values. In this regard the modified dimer model of Jeter et al.[6] gives nearly as good a representation of the experimental data as the larger cluster size models. However, on the basis of the structural data, we conclude that this is not a good physical picture of the material.

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Registry No. $Cu(NH_3)_2CO_3$, 21710-50-9.

Contribution from the Department of Physical Chemistry,
"Rudjer Bošković" Institute, Zagreb, Yugoslavia

Solubility and Equilibrium Constants of Mercury(II) in Carbonate Solutions (25 °C, I = 0.5 mol dm^{-3})[1a]

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Precipitation and dissolution studies of mercury(II) in carbonate solutions, performed at I = 0.5 mol dm^{-3} and 25 °C, complete the present knowledge of the state of inorganic divalent mercury in natural waters. The turbidity method was used to detect precipitation regions. Chemical analysis, IR spectra, and X-ray diffraction patterns were used to distinguish the various Hg salts in different concentration regions. The concentrations of mercury and hydrogen ions have been determined in solution in contact with the solid phase. From experimental data the following values for equilibrium constants are obtained: $\log [Hg^{2+}]^3 p(CO_2)[H^+]^{-6} = 5.40$; $\log [HgOH^+][H^+][Hg^{2+}]^{-1} = -3.38$; $\log [Hg(OH)_2{}^0][H^+][HgOH^+] = -2.56$; $\log [HgHCO_3{}^+][Hg^{2+}]^{-1}[CO_3{}^{2-}]^{-1} = 15.08$; $\log [HgCO_3{}^0][Hg^{2+}]^{-1}[CO_3{}^{2-}]^{-1} = 11.01$; $\log [HgOHCO_3{}^-][H^+][Hg^{2+}]^{-1}[CO_3{}^{2-}]^{-1} = 4.40$; $\log [Hg(CO_3)_2{}^{2-}][Hg^{2+}]^{-1}[CO_3{}^{2-}]^{-2} = 14.50$.

Introduction

There is limited information about the mercury(II) carbonate system in the literature, although it might be of interest in geochemistry. Several basic salts have been prepared.[2] The solubility product of $HgCO_3 \cdot 2HgO(s)$ has been determined at I = 3.0 mol dm^{-3}, independently by Hietanen and Högfeldt[3] and by Weber.[4] Soluble complexes were studied by Hietanen and Högfeldt.[5] They have calculated equilibrium constants for the three soluble mercury carbonate species $HgHCO_3{}^+$, $HgCO_3{}^0$, and $HgOHCO_3{}^-$. According to them the formation of $HgCO_3{}^0$ is somewhat uncertain considering the experimental uncertainty. In this work there is shown the concentration range of three stable solids, formed in mercury(II) carbonate system. Solubility of $HgCO_3 \cdot 2HgO(s)$ and equilibrium constants of soluble complexes are determined at I = 0.5 mol dm^{-3}. The values at I = 3.0 mol dm^{-3} obtained by Hietanen and Högfeldt[5] are recalculated and discussed.

Experimental Section

Chemicals. Solutions were prepared by dissolving the following chemicals in bidistilled water: $Hg(NO_3)_2$, $HClO_4$, $NaClO_4 \cdot H_2O$, $NaHCO_3$, NH_4OH (Merck, Darmstadt, Germany), pa; Na_2CO_3, EDTA, Zn metal powder (Kemika, Zagreb, Yugoslavia). Indicator buffer (Merck) was used for mercury determination. Stock solutions were standardized.

