parameters, namely, the occupation numbers of equipoints 2b, 2d, and 6h. These comprise the most reasonable available interstices in the mirror planes. By comparison, the idealized model of Figures 1–3 has two sodiums in equipoints 2b, chosen because their nearest-neighbor coordination is identical with that of the sodiums in the Beevers–Ross[3] model for β-alumina.

The results left the "Beevers–Ross" positions, 2b, nearly full, distributed nearly one more atom between equipoints 2d, and distributed another 0.96 atom among equipoints 6h. All are listed as sodiums in Table I. They add up to 3.9 sodiums per unit cell *vs.* only 2 for the idealized model and about 2.6 suggested by the chemical analyses carried out for Weber and Venero (see Introduction). The possibility that a fraction of these extra atoms in the mirror planes may be oxygens, rather than sodiums, must be kept in mind.

A suspicion that the extra scattering matter in the mirror planes might be water was tested experimentally by dehydrating a sample by heating to 700° under vacuum and then quickly sealing the sample into an X-ray type capillary. The ratios of the (002), (004), and (006) intensities were measured again, photographically, but they had not changed by more than 10%.

We conclude either that the (00*l*)'s and particularly (002) are affected by some unrecognized systematic error or that there are more atoms in the mirror plane than what one expects from chemical analysis and experience with other β-aluminas. These extra atoms are listed in Table I but are not indicated in the schematics of the idealized structures in Figures 2 and 3.

The idealized formula $Na_2O \cdot 4MgO \cdot 15Al_2O_3$ is obtained from the following considerations. The 2 spinel blocks of 6 oxygen layers, with 4 oxygens per layer, call for 48 oxygens. The 10 interstitial layers of 3 (Al or Mg) each, demanded by an ideal spinel arrangement, call for 30 (Al or Mg)'s. The two spacer columns, one across each basal mirror plane, call for 4 more (Al or Mg)'s and 2 more oxygens. The number of sodium ions per unit cell must be even, and 2 is by far the closest even integer to the analyses of Weber and Venero. One thus arrives at a total of 50 oxygens, 34 (Al or Mg)'s, and 2 Na's. Assigning standard valences then leads to 4 Mg's and 30 Al's.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS 02139

Inversion and Ligand-Exchange Kinetics of Tetrahedral Bis-Chelate Complexes of Zinc(II) and Cadmium(II)

BY S. S. EATON[1] AND R. H. HOLM*

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A series of bis(β-aminothionato)zinc(II) and -cadmium(II) complexes, $M(R\text{–}SC_6H_5HR_\alpha)_2$ (1), has been prepared by a nonaqueous chelation procedure for the purpose of investigating inversion rates of the tetrahedral enantiomers (Δ, Λ). The chirality of the molecular configuration renders the methyl groups of the *N*-isopropyl substituent diastereotopic and permits determination of the rates and activation parameters for the process of diastereotopic averaging (inversion) without prior separation of enantiomers. Kinetic data for this process were obtained for $Zn(i\text{-}C_3H_7\text{–}SC_6H_5HCH_3)(C_6H_5CH_2\text{–}SC_6H_5HH)$ and $Zn(i\text{-}C_3H_7\text{–}SC_6H_5HH)(C_6H_5CH_2\text{–}SC_6H_5HH)$ (formed by ligand exchange in solution) in chlorobenzene and for $Cd(i\text{-}C_3H_7\text{–}SC_6H_5HR_\alpha)_2$ (R_α = H, CH_3) in deuteriochloroform by line shape analysis of the exchange-broadened isopropyl methyl region of the pmr spectra. The inversion rates of the zinc(II) complexes are slower than those of the cadmium(II) complexes and the activation energies are 21 (Zn) and *ca.* 12–15 (Cd) kcal/mol. Ligand exchange was found to be slow relative to inversion for zinc(II) complexes, which undergo inversion by an intramolecular process. For cadmium(II) complexes thermodynamic parameters for diastereotopic averaging and ligand exchange are similar, suggesting that the former process may follow a bond rupture pathway. A "twist" mechanism is provisionally proposed for the inversion of zinc(II) complexes. Qualitiative comparison of the isopropyl methyl pmr spectra of the pair $Zn(i\text{-}C_3H_7\text{–}SC_6H_5HCH_3)_2$ and $Zn(i\text{-}C_3H_7\text{–}C_6H_5HCH_3)_2$ (2) indicates that replacement of oxygen by sulfur in the coordination sphere increases the inversion rate. Methyl pmr signals of $Zn[(+)CH_3CHC_6H_5\text{–}SC_6H_5HH]_2$ reveal that the stabilities of the Δ(+, +), Λ(+, +) diasteromers are essentially equal in $CDCl_3$ at ~30°

Introduction

Tetrahedral bis-chelate complexes derived from unsymmetrical ligands are enantiomeric with absolute configurations Δ and Λ.[2] Although partial resolution of various metal(II) complexes of this type have been reported, little quantitative information regarding rates of inversion at the metal center is available. A tabulation of optically active tetrahedral chelate complexes reported prior to 1958 is given by Basolo and Pearson.[3] Since that time there have been only four reports of partial resolution of other bis-chelate complexes,[4–8] and in one such case, a bis(formazyl)nickel(II) complex,[5] the optical isomerism does not arise from a tetrahedral structure.[9] Partially resolved complexes of Be(II), Cu(II), and Zn(II) as brucine and strychnine salts are reported to mutarotate to constant rotation within 15–25 min in chloroform solution.[10] Rapid mutarotation of the quinine salt of bis(salicylato)-

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[1] NSF Predoctoral Fellow, 1969–present.

[2] R. E. Ernst, M. J. O'Connor, and R. H. Holm, *J. Amer. Chem. Soc.*, **89**, 6104 (1967).

[3] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 1st ed, Wiley, New York, N. Y., 1958, p 284.

[4] E. Ferroni and R. Cini, *J. Amer. Chem. Soc.*, **82**, 2427 (1960).

[5] H. Irving, J. B. Gill, and W. R. Cross, *J. Chem. Soc.*, 2087 (1960).

[6] T.-M. Hseu, D. F. Martin, and T. Moeller, *Inorg. Chem.*, **2**, 587 (1963).

[7] J. Kratsmar-Smogrovic, *Acta Fac. Pharm. Bohemoslov.*, **10**, 27 (1965); *Chem. Abstr.*, **64**, 18937*d* (1966).

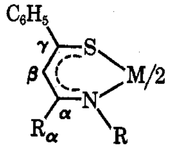
[8] O'Connor has confirmed certain of the results of Hseu, *et al.*,[6] and has also effected partial resolution of Co(II) and Ni(II) Schiff base complexes: M. J. O'Connor, private communication.

[9] D. Dale, *J. Chem. Soc. A*, 278 (1967); J. E. Parks and R. H. Holm, *Inorg. Chem.*, **7**, 1408 (1968).

