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 $p(CO_2) = 1$ atm (full line) and for $p(CO_2) = 0.5$ atm (dotted line) in Figure 5. The two curves coincide completely at $3 < pH < 6.5$, and a very small difference was obtained at pH < 3 and pH > 6.5. The influence of $p(CO_2)$ on the solubility of $HgCO_3 \cdot 2HgO(s)$ 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 < pH < 7.5, and our data are at 1.5 < pH < 4 and 7.9 < 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 The authors wish to thank Professor H. Gamsjäger for sending us unpublished results[4] and for useful discussion.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. Luić 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. $HgCO_3 \cdot 2HgO$, 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

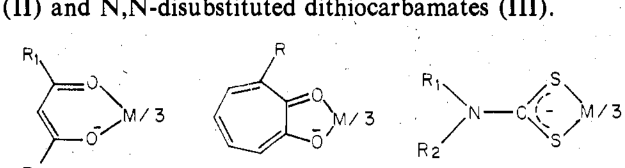
GEOFFREY A. LAWRANCE,*[1] MAXWELL J. O'CONNOR, SURAPONG SUVACHITTANONT, DONALD R. STRANKS, and PETER A. TREGLOAN

Received April 8, 1980

The pressure-dependent racemization of $Co(pyrdtc)_3$ (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 $Co(Ph_2\text{-dtc})_3$ complex (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).



$M(R_1,R_2\text{-}\beta\text{-dik})_3$ I $\quad$ $M(\alpha\text{-RT})_3$ II $\quad$ $M(R_1,R_2\text{-dtc})_3$ 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 $Al(acac)_3$ 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 $M(R_1,R_2\text{-dtc})_3$, where M = Ru(III), Fe(III), and Co(III), and $[Fe^{IV}(R_1,R_2\text{-dtc})_3](BF_4)$ complexes, have been subjected to NMR investigation by Pignolet and coworkers. Unique rearrangement modes have been assigned for $Ru(CH_3,PhCH_2\text{-dtc})_3$[12,13] and $[Fe^{IV}(CH_3,PhCH_2\text{-dtc})_3](BF_4)$,[14] and the most probable mechanism is a trigonal twist in each

(1) Address for correspondence: Research School of Chemistry, The Australian National University, Canberra, ACT 2600, Australia.

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Table I. Pressure-Dependent Racemization Rates of $(-)_{546}$-Co(pyrdtc)$_3$ in Various Solvents

solvent	pressure, bar	$10^4 k_{rac}$,[a] s^{-1}
ethanol[b]	1	5.58 ± 0.04 (4)
	345	4.91 ± 0.02 (4)
	690	4.50 ± 0.04 (3)
	1035	4.09 ± 0.06 (3)
	1380	3.85 ± 0.03 (3)
dimethylformamide[b]	1	3.47 ± 0.05 (5)
	345	3.24 ± 0.03 (4)
	690	3.10 ± 0.06 (3)
	1035	2.95 ± 0.04 (3)
	1380	2.86 ± 0.04 (2)
acetonitrile[c]	1	3.68 ± 0.01 (3)
	345	3.42 ± 0.02 (4)
	690	3.28 ± 0.02 (2)
	1035	3.12 ± 0.01 (3)
	1380	3.03 ± 0.03 (3)
toluene[d]	1	4.46 ± 0.04 (6)
	345	4.09 ± 0.05 (4)
	690	3.76 ± 0.02 (4)
	1035	3.53 ± 0.02 (3)
	1380	3.36 ± 0.05 (3)

[a] Standard error and number of independent runs (in parentheses) included. [b] At 43.0 °C. [c] At 41.0 °C. [d] At 55.4 °C.

case (Ph = phenyl). This mechanism is also favored for the Fe(CH$_3$,Ph-dtc)$_3$ complex.[15] Furthermore, the $\Delta G^‡$ values of a series of complexes Fe^{III}(R$_1$,R$_2$-dtc)$_3$ and Fe^{IV}(R$_1$,R$_2$-dtc)$_3^+$ are similar, providing further support for the same mechanistic assignment.[15] One cobalt(III) complex, Co(PhCH$_2$,PhCH$_2$-dtc)$_3$, has been studied by similar NMR techniques and the near-zero $\Delta S^‡$ value is in accord with a twist mechanism for inversion.[12,15]

A twist mechanism has also been proposed for the rearrangements of the mixed-ligand complexes bis(dithiocarbamato)(dithiolene)iron(II).[16,17] The observation that the structure of Fe(Et$_2$-dtc)$_2$(tfd) (tfd = perfluoromethyldithiolene = S$_2$C$_2$(CF$_3$)$_2$) is considerably distorted from an octahedral geometry of sulfur atoms toward a trigonal-prismatic geometry[18] has been used to support this mechanistic proposal.[16,17]