Solubility experiments were performed in two ways. (a) Prepared solid $HgCO_3 \cdot 2HgO$ was equilibrated with solutions of the composition $[H^+] = H$ mol dm^{-3}, $[Na^+] = (0.5 - H)$ mol dm^{-3}, $[ClO_4{}^-] = 0.5$ mol dm^{-3}, and $CO_2(g)$. In calculation of $p(CO_2)$, the partial pressure of water vapor of 23.75 torr was used. The dissolution time was 1–2 days. The reaction vessel and emf cell were the same as those described by Schindler, Reinert, and Gamsjäger.[6] In each equilibrated solution the concentrations of soluble mercury and free hydrogen ions were determined. (b) Solid $HgCO_3 \cdot 2HgO$ was precipitated by mixing a solution of mercury nitrate with a carbonate solution of the composition $[HCO_3{}^- + CO_3{}^{2-}]$ mol dm^{-3}, $[Na^+] = 0.5$ mol dm^{-3}, and $[ClO_4{}^-] = (0.5 - [HCO_3{}^- + 2CO_3{}^{2-}])$ mol dm^{-3}. Thirty days was allowed for equilibrium.

Table I. X-ray Powder Pattern[a] for $HgCO_3 \cdot 2HgO$

d_{obsd}, Å	I	d_{obsd}, Å	I
5.63	18	2.12	8
5.50	27	2.099	30
3.62	6	2.070	6
3.23	8	1.821	27
3.15	35	1.734	10
3.03	41	1.667	4
2.82	52	1.639	4
2.75	100	1.613	28
2.41	10	1.581	9
2.38	7	1.530	20
2.22	6	1.524	21
2.19	8	1.514	22

[a] The instrument used was a Philips PW 1050 X-ray diffractometer (Cu Kα radiation).

Instruments. The presence or absence of solid phases detected tyndallometrically[7] (a Zeiss tyndallometer in combination with a Pulfrich photometer) and color with the naked eye. X-ray diffraction patterns and IR spectra were used to distinguish the various Hg salts in different concentration regions. The concentration of soluble mercury was determined either by rapid DC polarography method[8] using Metrohm Polarecord E 261 or by a complexometric method.[9]

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(1) (a) This work has been presented in part at the Congress sur la protection des eaux de mer, lacs, et rivieres, Belgrade, Yugoslavia, Oct 26–30, 1976, and in part at the Conference on Electrolyte Precipitation in Aqueous Solution, Copenhagen, Denmark, Aug 16–18, 1978. (b) Dc polarographic measurements have been performed by H.B. at EAWAG, ETH-Dübendorf, Switzerland.

(2) "Gmelins Handbuch der Anorganischen Chemie", 8th ed., Verlag Chemie, GMBH Weinheim/Bergstr., West Germany, 1967, Part B, p 980. (b) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry", Vol. IV, Longmans, Green and Co., London, 1957, p 980.

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Table II. Homogeneous and Heterogeneous Equilibria in the Mercury(II)–Carbonate System[a]

eq	homogeneous equilibria	log *K* (*I* = 0.5 mol dm^{-3})	ref	log *K* (*I* = 3 mol dm^{-3})	ref	log *K*[b] (*I* = 3 mol dm^{-3})
1	$H_2O = H^+ + OH^-$	13.73	10	14.03	10	
2	$CO_2(g) + H_2O = H^+ + HCO_3^-$	−7.56 cor	11	−8.00	3	
3	$HCO_3^- = H^+ + CO_3^{2-}$	9.93 cor	10	9.56	16	
4	$Hg^{2+} + H_2O = HgOH^+ + H^+$	−3.38 ± 0.20	*c*	−3.55	17	
		−3.70	12	−3.49	10	
		−3.68	13	−3.23	10	
5	$HgOH^+ + H_2O = Hg(OH)_2^0 + H^+$	−2.56 ± 0.10	*c*			
		−2.60	12			
		−2.57	13			
4 + 5	$Hg^{2+} + 2H_2O = Hg(OH)_2^0 + 2H^+$			−6.21	17	
				−5.96	10	
				−6.16	10	
6	$Hg^{2+} + H^+ + CO_3^{2-} = HgHCO_3^+$	15.08 ± 0.10	*c*	15.05	5	14.72
7	$Hg^{2+} + CO_3^{2-} = HgCO_3^0$	11.01 ± 0.20	*c*	10.65	5	11.00
8	$Hg^{2+} + H_2O + CO_3^{2-} = HgOHCO_3^- + H^+$	4.40 ± 0.10	*c*	4.40	5	4.40
9	$Hg^{2+} + 2CO_3^{2-} = Hg(CO_3)_2^{2-}$	14.50 ± 0.20	*c*			14.00