[10] W. H. Mills and R. A. Gotts, *J. Chem. Soc.*, 3121 (1926).

beryllium(II) has also been observed,[7] and racemization of bis(benzoylacetonato)beryllium(II) has been found to be complete in 9 hr at room temperature.[11] Racemization of potassium bis(8-hydroxyquinolinato-5-sulfonate)zinc(II) in aqueous solution is complete within 4 hr at 100°.[12] Rate constants for racemization of bis(β-ketoaminato) complexes of nickel(II) and copper(II) varying from 0.12 to 1.06 hr^{-1} have been reported.[6] The most optically stable tetrahedral bis-chelate complex thus far described appears to be bis(*d*-benzoylcamphorato)beryllium(II)[13] which has been separated into its diastereomers and requires a catalyst for mutarotation in pure and dry solvents. The available information does not indicate any pattern of dependence of inversion rates on ligand structure or metal but does indicate that tetrahedral bis-chelate complexes often racemize readily.

In order to investigate inversion processes of tetrahedral chelate complexes under conditions where their coordination with solvent is likely to be weak or negligible, a number of bis(β-aminothionato)zinc(II) and -cadmium(II) complexes **1** (R_α = H, CH_3) have been prepared. These complexes are soluble in weakly polar solvents, but, because they are uncharged and since most of the tetrahedral zinc(II) species cited above racemize rapidly, no attempts at resolution and polarimetric determination of inversion rates have been made. Instead, the nitrogen substituent R has been selected such that it contains a pair of groups which are rendered diastereotopic by the chirality of the molecular configuration. For example, in complexes of type **1** with R = *i*-C_3H_7 the two methyl groups are magnetically nonequivalent (Figure 1). Chemical shift differences between them (diastereotopic splittings) will be averaged by any process which effects inversion at the metal center on the pmr time scale. Plausible processes include (i) intramolecular mechanisms involving rupture of one or more metal–ligand bonds or a "twist" motion generating a planar transition state and (ii) intermolecular pathways in which bond rupture or formation of a binuclear intermediate or transition state could be the rate-determining step. Mechanisms of the latter type should also lead to ligand exchange (*cf.* **3**–**7**).



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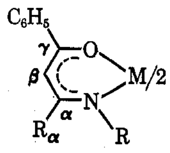

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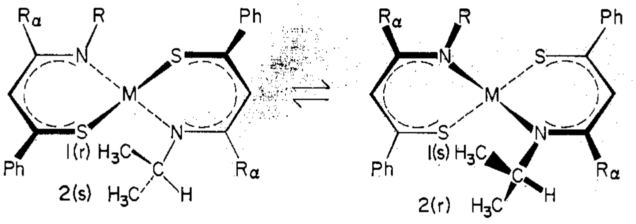

Δ - 1(r) 2(s)   Λ - 1(s) 2(r)

Figure 1.—Illustration of the Δ and Λ absolute configurations of a complex of type **1** and the interconversion of environments (r, s) of the diastereotopic methyls of an *N*-isopropyl group upon inversion of configuration.

This paper reports the results of a variable-temperature pmr investigation of the inversion reactions of zinc(II) and cadmium(II) complexes of type **1**, in which kinetic parameters have been obtained from a line shape analysis of isopropyl methyl signals in the intermediate-exchange region. Kinetic data for ligand exchange between two cadmium(II) species have also been obtained in order to estimate parameters for a bond rupture process. A point of additional interest in the use of the β-aminothione ligand system is that nickel(II) complexes of type **1** have been shown to populate the planar *vs.* the tetrahedral form to a significantly greater extent than their β-ketoamine analogs **2** (R_α = H, CH_3).[14] Inasmuch as the planar configuration is a possible transition state in the inversion of zinc(II) and cadmium(II) chelates, the relative rates of a pair of zinc(II) species of types **1** and **2** have been qualitatively established.

As previously,[2,14] bis(β-aminothionato)- and bis(β-ketoaminato)metal(II) complexes of types **1** and **2** are designated as $M(R\text{-}SC_6H_5HR_\alpha)_2$ and $M(R\text{-}C_6H_5HR_\alpha)_2$, respectively, and the R = α-phenylethyl group is designated as $CH_3CHC_6H_5$.

Experimental Section

Preparation of Compounds. (a) Ligands.—N-Substituted 1-phenyl-3-amino-2-propen-1-thiones were prepared from 3-phenyl-1,2-dithiolium perchlorate and the appropriate amine was prepared by the method reported earlier.[14] 1-Phenyl-3-isopropylamino-2-butene-1-thione was obtained by the reaction of 3.0 g of 1-phenyl-1-mercapto-1-buten-3-one, prepared by published procedures,[15] with excess neat isopropylamine at room temperature. Upon stirring, the reaction mixture turned brown and became warm. After stirring for 10 min 50 ml of *n*-heptane was added and the solution was heated to 50°. The clear red solution was decanted and upon cooling to room temperature deposited red crystals which were identified by their pmr spectrum; mp 81–82°, lit. mp[14] 81–82°. 1-Phenyl-3-(−)-α-phenylethylamino-2-buten-1-thione was prepared from the corresponding *O*-ethyl-β-ketoamine cation and sodium hydrosulfide in ethanol by the reported procedure.[14] Repeated recrystallizations failed to remove a small amount of the β-ketoamine; the slightly impure product (mp 74–75°) was identified by its pmr spectrum. Ligands used to prepare complexes with R = (+)- or (−)-$CH_3CHC_6H_5$ were obtained from samples of α-phenylethylamine of high optical purity: (+)-amine, $[\alpha]^{25}D$ +40.4° (neat), lit.[16] $[\alpha]^{25}D$ +40.1° (neat); (−)-amine, $[\alpha]^{25}D$ −39.6° (neat), lit.[17] $[\alpha]^{25}D$ −40.3° (neat).

(b) **Complexes.**—All zinc(II) and cadmium(II) complexes were prepared by a nonaqueous chelation reaction using *n*-butyllithium in tetrahydrofuran[14] and were obtained in pure form in yields ranging from 14 to 45% after recrystallization from toluene–*n*-heptane. Characterization data are given in Table I. The following rotations were obtained for zinc(II) complexes prepared from (+)-α-phenylethylamine: $Zn((+)CH_3CHC_6H_5\text{–}C_6H_5HCH_3)_2$, $[\alpha]^{25}D$ −905° (9.3×10^{-3} *M*, $CHCl_3$); $Zn((+)\text{-}CH_3CHC_6H_5\text{–}SC_6H_5HH)_2$, $[\alpha]^{25}D$ −93° (1.0×10^{-2} *M*, $CHCl_3$). $Cd((-)CH_3CHC_6H_5\text{–}SC_6H_5HCH_3)_2$ was prepared and identified by its pmr spectrum but could not be obtained in analytically pure form. Attempts to prepare $Zn(R\text{–}C_6H_5HH)_2$[14] and $Cd(R\text{–}C_6H_5\text{-}HR_\alpha)_2$ complexes (R_α = H, CH_3) by various nonaqueous chelation procedures were unsuccessful.

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[11] D. H. Busch and J. C. Bailar, Jr., *J. Amer. Chem. Soc.*, **76**, 5352 (1954).

[12] J. C. I. Lin and J. C. Bailar, Jr., *ibid.*, **73**, 5432 (1951).

[13] T. M. Lowry and R. C. Traill, *Proc. Roy. Soc., Ser. A*, **132**, 398 (1931).

[14] D. H. Gerlach and R. H. Holm, *J. Amer. Chem. Soc.*, **91**, 3457 (1969).