The rearrangement studies on the dithiocarbamate complexes mentioned above have involved NMR line-shape analysis on racemic species. Recently, optically active dithiocarbamate complexes of cobalt(III), Co(pyrdtc)$_3$ and Co(pedtc)$_3$, have been prepared (pe = α-phenylethyl) and their kinetics of racemization followed by polarimetric methods.[19,20] Activation parameters obtained for both these complexes are similar to those of Co(PhCH$_2$,PhCH$_2$-dtc)$_3$ determined by NMR techniques;[15] hence by analogies with the latter system, a trigonal-twist mechanism was proposed in each case.[19,20] Subsequently, a range of resolved Co(R$_1$,R$_2$-dtc)$_3$ complexes was prepared.[21] It was found that $\Delta S^‡$ for any one complex varies significantly upon changing the solvent.[21,22] Thus the interpretation of mechanism based on comparison of $\Delta S^‡$ alone should be approached with some caution.

The success of activation volumes ($\Delta V^‡$) in differentiating between a trigonal-twist and a bond-rupture mechanism has been demonstrated for the racemization reactions of a series of chromium(III) complexes.[23] Subsequently it was decided to apply this approach to mechanistic elucidation in racemization of Co(pyrdtc)$_3$ in a variety of nonaqueous solvents. Some results for a similar study of Co(Ph$_2$-dtc)$_3$ are also presented in this paper. These systems also offered an opportunity for the first study[24] of $\Delta V^‡$ for racemization of a metal complex in nonaqueous solvents by a polarimetric method.

Table II. Pressure-Dependent Racemization Rates of $(-)_{546}$-Co(Ph$_2$-dtc)$_3$ in Various Solvents

		$10^4 k_{rac}$, s^{-1}		
solvent	temp, °C	1 bar	610 bar	2600 bar
dimethylformamide	50.0	0.20_5	0.23_3	0.25_0
	70.0	2.9		3.5
chloroform	55.4	0.65		1.22
chlorobenzene	62.6	5.2		12.3
carbon tetrachloride	69.5	3.3		5.3
acetone	50.0	0.24		0.46

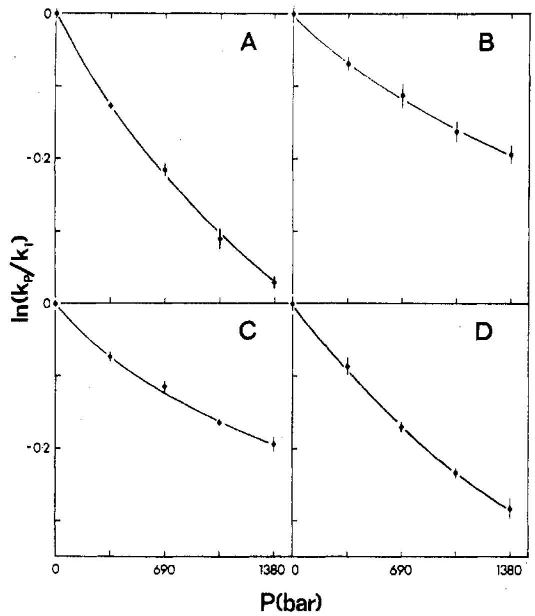

Figure 1. Pressure dependence of the isomerization of $(-)_{546}$-Co(pyrdtc)$_3$ in (A) ethanol, (B) dimethylformamide, (C) acetonitrile, and (D) toluene.

Results

In all cases, first-order racemization kinetics were observed, with ln (rotation) vs. time plots linear for at least 3 half-lives. All rate constants for racemization (k_{rac}) were evaluated by a standard least-squares method. Average rate constants and standard errors for racemization of Co(pyrdtc)$_3$ at various pressures are presented in Table I. Data were collected at five different pressures in each solvent over a pressure range of 1380 bar. Data collected for the (Ph$_2$-dtc) complex were obtained at only one elevated pressure for each solvent, except in the case of dimethylformamide as solvent; these limited data are presented in Table II.

