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Thio Derivatives of 1,3-Diketones and Their Metal Complexes. *O*-Ethyl Thioacetothioacetato Complexes of Tervalent Group VIII Metals

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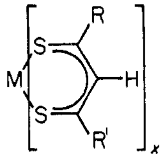
The syntheses and characterization of Co(III), Rh(III), Ir(III), Fe(III), Ru(III), and Os(III) neutral chelates of *O*-ethyl thioacetothioacetate, M(OEt-SacSac)$_3$, are described. The diamagnetic chelates of the cobalt triad form cis and trans isomers which are differentiated by their nmr spectra in benzene-d_6. Chemical shift values of the methine protons for the present and related complexes are discussed.

Introduction

1,3-Dithio chelates (**1**) of tervalent group VIII metals have received very little attention compared with that given to the chelates of bivalent metal ions. Indeed, the only 1,3-dithio ligand studied with all these metal ions is dithioacetylacetonate (**1a**).[1-3] The only other complex to fall into this category is Co(Ph-SacPh-Sac)$_3$ (**1b**) which was prepared by Uhlemann, *et al.*[4]



1a, R = R' = CH$_3$: M(SacSac)$_x$
b, R = R' = Ph: M(Ph-SacPh-Sac)$_x$
c, R = Me; R' = OEt: M(OEt-SacSac)$_x$

The deeply colored, monomeric dithioacetylacetonato complexes are prepared by the reaction of H$_2$S, acetylacetone, and the metal ion. Complete three-dimensional X-ray crystal structures have been described for Fe(SacSac)$_3$[5] and Rh(SacSac)$_3$.[6] Although neither complex possesses ideal geometry, the metal ions are approximately octahedrally coordinated. The acetylacetonato complexes of these trivalent metals are well-known and, with the apparent exception of Ir(III), representative 1,3-monothio complexes of these metals have also been synthesized recently. Complexes of these ligands have been extensively reviewed.[7-9]

The present paper describes an extension of the chemistry of 1,3-dithio chelates *via* the synthesis and characterization of tervalent group VIII metal complexes of the asymmetric ligand [OEt-SacSac]$^-$. The preparation and characterization of the free ligand and the divalent complexes of the Ni and Zn triads have been reported earlier.[10,11]

Experimental Section

Tris(1-ethoxy-1-thiolobut-1-ene-3-thione)cobalt(III), [Co(OEt-SacSac)$_3$]. A solution containing an excess of Na[OEt-SacSac][11] in water was added with stirring to a solution of K$_3$Co(CO$_3$)$_3$ in H$_2$O. The resulting black precipitate was collected and dried. Purification could only be achieved by chromatography. The compound was adsorbed on silica and elution with petroleum ether removed a yellow impurity band. The complex was then eluted with 10% benzene in petroleum ether. Following reduction of the volume of eluent to 5 ml and the addition of ethanol (5 ml) the solution was cooled and the black complex collected, washed, and dried; yield *ca.* 35%. Molecular weight, osmometric in benzene: found, 560; calcd for a monomer, 543. *Anal.* Calcd for C$_{18}$H$_{27}$CoO$_3$S$_6$: C, 39.9, H, 5.0; Co, 10.8; S, 35.4. Found: C, 40.4; H, 5.1; Co, 10.4; S, 34.1.

Tris(1-ethoxy-1-thiolobut-1-ene-3-thione)rhodium(III), [Rh(OEt-SacSac)$_3$]. Rhodium trichloride (1 g) was dissolved in EtOH (25 ml). To this solution was added a solution of sodium acetate (1.2 g) in H$_2$O (10 ml) and EtOH (10 ml) and the mixture was filtered. OEt-SacSacH (2.5 g) in EtOH (20 ml) was added to the mixture and the resulting solution was heated almost to boiling point for 10 min. On cooling, the solution was decanted from the gummy product which was washed with EtOH. The product was solidified by dissolving in benzene and precipitating with EtOH. Chromatography on silica with a 30:70 mixture of benzene and petroleum either (bp 40–60°) afforded the pure complex which was recrystallized from a mixture of EtOH and CH$_2$Cl$_2$ as bright orange-red crystals; yield *ca.* 30%. *Anal.* Calcd for C$_{18}$H$_{27}$O$_3$RhS$_6$: C, 36.9; H, 4.6; S, 32.8. Found: C, 36.5; H, 4.5; S, 32.3.