[15] E. Uhlemann and Ph. Thomas, *J. Prakt. Chem.*, **34**, 180 (1966); M. Renson and J. Bidaine, *Bull. Soc. Chim. Belg.*, **70**, 519 (1961).

[16] H. E. Smith, S. L. Cook, and M. E. Warren, Jr., *J. Org. Chem.*, **29**, 2265 (1964).

[17] W. Theilacker and H.-G. Winkler, *Chem. Ber.*, **87**, 690 (1954).

TABLE I

CHARACTERIZATION DATA FOR BIS(β-KETOAMINATO)- AND BIS(β-AMINOTHIONATO)ZINC(II) AND -CADMIUM(II) COMPLEXES

Complex	Mp, °C	% calcd			% found		
		C	H	N	C	H	N
$Zn[(-)CH_3CHC_6H_5\text{-}C_6H_5HCH_3]_2$[a]	228–230	72.78	6.11	4.72	72.51	6.23	4.52
$Zn(i\text{-}C_3H_7\text{-}SC_6H_5HCH_3)_2$	215–216	62.20	6.42	5.58	61.92	6.25	5.66
$Zn[(-)CH_3CHC_6H_5\text{-}SC_6H_5HCH_3]_2$	199–200	69.05	5.80	4.47	68.83	5.92	4.33
$Zn(i\text{-}C_3H_7\text{-}SC_6H_5HH)_2$	259–260	60.82	5.95	5.91	60.49	5.99	5.68
$Zn[(-)CH_3CHC_6H_5\text{-}SC_6H_5HH]_2$	146–148	68.27	5.39	4.68	68.25	5.31	4.57
$Zn(C_6H_5CH_2\text{-}SC_6H_5HH)_2$	169–170	67.41	4.97	4.91	67.17	4.92	4.92
$Cd(i\text{-}C_3H_7\text{-}SC_6H_5HCH_3)_2$	204–205	56.87	5.87	5.10	56.77	5.85	5.09
$Cd(i\text{-}C_3H_7\text{-}SC_6H_5HH)_2$	213–215	55.32	5.42	5.28	55.31	5.36	4.95
$Cd(C_6H_5CH_2\text{-}SC_6H_5HH)_2$	151–152	62.28	4.57	4.54	62.06	4.61	4.65

[a] Prepared by Dr. D. H. Gerlach.

TABLE II

CHEMICAL SHIFTS OF Zn(II) AND Cd(II) COMPLEXES IN $CDCl_3$ SOLUTION AT ~30°

Complex	$\Delta\nu$,[a] ppm			
	R_α	β-H	R_γ[b]	R
$Zn(i\text{-}C_3H_7\text{-}C_6H_5HCH_3)_2$	−2.08	−5.50	−7.30, −7.85	CH_3, −1.16 (d), −1.21 (d); CH, −3.94 (m)
$Zn[(-)CH_3CHC_6H_5\text{-}C_6H_5HCH_3]_2$	−1.98	−5.55	−7.30, −7.85	CH_3, −1.59 (d); CH, −4.93 (q); C_6H_5, −7.28 (m)
$Zn(i\text{-}C_3H_7\text{-}SC_6H_5HCH_3)_2$	−2.15	−6.38	−7.20, −7.60	CH_3, −1.28 (d), −1.40 (d); CH, −3.98 (d)
$Zn[(-)CH_3CHC_6H_5\text{-}SC_6H_5HCH_3]_2$	−2.00	−6.50	−7.30, −7.50	CH_3, −1.68 (d); CH, −4.90 (q); C_6H_5, −7.32 (m)
$Zn(i\text{-}C_3H_7\text{-}SC_6H_5HH)_2$	−7.88 (d)	−6.35 (d)	−7.25, −7.65	CH_3, −1.27 (d), −1.36 (d); CH, −3.70 (m)
$Zn[(-)CH_3CHC_6H_5\text{-}SC_6H_5HH]_2$	−7.78 (d)	−6.25 (d) −6.31 (d)	−7.25, −7.65	CH_3, −1.47 (d), −1.58 (d); CH, −4.72 (m); C_6H_5, −7.20 (m)
$Zn(C_6H_5CH_2\text{-}SC_6H_5HH)_2$	−7.60 (d)	−6.23 (d)	−7.25, −7.60	CH_2, −4.36; C_6H_5, −7.09
$Cd(i\text{-}C_3H_7\text{-}SC_6H_5HCH_3)_2$[d]	−2.14	−6.34	−7.25, −7.60	CH_3, −1.31 (broad d); CH, −4.05 (m)
$Cd[(-)CH_3CHC_6H_5\text{-}SC_6H_5HCH_3]_2$[c]	−2.02	−6.25	−7.20, −7.45	CH_3, −1.74 (d); CH, −3.91 (q); C_6H_5, −7.20 (m)
$Cd(i\text{-}C_3H_7\text{-}SC_6H_5HH)_2$[d]	−7.90 (d)	−6.26 (d)	−7.30, −7.62	CH_3, −1.31 (d); CH, −3.55 (m)
$Cd(C_6H_5CH_2\text{-}SC_6H_5HH)_2$[d]	−7.70 (d)	−6.19 (d)	−7.23, −7.60	CH_2, −4.35; C_6H_5, −7.15

[a] TMS internal reference. Abbreviations: d, doublet; q, quartet; m, multiplet. J_{HH}, $J_{H\text{-}CH_3}$ = 6–7 Hz. [b] Approximate centers of phenyl multiplets. [c] Slightly impure sample used. [d] Exchange-broadened spectra.

Pmr Spectra.—All spectra were obtained using a Varian HA-100 spectrometer equipped with a variable-temperature probe and operated at power levels at least *ca.* 5 db below saturation. Chlorobenzene used as the solvent in line shape studies was purified by the method previously described.[18] Temperatures were measured with a thermocouple mounted in the probe which was frequently calibrated with methanol and ethylene glycol. Temperatures are considered accurate to ±1°. Solutions were prepared under dry nitrogen immediately before use. Chemical shifts were measured with respect to chlorobenzene or TMS as internal standards. Shift data for zinc(II) and cadmium(II) complexes in $CDCl_3$ solution at ambient probe temperature are collected in Table II.

Kinetic Analysis.—With the exception noted below, rearrangement reactions of zinc(II) and cadmium(II) complexes 1 in chlorobenzene or deuteriochloroform solutions were investigated by measurement of the temperature dependences of isopropyl methyl signals, which under slow-exchange conditions appear as two spin doublets with $J_{H\text{-}CH_3}$ = 6.4–6.6 Hz depending on the complex. The methyl groups are diastereotopic and interchange environments upon inversion of the molecular configuration (Figure 1). Ligand exchange in the system $Cd(i\text{-}C_3H_7\text{-}SC_6H_5HCH_3)_2$–$Cd(C_6H_5CH_2\text{-}SC_6H_5HH)_2$ was followed with the $R_\alpha = CH_3$ signal in the pure and mixed species. Temperature regions of intermediate-exchange behavior under the solvent and concentration conditions employed were −25 to +40° and 85–140° for the cadmium(II) and zinc(II) inversions, respectively, and 30–90° for cadmium(II)–ligand exchange. In these regions spectra were recorded at *ca.* 5° intervals and several times at each temperature. Good spectral reproducibility was obtained when fresh samples were measured on different days. Instrumental tune was monitored by observation of the line widths of added cyclohexane (~0.2%) or non-exchange-broadened $R_\alpha = CH_3$ signals. In spite of careful purification of solvents and repeated recrystallization of complexes, small peaks due to free ligand were evident in many of the spectra. These peaks remained small and sharp in the intermediate- and fast-exchange regions and did not seriously interfere with analysis of line shapes.

