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Coordination Chemistry of Chromium(III) with Thiobis(ethylenenitrilo)tetraacetic Acid (TEDTA)

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The reaction between $Cr(ClO_4)_3$ and thiobis(ethylenenitrilo)tetraacetic acid (TEDTA) leads to two different geometrically isomeric complexes depending upon the pH of the reaction solution. Pure solutions of the two isomers were prepared and their spectra, pH titrations, anation by azide, reactions with heavy metal cations, and electrochemistry were investigated. For purposes of comparison, the behavior of analogous Cr(III) complexes of EDTA, oxybis(ethylenenitrilo)tetraacetic acid (EEDTA), and pentamethylenedinitrilotetraacetic acid (PMDTA) were also examined. The two isomers of CrTEDTA are concluded to have cis and trans configurations with respect to the coordinated nitrogen atoms. In the cis isomer, the ligand is pentadentate and a water molecule is coordinated to Cr(III). In the trans isomer, the ligand is hexadentate and the thioether sulfur atom occupies a coordination position. The position of the isomerization equilibrium appears to be governed by the difference in pK_a of the uncoordinated acetic acid group in the two isomers. Both isomers spontaneously adsorb on mercury electrodes and the adsorption of the trans isomer, in which the sulfur atom is coordinated to the Cr(III) center, is extraordinarily strong.

As part of a continuing investigation of the chemical factors that induce certain classes of complex ions to bind to the surface of electrodes by spontaneous adsorption,[1] we have sought ligands that can induce the adsorption of the widest possible variety of metal cations. Halide and pseudohalide anions are effective in inducing the adsorption of many d^{10} cations,[2] but large excesses of free ligand are usually necessary to stabilize these rather weak, labile complexes. As a result, analysis of the surface coordination chemistry involved is complicated by competition between these anions and their metal complexes for adsorption sites on the electrode surface. Thiocyanate anion induces the adsorption of certain transition-metal cations,[2] but the extent of adsorption is strongly dependent on the d electronic configuration of the transition metal–isothiocyanate complex and competitive ligand adsorption remains a problem with all substitutionally labile complexes. An attractive solution to this problem is to choose a ligand of high denticity and with an affinity for metallic cations sufficiently large that ligand excesses are not required to achieve essentially complete complexation. EDTA (ethylenedinitrilotetraacetic acid) is a good example of such a ligand but, with the exception of cobalt,[3] EDTA complexes of transition metal cations show little or no tendency to adsorb on the surface of mercury electrodes. In seeking a molecule with chelating capabilities similar to those of EDTA but with a greater tendency toward adsorption on mercury surfaces, we have investigated a sulfur-containing analogue of EDTA, thiobis(ethylenenitrilo)tetraacetic acid (TEDTA), $S[CH_2CH_2N(CH_2COOH)_2]_2$. We have found that a number of metal complexes of this ligand adsorb strongly on mercury surfaces. The present report concentrates on the coordination chemistry displayed by chromium(III) complexes of TEDTA. The results of a more detailed study of the electrochemistry of these complexes are described elsewhere.[4]

Experimental Section

Apparatus. pH titrations were performed by using a Beckman Model 76 Digital pH Meter. UV–visible absorption spectra were recorded on a Cary Model 17 or 118 spectrophotometer. A Beckman DU spectrophotometer was employed for precise absorbance measurements at a single wavelength. Elemental analyses were performed by Spang Microanalytical Laboratory (Eagle Harbor, MI) or the Caltech microanalytical laboratory. Cyclic voltammograms were obtained with a multipurpose electrochemical instrument of conventional design[5] or with PAR Model 173 and 175 instruments (Princeton Applied Research Corp., Princeton, NJ). All measurements were conducted at the laboratory temperature 25 ± 2 °C. The area of the hanging mercury drop electrode (Brinkmann Instruments) was 0.032 cm^2. Potentials were measured and are reported with respect to a sodium chloride saturated calomel electrode (−5 mV vs. SCE).