The rate of racemization of Co(pyrdtc)$_3$ in each solvent showed a significant retardation upon the application of pressure. However, a linear relationship of ln (k_{rac}) and pressure (P) was not observed over the pressure range studied. This nonlinear behavior (Figure 1) indicates that $\Delta V^‡$ is pressure dependent. Activation volumes and compressibility

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coefficients of activation ($\Delta\beta^{\ddagger}$) were subsequently calculated by least-squares analysis of the ln (k_{rac}) vs. P data using the expression

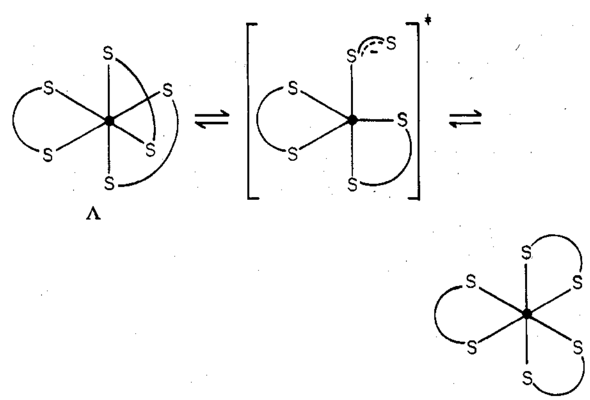
$$\ln k_p = \ln k_0 + bP + cP^2 \qquad (1)$$

where $\Delta V^{\ddagger} = -bRT$ and $\Delta\beta^{\ddagger} = 2cRT$. The calculated values of $\Delta V^{\ddagger}$, of $\Delta\beta^{\ddagger}$, and also of the compressibility of activation, $\Delta\kappa^{\ddagger}$ ($=\Delta\beta^{\ddagger}/\Delta V^{\ddagger}$), are collected in Table III; previously determined activation entropies and enthalpies[21] are also included for comparative purposes.

Limited data collected for the Co(Ph_2-dtc)$_3$ complex clearly indicated that the reaction in each solvent is accelerated upon the application of pressure. The one solvent in which data were collected at more than one elevated pressure indicates that appreciable curvature of the ln (k_{rac}) vs. P graph occurs for this complex as well. Activation volumes estimated for this system are included in Table III; they do not necessarily represent the $\Delta V^{\ddagger}$ values at zero pressure, however. Nevertheless, the marked change from positive $\Delta V^{\ddagger}$ values for Co(pyrdtc)$_3$ to negative $\Delta V^{\ddagger}$ for the Co(Ph_2-dtc)$_3$ complex has been established unequivocally, and it is this effect which plays an important role in the Discussion.

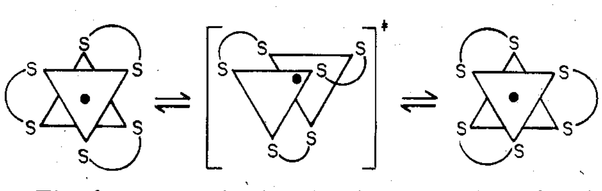
Discussion

Possible Mechanism for Racemization. The mechanism for racemization of Co(R_1,R_2-dtc)$_3$ complexes is intramolecular in nature since no exchange between free and coordinated ligands has been found.[15] Two intramolecular mechanisms have been considered as reasonable: a one-ended dissociative (eq 2) and a trigonal-twist (eq 3) mechanism. These two mechanisms are distinguished by whether or not there is bond breaking in the transition state.



(2)

Δ



(3)

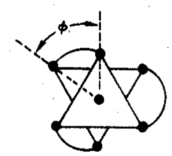
The former mechanism involves extension of a dithiocarbamate chelate arm into the solvent in the transition state. Arguments relating to $\Delta V^{\ddagger}$ prediction in this mechanism are essentially those developed previously.[23] Since the periphery of the molecule is presumably solvated, the only change in the instrinsic volume of the molecule in the transition state will arise from extension of the S donor atom into the solvent. For a dissociative mechanism where a negative charge resides at least partially on the dissociated arm, this small positive contribution (of the order of 2 cm^3 mol^{-1}) will be offset by a significantly negative contribution to $\Delta V^{\ddagger}$ due to solvent electrostriction about the new charge center generated by the dissociation. Therefore a negative $\Delta V^{\ddagger}$ is predicted for racemization of Co(R_1,R_2-dtc)$_3$ by this mechanism.

On the other hand, should the dissociative process occur with the charge residing entirely on the remaining coordinated sulfur, it could be argued that the dissociated arm is effectively neutral, leading to minimal electrostrictive effects. Therefore, a small positive $\Delta V^{\ddagger}$ would presumably be observed. In subsequent discussion, this latter prospect will be seen to be inconsistent with the experimental data; possibly the short lifetime of any ring-opened intermediate favors some retention of charge on the dangling arm.