Simulated spectra were calculated by a total line shape analysis using a modification[19] of the Whitesides–Lisle EXCNMR computer program,[20] which is based on the methods of Kubo and Sack.[21] Chemical shifts and line widths in the absence of exchange are required as input. Shifts of the zinc(II) and cadmium(II) complexes were measured in the slow-exchange region and plotted *vs.* temperature. As has been observed for other complexes,[18] chemical shifts were found to be temperature dependent. Isopropyl methyl shifts of $Cd(i\text{-}C_3H_7\text{-}SC_6H_5HR_\alpha)_2$ (R_α = H, CH_3) in the intermediate-exchange region in $CDCl_3$ solutions were obtained by linear extrapolation for the following reasons: (i) averages of extrapolated shifts agreed to within 0.3 Hz with those observed in the fast-exchange limit; (ii) linear temperature dependences were observed for the analogous zinc(II) complexes (slow exchange) in the same temperature interval; (iii) for the complexes $M(i\text{-}C_3H_7\text{-}SC_6H_5HH)_2$ the observed diastereotopic shift separation for M = Zn changes from 14 Hz at −45° to 8 Hz at 40° and for M = Cd the observed separation of 19 Hz at −50° extrapolated linearly to 10 Hz at 40°, giving approximately the same per cent change. In the case of $Cd(i\text{-}C_3H_7\text{-}SC_6H_5HCH_3)_2$ in $CDCl_3$ the separation of 17 Hz at −35° was extrapolated to 11 Hz at 50°, and in 1:1 $CDCl_3$–C_6H_5Cl the separation of 13 Hz at −30° is decreased, by extrapolation, to 8 Hz at 50°. For the complexes $Zn(i\text{-}C_3H_7\text{-}SC_6H_5HCH_3)(C_6H_5CH_2\text{-}SC_6H_5HH)$ and $Zn(i\text{-}C_3H_7\text{-}SC_6H_5HH)(C_6H_5CH_2\text{-}SC_6H_5HH)$ (formed by ligand exchange) and $Zn(i\text{-}C_3H_7\text{-}SC_6H_5HH)_2$ in chlorobenzene a slight curvature in extrapolating chemical shifts in the intermediate-exchange region was assumed in order to produce agreement with chemical shifts observed in the fast-exchange limit. Based on this slightly curved extrapolation the diastereotopic splitting in $Zn(i\text{-}C_3H_7\text{-}SC_6H_5HCH_3)(C_6H_5CH_2\text{-}SC_6H_5HH)$ decreased from 19 Hz at 60° to 14 Hz at 140°, in $Zn(i\text{-}C_3H_7\text{-}SC_6H_5HH)(C_6H_5CH_2\text{-}SC_6H_5HH)$ from 13 Hz at 60° to

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[18] J. G. Gordon, II, and R. H. Holm, *J. Amer. Chem. Soc.*, **92**, 5319 (1970).

[19] J. R. Hutchinson, J. G. Gordon, II, and R. H. Holm, *Inorg. Chem.*, **10**, 1004 (1971).

[20] G. M. Whitesides and J. S. Flemming, *J. Amer. Chem. Soc.*, **89**, 2855 (1967); J. S. Lisle, S.B. Thesis, Massachusetts Institute of Technology, 1968.

[21] R. Kubo, *Nuovo Cimento, Suppl.*, **6**, 1063 (1957); R. A. Sack, *Mol. Phys.*, **1**, 163 (1958).

9.0 Hz at 120°, and in $Zn(i\text{-}C_3H_7\text{–}SC_6H_5HH)_2$ from 6.0 Hz at 60° to 5.0 Hz at 120°. For the ligand-exchange process between $Cd(i\text{-}C_3H_7\text{–}SC_6H_5HCH_3)_2$ and $Cd(C_6H_5CH_2\text{–}SC_6H_5HH)_2$ in deuteriochloroform and chlorobenzene, the $R_\alpha = CH_3$ signals were analyzed. In chlorobenzene the chemical shift difference between the pure and mixed complexes is 12.9 ± 0.1 Hz from −21 to +29°. A constant separation was assumed throughout the exchange region.

Line widths of isopropyl methyl signals in zinc(II) complexes were found to change from 1.2 Hz in the slow-exchange limit to 1.0 Hz in the fast-exchange limit, and a linear extrapolation was used to obtain values in the intermediate-exchange region. Line widths in both the zinc(II) and cadmium(II) complexes were observed to increase as the temperature was decreased below *ca.* 30°. Below −50° the widths increase rapidly, presumably due to solvation effects and possible restricted rotation about the $N\text{–}C(i\text{-}C_3H_7)$ bond. Because the isopropyl methyl line widths of the cadmium(II) complexes in the fast- and slow-exchange limits are the same as the line widths of analogous zinc(II) complexes at the same temperatures, values for the latter between −45 and +30° were used for the former complexes in the intermediate-exchange region. For the ligand-exchange system specified above, the α-CH_3 line widths of $Cd(i\text{-}C_3H_7\text{–}SC_6H_5HCH_3)_2$, measured separately, were used as the nonexchanging line widths in both pure and mixed-ligand complexes. In chlorobenzene solution, initially 0.25 *M* in each of the pure complexes, curve fitting indicated that the ratio of pure to mixed complexes varied from 0.35:1.0 at −30° to 0.38:1.0 at 38°. This temperature dependence was extrapolated through the intermediate-exchange region.

The dynamic processes were treated as a simple two-site exchange between sites A and B which are not coupled to each other but are coupled (except the α-CH_3) to the methine proton with $J = 6.4\text{–}6.6$ Hz. The populations of sites A and B are equal, except in the cadmium(II)-ligand-exchange system, but can have different line widths. Line shape calculations were performed for the downfield component of each isopropyl methyl spin doublet, and the computed spectra were plotted as a superposition of the calculated line shape for the downfield components and an identical line shape displaced by 6.4–6.6 Hz for the upfield components. The area of the upfield component was 0.95 times that of the downfield component in all cases based on spectra in the slow- and fast-exchange limits. τ (sec) is defined as the mean pre-exchange lifetime of a methyl group in environment A or B and $k = 1/\tau$ is the exchange rate in sec^{-1} between A and B. Values of τ were obtained from visual comparison of computed and experimental isopropyl or α-methyl spectra in the intermediate-exchange region. Activation parameters were determined from weighted least-squares Arrhenius ($\ln k$ *vs.* $1/T$) and Eyring ($\ln (k/T)$ *vs.* $1/T$) plots. Points in the middle of the exchange region were given greater weight than the end points because in this region the computed line shapes are most sensitive to small changes in τ, errors in chemical shift extrapolation are likely to be smaller than in the high-temperature region, and for the cadmium(II) complexes line shapes in the middle of the exchange region proved to be least sensitive to the widths chosen for the non-exchange-broadened lines. Activation parameters are reported in Table III. In order to allow for errors in line widths and extrapolated shifts, errors are given as 3 times the standard deviation in the least-squares lines based on τ and temperature values uncertain to $\pm 20\%$ and $\pm 1°$, respectively. The estimated error in τ values from visual comparison is less than about 10%.