Tris(1-ethoxy-1-thiolobut-1-ene-3-thione)iridium(III), [Ir(OEt-SacSac)$_3$]. (NH$_4$)$_3$IrCl$_6$ (1 g) was dissolved in H$_2$O (10 ml) and sodium acetate (0.9 g) in H$_2$O (5 ml) was added. EtOH was added to the point of almost precipitating ionic products. OEt-SacSacH (1.5 g) in EtOH (10 ml) was added and the mixture was heated to 50° for 2 hr, cooled, and stirred for a further 3 days at 20°. The crude product was collected and purified by chromatography on silica with a 50% mixture of benzene and petroleum ether (bp 40–60°). The pure dark red complex was recrystallized from a mixture of CH$_2$Cl$_2$ and EtOH; yield *ca.* 25%. *Anal.* Calcd for C$_{18}$H$_{27}$IrO$_3$S$_6$: C, 32.0; H, 4.0; S, 28.5. Found: C, 32.2; H, 3.8; S, 28.9.

Tris(1-ethoxy-1-thiolobut-1-ene-3-thione)iron(III), [Fe(OEt-SacSac)$_3$]. A solution of Na[OEt-SacSac] in MeOH was filtered into ferrous perchlorate in MeOH. The resulting solution (50 ml) was added with stirring to H$_2$O (400 ml). The brown-black precipitate which separated was collected, washed with water, and dried at room temperature. This unstable complex could not be recrystallized owing to decomposition in solution. The composition of one preparation analyzed as indicated; yield *ca.* 40%. *Anal.* Calcd for C$_{18}$H$_{27}$FeO$_3$S$_6$: C, 40.1; H, 5.0; Fe, 10.4; S, 35.7. Found: C, 41.7; H, 5.3; Fe, 14.3; S, 32.9.

Tris(1-ethoxy-1-thiolobut-1-ene-3-thione)ruthenium(III), [Ru(OEt-SacSac)$_3$]. RuCl$_3$ (1.0 g), OEt-SacSacH (2.5 g), and sodium acetate (1.2 g) were mixed in EtOH (30 ml) and stirred for 24 hr. The crude product was collected and partially purified by dissolving in benzene and precipitating with EtOH. Elution with 10% CH$_2$Cl$_2$ in petroleum ether (bp 40–60°) removed a green solution of the complex from a silica column. The complex was recrystallized from a mixture of CH$_2$Cl$_2$ and EtOH as a dark green solid; yield *ca.* 25%. *Anal.* Calcd for C$_{18}$H$_{27}$O$_3$RuS$_6$: C, 37.0; H, 4.6; S, 32.9. Found: C, 37.3; H, 4.5; S, 33.5.

Tris(1-ethoxy-1-thiolobut-1-ene-3-thione)osmium(III), [Os(OEt-SacSac)$_3$]. Two grams of crude Na[OEt-SacSac][10] in H$_2$O (20 ml) was added with stirring to a warm solution of Na$_2$OsCl$_6$ (1.12 g) in warm water (20 ml) and the mixture was heated to boiling for 3 min. On cooling, the supernatant solution was decanted from the oily product which was solidified by precipitation from CH$_2$Cl$_2$ with EtOH. Elution with a 40:60 mixture of CH$_2$Cl$_2$ and petroleum ether removed the complex in a dark green band from a silica column. The dark green complex was recrystallized from CH$_2$Cl$_2$–EtOH; yield *ca.* 25%. *Anal.* Calcd for C$_{18}$H$_{27}$O$_3$OsS$_6$: C, 32.1; H, 4.0; S, 28.5. Found: C, 32.4; H, 4.0; S, 28.5. Instrumentation has been described previously.[10]