Materials. Reagent grade chemicals were used without further purification. Solutions were prepared with triply distilled water. Stock solutions of sodium perchlorate were prepared by neutralizing 60% $HClO_4$ with sodium carbonate. Stock solutions of chromium(III) perchlorate were prepared by reducing CrO_3 with excess H_2O_2 in perchloric acid and boiling to remove unreacted H_2O_2. These stock solutions were made 0.5–1 M in $HClO_4$ to minimize the formation of chromium(III) polymers. The extent of polymer formation was monitored spectrophotometrically by the method of Altman and King.[6] Cr(III) solutions were standardized spectrophotometrically following oxidation to Cr(VI).[7]

Thiobis(ethylenenitrilo)tetraacetic acid (TEDTA). The synthetic procedure of Smolin and co-workers[8] was followed with a few modifications that are given in detail elsewhere.[9] The purity of the product obtained was verified by elemental analysis and acidimetric titration.[9]

Chromium(III) Complexes of TEDTA. Two isomeric complexes, I and II, were prepared.

Isomer I. Stock solutions of this isomer with concentrations up to 25 mM were prepared by heating a small excess of TEDTA with a solution of $Cr(ClO_4)_3$ at pH 1.5–1.8 for ca. 90 min at 90 °C. The complexation reaction was judged to be complete when no precipitate (chromium hydroxide) formed upon raising the pH of an aliquot of the reaction mixture above 5. Violet solutions of isomer I were stored for 30 days at pH 1.5 without detectable decomposition. Slow decomposition ensued at pH values below 1.

If the initial pH of the reaction mixture was 3–3.5, little isomer I was formed. Instead, a reddish violet solution was obtained that appeared to contain a mixture of oxo-bridged species.[9] Although these species are slowly converted to isomer I by prolonged storage at pH 1.5, their formation is best avoided by careful control of the pH during the preparation of isomer I. Use of hydrated $Cr(NO_3)_3$ instead of $Cr(ClO_4)_3$ in the preparation of isomer I appeared to favor formation of the bridged complexes at all pH values and was avoided. Attempts to isolate isomer I as a solid by the addition of ethanol to concentrated solutions produced powders that did not exhibit the spectrum of pure isomer I when redissolved.

Isomer II. Stock solutions (10 mM) of this isomer were prepared by boiling solutions of isomer I at pH 4–4.5 for ca. 3 h. (If the pH reached 5 or above during the heating period, oxo-bridged species were sometimes detected.) The resulting solution contained ca. 80% isomer II and 20% isomer I. It was cooled to room temperature and the pH adjusted to 6.8–7.0 where the conversion of residual isomer I to isomer II was complete after a few weeks. Alternatively, a pure solution of deep pink isomer II could be obtained immediately by anion exchange as described in the Results and Discussion section.

Pentamethylenedinitrilotetraacetic Acid (PMDTA). This ligand was synthesized from 1,5-diaminopentane (Aldrich) by a procedure very similar to that employed for TEDTA.[8,9] The colorless product obtained had the correct proportions of carbon and nitrogen but

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appeared to contain ca. 20% of an inorganic impurity which persisted through repeated recrystallizations. However, the impurity did not appear to interfere with the preparation of Cr(III) complexes from the impure ligand.

Chromium(III) Complexes of PMDTA. Two different isomers were prepared. A 10 mM stock solution of a violet isomer was obtained by heating a small excess of the ligand with Cr(III) at pH 1.5–1.8. The second isomer was obtained by maintaining the pH of a solution of the violet isomer between 6.4 and 6.6 while the solution was boiled for ca. 22 h. During this period the color of the solution gradually became peach. The final solution at pH 6.5 appeared indefinitely stable at room temperature.

Chromium(III) Complex of Oxybis(ethylenenitrilo)tetraacetic Acid (EEDTA). A solution of $Cr(ClO_4)_3$ (10 mM) and EEDTA (Ciba-Geigy: from a 10-year old stock in this laboratory; the material is apparently no longer commercially available) were mixed in stoichiometric quantities. The mixture, at pH 1.8, was heated for ca. 90 min at 90 °C. The resulting blue-green solution turned violet on cooling to room temperature. The violet solution was stored at pH 1.6 and appeared to be quite stable.

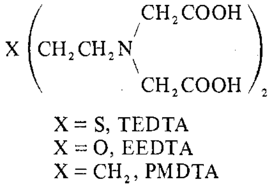
Ion-Exchange Resins. Selectacel DEAE anion-exchange resin was purified,[10] converted to the perchlorate form by stirring with 1 M $HClO_4$, and rinsed thoroughly with distilled water. AG 1-X8 and AG 50W-X8 ion-exchange resins were purified by oxidation with a strongly alkaline solution of H_2O_2, followed by washing with 1 M HCl and distilled water.

