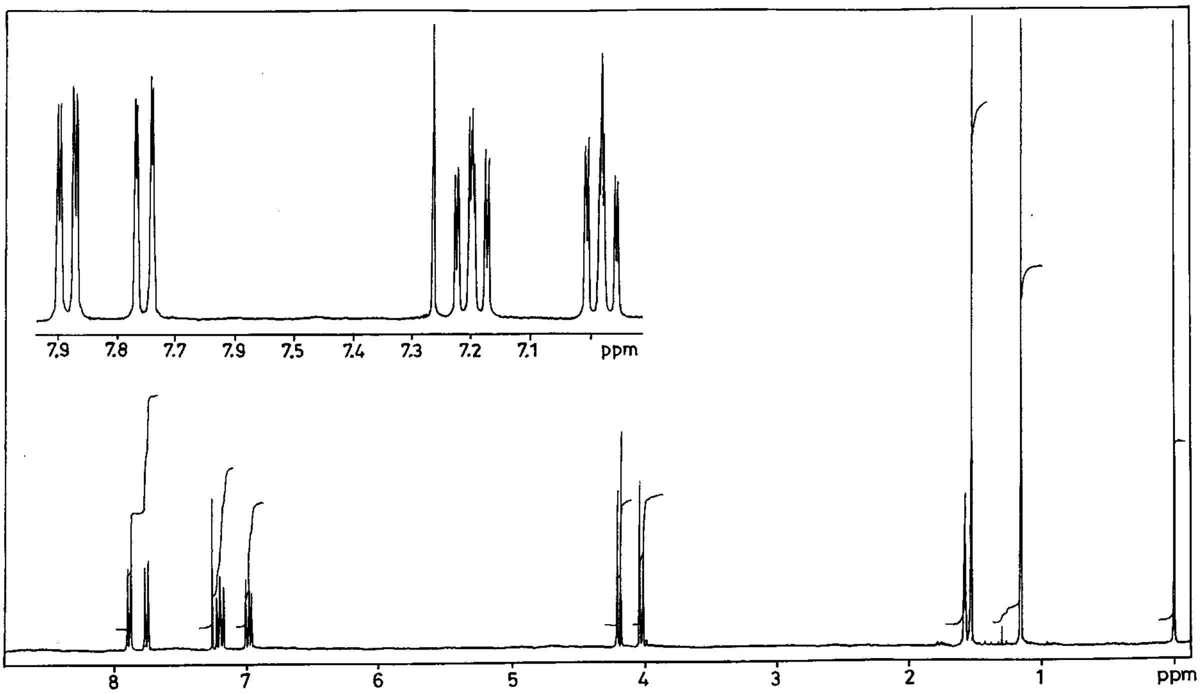


Figure 1. Room-temperature ^{1}H-NMR spectrum of **4a** ($CDCl_3$, 300 MHz)

for the methyl group carbon atoms clearly indicate that the two methyl groups present in the complex are nonequivalent.

Mass-Spectrometric Studies and Thermal Behavior

The mass spectra were recorded for complexes **4** and **5**. The mass spectra of complexes **4** and **5** are indicative of the presence of both monomeric and dimeric species in the gas phase {**4**; *m*/*z*: 477 $[Zn(SOx)_2^+]$, 750 $[Zn_2(SOx)_3^+]$; **5**; *m*/*z*: 525 $[Cd(SOx)_2^+]$, 844 $[Cd_2(SOx)_3^+]$}. The molecular ion peaks and the peaks due to other fragments containing S and M exhibit the expected isotope patterns.

The complexes have sharp melting points in the range 120−195°C giving clear liquids. To further know the volatility of the complexes and the decomposition pathway, TGA and DTA were recorded for all three complexes. The DTA curves of complexes **4**, **5** and **6** showed a phase transition (endothermic peak) in the range 130−200°C which corresponds to their melting. The TGA of complexes **4** and **5** showed the formation of expected metal sulfides (MS: M = Zn, Cd) at 530 and 390°C, respectively at ambient pressure. The mercury complex **6** showed complete weight loss in this temperature range probably due to the high volatility of this complex.

Molecular Structure of Compound 3

The crystal structure of **3** is shown in Figure 3 and the bond lengths and angles are given in Table 1. The interesting feature in this structure is that compound **3** crystallizes in the chiral space group $P2_12_12_1$ of the orthorhombic system. The structure is different from that of the corresponding diselenide[4f] and ditelluride[7] which are not chiral. Refinement of the Flack enantiopole parameter[10] shows that the compound has crystallized in enantiomerically pure form. Generally, the S···N interactions are expected to be weak compared with Se···N and Te···N interactions. However, in compound **3** the S···N interactions are found to be quite strong. The S(1)···N(1) and S(2)···N(2) bond lengths (2.815 and 2.787 Å) are considerably shorter than the sum of the van der Waals radii (3.35 Å) of these two atoms. In contrast to the selenium and tellurium analogues, the two S···N distances are almost equal. The S−S bond length of 2.053(1) Å is comparable to the single-bond covalent radii (2.08 Å).[11] The S(1)−C(11) and S(2)−C(21) bond lengths [1.798(3) Å and 1.790(3) Å] are also comparable to the corresponding single-bond covalent radii (1.81 Å). The angles N(1)···S(1)−S(2) and S(1)−S(2)···N(2) are 173.5° and 172.9°, respectively, indicating an almost linear arrangement of N···S−S···N atoms. The torsion angle C(11)−S(1)−S(2)−C(21) is −79.47°.

Molecular Structure of Compound 4

Complex **4** crystallizes in two different enantiomorphs (**4a** and **4b**). The structures of both crystalline modifications were determined.