Results and Discussion

The present tervalent complexes are, unfortunately, much less stable than the corresponding dithioacetylacetonato complexes. Ru(OEt-SacSac)$_3$ and Os(OEt-SacSac)$_3$ exhibit thermal instability at ~60°. Crystalline Co(OEt-SacSac)$_3$ is relatively stable but decomposes slowly in solution. The

Table I. Nmr Spectra in $CDCl_3$

Compd	Chem shift (δ),[a] ppm				$J_{CH_3-CH_2}$, Hz
	CH_3———	———CH_2	CH_3	H	
$Co(OEt\text{-}SacSac)_3$ A[b]	1.37	4.56[c]	2.29	6.36	7.2
B	1.35	4.56[c]	2.32	6.34	7.2
$Rh(OEt\text{-}SacSac)_3$	1.37	4.49	2.31	6.48	7.2
$Ir(OEt\text{-}SacSac)_3$[d]	1.39	4.42	2.11	6.48	7.0

[a] With reference to TMS at 0.0 ppm. [b] A and B represent the two sets of absorptions observed in the intensity ratio of ~3:2 as evaluated for the ~1.4-ppm resonances. [c] Poorly resolved absorption. [d] All absorptions show slight asymmetry.

Table II. Nmr Absorptions in Benzene-d_6

Compd	Chemical shift (δ),[a] ppm			
	CH_3———	———CH_2	CH_3	H
cis-$Co(OEt\text{-}SacSac)_3$	0.94[b]	~4.2	2.09	6.48
trans-$Co(OEt\text{-}SacSac)_3$	0.90[b] 0.94	~4.2	2.06, 2.17, 2.19	6.40, 6.48?, 6.54
cis-$Rh(OEt\text{-}SacSac)_3$	0.92	4.16[c]	2.08	6.52
trans-$Rh(OEt\text{-}SacSac)_3$	0.89 0.92	~4.13	2.05, 2.11, 2.15	6.44, 6.52?, 6.59
cis-$Ir(OEt\text{-}SacSac)_3$	0.93	~4.1	1.91	6.56
trans-$Ir(OEt\text{-}SacSac)_3$[d]	0.91 0.93	~4.1	1.87, 1.94, 1.98	6.49, 6.56?, 6.63

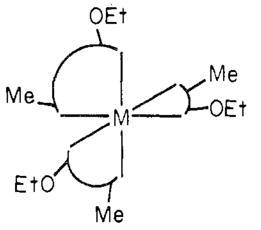
[a] With reference to TMS at 0.00 ppm; all $J_{CH_2-CH_3}$ values 7.0 Hz. [b] Tentative isomer assignment; see text. [c] Two quartets (J = 7.0 Hz) centered at *ca.* 4.16 ppm separated by 2.0 Hz. [d] See Figure 1.

rhodium(III) and iridium(III) analogs appear to be stable. At room temperature the product thought to be $Fe(OEt\text{-}SacSac)_3$ quickly decomposes to a tacky product. The complex is extremely difficult to work with and has not been adequately characterized. By comparison with $M(SacSac)_3$ complexes, some of the present complexes are less intensely colored: *e.g.*, $Rh(OEt\text{-}SacSac)_3$, orange-red; $Ir(OEt\text{-}SacSac)_3$, reddish; $Os(OEt\text{-}SacSac)_3$, green. There is no evidence to suggest these compounds are not structurally analogous to the dithioacetylacetonato complexes with the central metal being approximately octahedrally surrounded by six sulfur atoms.

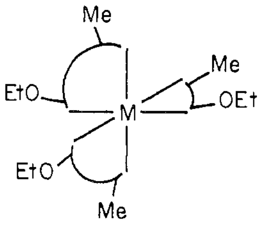
The ir spectra of the tervalent complexes are remarkably similar both to each other and to those of the bivalent complexes of $[OEt\text{-}SacSac]^-$.[10,11] The assignments proposed for the vibrations of $Ni(OEt\text{-}SacSac)_2$[11] are readily transferred to the spectra of the present complexes on the basis of the 1:1 correspondence of energies for all vibrations. Increasing the positive charge on the central metal ion from the bivalent to the tervalent complexes reduces the band energy attributed to $\nu(C\overset{\cdots}{-}C)$ in the backbone of the ring from ~1509 to ~1489 cm^{-1}, respectively. This trend has also been noted for the corresponding dithioacetylacetonato complexes.[1,2]