eq	heterogeneous equilibria	log *K* (*I* = 0.5 mol dm^{-3})	ref	log *K* (*I* = 3 mol dm^{-3})	ref
10	$HgCO_3 \cdot 2HgO(s) + 6H^+ = 3Hg^{2+} + CO_2(g) + 3H_2O$	5.40 ± 0.25	*c*	7.20	3
		7.02 ± 0.25 (*I* = 0 mol dm^{-3})	*b*	7.12	5
				7.26	4
11	$HgO(s) + H_2O = Hg^{2+} + 2OH^-$	−24.87 ± 0.05	*c*	25.59	10

[a] At 25 °C. [b] Recalculated in this work. [c] This work.

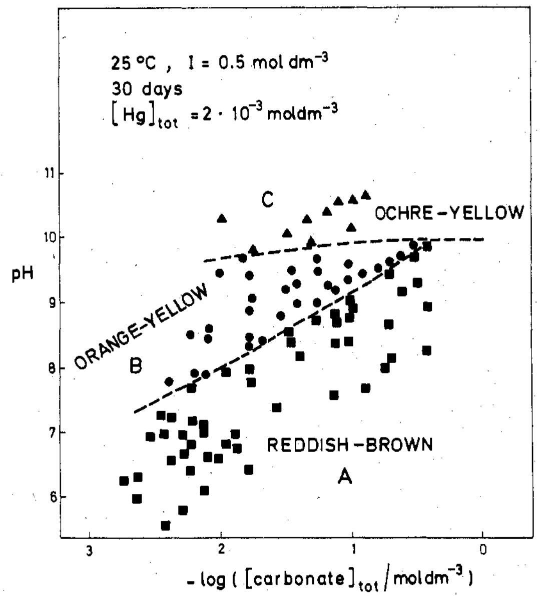

Figure 1. Precipitation diagram of mercury(II) salts formed in carbonate solutions at different pH values (25 °C, I = 0.5 mol dm^{-3} ($NaClO_4$), 30 days' aging).

The concentration of $[H^+]$ was determined by a Radiometer 26 pH-meter with a G 202 C glass electrode and an Ag/AgCl reference electrode. The standard potential of a glass electrode was determined after each experiment. A correction for liquid junction potential (at I = 0.5 mol dm^{-3}, $E_j' = 100.2[H^+]$) was added to the measured E values.

Results

In Figure 1 is presented the precipitation diagram of various mercury salts. At constant mercury concentration, 2 × 10^{-3} mol dm^{-3}, total carbonate varied from 2 × 10^{-3} to 3 × 10^{-1} mol dm^{-3} and the pH varied from 5.5 to 10.8. With use of chemical analysis, IR spectra, and X-ray diffraction patterns, three precipitation regions were differentiated: (A) reddish brown $HgCO_3 \cdot 2HgO$, (B) an orange-yellow precipitate with

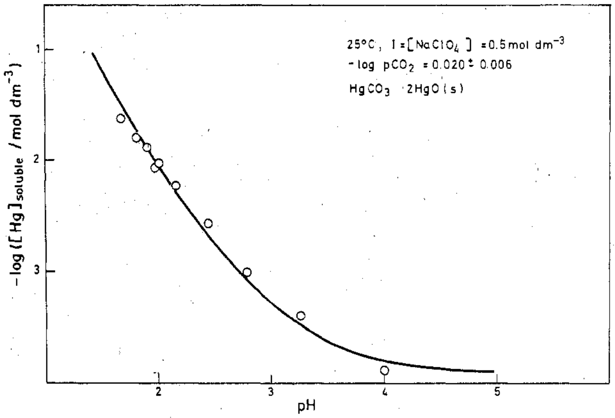

Figure 2. Solubility of $HgCO_3 \cdot 2HgO(s)$ in acid solutions in the presence of $p(CO_2) \approx 1$ atm. Equilibrium constants presented by eq 4–7 and 10 (Table II) have been obtained from experimental data.