Procedures for pH Titrations. The substitutional inertness of chromium(III) complexes made it necessary to heat mixtures of each ligand and $Cr(OH_2)_6^{3+}$ until complexation equilibrium was attained before commencing each titration. For the titrations of isomer I (and the complex with EDTA) the procedure was as follows. A stoichiometric quantity of the solid ligand in the tetraacid form was added to a 10 mM solution of $Cr(ClO_4)_3$ which also contained perchloric acid (cf. Materials section). The mixture was heated for ca. 60–90 min at 90 °C while its volume was maintained by addition of distilled water. The absence of any oxo-bridged species was verified spectrally[11] and the resulting solution was titrated with standard base. The concentration of perchloric acid present in the stock solution of $Cr(ClO_4)_3$ was determined by titrating a mixture of $Cr(ClO_4)_3$ and EDTA prepared similarly. Formation of the CrEDTA complex is known to produce 4 mol of protons/mol of Cr(III) for titration to the first end point.[12]

For isomer II a different procedure was followed. The pH of a 10 mM solution of isomer I was increased to 4–4.5 by addition of a measured volume of 0.01 M NaOH. The solution was heated to 95 °C and the pH (monitored with pH paper) was maintained at 4–4.5 by continual quantitative addition of base. After ca. 3 h, 3.7–3.9 mol of base/mol of chromium had been added and the pH had stopped decreasing. The resulting solution was cooled and titrated with standard base to obtain the titration curve shown in Figure 2A. The spectrum of the solution titrated to pH 7 was quite close to that of a solution of pure isomer II which had been obtained by prolonged storage at pH 7. However, since equilibration at pH 4 at room temperature produced a solution containing ca. 80% isomer II and 20% isomer I, solutions containing only isomer II probably cannot be prepared by heating at pH 4.

Results and Discussion

Structures and abbreviations of the three related ligands under discussion are as follows:

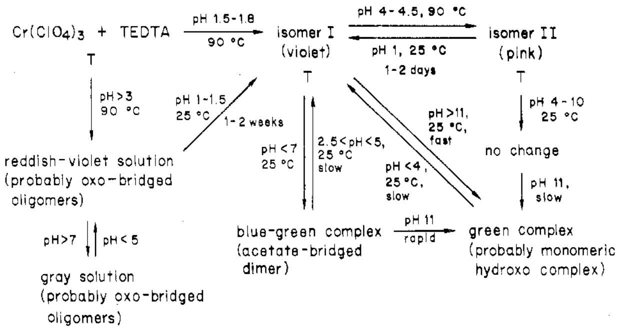


$$X\left(CH_2CH_2N\begin{matrix}CH_2COOH\\ \\ CH_2COOH\end{matrix}\right)_2$$

X = S, TEDTA
X = O, EEDTA
X = CH_2, PMDTA

The products that result when a solution of $Cr(ClO_4)_3$ and TEDTA is heated depend on the pH of the reaction mixture (Scheme I). When the pH is maintained between 1.5 and 1.8, a stable, violet complex (isomer I) is obtained. Solutions of this complex become blue-green at pH 7. If the initial pH of the reaction mixture is between 3 and 4, the color of the resulting solution is redder than that characteristic of isomer I at the same pH and the color is gray instead of blue-green at pH 7. The gray solutions are believed to contain hydroxo- or oxo-bridged complexes which convert to monomeric isomer I very slowly at pH 1–1.5.[9]

Scheme I



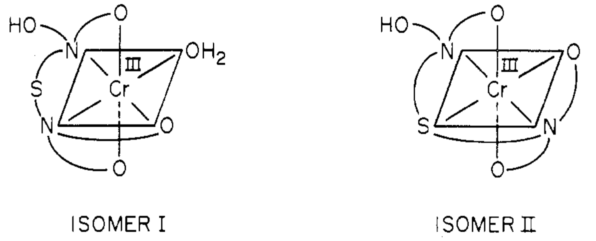


Figure 1. Proposed structures of isomers I and II. Curved lines are used to represent the atoms between the nitrogen and oxygen atoms (i.e., $-CH_2CO-$) and the nitrogen and sulfur atoms (i.e., $-CH_2CH_2-$).

Conversion of isomer I to isomer II results when a solution of the former is heated for ca. 3 h while the pH was maintained between 4 and 4.5. Isomer II spontaneously reverts to isomer I after a few days at pH 1.5.