Results and Discussion

In the type **1** complexes the methyl groups of the *N*-isopropyl substituent are diastereotopic with nonequivalent environments arbitrarily labeled as r and s as illustrated in Figure 1. Upon inversion of the molecular configuration the environment of a particular group is changed in a simple two-site exchange process, which may be studied by a pmr line shape analysis of experimental spectra recorded in a temperature interval encompassing the intermediate-exchange region. In the slow-exchange region the spectrum consists of two spin doublets, the separation between which is the diastereotopic splitting. In the fast-exchange region, the spectrum collapses to a single doublet. A number of bis(β-aminothionato)zinc(II) and -cadmium(II) complexes have been prepared which exhibit sufficiently large diastereotopic splittings in certain solvents to permit meaningful line shape analysis of their exchange-broadened spectra. In order to investigate relative rearrangement rates of zinc(II) and cadmium(II) species with identical, or closely similar, ligand systems, complexes of type **1** were selected. The zinc(II) and cadmium(II) type **1** complexes, $M(R\text{–}SC_6H_5HR_\alpha)_2$, can be prepared by nonaqueous chelation techniques.[14] Other potentially suitable systems are of the bis(salicylaldiminato) or bis(β-ketoaminato) type (**2**), which can be prepared with a diastereotopic group such as isopropyl bonded to the coordinated nitrogen. While zinc(II) complexes of these types can be synthesized,[14,22–24] a number of attempts in this laboratory to prepare the corresponding cadmium(II) complexes have failed.

Zinc(II) Complexes.—In a search for conditions producing large diastereotopic splittings, the pmr spectra of the complexes in Table II were examined in a number of different solvents, including 1,1,2,2-tetrachloroethane, 1,1,2,3,3-pentachloropropane, deuteriochloroform, and chlorobenzene. Chemical shifts in deuteriochloroform solution are given in this table. Although diastereotopic splittings of $R = i\text{-}C_3H_7$ methyl groups are larger in the first three solvents than in chlorobenzene, decomposition in the first two solvents even when carefully purified and the temperature range (85–140°) of exchange broadening led to the use of chlorobenzene as the solvent for the line shape studies.

In chlorobenzene it was observed that the ligand-exchange reactions 1 and 2 reached equilibrium within a few minutes at ~30°. The equilibrium constant, $[\text{mixed}]^2/[\text{pure}_1][\text{pure}_2]$, at 60° is approximately equal to the statistical value of 4 for reaction 2 but is ~11 for reaction 1. Limited observations under slow-exchange conditions indicated no appreciable temperature dependence of K_{eq} in either case. The important

$$Zn(i\text{-}C_3H_7\text{–}SC_6H_5HCH_3)_2 + Zn(C_6H_5CH_2\text{–}SC_6H_5HH)_2 \rightleftharpoons 2Zn(i\text{-}C_3H_7\text{–}SC_6H_5HCH_3)(C_6H_5CH_2\text{–}SC_6H_5HH) \quad (1)$$

$$Zn(i\text{-}C_3H_7\text{–}SC_6H_5HH)_2 + Zn(C_6H_5CH_2\text{–}SC_6H_5HH)_2 \rightleftharpoons 2Zn(i\text{-}C_3H_7\text{–}SC_6H_5HH)(C_6H_5CH_2\text{–}SC_6H_5HH) \quad (2)$$

property of the mixed-ligand species in this solvent is that the diastereotopic splittings are considerably larger than those of the pure complexes from which they are derived.[25] For example, at 50° the splittings of the mixed-ligand complexes in reactions 1 and 2 are 19 and 13 Hz, respectively, compared to 2.2 Hz in $Zn(i\text{-}C_3H_7\text{–}SC_6H_5HCH_3)_2$ and 6.2 Hz in $Zn(i\text{-}C_3H_7\text{–}SC_6H_5HH)_2$. The isopropyl methyl region for mixed-ligand system 1 at slow exchange is shown in Figure 2, where the chemical shift separations $P_2\text{–}P_3$ and $M_2\text{–}M_3$ are the diastereotopic splittings of the pure and mixed-ligand complexes, respectively. Shown in Figure 3 are the

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[22] M. J. O'Connor, R. E. Ernst, J. E. Schoenborn, and R. H. Holm, *J. Amer. Chem. Soc.*, **90**, 1744 (1968).

[23] D. H. Gerlach and R. H. Holm, *Inorg. Chem.*, **9**, 588 (1970).

[24] R. H. Holm and M. J. O'Connor, *Progr. Inorg. Chem.*, **14**, 408 (1971).

[25] Diastereotopic splittings refer to isopropyl methyl groups. Methylene protons of $R = CH_2C_6H_5$ groups are also diastereotopic but chemical shift differences between them in pure zinc(II) and cadmium(II) complexes could not be resolved at 100 MHz; multiplets were observed in mixed-ligand complexes.

TABLE III

KINETIC PARAMETERS FOR DIASTEREOTOPIC AVERAGING OF ISOPROPYL METHYL GROUPS AND LIGAND EXCHANGE OF BIS(β-AMINOTHIONATO)ZINC(II) AND -CADMIUM(II) COMPLEXES

Complex	Solvent (*M*)	$\Delta G^{\ddagger}_{298°}$, kcal/mol	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	E_a, kcal/mol	Log [*A* (sec^{-1})]	$k_{298°}$, sec^{-1}
Zn(*i*-C_3H_7–$SC_6H_5CH_3$)-($C_6H_5CH_2$–SC_6H_5HH)	C_6H_5Cl (0.13,[a] 0.27[a])	20.5 ± 1.1	20.6 ± 1.3	0.2 ± 4.0	21.4 ± 1.4	13.4 ± 1.0	7.0×10^{-3} [d]
Zn(*i*-C_3H_7–SC_6H_5HH)-($C_6H_5CH_2$–SC_6H_5HH)[b]	C_6H_5Cl (0.27[a])	20.1 ± 1.5	20.2 ± 1.5	0.1 ± 4.0	21.0 ± 1.5	13.2 ± 1.0	6.5×10^{-3} [d]
Cd(*i*-C_3H_7–$SC_6H_5HCH_3$)$_2$	$CDCl_3$ (0.27[f])	15.1 ± 1.5	13.9 ± 1.5	−4.0 ± 4.0	14.5 ± 1.5	12.3 ± 1.0	5.6×10
	$CDCl_3$–C_6H_5Cl[e] (0.27[f])	14.6 ± 1.5	12.3 ± 1.5	−7.5 ± 4.0	12.8 ± 1.5	11.8 ± 1.0	1.3×10^2
Cd(*i*-C_3H_7–SC_6H_5HH)$_2$	$CDCl_3$ (0.15[f])	14.0 ± 1.5	11.0 ± 1.5	−10.1 ± 4.0	11.5 ± 1.0	11.0 ± 1.0	2.9×10^2
Cd(*i*-C_3H_7–$SC_6H_5HCH_3$)$_2$–Cd(*i*-C_3H_7–$SC_6H_5HCH_3$)-($C_6H_5CH_2$–SC_6H_5HH)[c]	C_6H_5Cl (0.25[a,f])	16.6 ± 1.8	13.7 ± 1.5	−9.5 ± 4.5	14.3 ± 1.6	11.1 ± 1.1	4.0[d]

[a] Initial concentration of each pure complex used in the formation of mixed-ligand species. [b] Kinetic data are also applicable to Zn(*i*-C_3H_7–SC_6H_5HH)$_2$ in chlorobenzene. [c] Data refer to ligand exchange. [d] Extrapolated values. [e] 1:1 v/v. [f] Saturated solution at low-temperature limit of measurement.