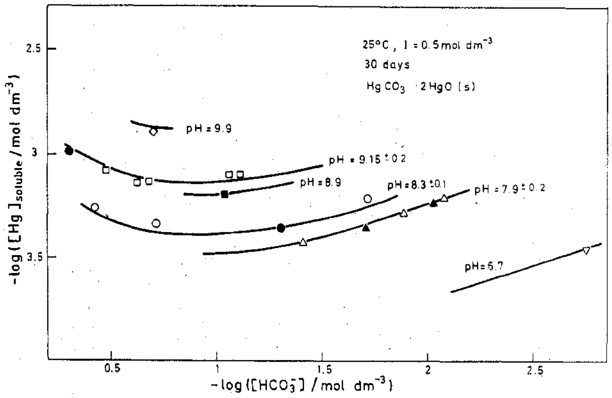

Figure 3. Complex solubility of $HgCO_3 \cdot 2HgO(s)$ in carbonate solutions. Equilibrium constants for eq 8 and 9 for I = 0.5 mol dm^{-3} in Table II have been obtained from experimental data. Constants presented by eq 4–7 have been used as unchanged in the iteration process. Solubility is explained by iso-pH curves.

variable composition (Hg = 81.4–86.6%, C < 1%, and N ≈ 0%), and (C) yellow HgO.

Characteristic IR spectra of the precipitates in regions A and B show the splitting of the degenerate vibrations of car-

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(9) "Komplexometrische Bestimmunsmethoden mit Titriplex", Merck, AG-Darmstadt, West Germany, 1961.

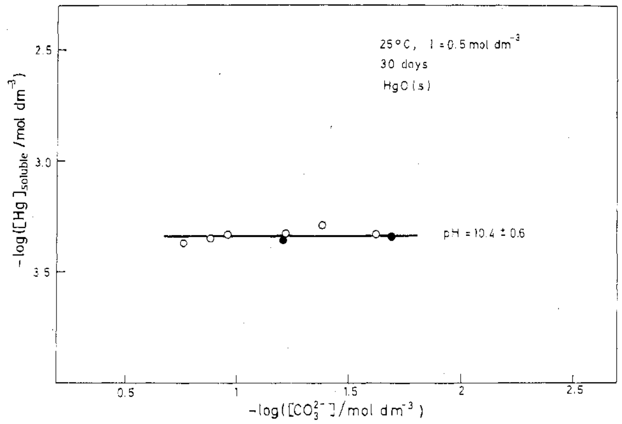

Figure 4. Solubility of yellow HgO(s) in carbonate solutions (I = 0.5 mol dm^{-3} ($NaClO_4$), 25 °C). The equilibrium constant presented by eq 11 is presented in Table II.

bonate, which could correspond to unidentate rather than to bidentate binding.[17]

In Table I there are given d values and intensities for $HgCO_3$·2HgO, obtained by X-ray powder diffraction method. Precipitates in region B show an X-ray diffraction pattern almost identical with that of HgO, with an additional strong line at d = 2.88 Å.

In Table II there are listed all reported homogeneous and heterogeneous equilibria in the mercury(II)–carbonate system, including the values of equilibrium constants and the references. Equilibrium constants at I = 0.5 mol dm^{-3} have been calculated from the solubility experiments presented in Figures 2 and 3 of this paper. The data were analyzed as earlier described[14] to give the simplest polynominal in [H^+] which can explain the experimental solubility.