Molecular Structure of Compound 4a

The structure of complex **4a** is consistent with the solution data. Interestingly, complex **4a** crystallizes in a chiral space group $P2_1$ with two molecules per unit cell. Crystals

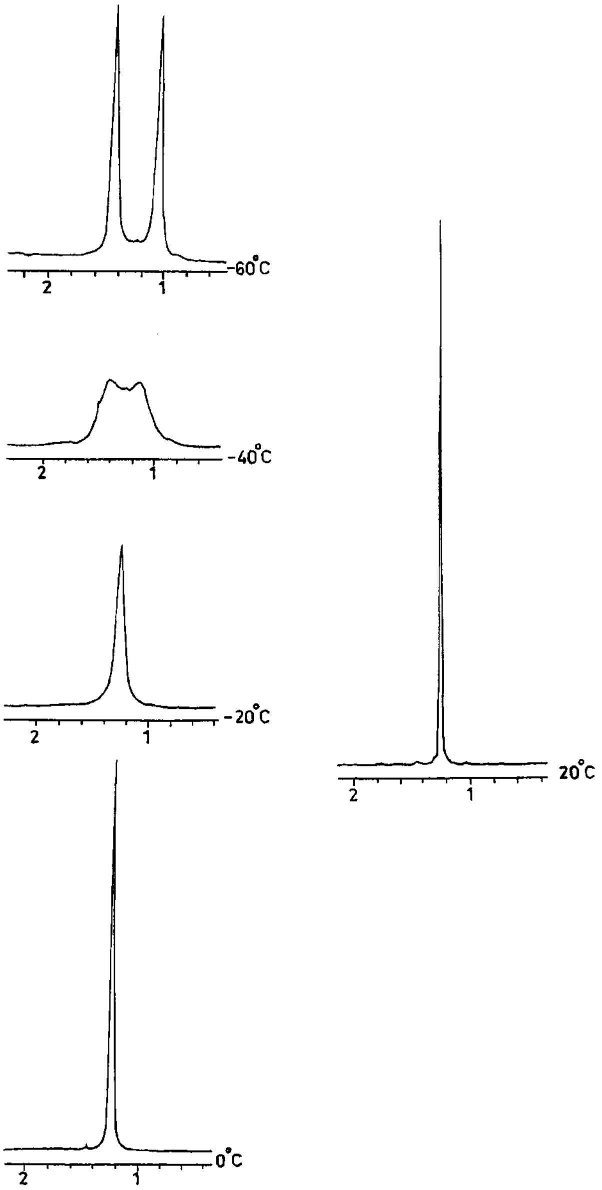


Figure 2. Variable-temperature ^{1}H-NMR ($CDCl_3$, 300 MHz) spectra (in part only) of **5**; at −60°C, the signals due to the CH_3 protons split into two singlets

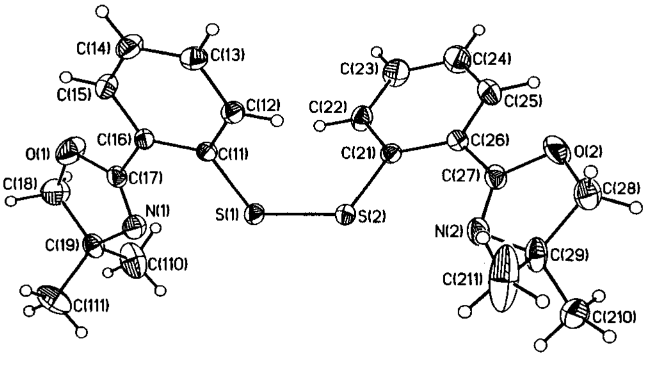


Figure 3. Crystal structure of disulfide **3**

Table 1. Selected bond lengths [Å] and angles [°] for **3**

S(1)−N(1)	2.815(3)	S(2)−N(2)	2.787(3)
S(1)−C(11)	1.798(3)	S(2)−C(21)	1.790(3)
O(1)−C(17)	1.357(4)	O(1)−C(18)	1.437(6)
O(2)−C(27)	1.352(4)	O(2)−C(28)	1.438(6)
N(1)−C(17)	1.244(4)	N(1)−C(19)	1.485(4)
N(2)−C(27)	1.254(4)	N(2)−C(29)	1.492(4)
S(1)−S(2)	2.053(1)		
C(26)−C(21)−S(2)	119.4(2)	C(12)−C(11)−S(1)	121.0(2)
C(11)−S(1)−S(2)	105.6(1)	C(16)−C(11)−S(1)	119.7(2)
C(21)−S(2)−S(1)	105.5(1)	C(22)−C(21)−S(2)	121.5(2)

of the complex **4a** belong to the monoclinic system. The ORTEP[12] view of the molecule is shown in Figure 4 and selected bond lengths and angles are given in Table 2. The structure is similar to that of the corresponding zinc selenolate complex,[6] which also crystallized in the same space group and almost with same cell parameters [the cell in **4** corresponds to $P2_1$ with a = 9.371(1), b = 11.397(1), c = 10.881(1) Å and β = 97.351(9)°; the cell in selenolate[6] corresponds to $P2_1$ with a = 9.390(1), b = 11.618(2), c = 10.882(1) Å and β = 98.245(8)°] and, therefore, the two compounds appear to be isostructural. Although, tetrahedral complexes with AB-type chelate ligands are expected to be chiral, to our knowledge, no optically pure chiral tetrahedral thiolatozinc complexes have been reported so far (generally they crystallize as racemates). Refinement of the Flack enantiopole parameter[10] led to a value of ca. zero for **4a** thus confirming the enantiomeric purity of the crystals.