Like the bivalent complexes, the present diamagnetic, tervalent complexes exhibit simple, characteristic nmr spectra in $CDCl_3$. Basic assignments (Table I) are readily deduced from intensity data and the characteristic quartet–triplet spectrum of the $-CH_2-CH_3$ group. In $CDCl_3$ the rhodium(III) and iridium(III) complexes exhibit single absorptions for all resonances. On the other hand, $Co(OEt\text{-}SacSac)_3$ shows two sets of peaks for all protons except those of the methylene group although it is conceivable that the poor resolution of this group may arise from multiple, closely spaced sets of methylene resonances. As measured on the reasonably well-resolved methyl resonances at ~1.4 ppm, these peaks are present in the approximate intensity ratio 2:3 although the accuracy of this value is limited as the two peaks with the small chemical shift difference (0.02 ppm) overlap markedly.

With the asymmetric ligand $[OEt\text{-}SacSac]^-$ these presumably octahedral tris complexes may exhibit a variety of isomers, both geometric and optical. Geometric isomers have been detected for the square-planar complexes $M(OEt\text{-}SacSac)_2$ (M = Pd and Pt). *cis*- and *trans*-$Pt(OEt\text{-}SacSac)_2$ have been isolated[11] and characterized by X-ray crystallography.[12] For the octahedral complexes the geometric isomers **2** and **3** may be distinguished by nmr spectroscopy.

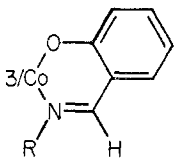


2, cis isomer



3, trans isomer

Chakravorty and Holm[13] have found that only one isomer (trans) forms with a series of tris(*N*-R-salicylaldimine)cobalt(III) complexes (**4**) and have ascribed the formation of a single isomer to the unfavorable steric crowding of the R groups in the cis isomer.



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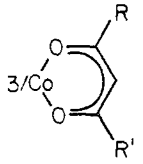

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However, this consideration is unlikely to be important with ligands of the present geometry where the substituent groups are further removed from the coordination site (**5**). Thus Fay and Piper[14-16] have detected and isolated cis and trans isomers of unsymmetrical β-diketonates. Unfortunately, the results on the isomeric properties of the present compounds in $CDCl_3$ are inconclusive.

Attempts to identify fully the isomers by the use of lanthanide shift reagents through interaction at the C–O–Et linkages were unsuccessful. With $Rh(OEt\text{-}SacSac)_3$ in $CDCl_3$ quite high concentrations of $Eu(fod)_3$ induced no shifts or splittings in the spectrum. However, we have previously reported that benzene-d_6 differentiates the resonances for square-planar cis and trans isomers of $Pd(OEt\text{-}SacSac)_2$ and $Pt(OEt\text{-}SacSac)_2$.[11] Accordingly, this solvent has been used again with the present isomers.

In benzene-d_6 the diamagnetic complexes show splittings of the nmr absorptions which are readily rationalized in terms of isomers (Table II). On the basis of peak areas the spectrum of $Ir(OEt\text{-}SacSac)_3$ (Figure 1) is most easily interpreted with

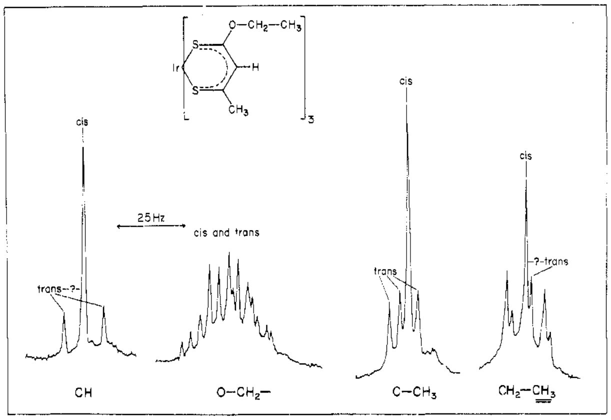


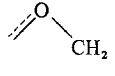
Figure 1. Nmr spectrum of a mixture of *cis*- and *trans*-Ir(OEt-SacSac)$_3$ in benzene-d_6. See Table II for chemical shift values.