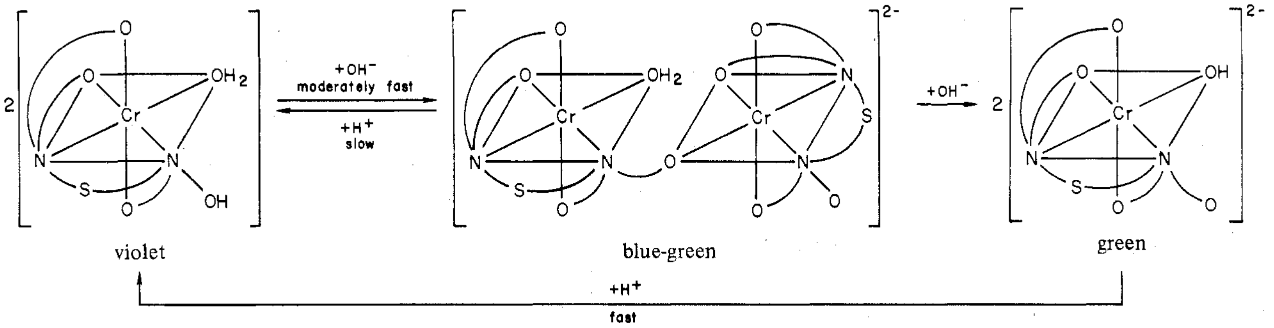
Isomers I and II and any bridged oligomers present are readily separable with Selectacel DEAE anion-exchange resin in the perchlorate form. Isomer I exhibits little affinity for this resin and elutes rapidly with 0.01 M $NaClO_4$ or 0.01 M $HClO_4$. Isomer II and oligomers are much more tightly bound but can be eluted with 1 M $NaClO_4$, isomer II moving somewhat faster.

Proposed structures for the two isomeric CrTEDTA complexes are shown in Figure 1. In isomer I, we believe that TEDTA behaves as a pentadentate ligand with one of the carboxylate groups remaining uncoordinated. A water molecule occupies the sixth coordination position on Cr(III) as in CrEDTA.[12–16] In isomer II, TEDTA is believed to act as a sexadentate ligand with three of the carboxylate groups, the thioether sulfur atom and the two nitrogen atoms (occupying trans positions) coordinated to Cr(III). The evidence and reasoning upon which these proposed structures are based will be elaborated in what follows.

pH Behavior. Figure 2 contains pH titration curves for both isomers of CrTEDTA along with those for the related Cr(III) complexes of EDTA and EEDTA. Since the reaction solutions were heated to drive the complexation of substitutionally inert Cr(III) largely to completion before the pH titrations were conducted, the titration curves do not reflect the equilibrium pH dependence of the Cr(III)–ligand reactions. Nevertheless, the stoichiometric ratio of total base consumed to moles of chromium(III) present has diagnostic utility.

The titration curve for CrEDTA (Figure 2B) has two sharp inflections at 4 and at 5 mol of base/mol of Cr(III). The first inflection has been identified[12] with the combined titration of free protons and the single, uncoordinated carboxyl group present.

Scheme II. Colors and Reactions of Isomer I as a Function of pH



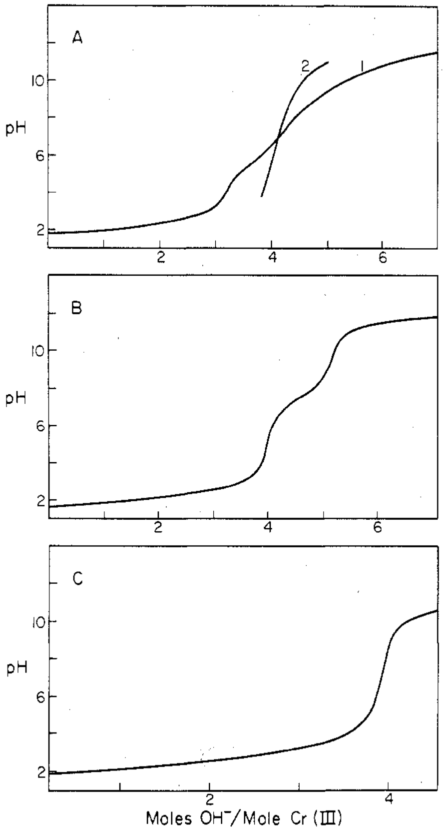


Figure 2. pH titration curves for Cr(III) complexes with several chelating ligands. All solutions were approximately 10 mM in Cr(III). See text for preparation of the solutions titrated: (A) CrTEDTA isomer I (curve 1) and isomer II (curve 2); (B) CrEDTA; (C) CrEEDTA.