It is most likely that for a one-ended dissociative racemization mechanism with dominant electrostrictive contribution $\Delta V^{\ddagger}$ would be markedly solvent dependent since each solvent will exhibit different solvating properties. This argument is well supported by the study of solvent effects on the rate of the addition reaction of methyl iodide to chlorocarbonylbis(triphenylphosphine)iridium(I) under pressure.[25] In that study a solvent parameter, q_p, described by the pressure derivative of the Kirkwood formula was used as a measure of the contribution to the experimental $\Delta V^{\ddagger}$ due to solvent electrostriction, and a trend where $\Delta V^{\ddagger}$ decreased in the same sense as q_p was observed. For example, the measured $\Delta V^{\ddagger}$ values in toluene and dimethylformamide were −28.2 and −15.2 cm^3 mol^{-1}, respectively. The corresponding q_p values were estimated as 14.7 × 10^{-6} and 1.7 × 10^{-6} atm^{-1}, respectively. Therefore, it has been suggested that this reaction proceeds via a polar transition state. On the other hand, the oxygen addition reaction of this complex showed small solvent effects and a reaction proceeding without bond rupture of the O–O bond has been proposed.[25]

The arguments relating to racemization by the alternative trigonal-twist mechanism have been presented previously in detail.[23] This mechanism can be considered to a first approximation to occur without bond lengthening, in the absence of any spin-state preequilibrium, and only with bond angle deformation. For example, the trigonal-prismatic intermediate can be generated simply by twisting about the C_3 axis (eq 3). Subsequently, a near-zero $\Delta V^{\ddagger}$ is predicted. While solvent molecules in the V-shaped cavities between the chelates may be squeezed out during twisting, the neutral complex is unlikely to be strongly solvated, and this contribution should be small.

Structural and Electronic Considerations. A relationship between the easily visualized twist angle (ϕ) of the ground-state structure (defined in IV) and the activation enthalpy or energy



IV

has been used previously in mechanistic arguments.[26] For a tris-chelate complex, idealized trigonal-prismatic and octahedral geometries have ϕ = 0 and 60°, respectively. Thus the twist angle reflects the extent of twist from an octahedral toward trigonal-prismatic geometry. The mechanistic argument is simply that if ϕ is much less than 60°, then a trigonal-twist mechanism is energetically favored. For example, Co(acac)$_3$ apparently racemized via a bond-rupture mechanism and has an associated twist angle to approximately 60°, while the corresponding value for Co(Et_2-dtc)$_3$ is 43.0°.[27,28] These observations suggest that a trigonal-twist mechanism for inversion of the latter complex may be favored.

Structural arguments based on the ϕ concept alone, however, can lead to erroneous mechanistic predictions, and it has been

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Table III. Activation Parameters for Racemization of $Co(pyrdtc)_3$ and $Co(Ph_2\text{-dtc})_3$ in Various Solvents[a]

solvent	$\Delta V^\ddagger$	$\Delta\beta^\ddagger$	$\Delta\kappa^\ddagger$	$\Delta H^{\ddagger b}$	$\Delta S^{\ddagger b}$
		$Co(pyrdtc)_3$			
ethanol	+9.8 (±0.5)[c]	+4.0 (±0.9)	0.41	105 (±4)	+18 (±14)
dimethylformamide	+5.2 (±0.7)[c]	+2.2 (±1.0)	0.42	112 (±4)	+35 (±11)
acetonitrile	+5.4 (±0.5)[c]	+2.5 (±0.8)	0.46	103 (±4)	+11 (±13)
toluene	+7.8 (±0.6)[c]	+3.1 (±0.9)	0.40	121 (±9)	+51 (±29)
		$Co(Ph_2\text{-dtc})_3$			
dimethylformamide	−2.0[d]			116 (±3)	+19 (±10)
	−5.7[e]	~−3			
chloroform	−6.6[d]			99 (±4)	−31 (±12)
chlorobenzene	−9.3[d]			86 (±12)	−66 (±35)
carbon tetrachloride	−5.2[d]			129 (±10)	+60 (±30)
acetone	−6.8[d]				

[a] Units of $\Delta V^\ddagger$, $\Delta\beta^\ddagger$, $\Delta\kappa^\ddagger$, $\Delta H^\ddagger$, and $\Delta S^\ddagger$ are $cm^3\ mol^{-1}$, $cm^3\ kbar^{-1}\ mol^{-1}$, $kbar^{-1}$, $kJ\ mol^{-1}$, and $J\ K^{-1}\ mol^{-1}$, respectively. [b] Data from ref 21. [c] Activation volume at room pressure. [d] Activation volume at 2600 bar. [e] Activation volume at 610 bar; $\Delta\beta^\ddagger$ estimated from combined rate data.

shown[5] that the propeller pitch angle (ψ) is a more successful indicator of distortion toward trigonal-prismatic geometry. Idealized O_h geometry has $\phi = 60°$ and $\psi = 35.3°$ and a bite angle (α) of the chelate of 90° and also requires mutual orthogonality of the three chelate rings. This latter requirement can be maintained by decreasing α, which in turn generates a lower value of ϕ but retains ψ at the idealized O_h value. Thus a small value of ϕ does not necessarily indicate a twist toward D_3 (since α may be small), whereas a small value of ψ always does.[5] For the $Co(Et_2\text{-dtc})_3$ complex $\psi = 30.7°$, which is also less than the idealized O_h value; subsequently, structural arguments favoring a trigonal-twist mechanism are retained.