the singular, most intense spectral set of absorptions being assigned to *cis*-Ir(OEt-SacSac)$_3$ due to the equivalence of the ligands in this isomer. *trans*-Ir(OEt-SacSac)$_3$ has no symmetry and all nmr absorptions may be inequivalent. This fact is illustrated best by the $-CH_3$ absorption with the appearance of three peaks of equal intensity at 1.87, 1.94, and 1.98 ppm. The methine proton only shows two peaks of equal intensity and it is assumed the third peak has the resonance of *cis*-Ir(OEt-SacSac)$_3$ superimposed on it. The CH_3 group of the OCH_2CH_3 unit shows one set of triplets attributable to *trans*-Ir(OEt-SacSac)$_3$ while others must coincide with the resonances of the cis isomer. The $-CH_2-$ resonances are quite complex, exhibiting at least 13 discernible absorptions. Attempts to decouple completely the $-CH_3$ groups giving rise to these multiplets were unsuccessful.

Assignment of isomers for the other diamagnetic tris complexes is analogous to those of Ir(OEt-SacSac)$_3$. For Co(OEt-SacSac)$_3$ intensity data do not provide unique assignments of the $-CH_2CH_3$ absorptions. Hence the absorptions of the cis isomers are tentatively assigned to the downfield absorption by analogy with the unambiguous pattern noted for the Rh(III) and Ir(III) isomers.

Careful chromatography and recrystallization of Rh(OEt-SacSac)$_3$ has afforded a sample of predominantly *cis*-Rh(OEt-SacSac)$_3$. With the exception of the $-CH_2-$ absorption, this complex exhibits single absorptions as expected for a cis complex. The appearance of the methylene resonance as two quartets of equal intensity separated by 2 Hz reflects the diastereoisomerism of this isomer.

The eight-line spectrum of the $-CH_2-$ moiety is analogous to that observed for the square-planar complex Ni(OEt-SacSac)$_2$ which exhibits a similar spectrum in $CDCl_3$ at −40°.[11] Although this spectrum was initially suggested to be indicative of cis and trans isomers of Ni(OEt-SacSac)$_2$, it now appears that this behavior may also be interpreted in terms of geometric isomerism at the



unit within a single isomer. No other lines in the spectrum of Ni(OEt-SacSac)$_2$ showed evidence of isomers as observed with analogous Pd(II) and Pt(II) complexes.

The chemical shift values of diamagnetic acetylacetonato complexes have received close attention and many rationalizations have been attempted. These shifts in symmetrically substituted complexes are relatively insensitive to the effects of the metal ion such as charge, size, π-bonding ability, and electronegativity.[17,18] Aromatic and anisotropic behavior of the six-membered ring has often been considered[19,20] as has the nature of the central atom and the orbitals it uses in σ and π bonding to the ligand.[17,21,22]

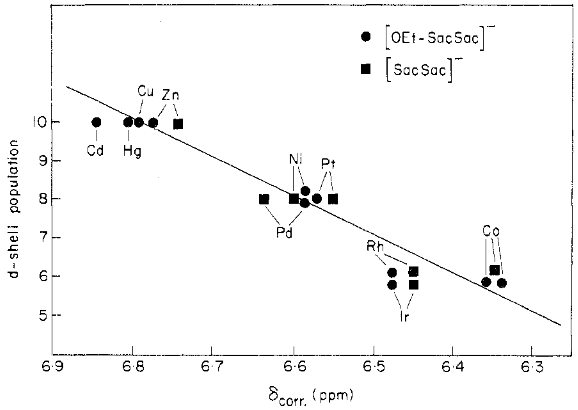


Figure 2. Groupings of methine chemical shift values of 1,3-dithio chelates[2,10,11,25] into triads. Solvent is $CDCl_3$. Values for [SacSac]$^-$ complexes have been corrected for substituent effects by subtraction of 0.5 ppm.