$$\underset{\text{violet}}{\mathrm{CrHEDTA(OH_2)}} + \mathrm{OH^-} \overset{pK_1 = 3.1}{\rightleftharpoons} \underset{\text{violet}}{\mathrm{CrEDTA(OH_2)^-}} + \mathrm{H_2O} \quad (1)$$

The second inflection corresponds to the conversion of the coordinated water molecule to hydroxide.[12]

$$\underset{\text{violet}}{\mathrm{CrEDTA(OH_2)^-}} + \mathrm{OH^-} \overset{pK_2 = 7.5}{\rightleftharpoons} \underset{\text{blue}}{\mathrm{CrEDTA(OH)^{2-}}} + \mathrm{H_2O} \quad (2)$$

Recent experiments by Thorneley et al.[16] support this interpretation.

The titration of CrEEDTA produces a curve with a single inflection (Figure 2C) corresponding to the neutralization of 4 mol of protons/mol of Cr(III). The apparent absence of a titratable coordinated water molecule in this complex indicates that all six coordination positions about the metal are occupied by the ligand at the point where 4 mol of acid has been neutralized. However, the color of the solution changes from violet to blue-green during the addition of the fourth equivalent of base, suggesting that, unlike EDTA, EEDTA displaces an initially coordinated water molecule and becomes hexadentate as the pH is increased during the titration. This proposal is supported by the relative inertness of the resulting coordination environment as demonstrated by the slow return of the violet color when the pH of a solution of CrEEDTA is abruptly decreased from 8 to 2.

Isomer I produced titration curves with two poorly defined inflections (Figure 2A, curve 1). The positions of the inflections correspond reasonably well to the points where 3 and 4 mol of base/mol of Cr(III) had been consumed. (The precise values in Figure 2A were 3.1 and 4.1, respectively.)

The low pH values preceding the first inflection indicate that the protons released by the coordination of three carboxylate groups are being titrated up to this point. The drawn out shape of the remainder of the titration curve with no sharp second inflection suggests that the coordination chemistry accompanying further increases in pH is more complex than is the case with either CrEDTA or CrEEDTA. There is electrochemical evidence for the formation of a dimeric species at pH values above 5.[4] We believe that the uncoordinated acetate group on one complex replaces the coordinated water molecule on a second complex, forming an acetate-bridged dimer. The proposed reactions are summarized in Scheme II. There are three possible sources of acid to consume the base added after the pH inflection at 3 mol of base/mol of Cr(III): the proton released from the bridging acetate group, the proton on the nonbridging, uncoordinated acetate group, and the water molecule coordinated to the Cr(III) center that donates the acetate bridge. The neutralization of these three different acids is believed to be responsible for the drawn out shape of the titration curve.

The color changes that occur during the titration of isomer I are also consistent with the interpretation depicted in Scheme II. The solution retains its original violet color until 3 mol of base/mol of Cr(III) has been added. Further addition of base causes the color to turn blue-green, indicating the formation of the acetate-bridged dimer. If the pH of the solution is abruptly decreased, the original violet color is only slowly regained, as would be anticipated if the acid-promoted aquation of the acetate bridge were a sluggish reaction.

The formation of acetate-bridged binuclear complexes similar to the one proposed here has been demonstrated recently by Ogino et al.,[17] who reacted the pentadentate EDTA complexes of Cr(III), Co(III), and Ni(II) with $\mathrm{Co(NH_3)_5OH_2^{3+}}$ to obtain acetate-bridged binuclear products.

The relatively rapid formation of the proposed acetate-bridged dimer by isomer I depends upon the well established[18-20] ability of an uncoordinated carboxylate group in CrEDTA complexes to labilize the water molecule coordinated to the Cr(III) center.

Solutions of isomer I are green above pH 11. Upon sudden acidification, those solutions rapidly return to their original violet color. This behavior can be explained by assuming that both the violet form of isomer I and the acetate-bridged dimer are converted to a monomeric hydroxo complex at sufficiently high pH. The coordinated hydroxide ion is protonated rapidly upon acidification to restore the violet, low-pH form of isomer I. Electrochemical evidence in support of this interpretation can also be cited: Above pH 8, CrEDTA exists primarily as the hydroxo complex and no voltammetric reduction wave is observed,[21] presumably because reduction of the hydroxo complex requires a potential cathodic of that at which reduction of the supporting electrolyte commences. Isomer I behaves similarly at pH 11 or higher, but between pH 4 and 9 where a mixture of the violet and blue-green forms of isomer I is present, as many as three waves appear in the cyclic voltammograms and their sum accounts for all of the chromium present.[4] This behavior suggests that an irreducible hydroxo complex is not formed in this pH range.