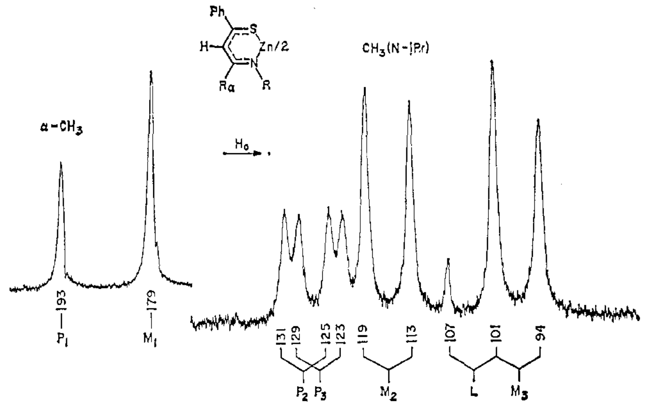

Figure 2.—Methyl resonances in an equimolar mixture of Zn(*i*-C_3H_7–$SC_6H_5HCH_3$)$_2$ and Zn($C_6H_5CH_2$–SC_6H_5HH)$_2$ in chlorobenzene solution at 57° (slow exchange). Zn(*i*-C_3H_7–$SC_6H_5HCH_3$)$_2$: P1, α-CH_3; P_2, P_3, diastereotopic *i*-C_3H_7 methyl doublets. Zn(*i*-C_3H_7–$SC_6H_5HCH_3$)($C_6H_5CH_2$–SC_6H_5HH): M_1, α-CH_3; M_2, M_3, diastereotopic *i*-C_3H_7 methyl doublets. L is a ligand impurity. Chemical shifts in hertz are downfield of the TMS reference.

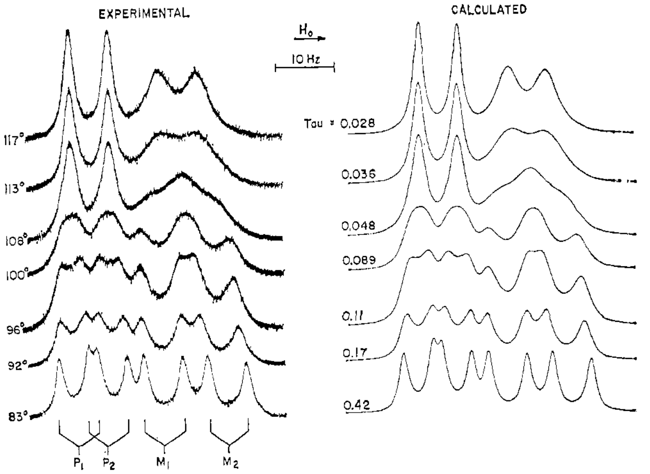

Figure 3.—Experimental and calculated isopropyl methyl spectra illustrating changes in the intermediate-exchange region for a chlorobenzene solution of Zn(*i*-C_3H_7–SC_6H_5HH)$_2$ and Zn(C_6H_5-CH_2–SC_6H_5HH)$_2$: P_1, P_2, Zn(*i*-C_3H_7–SC_6H_5HH)$_2$; M_1, M_2, Zn(*i*-C_3H_7–SC_6H_5HH)($C_6H_5CH_2$–SC_6H_5HH). τ values are in seconds.

exchange-broadened methyl spectra of Zn(*i*-C_3H_7–S-C_6H_5HH)$_2$ and Zn(*i*-C_3H_7–SC_6H_5HH)($C_6H_5CH_2$–SC_6H_5-HH), reaction 2. The fast-exchange spectrum consists of two doublets which attain minimum line width at *ca.* 125° and are separated by 15 Hz. Below this temperature the $\Delta \rightleftharpoons \Lambda$ averaging process is intramolecular. At higher temperatures these doublets undergo exchange broadening and coalesce at about 170° in solutions initially 0.14 *M* in the pure complexes, due to intermolecular ligand exchange. The behavior of the system represented by reaction 1 is slightly different. The spectrum simplifies to two doublets at fast exchange, but up to 175° these features, as well as the α-CH_3 signals of the pure and mixed complexes, exhibit no broadening, indicating that intramolecular rearrangement is much faster than ligand exchange.

Simulated methyl spectra for the reaction 2 system are depicted in Figure 3. Agreement between the calculated and observed spectra was best when the same value of τ was used for both the pure and the mixed complexes. For reaction 1 line shape analysis was restricted to the mixed complex because of the small diastereotopic splitting of Zn(*i*-C_3H_7–$SC_6H_5HCH_3$)$_2$. Activation parameters obtained from least-squares fits of the τ values to the Arrhenius equation and the Erying equation are collected in Table III. Parameters for the different complexes are identical within the estimated errors.[26]

Several other observations of interest have been made on zinc(II) chelates. It was reported earlier[23] that the β-ketoamine complex Zn(*i*-C_3H_7–$C_6H_5HCH_3$)$_2$ exhibited diastereotopic splitting and that in deuteriochloroform solution the two doublets coalesced above 120°. Coalescence behavior of Zn(*i*-C_3H_7–$C_6H_5HCH_3$)$_2$ and Zn-(*i*-C_3H_7–$SC_6H_5HCH_3$)$_2$ has been qualitatively examined in 1,1,2,2-tetrachloroethane. Under slow-exchange conditions (*e.g.*, 60°) the diastereotopic splittings of these complexes are 4 and 10 Hz, respectively. The two doublets coalesce at ~100° for the latter and at ~170° for the former even though its splitting is smaller. Because the two complexes differ only in the composition of the donor atom set, these results indicate that inversion of configuration occurs more readily for an N_2S_2 than an N_2O_2 complex. Because of the small

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(26) This result substantiates interpretation of the averaging processes as $\Delta \rightleftharpoons \Lambda$ inversion. Molecular models of complexes containing an *i*-C_3H_7–$SC_6H_5HR_\alpha$ chelate ring suggest the possibility of restricted rotation about the N–C(*i*-C_3H_7) bond when R_α = CH_3 due to steric interactions. This effect would be compatible with the pmr spectra, which could be interpreted without inversion of configuration. However, in the case of R_α = H the steric interactions are greatly diminished and any rotational barrier should be extremely small. Further, the large differences between the activation parameters for the zinc(II) and cadmium(II) complexes strongly indicate an effect other than N–C(*i*-C_3H_7) restricted rotation. The rapid increase in isopropyl methyl line widths below −50°, noted earlier, may be due in part to restricted rotation.

splitting and high coalescence temperature of $Zn(i\text{-}C_3H_7\text{–}C_6H_5HCH_3)_2$, other β-ketoamine complexes were not investigated.