The present 1,3-dithio chelates provide a favorable alternative system to examine the trends in these resonances. Using nmr chemical shift values of the methine (ring) proton as an indication of the electronic environment of this proton, the present comparison between the free ligand and the metal complexes indicates that the chemical shift of this proton in the protonated ligand (6.44 ppm) falls *within* the range of values observed for the diamagnetic metal complexes (6.34–6.85 ppm).[10,11]

For Pd(SacSac)$_2$, Kawanishi, *et al.*,[23] have suggested that the downfield methine absorption (with respect to the monothio analog Pd(Sacac)$_2$) reflects a considerable quasiaromaticity in Pd(SacSac)$_2$. Schneller[24] also suggested that a similar trend in the methine resonances in the series Ni(*t*-Bu-ac-*t*-Bu-ac)$_2$, Ni(*t*-Bu-Sac-*t*-Bu-ac)$_2$, and Ni(*t*-Bu-Sac-*t*-Bu-Sac)$_2$ substantiates the presence of a ring current in β-dithiodiketone complexes. However, it would seem that the situation with these compounds is exactly analogous to the present compounds; *i.e.*, the relative downfield shift of the methine proton observed in the dithio complexes compared with those of the oxygen analogs is largely paralleled by the chemical shift change in the protonated ligands. The mere comparison of methine chemical shift values for 1,3-dioxo, monothio, and dithio complexes in search of quasiaromaticity is not justified since the deshielding effect of the substituted thio groups appears to be the dominant factor in these resonance shifts: *cf.* OEt-acacH, 4.97 ppm; OEt-acSacH, 5.75 ppm; OEt-SacSacH, 6.44 ppm.[10]

Furthermore, for 1,3-dithio ligands, the methine resonance is dependent on the metal ion or geometry. To this end, the results gathered for this resonance from earlier papers and those of the cobalt triad are plotted against d-shell population in Figure 2. The methine chemical shift values of the diamagnetic complexes of [SacSac]$^-$ are also included in the figure. The methine resonances of the [SacSac]$^-$ complexes fall approximately 0.5 ppm downfield compared with the same resonances in the corresponding [OEt-SacSac]$^-$ complexes. This difference is considered to be due to the relative substituent effects of $-OEt$ and $-CH_3$ and has been neutralized in the present figure by subtracting 0.5 ppm from the methine resonance positions of all the [SacSac]$^-$ complexes. Obviously the groupings depicted in Figure 2 are real. The chemical shift values of the $-CH_3$ groups exhibit a trend in the same direction (*i.e.*, downfield shift on increasing d-shell population) although the range of shift values is smaller. This is not unexpected as the effect of the shift, whether it arises from a psuedoaromaticity or is metal ion induced, is expected to be attenuated at the more distant and σ bonded $-CH_3$ unit. It should be noted that the presentation of the data in Figure 2 does not necessarily imply a relationship between d-electron population and chemical shift values. For example, it will be noted that the chemical shifts fall into groups depending on whether the stereochemistry of the complex is tetrahedral, square planar, or octahedral. Unfortunately, rationalizations such as those examined for [acac]$^-$ complexes and outlined at the commencement of this discussion do not singularly account for the observed groupings of the chemical shift values of the 1,3-dithio chelates.

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Registry No. *cis*-Co(OEt-SacSac)$_3$, 54340-43-1; *trans*-Co(OEt-SacSac)$_3$, 54382-40-0; *cis*-Rh(OEt-SacSac)$_3$, 54340-44-2; *trans*-Rh(OEt-SacSac)$_3$, 54382-41-1; *cis*-Ir(OEt-SacSac)$_3$, 54365-68-3; *trans*-In(OEt-SacSac)$_3$, 54422-35-4; Fe(OEt-SacSac)$_3$, 54365-69-4; Ru(OEt-SacSac)$_3$, 54365-70-7; Os(OEt-SacSac)$_3$, 54365-71-8.