The complex is monomeric with the zinc atom coordinated to two nitrogen and two sulfur atoms forming a distorted tetrahedron. As a consequence of the interaction of the two chelating ligands which causes the complex to distort in a helical way, chirality is induced at the metal center. The average Zn−S bond length 2.270(1) Å is close to the Zn−S length reported for an $(N_2S_2)Zn^{II}$ Schiff base complex incorporating pyrazole [Zn−S: 2.293(1) Å][13] but slightly shorter than that reported for a chiral five-coordinate Zn^{II} complex (2.34 Å)[8a] and for $Zn(SAr)_2(imid)_2$ (2.315 Å).[14] The Zn−N bond lengths [Zn−N(1): 2.043(3); Zn−N(2): 2.036(4) Å] are very close to the Zn−N length reported for the pyrazole Schiff base complex [2.039(3) Å][13] and for $Zn(SAr)_2(imid)_2$ (2.048Å)[14] and that reported for zinc and typical N-donor ligands which normally range from 2.04 Å to 2.14 Å. However, this bond is much stronger than the Zn−N bond reported for the chiral five-coordinate Zn^{II} complex (2.21 Å).[8a] The C−S bond lengths [S(1)−C(11): 1.758(4) Å; S(2)−C(21): 1.756(5) Å] are intermediate between that of a thione (C−C=S: 1.6 Å) and that of a thiol (C−C−SH 1.8 Å)[15] which is normal for N_2S_2 Schiff base complexes.[16] The chelate bite angles of S(1)−Zn−N(1) and S(2)−Zn−N(2) are 96.16(9) and 97.18(9)°, respectively. The larger bite angle leads to relatively smaller N−Zn−N and S−Zn−S angles of 106.45(14) and 116.47(9)°, respectively.

Interestingly, in the case of the selenium analogue[6] of **4**, the N−Zn−N and Se−Zn−Se bond angles [106.6(2)° and 113.49(4)°] are close to ideal tetrahedral angles and in this case we have isolated optically pure complex whereas in the oxygen analogue, the deviation from the ideal tetrahedral

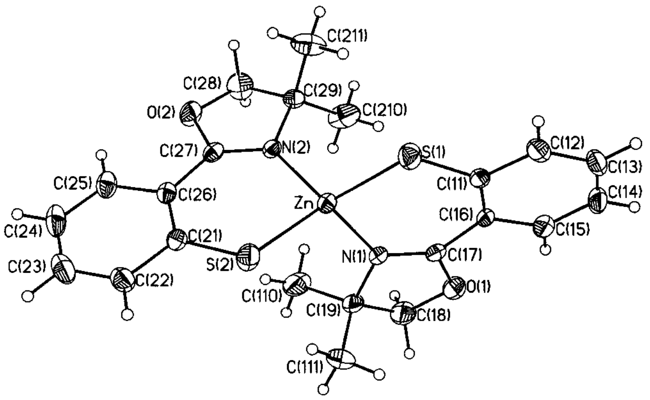


Figure 4. Crystal structure of monomeric Zn^{II} complex **4a**

Table 2. Selected bond lengths [Å] and angles [°] for **4a**

Zn−N(2)	2.036(4)	Zn−N(1)	2.043(3)
Zn−S(2)	2.268(1)	Zn−S(1)	2.273(1)
S(1)−C(11)	1.758(4)	S(2)−C(21)	1.756(5)
O(1)−C(17)	1.350(4)	O(1)−C(18)	1.442(5)
O(2)−C(27)	1.357(5)	O(2)−C(28)	1.456(6)
N(1)−C(17)	1.277(5)	N(1)−C(19)	1.493(5)
N(2)−C(27)	1.282(5)	N(2)−C(29)	1.501(5)
N(2)−Zn−N(1)	106.5(1)	N(2)−Zn−S(2)	97.18(9)
N(1)−Zn−S(2)	120.98(9)	N(2)−Zn−S(1)	120.9(1)
N(1)−Zn−S(1)	96.16(9)	S(2)−Zn−S(1)	116.47(7)

geometry is even higher [N−Zn−N: 121.13(9); O−Zn−O: 117.73(9)] and in this case no optically pure enantiomer could be isolated.[17]

Molecular Structure of Compound 4b

The colorless crystals of complex **4b** belong to the space group *Pbca* of the orthorhombic system with 8 molecules per unit cell. Surprisingly, although the crystals of **4b** exhibited optical rotation, the space group indicates the formation of racemic crystals. This indicates that **4b** is probably a mixture of optically pure and racemic forms. An ORTEP view of the structure is shown in Figure 5 and selected bond lengths and angles are given in Table 3. The geometry around the metal center is distorted tetrahedral. Although the bond lengths around the metal ion are found to be similar to that of **4a**, the bond angles show significant differences. The N(1)−Zn−N(2) [110.6(1)°] and S(1)−Zn−S(2) [118.34(6)°] angles are slightly larger than the corresponding angles observed in complex **4a**. The N(1)−Zn−S(2) [114.4(1)°] and N(2)−Zn−S(1) [117.0(1)°] bond angles are considerably smaller than the corresponding angles observed in **4a** [N(1)−Zn−S(2): 120.98(9)°; N(2)−Zn−S(1): 120.9(1)°]. The average chelate bite angle of 98.6° is larger than that of **4a** [96.67(9)°].