Adjustment of a solution of isomer I to pH 4 required about 3 mol of base/mol of Cr(III). Upon heating of the mixture, the resulting solution slowly liberated protons as isomer I was converted to isomer II. When the release of acid had ceased, almost one additional mole of base had been added to maintain the pH at 4. Titration of this solution with base produced curve 2 in Figure 2A with the almost immediate inflection at the point corresponding to 4 mol of base/mol of Cr(III). (The pK_a values of the acid form of TEDTA are 1.8, 2.5, 8.5, and 9.4.[22]) The color of the solution of isomer II changed only slightly during the titration. However, on standing overnight at pH 11, the solution took on the green color characteristic of isomer I at the same pH.

Although the liberation of acid accompanying the slow conversion of isomer I to isomer II would be consistent with the coordination of the fourth carboxylic acid group in isomer I, we do not believe that this is the case. One reason for doubting this interpretation is the relative ease with which the coordination of the fourth carboxylate group in the CrEEDTA complex proceeds at room temperature as the pH is increased. It seems quite unlikely that the same substitution reaction for isomer I would require so much greater activation. Instead, the release of acid during the conversion of isomer I to isomer II is believed to result from a significant decrease in the pK_a of the fourth carboxylate group when the configuration of the two nitrogen atoms changes from cis to trans. Such a decrease in pK_a would cause the uncoordinated carboxylic acid in isomer II to be almost fully neutralized at pH 4, wich would account for the almost immediate inflection in curve 2 of Figure 2A.

As a pure sample of PMDTA was not available, titration curves for the CrPDMTA complexes were not recorded. However, the response of these complexes to changes in pH was similar to those of the two isomers of CrTEDTA. The violet isomer, formed at low pH, exhibited color changes as the pH was increased that were indistinguishable from those of isomer I. The peach-colored isomer, formed from the violet isomer by heating at higher pH, behaved similarly to isomer II, undergoing only minor variations in color between pH 2 and 11.

Reactions with Azide Ion. The water molecule that occupies the sixth coordination position in the pentadentate EDTA complex of Cr(III) is relatively labile and can be readily replaced by another ligand such as acetate[18,19] or azide.[19,20] Tanaka and co-workers[19] have shown that such anation by azide produces an intensification and red shift of the two prominent absorption bands of the CrEDTA complex. The two isomers of CrTEDTA were therefore reacted with azide to compare their behavior with that of the EDTA complex.

Reaction of a 10 mM solution of isomer I with 0.5 M NaN_3 at 60 °C and pH 4.3 produced an immediate color change from violet to blue violet. After 1 h, the solution was blue-green and the two absorption maxima had increased in intensity and shifted toward the red: λ_{max} (ϵ) 582 nm (136), 424 nm (91) (compare with Table I). However, if the pH of the solution was raised to 7 (producing a color change to blue-green) before exposure to azide, no anation was observed. This similarity in the reactions of isomer I and CrEDTA with azide ion confirms the presence of a labile water molecule in the coordination sphere of the violet form of isomer I. The apparent lack of reaction between azide and the blue-green form of isomer I is consistent with its being formulated as an acetate-bridged dimer. The half of the dimer containing the potentially replaceable water molecule (Scheme II) lacks the labilizing, uncoordinated acetate group while the other half of the dimer has no open coordination site available.

Heating a 10 mM solution of isomer II with 0.5 M NaN_3 at pH 7–8 for 1 h produced a solution with a color indistinguishable from that of an azide-free solution at the same pH. The failure of isomer II to react with azide under conditions where isomer I and the CrEDTA complex were readily anated is strong evidence that isomer II has no open coordination position and, therefore, that TEDTA acts as a hexadentate ligand in this isomer.

At pH 4.5 where solutions of CrEEDTA are blue-green, this complex shows no apparent reaction with azide. However, at lower pH values where the complex is violet, anation by azide proceeds. This pH-dependent response of the CrEEDTA complex is in accord with the proposal that the violet complex is pentadentate and the blue-green complex is hexadentate.