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Kinetics and Mechanism of the Chloride Anation of *trans*-Diaquobis(ethylenediamine)rhodium(III) Complex Ion in Aqueous Solution

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The kinetics of the chloride anation of *trans*-Rh(en)$_2$(H$_2$O)$_2^{3+}$ in aqueous solution have been studied at 40, 50, and 65° with 0.02 $M <$ (H$^+$) $<$ 0.2 M and 0.2 $M <$ (Cl$^-$) $<$ 1.0 M at unit ionic strength. Under all conditions *trans*-Rh(en)$_2$Cl$_2^+$ is the only observed product indicating that the substitution of the first Cl$^-$ is rate determining. The rate shows a strong inverse dependence on (H$^+$) indicating that the base form of the complex, *trans*-Rh(en)$_2$(OH)(H$_2$O)$^{2+}$, is some 10^3 times more reactive than the conjugate acid form, *trans*-Rh(en)$_2$(H$_2$O)$_2^{3+}$. This behavior allows a kinetic distinction to be made between two possible explanations of the less than first-order dependence of the rate on (Cl$^-$). It is found that the data cannot be fitted to an interchange stoichiometric mechanism rate law but can be fitted to a dissociative stoichiometric mechanism rate law. Therefore, by default, it is assumed that *trans*-Rh(en)$_2$(H$_2$O)$_2^{3+}$ and/or *trans*-Rh(en)$_2$(OH)(H$_2$O)$^{2+}$ anates *via* a dissociative stoichiometric mechanism. Comparing this result with those obtained for related complexes indicates that the substitution mechanism of an octahedral complex is far more sensitive to the nature of the inert ligands when the central atom is rhodium(III) than when the central atom is cobalt(III).

Introduction

Studies of the substitution reactions of octahedral complexes have been extensive and have yielded a fairly clear picture of the general mechanisms by which these complexes undergo reaction.[1,2] They seem to react either *via* a dissociative or an interchange stoichiometric mechanism, with either associative or dissociative activation occurring in an interchange mechanism.[3] However, our knowledge of the specific factors that determine which of these mechanisms is used by a complex is still extremely shallow. It is believed that such a knowledge can be obtained if the reaction mechanisms of a series of related complexes are known. For example, data indicate that Rh(NH$_3$)$_5$H$_2$O^{3+} anates *via* an associative interchange mechanism[4–6] while RhCl(H$_2$O)$_5^{2+}$ and/or RhCl(OH)(H$_2$O)$_4^+$ anates *via* a dissociative mechanism.[7] Some idea as to what is causing this difference in mechanism between these fairly dissimilar complexes could be obtained if the substitution mechanism employed by *trans*-Rh(en)$_2$(H$_2$O)$_2^{3+}$ were known. This latter complex can be thought of as intermediate between the others since it predominantly contains amine ligands as does Rh(NH$_3$)$_5$H$_2$O^{3+} but does have an inert oxygen-bonded ligand as do the chloroaquo complexes. This particular example prompted the present research which is an attempt to elucidate the substitution mechanism of *trans*-Rh(en)$_2$(H$_2$O)$_2^{3+}$.

Three experimental approaches are available which allow a fairly unambiguous distinction to be made between the interchange and dissociative stoichiometric mechanisms for anation reactions of octahedral complexes. These are the independent determination of apparent ion-pair constants,[5,8] a reverse kinetic saturation technique,[9] and the determination of the kinetic behavior of diaquo complexes as a function of acidity.[7] It is this last approach that is used in the present study to judge the mechanism of the Cl$^-$ anation of *trans*-Rh(en)$_2$(H$_2$O)$_2^{3+}$ and its conjugate base *trans*-Rh(en)$_2$(OH)(H$_2$O)$^{2+}$.

Experimental Section

Materials. Deionized water with a specific resistance greater than 100 megohm cm was obtained by passing tap water through a commercial charcoal and mixed-bed ion exchanger. Stock solutions of HClO$_4$, HCl, NaOH, and NaCl were prepared by dissolving reagent grade chemicals in deionized water. The concentrations of the NaCl solutions were determined from the weight of reagent added whereas those of the HClO$_4$, HCl, and NaOH solutions were de-