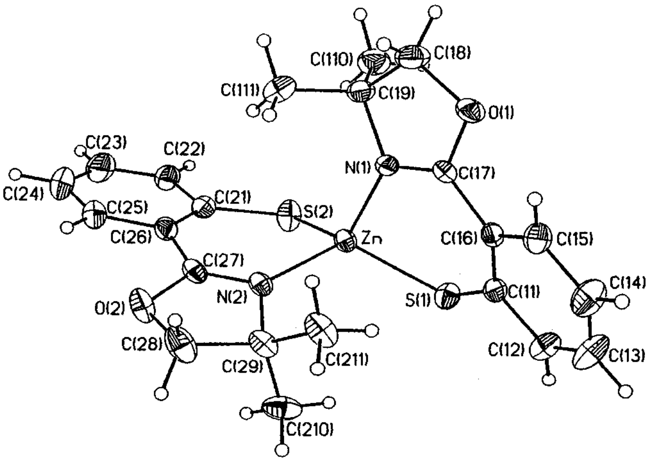


Figure 5. Crystal structure of monomeric Zn^{II} complex **4b**

Table 3. Selected bond lengths [Å] and angles [°] for **4b**

Zn−N(2)	2.021(3)	Zn−N(1)	2.027(3)
Zn−S(2)	2.271(1)	Zn−S(1)	2.264(1)
S(1)−C(11)	1.739(5)	S(2)−C(21)	1.745(5)
O(1)−C(17)	1.357(5)	O(1)−C(18)	1.436(6)
O(2)−C(27)	1.353(4)	O(2)−C(28)	1.441(6)
N(1)−C(17)	1.287(5)	N(1)−C(19)	1.497(5)
N(2)−C(27)	1.286(5)	N(2)−C(29)	1.498(5)
N(2)−Zn−N(1)	110.6(1)	N(2)−Zn−S(2)	98.6(1)
N(1)−Zn−S(2)	114.4(1)	N(2)−Zn−S(1)	117.0(1)
N(1)−Zn−S(1)	98.6(1)	S(2)−Zn−S(1)	118.34(6)

Molecular Structure of Compound 5

The colorless crystals of **5** belong to the space group *Pbca* of the orthorhombic system with 8 molecules per unit cell. From the space group and the cell parameters, complex **5** can be considered as isostructural with the corresponding selenolate.[6] An ORTEP diagram of the structure is shown in Figure 6. The bond lengths and angles are given in Table 4. The geometry around the metal center is distorted tetrahedral. In contrast to other cadmium thiolates, **5** is monomer without any close intermolecular contacts. The Cd−S bond lengths [Cd(1)−S(1): 2.453(3); Cd(1)−S(2): 2.459(3) Å] are much smaller than the corresponding lengths reported for $[Cd(C_5H_4NS)_2]_n$ (2.81 Å)[18] and $[Cd(C_7H_4N_2S)_2]_n$ (2.55 Å).[18] The Cd−N bond lenghts [Cd(1)−N(1): 2.286(8); Cd(1)−N(2): 2.261(8) Å] are, however, comparable to that reported for $[Cd(C_5H_4NS)_2]_n$ (2.34 Å) and $[Cd(C_7H_4N_2S)_2]_n$ (2.28 Å). The bond angle S(1)−Cd−S(2) [139.1(1)°] and the chelate ring bite angle S−Cd−N [88.2(2)°] are much larger than that of $[Cd(C_5H_4NS)_2]_n$ in which the S−Cd−S bond angle is 103.4(3)° and the chelate bite angle is 60.80°. In contrast to the zinc complex **4**, complex **5** is not chiral which indicates that the interactions between the nitrogen atom and the cadmium ion are not strong enough to create the required distortion around the metal center.

The bond lengths and angles for the oxazoline rings in all the cases reflect certain similarities with other five-membered heterocycles containing O and N atoms such as isoxazoline[19] and oxazolo[20] compounds. The O(1)−C(17) lengths [1.357(4) Å and 1.36(1) Å] in complexes **4a** and **4b**, respectively are significantly shorter than the O(1)−C(18) bond lengths [1.442(5) Å and 1.46(1) Å], while the same is

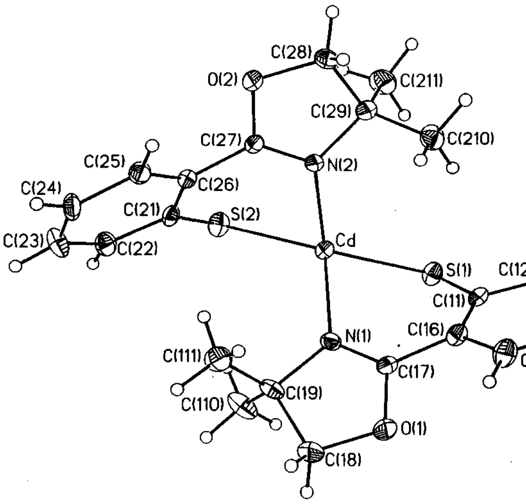


Figure 6. Crystal structure of monomeric Cd^{II} complex **5**

Table 4. Selected bond lengths [Å] and angles [°] for **5**

Cd(1)−N(1)	2.286(8)	Cd(1)−N(2)	2.261(8)
Cd(1)−S(1)	2.453(3)	Cd(1)−S(2)	2.459(3)
S(2)−C(21)	1.763(10)	S(1)−C(11)	1.766(10)
O(1)−C(17)	1.357(11)	O(1)−C(18)	1.464(14)
O(2)−C(27)	1.350(11)	O(2)−C(28)	1.440(12)
N(1)−C(17)	1.257(12)	N(1)−C(19)	1.508(12)
N(2)−C(27)	1.294(11)	N(2)−C(29)	1.49 (1)
N(2)−Cd−N(1)	107.0(3)	N(2)−Cd(1)−S(2)	88.1(2)
N(1)−Cd−S(1)	88.3(2)	N(2)−Cd(1)−S(1)	116.7(2)
N(1)−Cd(1)−S(2)	116.4(2)	S(1)−Cd(1)−S(2)	113.1(1)

true for the N(1)−C(17) lengths [1.244(4) Å and 1.26(1) Å] with respect to the N(1)−C(19) bond lengths [1.485(4) Å and 1.51(1) Å]. This indicates a similar double-bond character in both O(1)−C(17) and N(1)−C(17). The O(1)−C(17) bond lengths are slightly shorter than the corresponding length observed for the zinc selenolate [1.362(8) Å].[6] Complex **5** also shows similar double-bond character in both O(1)−C(17) and N(1)−C(17).