In Figure 2 there are presented experimental results for solubility of $HgCO_3$·2HgO(s) in acid solutions in the presence of $p(CO_2) \approx 1$ atm. Experimental data are plotted as $-\log [Hg]_{soluble}$ vs. the pH. The solubility curve which fits experimental points is calculated by using equilibria 4–7 and 10 for I = 0.5 mol dm^{-3} in Table II. Under the experimental conditions investigated, the following species predominate in solution: Hg^{2+}, $HgOH^+$, $Hg(OH)_2^0$, $HgHCO_3^+$, and $HgCO_3^0$. Precipitates from region B were unstable under the same experimental conditions ($p(CO_2) \approx 1$ atm), being slowly transformed to $HgCO_3$·2HgO.

In Figure 3 there are presented experimental results for precipitation of $HgCO_3$·2HgO(s) from carbonate solutions. Solubility data are plotted as $-\log [Hg]_{soluble}$ vs. $-\log [HCO_3^-]$. The concentration of HCO_3^- was calculated from the pH and total carbonate concentration,[15] with use of eq 2 and 3 for I = 0.5 mol dm^{-3} from Table II. Theoretical solubility iso-pH curves were calculated by using equilibria 4–10 and constants for I = 0.5 mol dm^{-3}. Black points present the data in which mercury was determined by a DC polarographic method.[8] In the rest of the experimental points mercury was determined complexometrically.[9] Very good agreement was obtained by the two analytical methods. Under the experimental conditions studied, the complexes $Hg(OH)_2^0$, $HgOHCO_3^-$, and $Hg(CO_3)_2^{2-}$ exist in equilibrium with $HgCO_3$·2HgO(s).

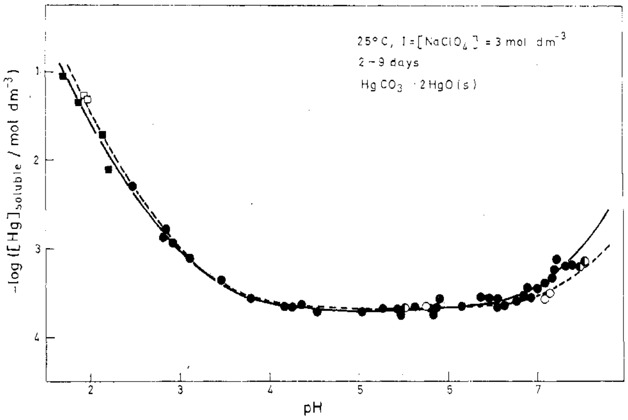

Figure 5. Reinterpretation of literature values[4,5] performed for solubility of $HgCO_3$·2HgO(s) at I = 3.0 mol dm^{-3}. Solubility curves are calculated for $p(CO_2)$ = 1 atm (full line) and for $p(CO_2)$ = 0.5 atm (dotted line).

In Figure 4 there are presented experimental results for precipitation of yellow HgO(s) in carbonate solutions (region C, Figure 1). Solubility data are plotted as $-\log [Hg]_{soluble}$ vs. $-\log [CO_3^{2-}]$. The concentration of [CO_3^{2-}] was calculated from the pH and total carbonate concentration,[15] with use of eq 2 and 3 and constants for I = 0.5 mol dm^{-3} from Table II. Dots present the data obtained by dc polarography and circles by complexometric titration, as analytical methods for mercury determination. From experimental solubility data in Figure 4 and equilibrium constants for eq 4–9, for I = 0.5 mol dm^{-3} in Table II, it was possible to calculate the solubility product of HgO. The value is presented by eq 11 in Table II and is in very good agreement with the existing literature.[10] Thus it was proved by an independent experiment at pH 10.4 ± 0.6, the validity of equilibrium constants determined for I = 0.5 mol dm^{-3} and presented by eq 3–9 in Table II. Complex $Hg(OH)_2^0$ predominates in solution in the whole region of carbonate concentrations.