A diastereomeric splitting of 11 Hz for the methyl group in $Zn[(+\text{ or }-)CH_3CHC_6H_5\text{–}SC_6H_5HH]_2$ was observed in deuteriochloroform solution at $\sim 30°$. These features arise from species such as $\Delta(+,+)$ and $\Lambda(+,+)$. Within the accuracy of planimetric integration the two doublets are of equal intensity, indicating the absence of stereoselective effects due to the asymmetric α-phenylethyl group. Under similar conditions (*cf.* Table II) no diastereomeric splittings were resolvable for other $R = CH_3CHC_6H_5$ complexes. Insufficient solubility of $Zn(CH_3CHC_6H_5\text{–}SC_6H_5HH)_2$ in chlorobenzene prevented a detailed study of rearrangement reactions.

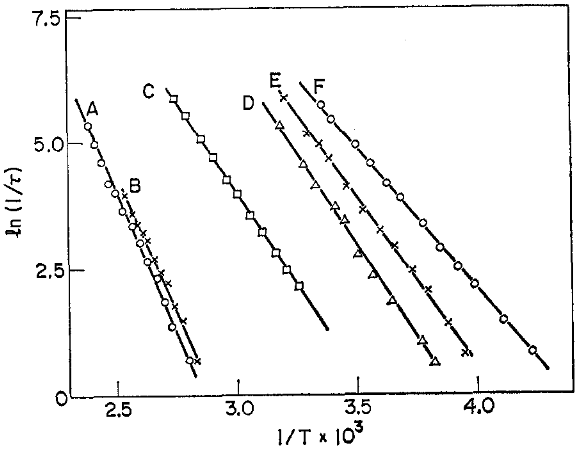

Figure 4.—Arrhenius plots for molecular rearrangements: A, inversion of $Zn(i\text{-}C_3H_7\text{–}SC_6H_5HCH_3)(C_6H_5CH_2\text{–}SC_6H_5HH)$ in C_6H_5Cl; B, inversion of $Zn(i\text{-}C_3H_7\text{–}SC_6H_5HH)_2$ and $Zn(i\text{-}C_3H_7\text{–}SC_6H_5HH)(C_6H_5CH_2\text{–}SC_6H_5HH)$ in C_6H_5Cl; C, ligand exchange of $Cd(i\text{-}C_3H_7\text{–}SC_6H_5HCH_3)_2$ and $Cd(C_6H_5CH_2\text{–}SC_6H_5HH)_2$ in C_6H_5Cl; D, inversion of $Cd\ (i\text{-}C_3H_7\text{–}SC_6H_5HCH_3)_2$ in $CDCl_3$; E, inversion of $Cd(i\text{-}C_3H_7\text{–}SC_6H_5HCH_3)_2$ in 1:1 $CDCl_3\text{–}C_6H_5Cl$; F, inversion of $Cd\ (i\text{-}C_3H_7\text{–}SC_6H_5HH)_2$ in $CDCl_3$.

Cadmium(II) Complexes.—The intermediate-exchange regions (−25 to +40° for inversion, 30–90° for ligand exchange with initial concentrations 0.25 *M* in each pure complex) occur at lower temperatures than those for zinc(II) complexes. Both diastereotopic averaging and ligand exchange were studied by line shape analysis. In deuteriochloroform diastereotopic splittings of the complexes $Cd(i\text{-}C_3H_7\text{–}SC_6H_5HR_\alpha)_2$ ($R_\alpha = CH_3$, H) are 17 Hz at −35° (slow exchange) which are sufficiently large to allow analysis of the exchange-broadened spectra. The temperature-dependent spectra are quite similar in appearance to those of the zinc(II) systems and coalescence of the two doublets occurred at $\sim 15°$ (CH_3) and $\sim -10°$ (H). Kinetic parameters are given in Table III. Comparison with the data for related zinc(II) complexes in chlorobenzene[27] reveals that rate constants for diastereotopic averaging are *ca.* 10^4 larger and activation energies are *ca.* 6–9 kcal/mol smaller for cadmium(II) than for zinc(II).

The ligand-exchange reaction (eq 3) was followed by observation of the temperature dependence of the α-CH_3 signals of the pure and mixed species in deuteriochloroform and chlorobenzene, where α-CH_3 chemical

$$Cd(i\text{-}C_3H_7\text{–}SC_6H_5HCH_3)_2 + Cd(C_6H_5CH_2\text{–}SC_6H_5HH)_2 \rightleftharpoons 2Cd(i\text{-}C_3H_7\text{–}SC_6H_5HCH_3)(C_6H_5CH_2\text{–}SC_6H_5HH) \quad (3)$$

shift differences are 21 and 13 Hz, respectively, at −21°. In chlorobenzene the equilibrium constant equals 8.2 at −30° and 6.9 at 38°. Ligand-exchange rates in deuteriochloroform were found to be strongly dependent upon solvent purity and times of heating above *ca.* 70°. Addition of a trace of dry hydrogen chloride accelerated rates by a factor of about 100. Due to difficulties in purification of deuteriochloroform, full line shape analysis was performed only on the spectra of chlorobenzene solutions. Kinetic data are given in Table III. Ligand-exchange rates were estimated in deuteriochloroform solution[28] using a less complete line shape analysis and were found to be comparable with the more reliable values in chlorobenzene. Solubility and spectrometer sensitivity restrictions prevented the variation of concentrations required to establish the kinetic order of reaction 3 in each of the pure complexes. However, variation of the equimolar concentrations of these species by factors of about 2 and 4 in chlorobenzene and deuteriochloroform, respectively, indicated that ligand-exchange rates are, approximately, directly proportional to total concentration.

Rearrangement Mechanisms.—Although the information summarized above does not permit an unambiguous determination of mechanism in any case, it does allow formulation of reaction pathways consistent with two key observations. (i) For zinc(II) complexes ligand exchange is significantly slower than diastereotopic averaging, which is therefore primarily intramolecular. (ii) For cadmium(II) complexes kinetic parameters, especially $\Delta H^{\ddagger}$, for ligand exchange and diastereotopic averaging are closely comparable and the ligand-exchange reaction is second order overall.

Plausible reaction pathways are illustrated in Scheme I with the Δ form **3** taken as the initial enantiomer. Pathway (a) involves a twist motion of the rings to form a planar transition state **4**, which upon further twisting causes inversion of the initial configuration to the Λ form **5**. Pathway (b) requires rupture (presumably heterolytic) of one metal–ligand bond (illustrated here as M–S) to yield a formally tricoordinate species **6**, which can generate **5** by bond formation. In pathway (c) two complexes interact to produce the binuclear intermediate **7**, followed by collapse to **5**. The formation and breakdown of **7** involves a sequence of bond formation and rupture *via* inter- and intramolecular Cd···S interactions along with rupture and reformation of two Cd–N bonds, resulting in ligand exchange and racemization. The intermediate **7** is proposed to