Conclusion

The intramolecularly coordinating 2-(4,4-dimethyloxazolino)benzenethiolate ligand can be successfully used for the isolation of a series of monomeric four-coordinate Group 12 metal thiolate complexes, including the rare example of a "helically" chiral zinc complex. The high affinity of zinc ions towards thiolates and the strong coordination of the imine nitrogen atom to the metal center facilitate the separation of two enantiomorphs by crystallization. The AB spin behavior of methylene protons present in the oxazoline ring can be used as a diagnostic probe of chirality in the complexes. The thiolate ligand shows chirality only with the zinc ion, whereas the selenolate and tellurolate ligands show chirality with the zinc and cadmium ions. The isolation of "helically" chiral zinc complex is much more facile in the case of thiolate compared with selenolate and tellurolate. However, the chirality observed in these complexes at either room temperature or low temperatures shows the general tendency of the oxazoline ligand to form "helical" metal complexes. As expected, the stability of the Group 12 metal complexes decreases in the order S > Se > Te. In addition, the low molecularity, excellent solubility in hydrocarbon solvents, low melting points and relatively high volatility of the complexes render them of interest as single-source precursors to Group 12−16 thin-film semiconductors.

Experimental Section

General Procedures: All reactions were carried out under nitrogen or argon using standard vacuum-line techniques. Solvents were purified by standard procedures[21] and were freshly distilled prior to use. Mercury and $ZnCl_2$ were purified prior to use.[21] Commercially available $CdCl_2$ and $HgCl_2$ were used as received. − Melting points were recorded in capillary tubes and are uncorrected. − ^1H- and ^{13}C-NMR spectra were obtained at 300 and 75.42 MHz, respectively, in $CDCl_3$ with a Varian VXR 300S spectrometer. Chemical shifts are cited with respect to $SiMe_4$ as internal standard. − Elemental analyses were performed with a Carlo-Erba model 1106 elemental analyzer. − Fast atom bombardment (FAB) mass spectra were recorded at room temperature with a JEOL SX 102 DA-6000 mass spectrometer/data system with xenon (6 kV, 10 mV) as the bombarding gas. The acceleration voltage was 10 kV and *m*-nitrobenzyl alcohol was used as the matrix with positive-ion detection. In case of isotopic patterns the value given is for the most intense peak. − Thermal analyses were performed at atmospheric presure with a Shimadzu D30 thermal analyser under nitrogen with the heating rate of 10°C/min. − Optical rotations were measured with a JASCO Model DIP 370 digital polarimeter.

Synthesis of Ox_2S_2 (3): To a suspension of 4,4-dimethyl-2-oxazolinylphenyl lithium[6] (1.82 g, 10 mmol) in dry ether (30 mL), elemental sulfur (0.32 g, 10 mmol) was added rapidly at 0°C. After 3 h, all sulfur was consumed to give a yellow solution of **2**. To this, distilled water (10 mL) was added and complete oxidation was affected by passing oxygen through the mixture for 2 h. The resulting organic layer and the ether extracts from the aqueous layer were combined, dried with anhydrous sodium sulfate, and concentrated in vacuo to give a yellow oil. Crystallization of this from chloroform/methanol (1:1) afforded **3** as white needles. Yield: 0.8 g, (40%); m.p. 142−144°C. − $C_{22}H_{24}N_2O_2S_2$ (412.6): calcd. C 63.98, H 5.82, N 6.79; found C 63.86, H 5.42, N 5.94. − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.44 (s, 12 H, CH_3), 4.12(s, 4 H, CH_2), 7.17−7.22 (m, 2 H, Ar-H), 7.26−7.35 (m, 2 H, Ar-H), 7.71−7.74 (m, 2 H, Ar-H), 7.78−7.81 (m, 2 H, Ar-H). − ^{13}C NMR ($CDCl_3$): δ = 27.97, 68.68, 78.70, 124.66, 125.81, 126.69, 128.97, 131.64, 138.51, 160.57.

Synthesis of $Zn[S(Ox)]_2$ (4): To the lithium arenethiolate (2.14 g, 10 mmol), prepared as described above, was added anhydrous $ZnCl_2$ (0.68 g, 5 mmol) and stirring was continued for 1 h at 0 °C and 18 h at room temperature. The resulting solution was filtered through Celite and concentrated to give a yellow compound. The compound was recrystallized from a chloroform/hexane (1:1) mixture to give **4**. The spontaneous resolution of the racemate was observed during the crystallization process. The crude yellow compound (1.62 g) was dissolved in chloroform (20 mL) and hexane (20 mL) was added. Evaporation of the solvent at room temperature afforded the crystals of the two enantiomorphs. Fast crystallization (in 24 h) in an open vessel resulted in pale yellow crystals (**4a**) whereas slow evaporation of the remaining solvent (in 5 d) in a flask covered with a rubber septum with a small hole resulted in white crystals (**4b**).