Nevertheless, structural arguments alone cannot explain the significant difference between the energy barrier to inversion of $Fe(CH_3,Ph\text{-dtc})_3$ ($\Delta H^\ddagger = 36\ kJ\ mol^{-1}$) and that of $Co(Et_2\text{-dtc})_3$ ($\Delta H^\ddagger = 107\ kJ\ mol^{-1}$), in which both twist and pitch angles are quite similar.[15] The difference between these barriers has been interpreted in terms of the difference between the ligand field stabilization energy of the octahedral and trigonal-prismatic geometries (Δ(LFSE)).[15] A trend has also been observed in which the high-spin complexes have lower values of $\Delta H^\ddagger$ (and also of Δ(LFSE)) than the low-spin complexes. The low-spin iron(II) and cobalt(III) complexes have the largest $\Delta H^\ddagger$ values, while significantly smaller $\Delta H^\ddagger$ values have been found for the iron(III) and several high-spin iron(II) complexes.

Mechanism for Racemization of $Co(pyrdtc)_3$. Activation volumes for racemization of $Co(pyrdtc)_3$ in four solvents are all positive and reasonably consistent in magnitude, indicating that a common mechanism is operating for all the solvents, as previously suggested from isokinetic relationship considerations.[21] The magnitude of the corresponding activation entropy, however, varies considerably. A rotational contribution associated with solvent rearrangement may account for the variation in $\Delta S^\ddagger$ and need not be reflected in $\Delta V^\ddagger$. However, the significantly positive $\Delta V^\ddagger$ in each solvent is not consistent with predictions for either a one-ended dissociation (negative $\Delta V^\ddagger$ for a charge-carrying chelate arm) or a simple twist mechanism (near-zero $\Delta V^\ddagger$). The possibility of a low-spin $\rightleftharpoons$ high-spin preequilibrium for dithiocarbamate complexes of cobalt(III) has not been assessed, however.

The concept of a spin preequilibrium has been proposed previously for racemization and aquation of $Fe(phen)_3^{2+}$ and aquation of $Fe(bpy)_3^{2+}$.[29-31] In the case of $Fe(phen)_3^{2+}$ racemization, a low-spin $\rightleftharpoons$ high-spin preequilibrium with general metal–ligand bond lengthening has been considered to precede twisting in the expanded high-spin state.[30] A positive molar volume change of the order of 10 $cm^3\ mol^{-1}$ has been assigned to this process. Such a spin preequilbrium would make a substantial positive contribution to $\Delta S^\ddagger$ as well as $\Delta V^\ddagger$.

For certain iron(III) complexes containing dithiocarbamate ligands, pressure as well as temperature variations can cause substantial changes in their magnetic moments.[32] Such an observation is known to arise as a consequence of a spin crossover between the two possible electronic states, low spin ($^2T_2$) and high spin ($^6A_1$), which are separated by an energy of approximately k_BT. Mössbauer spectra[33] and redox properties[34] of these complexes seem to support this view. The pressure dependence of the low-spin $\rightleftharpoons$ high-spin equilibrium of a series of tris(*N*,*N*-disubstituted-dithiocarbamato)iron(III) complexes in solution has been reported.[32] The results indicate that a positive ΔV° value of 5–6 $cm^3\ mol^{-1}$ can be assigned to the low-spin to high-spin state conversion. This value, somewhat less than that proposed for the $Fe(phen)_3^{2+}$ (d^6) system, represents a general expansion of the Fe–S bonds by a distance of about 10 pm.

It is important to note that the pyrrolidinecarbodithioate ligand chosen for this study forms a high-spin iron(III) complex at room temperature.[32] There is evidence indicating that the ligand-field characteristics of the dithiocarbamate ligands in the $Fe(R_1,R_2\text{-dtc})_3$ complexes may be reflected in the low-spin $Co(R_1,R_2\text{-dtc})_3$ analogues;[32] hence a spin preequilibrium twist mechanism could be considered. The implication is that the low-spin $Co(pyrdtc)_3$ complex could be most susceptible to a spin preequilibrium in the transition state, by analogy with the iron(III) complex. Recently, the first report of a high-spin $\rightleftharpoons$ low-spin equilibrium in a six-coordinate cobalt(III) complex with an octahedral CoO_6 chromophore, determined from temperature-dependent magnetic moment studies, has appeared.[35] A quintet–singlet spin equilibrium has been proposed in that case.