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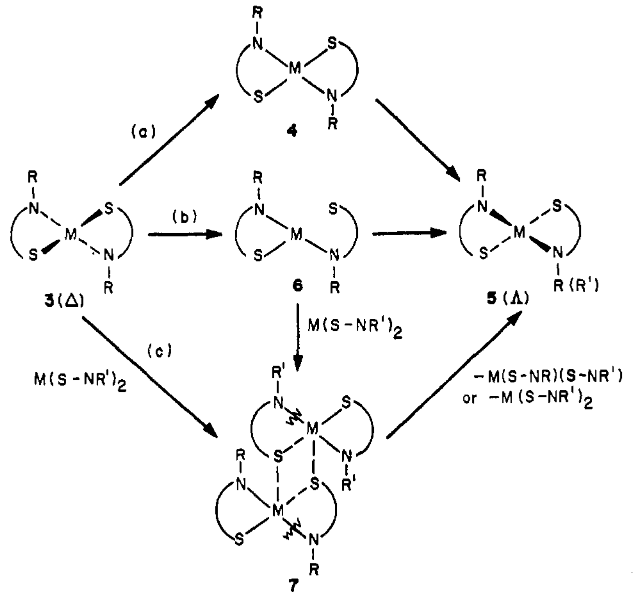
[27] Attempts to obtain accurate kinetic data for inversion of the cadmium(II) complexes in chlorobenzene were hampered by smaller diastereotopic splittings and the freezing point of the solvent (−45°). However, it was established that the rates of diastereotopic averaging for $Cd(i\text{-}C_3H_7\text{–}SC_6H_5HCH_3)_2$ in chlorobenzene are within a factor of 2 of those determined in $CDCl_3$. For the mixed complex $Cd(i\text{-}C_3H_7\text{–}SC_6H_5HCH_3)(C_6H_5CH_2\text{–}SC_6H_5HH)$ in chlorobenzene the diastereotopic splitting is *ca.* 40 Hz (−43°), but the slow-exchange limit is not reached before the solvent freezes. Approximate τ values for this complex indicate that diastereotopic averaging rates at several temperatures are comparable to those given in Figure 4 for $Cd(i\text{-}C_3H_7\text{–}SC_6H_5HH)_2$ in $CDCl_3$. The data in Table III for $Cd(i\text{-}C_3H_7\text{–}SC_6H_5HCH_3)_2$ show that change of solvent from $CDCl_3$ to 1:1 $CDCl_3\text{–}C_6H_5Cl$ does not significantly alter the kinetic parameters.

[28] Fresh commercial samples of $CDCl_3$ further purified by passage through an alumina column were used. Inversion rates of the two cadmium complexes in Table III were unaffected by this purification step.

Scheme I



involve bridging Cd···S rather than Cd···N interactions by analogy with sulfur-bridged dimers of certain cadmium(II) chelates.[24,29] An alternative mechanism for the formation of the intermediate **7** involves bond rupture to generate **6** succeeded by reaction with an intact complex $M(S\text{-}NR')_2$.

Observation (i) is consistent with either pathway (a) or (b). The concentration dependence of cadmium(II)-ligand exchange (observation (ii)) is most simply accommodated by pathway (c).

Whatever the exact nature of the ligand-exchange process, it cannot involve complete removal of the ligand from the coordination sphere of cadmium(II). When excess ligand was added to pure complexes, in a wide range of concentration ratios, the exchange-broadened spectra of the pure complexes were not affected, and the spectra of the free ligand remained sharp. Under these conditions if uncomplexed ligand anion were present, it would undergo proton exchange with free ligand, averaging the signals of ligand and complex in the intermediate-exchange region.

The similarity between the thermodynamic parameters for ligand exchange and inversion of $Cd(i\text{-}C_3H_7\text{-}SC_6H_5HCH_3)_2$ suggests but does not require that the latter process occurs *via* bond rupture (pathway (b)) accompanied by ligand exchange (pathway (c)) at a somewhat slower rate. The data provide no information on whether a Cd–S or a Cd–N bond is broken. Attempts to correlate the mechanisms of the inversion and ligand-exchange processes by an investigation of the concentration dependence of diastereotopic averaging were thwarted by the low solubilities of the two $Cd(i\text{-}C_3H_7\text{-}SC_6H_5HR_\alpha)_2$ species studied (Table III).

The higher activation energies and slower rates for diastereotopic averaging of zinc(II) than of cadmium(II) complexes may indicate different rearrangement mechanisms but may also merely reflect changes in bond strengths. The rates and thermodynamic parameters for inversion of the two mixed complexes of zinc(II) are equal within experimental error, but the rates of ligand exchange (which must proceed by bond rupture) in the two systems are considerably different, suggesting but not requiring that the zinc(II) inversion reaction may proceed by a twist mechanism (pathway (a)), rather than bond rupture (pathway (b)). The slower rate of diastereotopic averaging in the $Zn\text{-}N_2O_2$ compared to the $Zn\text{-}N_2S_2$ case is consistent with a transition state whose planar geometry is stabilized to a greater extent by sulfur than by oxygen donor atoms.[14,24]

The observation of increased rates of rearrangement with increasing ionic radius (Zn^{2+}, 0.74 Å; Cd^{2+}, 0.97 Å) of the metal ion is consistent with previous observations on d^0 and d^{10} chelate complexes and appears to be a general property. The same trend has been found for the geometrical isomerization reactions of $M(tfac)_3$[30] (M = Al, Ga, In), $M(acac)_2X_2$[31] (M = Ti, Zr, Hf), and tris(1-phenyl-5-methylhexane-2,4-dionato)metal(III)[19] complexes ($M(pmhd)_3$, M = Al, Ga, Sc).

Finally, a number of nickel(II) complexes of the $Ni(R\text{-}R_\gamma HR_\alpha)_2$, $Ni(R\text{-}SR_\gamma HR_\alpha)_2$, and bis(*N*-R-salicylaldiminato) types[2,14,24,32] containing (+)- or (−)-R groups have been prepared and have been shown to be involved in dynamic planar (diamagnetic) $\rightleftharpoons$ tetrahedral (paramagnetic) equilibria. The structural change is fast on the pmr time scale and an upper limit for the lifetime of either stereoisomer has been estimated as *ca.* 10^{-4} sec. The failure to observe separate signals for active ((+,+) or (−,−)) complexes has been interpreted in terms of rapid racemization of tetrahedral diastereomers *via* a planar intermediate. If correct, the apparent order of inversion is Zn < Cd < Ni, at least for β-aminothione complexes where a full comparison can be made. However, it has not yet been demonstrated that the diamagnetic form in solution is strictly planar, *i.e.*, achiral at the metal center, and that one cycle of the change, paramagnetic → diamagnetic → paramagnetic, *necessarily* inverts the molecular configuration. The results of Hseu, *et al.*,[6] for metal(II) β-ketoamines, including $Ni(H\text{-}CH_3HCH_3)_2$, suggest that certain diamagnetic nickel(II) complexes in solution may not be strictly planar and that an appreciable activation energy may be required to achieve this configuration in an inversion process which proceeds by a twist pathway. This matter is being actively investigated in another laboratory.[8]

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(29) D. Coucouvanis, *Progr. Inorg. Chem.*, **11**, 233 (1970); R. Eisenberg, *ibid.*, **12**, 295 (1970).

(30) R. C. Fay and T. S. Piper, *Inorg. Chem.*, **3**, 348 (1964).

(31) R. C. Fay and R. N. Lowry, *ibid.*, **6**, 1512 (1967); T. J. Pinnavaia and R. C. Fay, *ibid.*, **7**, 502 (1968).

(32) R. H. Holm, *Accounts Chem. Res.*, **2**, 307 (1969), and references therein.