4a: Yellow crystals. Yield: 1.07 g (45%); m.p. 192−194°C. − $C_{22}H_{24}N_2O_2S_2Zn$ (477.9): calcd. C 55.30, H 5.03, N 5.87; found C 54.68, H 4.82, N 5.12. − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.16 (s, 6 H, CH_3), 1.38 (s, 6 H, CH_3), 4.01−4.18 (dd, 4 H, CH_2), 6.95−6.98 (m, 2 H, Ar-H), 7.00−7.22 (m, 2 H, Ar-H), 7.73−7.77 (m, 2 H, Ar-H), 7.86−7.90 (m, 2 H, Ar-H). − ^{13}C NMR ($CDCl_3$): δ = 26.99, 28.28, 68.50, 78.15, 121.97, 122.78, 131.30, 131.62, 136.54, 150.45, 167.46. − MS; *m/z* (%): 652 [$C_{33}H_{36}N_3O_3S_3Zn_2^+$], 587 [$C_{33}H_{36}N_3O_3S_3Zn^+$], 477 [$M^+$, $C_{22}H_{24}N_2O_2S_2Zn^+$], 412 [$C_{22}H_{24}N_2O_2S_2^+$], 380 [$C_{22}H_{24}N_2O_2S^+$], 206 (100) [$C_{11}H_{12}NOS^+$]. − $[\alpha]_D^{25} = -6.158$ (c = 1.0, $CHCl_3$).

4b: White crystals. Yield: 0.48 g (20%). m.p. 190−192°C. − $C_{22}H_{24}N_2O_2S_2Zn$ (477.9): calcd. C 55.30, H 5.03, N 5.87; found C 55.50, H 5.02, N 5.25. − $[\alpha]_D^{25} = +5.080$ (c = 1.0, $CHCl_3$). − ^1H- and ^{13}C-NMR chemical shifts are in full accordance with the values reported for **4a**.

Synthesis of Cd[S(Ox)]$_2$ (5): Compound **5** was prepared according to the method described for **4** using 1.82 g (10 mmol) of 4,4-dimethyl-2-oxazolinylphenyllithium,[6] 0.32 g (10 mmol) of elemental sulfur and 0.917 g (5 mmol) of anhydrous $CdCl_2$. The crude product was recrystallized from a chloroform/hexane (1:1) mixture to give white crystals of **5**. Yield: 1.36 g (52%); m.p. 186−188°C. − $C_{22}H_{24}CdN_2O_2S_2$ (524.9): calcd. C 50.34, H 4.58, N 5.34; found C 50.49, H 4.45, N 5.28. − ^1H NMR(300 MHz, $CDCl_3$): δ = 1.25 (s, 12 H, CH_3), 4.09(s, 4 H, CH_2), 6.97−7.02 (m, 2 H, Ar-H), 7.15−7.20 (m, 2 H, Ar-H), 7.73−7.76 (m, 2 H, Ar-H), 7.75−7.81 (m, 2 H, Ar-H). − ^{13}C NMR ($CDCl_3$): δ = 27.91, 68.18, 77.82, 122.66, 124.99, 130.77, 131.30, 137.17, 147.66, 167.11. − MS; *m/z* (%): 746 [$C_{33}H_{36}Cd_2N_3O_3S_3^+$], 524 [$M^+$, $C_{22}H_{24}CdN_2O_2S_2^+$], 380 [$C_{22}H_{24}N_2O_2S^+$], 318 [$C_{11}H_{12}CdNOS^+$], 206 (100) [$C_{11}H_{12}NOS^+$].

Synthesis of Hg[S(Ox)]$_2$ (6). − Method A: Synthesis of compound **6** was approached by the method described for **4** from 10 mmol of 4,4-dimethyl-2-oxazolinylphenyllithium,[6] 0.32 g (10 mmol) of elemental sulfur and 1.358 g (5 mmol) of anhydrous $HgCl_2$. Elemental analysis and other analytical data for the white solid obtained from the reaction indicated the formation of the disulfide **3**. The crude product was recrystallized from a chloroform/hexane (1:1) mixture. Yield: 2.12 g (60%). All analytical data are in full accordance with the values reported for **3**.

Method B: To a stirred solution of **3** (0.413 g, 1 mmol) in methanol (20 mL) was added an excess of mercury (1 g, 5 mmol) at room temperature. The reaction mixture was stirred for 5 d to give an almost colorless solution. This was filtered through a Celite-padded filter frit to remove the unchanged mercury. The filtrate was concentrated to give a colorless crystalline product (0.5 g). This was recrystallized from a chloroform/methanol (1:1) mixture to give colorless crystals of **6**. Yield: 0.37 g (60%); m.p. 122−124°C. − $C_{22}H_{24}HgN_2O_2S_2$ (612.6): calcd. C 43.12, H 3.92, N 4.52; found C 42.95, H 3.86, N 4.10. − ^1H NMR (300 MHz, $CDCl_3$): δ = 1.17 (s, 12 H,CH_3), 3.99 (s, 4 H, CH_2), 7.06−7.11 (m, 2 H, Ar-H), 7.24−7.28 (m, 2 H, Ar-H), 7.67−7.71 (m, 2 H, Ar-H), 7.74−7.78 (m, 2 H, Ar-H). − ^{13}C NMR ($CDCl_3$): δ = 28.05, 68.53, 77.92, 124.76, 126.87, 132.67, 133.35, 139.32, 148.93, 165.23.

Caution: Cadmium and mercury complexes are expected to be toxic and must be handled with care.