Discussion

Equilibrium constants determined in this work for I = 0.5 mol dm^{-3} ionic strength can be compared in Table II with the very few literature values. Correction of the constant for eq 10 from I = 0.5 mol dm^{-3} to the ionic strength I = 0 mol dm^{-3} was performed by using the Davies equation.[15] The value log K = 7.02 ± 0.25 can be approximately compared with the values determined at I = 3.0 mol dm^{-3}. Very good agreement exists. Hydrolysis constants of mercury compared for I = 0.5 and 3.0 mol dm^{-3} in Table II show fairly good agreement. About mercury carbonate complexes there is only one paper for comparison.[5] It contains equilibrium constants for $HgHCO_3^+$, $HgCO_3^0$, and $HgOHCO_3^-$ complexes at I = 3.0 mol dm^{-3}, assuming large experimental uncertainty for $HgCO_3^0$, as concluded by the authors.[5] In our paper, we have found an additional complex $Hg(CO_3)_2^{2-}$, because of the broader pH region investigated.

Experimental data of Hietanen and Högfeldt[5] presented by circles and of Weber[4] presented by squares in Figure 5 can be discussed. The data are presented analogously to Figure 2 in the form $-\log [Hg]_{soluble}$ vs. pH and show excellent precision in the whole region of pH. Data were analyzed to find out the simplest polynomial which could explain solubility data at $p(CO_2) \approx 1$ atm (black points) and at $p(CO_2) \approx 0.5$ atm (empty points). Experimental data for $p(CO_2) \approx 0.8$ atm are presented with half black points and are between the two calculated curves. For the best set of carbonate constants, the following log K values for I = 3 mol dm^{-3} from Table II have

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been used as unchanged: 14.03 (eq 1), −8.00 (eq 2), 9.56 (eq 3), −3.55 (eq 4), 6.21 (eq 4 and 5), and 7.20 (eq 10). Other values have been iterated; the best recalculated values for eq 6–9 have been found for $I = 3.0$ mol dm^{-3} presented in Table II. The two solubility curves have been calculated for the same set of equilibrium constants, for $p(\mathrm{CO_2}) = 1$ atm (full line) and for $p(\mathrm{CO_2}) = 0.5$ atm (dotted line) in Figure 5. The two curves coincide completely at $3 < \mathrm{pH} < 6.5$, and a very small difference was obtained at pH < 3 and pH > 6.5. The influence of $p(\mathrm{CO_2})$ on the solubility of $\mathrm{HgCO_3{\cdot}2HgO(s)}$ was found to be insignificant. The normalization used by Hietanen and Högfeldt was not necessary.[5] The recalculated values for $I = 3.0$ mol dm^{-3} are in very good agreement with our values for $I = 0.5$ mol dm^{-3}. Experimental data from Weber[4] cover the pH region from 1.5 to 2.5, those of Hietanen and Högfeldt[5] cover the region $2.5 < \mathrm{pH} < 7.5$, and our data are at $1.5 < \mathrm{pH} < 4$ and $7.9 < \mathrm{pH} < 9.9$, presenting together a complementary picture of the mercury–carbonate system.

Acknowledgment. The authors wish to thank Professor H. Gamsjäger for sending us unpublished results[4] and for useful discussion. X-ray diffraction patterns by Miss M. Luič are appreciated. Our work was supported in part by the Self-Management Council for Scientific Research of S. R. Croatia and in part by the Swiss National Foundation. The suggestion of this study by Professor Werner Stumm is greatly appreciated.

Registry No. $\mathrm{HgCO_3{\cdot}2HgO}$, 58800-00-3; HgO, 21908-53-2.