A proposed mechanism for racemization of $Co(pyrdtc)_3$ is thus a twist mechanism preceded by a spin preequilibrium, as represented in eq 4. This mechanism is similar to the one previously proposed for the d^6 $Fe(phen)_3^{2+}$ racemization reaction.[30]

A contribution from the spin preequilibrium of the order of +6 $cm^3\ mol^{-1}$ can perhaps be estimated by analogy to ΔV° determined for the spin equilibrium of $Fe(R_1,R_2\text{-dtc})_3$,[32] although it is obvious that the value for the cobalt(III) system

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$$\Lambda\text{-}Co(pyrdtc)_3 \rightleftharpoons [\Lambda\text{-}Co\cdots(pyrdtc)_3]^{\ddagger} \xrightarrow{\text{twist}}$$
low spin   high spin

$$[\Delta\text{-}Co\cdots(pyrdtc)_3]^{\ddagger} \rightarrow \Delta\text{-}Co(pyrdtc)_3 \quad (4)$$
high spin   low spin

need not be the same. Nevertheless, such a positive contribution would leave a near-zero or small positive component of the experimental $\Delta V^{\ddagger}$ ascribable to the racemization process in each solvent, consistent with a twist mechanism.

The proposed mechanism is also supported by comparison of the observed pressure dependence of the activation volume ($\Delta\beta^{\ddagger} \neq 0$) in each solvent. The compressibility of activation ($\Delta\kappa^{\ddagger}$), defined as $\Delta\beta^{\ddagger}/\Delta V^{\ddagger}$, is essentially independent of solvent ($\Delta\kappa^{\ddagger} = 0.43 \pm 0.03$ kbar^{-1}). This need not be the case for a one-ended dissociation since the compressibilities of the solvents are different (e.g., at 40 °C, the isothermal compressibilities of ethanol and toluene are 127.4×10^{-6} and 103.3×10^{-6} bar^{-1}, respectively), and solvent electrostriction is an important and perhaps dominant component of the experimental $\Delta V^{\ddagger}$ for that mechanism. Since we are dealing with a formally neutral complex, arguments relating to the essential incompressibility of ionic complexes[37] need not be invoked. In particular, a spin-preequilibrium mechanism should be associated in the case of a neutral complex with an appreciable change in compressibility from precursor to activated state, which should nevertheless be essentially solvent independent. This is borne out by the experimental results.

Racemization of $Co(Ph_2\text{-}dtc)_3$. Generally, the so-called isokinetic plot of $\Delta H^{\ddagger}$ vs. $\Delta S^{\ddagger}$ of a chemical reaction in various solvents can be used to infer a uniform solvation or a common reaction mechanism.[38] For a particular solvent, resulting in activation parameters which do not fall in the line of such a plot, it is expected that the solvent–solute interaction differs or alternatively another mechanism could be considered. Linear correlations of $\Delta H^{\ddagger}/\Delta S^{\ddagger}$ in the isokinetic plots for racemization of a series of $Co(R_1,R_2\text{-}dtc)_3$ complexes in various solvents indicate that, for any one complex, the mechanism does not change on changing the solvent.[22] However, when all the complexes and solvents are taken into consideration, the correlation line of the diphenyl- and diisopropyl-substituted complexes differs significantly from the line exhibited by, among others, the pyrdtc complex. An explanation of these observations in terms of differences in solvent–solute interaction effects was proposed.[22] An alternative explanation in terms of a mechanistic difference was also possible, but there were insufficient grounds to suggest that this may be the case. Subsequently, in view of this possibility of a mechanistic difference, a brief study of the pressure-dependent racemization of the $Co(Ph_2\text{-}dtc)_3$ complex was undertaken to supplement the detailed study of the $Co(pyrdtc)_3$ system.

The activation volumes for racemization of the diphenyl complex in a range of solvents (Table III) differ markedly from those determined for the pyrrolidyl complex. Values of $\Delta V^{\ddagger}$ (at 2600 bar) of between −2 and −9.3 cm^3 mol^{-1} were observed. Apart from the appreciable solvent dependence of $\Delta V^{\ddagger}$ (which nevertheless is always negative), the one study in dimethylformamide at various pressures indicated that $\Delta V^{\ddagger}$ is appreciably pressure dependent (i.e., $\Delta\beta^{\ddagger} \neq 0$). These observations are most consistent with the predicted behavior for a one-ended dissociative mechanism with the dangling arm charged.