X-ray Crystallographic Studies: The diffraction measurements for compounds **3**, **4a**, **4b**, and **5** were performed at room temperature (293 K) with a Siemens R3m/V diffractometer using graphite-monochromated Mo-K_α radiation (λ = 0.7170 Å). The unit cell was determined from 25 randomly selected reflections using the automatic search index and least-squares routine. For **3**, the θ range for data collection was from 2.61 to 30.00° whereas for **4a**, **4b**, and **5** it ranged from 2.60 to 27.50°, 2.52 to 27.50° and 2.53 to 27.50°, respectively. The index range for **3** was $0 \le h \le 11$, $0 \le k \le 21$, $0 \le l \le 23$ while for **4a**, **4b**, and **5** it was $0 \le h \le 12$, $-14 \le k \le 0$, $-14 \le l \le 14$; $0 \le h \le 11$, $-26 \le k \le 0$, $0 \le l \le 30$; and $-16 \le h \le 0$, $0 \le k \le 23$, $0 \le l \le 27$, respectively. The data for **4b** and **5** were corrected for Lorentz, polarization and absorption effects. The maximum/minimum transmission values of the correction factors for compounds **4b** and **5** were 0.9471/0.5626 and 0.8588/0.5163, respectively. The data were monitored by measuring two standard reflections every 60 min of X-ray exposure time. The structures were solved by routine heavy-atom (using SHELXS 86[22]) and Fourier methods and refined by full-matrix least squares

Table 5. Crystal data and structure refinement for **3**, **4a**, **4b**, and **5**

	3	**4a**	**4b**	**5**
empirical formula	$C_{22}H_{24}N_2O_2S_2$	$C_{22}H_{24}N_2O_2S_2Zn$	$C_{22}H_{24}N_2O_2S_2Zn$	$C_{22}H_{24}CdN_2O_2S_2$
mol. mass	412.55	477.92	477.92	524.95
crystal system	orthorhombic	monoclinic	orthorhombic	orthorhombic
space group	$P2_12_12_1$	$P2_1$	*Pbca*	*Pbca*
a [Å]	8.657(1)	9.371(1)	9.531(2)	12.504(2)
b [Å]	15.581(2)	11.397(1)	20.118(2)	17.773(2)
c [Å]	16.387(2)	10.881(1)	23.351(3)	21.019(3)
β [°]	90	97.35(1)	90	90
V [Å^3]	2210.3(5)	1152.6(2)	4477.5(11)	4671(10)
Z	4	2	8	8
D(calcd.) [Mg/m^3]	1.260	1.377	1.418	1.493
crystal size [mm]	0.36×0.99×0.50	0.24×0.52×0.30	0.23×0.82×0.40	0.27×0.82×0.72
abs. coeff. [mm^{-1}]	0.240	1.266	1.304	1.333
obsd. reflxns. [$I > 2\sigma$]	3486	2746	4944	4847
final $R(F)$ [$I > 2\sigma(I)$][a]	0.0454	0.0307	0.0500	0.0633
$wR(F^2)$ indices [$I > 2\sigma(I)$]	0.1161	0.0638	0.1002	0.1458
absolute structure parameter	0.11(11)	0.96(3)	−	−
data/restrains/parameters	3480/0/281	2745/1/291	4944/0/290	4783/0/290
goodness of fit on F^2	1.04	1.04	1.02	1.19

[a] Definitions: $R(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $wR(F_o^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_c^2)^2\}^{1/2}$.

with the nonhydrogen atoms anisotropic and hydrogen atoms with fixed isotropic thermal parameters of 0.07 Å^2 using the SHELXL 93 program.[23] The hydrogen atoms were partially located from difference electron density maps and the rest were fixed at calculated positions. Scattering factors were from common sources.[24] Only the observed reflections were used in the final refinements. Some details of data collection and refinement are given in Table 5. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-111948 (**3**), -111950 (**4a**), -111949 (**4b**), -111951 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We are grateful to the Department of Science and Technology (DST), New Delhi and Board of Research in Nuclear Sciences (BRNS), Department of Atomic Energy, Bombay for funding this work. Additional help from the Regional Sophisticated Instrumentation Centre (RSIC), Indian Institute of Technology (IIT), Bombay for 300-MHz NMR spectroscopy, RSIC, Central Drug Research Institute (CDRI), Lucknow for Mass spectra and Tata Institute of Fundamental Research (TIFR), Bombay for 500-MHz NMR spectroscopy is gratefully acknowledged. R. J. B. wishes to acknowledge the DoD-ONR program for funds to upgrade the diffractometer.

---

[1] [1a] A. Müller, E. Diemann, in *Comprehensive Coordination Chemistry* (Ed.: G. Wilkinson), Pergamon, London, **1987**, vol. 2, p. 515. − [1b] I. G. Dance, *Polyhedron* **1986**, *5*, 1037. − [1c] P. G. Blower, J. R. Dilworth, *Coord. Chem. Rev.* **1987**, *76*, 121. − [1d] J. Arnold, “The Chemistry of Metal Complexes with Selenolate and Tellurolate Ligands” in *Progress in Inorganic Chemistry* (Ed.: K. D. Karlin), John Wiley & Sons, Inc.,**1995**, vol. 43, p. 353.

[2] [2a] J. G. Brennan, T. Siegrist, S. Stuczynski, C. Carroll, L. Brus, M. Steigerwald, *Chem. Mater.* **1990**, *2*, 403. − [2b] M. B. Hursthouse, M. A. Malik, M. Motevalli, P. O′Brien, *Organometallics* **1991**, *10*, 730. − [2c] M. A. Malik, M. Motevalli, J. R. Walsh, P. O′Brien, *Organometallics* **1992**, *11*, 3136. − [2d] M. A. Malik, M. Motevalli, T. Saeed, P. O′Brien, *Adv. Mater.* **1993**, *5*, 653. − [2e] M. Bochmann, *Chem. Vap. Deposition* **1996**, *2*, 85. − [2f] H. B. Singh, N. Sudha, *Polyhedron* **1996**, *15*, 745. − [2g] A. L. Seligson, J. Arnold, *J. Am. Chem. Soc.*, **1993**, *115*, 8214. − [2h] P. J. Bonasia, J. Arnold, *Inorg. Chem.* **1992**, *31*, 2508.