Contribution from the Department of Inorganic Chemistry, University of Melbourne, Parkville, 3052, Australia,
and the Department of Inorganic and Analytical Chemistry, La Trobe University, Bundoora, 3083, Australia

Pressure-Dependent Racemization Reactions of Tris(dithiocarbamato)cobalt(III) Complexes in Nonaqueous Solvents

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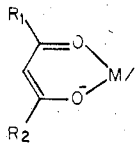
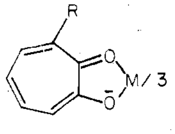
The pressure-dependent racemization of $\mathrm{Co(pyrdtc)_3}$ (pyrdtc = pyrrolidinecarbodithioate) determined over the pressure range 1–1380 bar yielded activation volumes ($\Delta V^{\ddagger}$) of +9.8 (±0.5) cm^3 mol^{-1} (in ethanol), +5.2 (±0.7) cm^3 mol^{-1} (dimethylformamide), +5.4 (±0.5) cm^3 mol^{-1} (acetonitrile), and +7.8 (±0.6) cm^3 mol^{-1} (toluene). The activation volume in each solvent is pressure dependent; hence nonzero compressibility coefficients of activation ($\Delta\beta^{\ddagger}$) are observed in each solvent. The compressibility of activation ($\Delta\kappa^{\ddagger}$) is independent of solvent at 0.43 (±0.03) kbar^{-1}.. A twist mechanism involving a low-spin ⇌ high-spin preequilibrium is proposed on the basis of the experimental data. The $\mathrm{Co(Ph_2\text{-}dtc)_3}$ complex ($\mathrm{Ph_2}$-dtc = diphenyldithiocarbamate), by contrast, exhibits negative $\Delta V^{\ddagger}$ values of between −2 and −9.3 cm^3 mol^{-1} in five different nonaqueous solvents. The alternative one-ended dissociative mechanism is favored for this complex.

Introduction

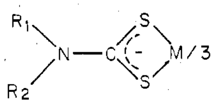
Rearrangement reactions of six-coordinate chelate complexes, involving racemization and isomerization, have been extensively studied. However, most of the early work in this area was confined to the inert metal complexes of cobalt(III) and chromium(III) and of iron(II) and nickel(II) complexes containing oxalate (ox), 1,10-phenanthroline (phen), and 2,2′-bipyridyl (bpy) ligands.[2] During the past decade much effort has been devoted to the study of the intramolecular metal-centered rearrangement reactions of complexes involving various other types of ligands, using variable-temperature nuclear magnetic resonance techniques in particular.[2-5] These complexes are the β-diketonates (I), α-substituted tropolonates (II) and N,N-disubstituted dithiocarbamates (III).



$\mathrm{M(R_1,R_2\text{-}\beta\text{-dik})_3}$
I



$\mathrm{M(\alpha\text{-RT})_3}$
II



$\mathrm{M(R_1,R_2\text{-dtc})_3}$
III

Generally, racemization and isomerization of unsymmetrical (β-diketonato)cobalt(III) complexes have been found to occur via a bond-rupture mechanism, involving a trigonal-bipyramidal transition state.[6,7] On the other hand, a twist mechanism has been assigned to rearrangement of α-substituted tropolonates of cobalt(III) as well as of aluminum(III) and gallium(III).[8,9] For the symmetrical tris(trifluoroacetylacetonato)cobalt(III), -aluminum(III), and -gallium(III) complexes a bond-rupture mechanism has been suggested, although not definitely proved.[10] Recently, the $\mathrm{Al(acac)_3}$ complex was optically resolved and the racemization followed by circular dichroism.[11] The large positive value of $\Delta S^{\ddagger}$ (+220 J K^{-1} mol^{-1}) for this reaction is not consistent with a twist mechanism; consequently an intramolecular bond-rupture mechanism was proposed.

The rearrangement reactions of disubstituted dithiocarbamates $\mathrm{M(R_1,R_2\text{-dtc})_3}$, where M = Ru(III), Fe(III), and Co(III), and $\mathrm{[Fe^{IV}(R_1,R_2\text{-dtc})_3](BF_4)}$ complexes, have been subjected to NMR investigation by Pignolet and coworkers. Unique rearrangement modes have been assigned for $\mathrm{Ru(CH_3,PhCH_2\text{-dtc})_3}$[12,13] and $\mathrm{[Fe^{IV}(CH_3,PhCH_2\text{-dtc})_3](BF_4)}$,[14] and the most probable mechanism is a trigonal twist in each

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