It is noted that the corresponding iron(III) complexes of Ph_2-dtc and pyrdtc exhibit low-spin and high-spin character, respectively. A spin preequilibrium for the low-spin $Co(Ph_2\text{-}dtc)_3$ complex may subsequently be less facile, and the alternative ring-opening mechanism may become favored. Should a spin preequilibrium occur also for the Ph_2-dtc complex, the positive ΔV° contribution (of perhaps +6 cm^3 mol^{-1}) would require an even more negative component to be assigned to the racemization process; this can be accommodated for a one-ended dissociative mechanism but makes a twist mechanism less likely. Other minor effects do not alter the above arguments. For example, although $\Delta V^{\ddagger}$ values were determined at different temperatures, the temperature dependence of $\Delta V^{\ddagger}$ has generally been observed to be small. In the case of the diphenyl complex, the values determined at 50 and 70 °C are essentially identical. Further, although the $\Delta V^{\ddagger}$ values reported for the diphenyl complex are those at 2600 bar and not at zero (or room) pressure, the effect is to make the values appear less rather than more negative, since the slope of the curve of ln (k_{rac}) vs. pressure decreases with increased pressure. This is exemplified by a $\Delta V^{\ddagger}$ of −2 cm^3 mol^{-1} in dimethylformamide at 2600 bar and a value of −5.7 cm^3 mol^{-1} at 610 bar.

Consequently, on the basis of activation volume data, a differentiation between a one-ended dissociative mechanism for racemization of $Co(Ph_2\text{-}dtc)_3$ and a spin-preequilibrium twist mechanism for $Co(pyrdtc)_3$ racemization is indicated. Such information cannot be obtained from the analysis of $\Delta H^{\ddagger}/\Delta S^{\ddagger}$ correlations or $\Delta S^{\ddagger}$ data alone.

Previously, a correlation between $\Delta S^{\ddagger}$ and $\Delta V^{\ddagger}$ for isomerization and racemization reactions was established[39] and the possibility of using such a relationship to differentiate between twist and one-ended dissociative mechanisms raised. While a close correlation was not observed nor should be expected, deviation in the case of reactions asserted to proceed by simple twist mechanisms was quite large and was suggested as a mechanistic guide. The twist mechanism proposed for racemization of $Fe(phen)_3^{2+}$ and $Co(pyrdtc)_3$ has been predicted to involve a low-spin $\rightleftharpoons$ high-spin preequilibrium, however. This process will contribute positively to both $\Delta V^{\ddagger}$ and $\Delta S^{\ddagger}$. Thus it should be noted that a lack of correlation between $\Delta V^{\ddagger}$ and $\Delta S^{\ddagger}$ supporting a twist mechanism would be marked only for a simple twist mechanism where there is no spin preequilibrium involved.

Experimental Section

Preparation of Compounds. The sodium salts of the dithiocarbamate ligands pyrrolidinecarbodithioate (pyrdtc) and diphenyldithiocarbamate (Ph_2-dtc) were prepared as previously described and analyzed successfully.[40] Optically active tris(dithiocarbamato)cobalt(III) complexes were prepared by reaction of $(+)_{546}$-$Na[Co(EDDS)]\cdot H_2O$[41] with the ligands as previously described.[42] Solvents selected for kinetic experiments were of analytical reagent grade quality and were used without further purification.

Kinetic Measurements. Racemization kinetics at various pressures were carried out in a high-pressure sampling vessel immersed in an oil bath thermostated to the required temperature (±0.1 °C).[43] Each reaction was performed with complex concentration of approximately 5×10^{-4} M. From 10 to 15 min was allowed for temperature and pressure equilibration of the reaction solution before the first sample was collected. Aliquots of solution (~2 cm^3) were collected from the steel container via a bleed valve at regular time intervals (5–10 min). The optical rotation of each sample was measured immediately on an adjacent Perkin-Elmer 241MC polarimeter in a 1-dm path length microcell at 546 nm. All reactions were followed over at least 3 half-lives. Rate constants were determined by graphical and standard linear least-squares methods. Activation volumes and compressibility coefficients were determined as described earlier.[44] Data were collected in the case of the Ph_2-dtc complex at only one high pressure generally; hence the determined $\Delta V^{\ddagger}$ is the value over that pressure range (2600 bar) and not at zero or room pressure, and an accurate

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error estimate cannot be provided. Activation volumes reported for the pyrdtc complex are those calculated at room (or effectively zero) pressure; since data were collected at five pressures up to 1380 bar in each solvent, accurate error estimates were obtained.