[3] [3a] I. G. Dance, R. G. Garbutt, D. C. Craig, M. L. Scudder, *J. Chem. Soc., Chem. Commun.* **1987**, 1164. − [3b] I. G. Dance, R. G. Garbutt, T. D. Bailey, *Inorg. Chem.* **1990**, *29*, 603. − [3c] I. G. Dance, R. G. Garbutt, M. L. Scudder, *Inorg. Chem.* **1990**, *29*, 1571. − [3d] T. Alsina, W. Clegg, K. A. Fraser, J. Sola, J. *J. Chem. Soc., Dalton Trans.* **1992**, 1393.

[4] [4a] H. B. Singh, N. Sudha, *Coord. Chem. Rev.* **1994**, *135−136*, 469. − [4b] R. Kaur, H. B. Singh, R. J. Butcher, *Organometallics* **1995**, *14*, 4755. − [4c] S. C. Menon, H. B. Singh, J. M. Jasinski, J. P. Jasinski, R. J. Butcher, *Organometallics* **1996**, *15*, 1707. − [4d] R. Kaur, S. C. Menon, H. B. Singh, *Proc. Indian Acad. Sci. (Chem. Sci.)* **1996**, *108*, 159. − [4e] S. C. Menon, H. B. Singh, R. P. Patel, K. Das, R. J. Butcher, *Organometallics* **1997**, *18*, 563. − [4f] G. Mugesh, A. Panda, H. B. Singh, N. S. Punekar, R. J. Butcher, *Chem. Commun.* **1998**, 2227. − [4g] G. Mugesh, H. B. Singh, R. J. Butcher, *Tetrahedron: Asymm.* **1999**, *10*, 237. − [4h] G. Mugesh, A. Panda, H. B. Singh, R. J. Butcher, *Chem. Eur. J.* **1999**, *5*, 1411.

[5] R. Kaur, H. B. Singh. R. P. Patel, S. K. Kulshreshtha, *J. Chem. Soc., Dalton Trans.* **1996**, 461.

[6] G. Mugesh, H. B. Singh, R. P. Patel, R. J. Butcher, *Inorg. Chem.* **1998**, *37*, 2663.

[7] G. Mugesh, H. B. Singh, R. J. Butcher, *J. Organomet. Chem.* **1999**, *577*, 243.

[8] [8a] L. F. Lindoy, D. H. Busch, V. Goedken, V. *J. Chem. Soc., Chem. Commun*. **1972**, 683. − [8b] T. Adatia, N. Beynek, B. P. Murphy, *Polyhedron* **1995**, *14*, 335. − [8c] R. Chotalia, E. C. Constable, M. Neuburger, D. R. Smith, M. Zehnder, *J. Chem. Soc., Dalton Trans.* **1996**, 4207.

[9] [9a] S. Ruttimann, C. Piguet, G. Bernardinelli, B. Bocquet, A. F. Williams, *J. Am. Chem. Soc.* **1992**, *114*, 4230. − [9b] A. Bilyk, M. M. Harding, *J. Chem. Soc., Dalton Trans.* **1994**, 77.

[10] H. Flack, *Acta Crystallogr., Sect. A* **1983**, *39*, 876.

[11] L. Pauling, in *The Nature of the Chemical Bond*, 3rd ed. Cornell University Press, Ithaca, New York, **1960**, p. 224.

[12] C. K. Johnson, *ORTEPII*; Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, **1976**.

[13] O. P. Anderson, A. la Cour, M. Findeisen, L. Hennig, O. Simonsen, L. F. Taylor, H. Toftlund, *J. Chem. Soc., Dalton Trans.* **1997**, 111.

[14] M. Bochmann, G. C. Bwembya, R. Grinter, A. K. Powell, K. J. Webb, M. B. Hursthouse, K. M. A. Malik, M. A. Mazid, *Inorg. Chem.* **1994**, *33*, 2290.

[15] F. H. Allen, O. Kennard, D. G. Watson, L. Bremmer, A. G. Orpen, R. Taylor, *J. Chem. Soc., Perkin Trans. 2* **1987**, S1.

[16] A. D. Garnowski, A. L. Nivorozhkin, V. I. Minkin, *Coord. Chem. Rev.* **1993**, *126*, 1.

[17] G. Mugesh, H. B. Singh, R. J. Butcher, *Inorg. Chem.*, under revision.

[18] M. B. Hursthouse, O. F. Z. Khan, M. Mazid, M. Motevalli, P. O′Brien, *Polyhedron* **1990**, *9*, 541.

[19] [19a] D. C. Rodiou, S. C. Kokkou, P. J. Rentzeperis, *Acta Crystallogr., Sect. B* **1978**, 13. − [19b] A. P. Bozopoulos, S. C. Kokkou, P. J. Rentzeperis, *Acta Crystallogr., Sect. B* **1980**, 1326.

[20] [20a] R. Jaunin, W. E. Oberhansli, J. Hellerbach, *Helv. Chim. Acta* **1972**, *55*, 2975. − [20b] K. Kamiya, Y. Wada, M. Nishikawa, *Chem. Pharm. Bull.* **1973**, *21*, 1520.

[21] D. D. Perrin, W. L. F. Armarego, D. R. Perrin, *Purification of Laboratory Chemicals*, 2nd ed., Pergamon, Oxford, **1980**.

[22] G. M. Sheldrick, *Crystallographic Computing 3*, Oxford University Press, Oxford, **1985**, p 175.

[23] G. M. Sheldrick, *SHELX 93*, Program for Crystal Structure Determination, University of Göttingen, **1993**.

[24] *International Tables for X-ray Crystallography*, Kynoch Press, Birmingham, **1974**, vol. 4, pp. 99, 149.

Received December 10, 1998
[I98424]