Acknowledgment. We thank the Australian Research Grants Committee for financial support and Jean-Michel Lucie for technical assistance during part of this project. Surapong Suvachittanont thanks the Prince of Songkla University, Thailand, for a leave of absence. Geoffrey A. Lawrance thanks the Research School of Chemistry, The Australian National University, for facilities provided during manuscript preparation.

Registry No. $(-)_{546}$-Co(pyrdtc)$_3$, 69176-69-8; $(-)_{546}$-Co(Ph$_2$-dtc)$_3$, 74645-14-0.

Contribution from the Anorganisch Chemisch Laboratorium, University of Amsterdam, J. H. van't Hoff Instituut, 1018 WV Amsterdam, The Netherlands

UV Photoelectron Spectroscopic Studies of the Metal–Olefin Bond. 2. Bonding in (β-Diketonato)rhodium(I) and -iridium(I) Carbonyl and Olefin Complexes[1]

HENK VAN DAM, ANDRIES TERPSTRA, DERK J. STUFKENS, and AD OSKAM*

Received November 9, 1979

The He I and He II photoelectron spectra of series of (β-diketonate)ML$_2$ complexes (β-diketonate = enolate anion of 2,4-pentanedione, 2,2,6,6-tetramethyl-3,5-heptanedione, 1,1,1-trifluoro-2,4-pentanedione, or 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, M = Rh or Ir, L = CO, ethylene, or propylene) are reported. Assignments are proposed, on the basis of He I/He II intensity differences, on MO calculations, on related complexes, and on empirical comparisons. The electronic structure of the complexes is discussed, and conclusions can be drawn about the trends in σ donation and π back-donation in the metal–olefin bond in the various complexes.

Introduction

As an extension of previous investigations in our laboratory of metal–olefin complexes,[2-4] we studied a series of Rh and Ir olefin complexes with UV photoelectron spectroscopy (UPS). These complexes have already been the subject of thermochemical, IR/Raman, and NMR investigations.[5]

Thorough studies of the He I spectra of a large number of β-diketonate transition-metal complexes have been reported,[6-9] but information about the monovalent rhodium and iridium β-diketonate dicarbonyl and diolefin complexes is lacking. In fact, to our knowledge, no gas-phase UPS data of square-planar Ir(I) and Rh(I) complexes have been published.

We now report the He I and He II photoelectron spectra of a series of LMX$_2$ complexes, where L is the enolate anion of a β-diketone [2,4-pentanedione, commonly known as acetylacetone (acac), 1,1,1-trifluoro-2,4-pentanedione (tfa), 1,1,1,5,5,5-hexafluoro-2,4-pentanedione (hfa), or 2,2,6,6-tetramethyl-3,5-heptanedione (tmh)], M = Rh or Ir, and X = CO, ethylene, or propylene. The structures of the complexes are shown in Figure 1. All complexes under study here are assumed to have C_{2v} symmetry, except of course the complexes with the asymmetric tfa ligand and the propylene complexes which can exist as many isomers.[5] All the complexes are square planar coordinated while the olefins are perpendicular to the molecular plane.

The aim of this investigation is to extend our knowledge of the nature of the metal–olefin bond and in particular to investigate the influence exerted on this bond by variation of the β-diketonate ligand and substitution of the olefin. The assignments are made by using He I/He II cross-section variations and by using some results of extended CNDO calculations on model cobalt complexes.

Experimental Section

Synthesis. The complexes were prepared according to the literature.[5,10,11] They were purified by recrystallization and vacuum sublimation, and their purity was checked by elementary analysis, ^{1}H NMR, and IR. Jesse[5] studied the behavior of these complexes upon heating in vacuo in a Mettler Type 1 thermoanalyzer and found no decomposition.

We failed to record PE spectra of a series of complexes in which the β-diketone is 1,3-diphenyl-1,3-propanedione. These complexes have almost no vapor pressure, and decomposition occurred upon heating. Decomposition also occurred in complexes in which the olefin was varied to methyl acrylate, vinyl chloride, styrene, and vinyl acetate.

Photoelectron Spectra. The spectra were recorded on a Perkin-Elmer PS 18 photoelectron spectrometer modified with a Helectros He I/He II source. The spectra were calibrated with respect to Ar and Xe lines as internal calibrants. Due to strongly overlapping bands in the spectra, so that no accurate deconvolution of the peaks could be achieved, the intensity arguments used as an assignment criterion are based on spectra uncorrected for analyzer dependence.

Results

In order to assign the spectra we require a molecular orbital scheme for these molecules. Extended CNDO calculations[12] have been performed on two model systems [acacCo(CO)$_2$] and [acacCo(C$_2$H$_4$)$_2$].[13] These calculations gave some indication of the character and the relative ordering of the molecular orbitals, and these results were used in the assign-

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