The violet, presumably pentadentate isomer of CrPMDTA reacted rapidly with azide as expected. The peach-colored isomer that is believed to be hexadentate also underwent slow anation by azide. We believe that the hydrocarbon backbone connecting the (presumably) trans nitrogen atoms in the peach complex may crowd two of the coordinated acetate groups, thus increasing their lability. Such labilization through steric interactions has been found in a variety of transition-metal complexes.[23]

The TEDTA and PMDTA ligands are very nearly the same size and both appear to form hexadentate complexes: isomer II and the peach-colored isomer of CrPMDTA. Therefore, the fact that isomer II resists anation by azide while the peach-colored isomer of CrPMDTA can be slowly anated suggests that the coordination geometry in these two complexes is not the same and supports the proposal that the sulfur atom, rather than the fourth acetate group, completes the coordination of Cr(III) in isomer II.

Visible and UV Absorption Spectra. Spectral evidence can also be marshaled in support of the cis and trans configurations of the nitrogen atoms proposed in the two isomers of CrTEDTA. Wilkins and Williams[24] have summarized the ways in which the absorption spectra of octahedral transition-metal complexes have been used to distinguish between cis and trans isomers. Splitting of the e and t_2 levels is predicted to be greater in the trans isomer. Commonly, the two bands of the cis isomer are somewhat broadened while the lower energy band of the trans isomer splits into two bands. The extinction coefficients of the trans isomer are usually smaller than those for the cis isomer. For example, *cis*-$Cr(en)_2(OH_2)_2^{3+}$ displays maxima at 366 nm (43.7) and 485 nm (67.6) while the trans isomer has three maxima at 361 nm (39.2), 442 nm (39.3), and 508 nm (22.5).[25]

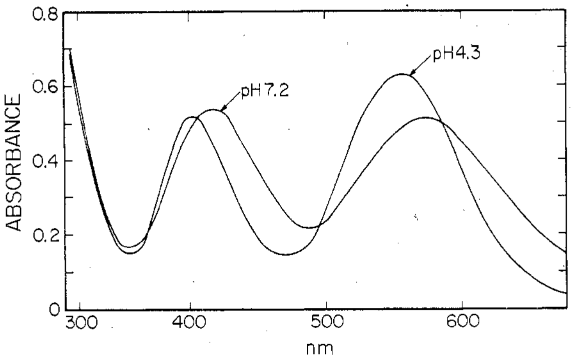


Figure 3. Visible spectra of isomer I at pH 4.3 (violet solution) and pH 7.2 (blue-green solution). Solutions were 10 mM; optical path length was 1 cm.

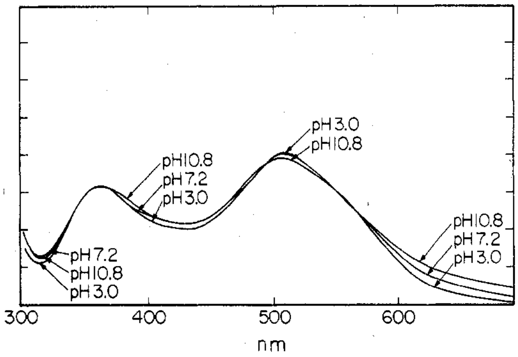


Figure 4. Visible spectra of isomer II at pH 3.0, pH 7.2, and pH 10.8. Solutions were 10 mM; optical path length was 1 cm.

Table I. Spectral Data[a]

	pH	$\lambda_{\max}$, nm (ϵ, M^{-1} cm^{-1})[b]
CrTEDTA		
isomer I	4.3	558 (65), 393 (51)
	4.5	195 (8650)
	7.2	584 (54), 414 (58)
	7.1	195 (17 800)
isomer II	3.0	513 (40), 365 (30), ~415 w, sh
	4.7	240 (1050), 195 (19 100)
	7.2	512 (41), 365 (31), ~415 w, sh
	10.8	509 (37), 365 (29), ~415 w, sh
CrEEDTA	1.8	561 (53), 396 (47)
	4.7	585 (78), 415 (78), 203 sh (~4800)
CrPMDTA		
violet isomer	1.7	557 (64), 393 (51)
peach isomer	6.4	514, 410,[c] 370[c] (ϵ's ~60% of those for violet isomer)

[a] Visible spectra were obtained with 10 mM solutions of the complexes in 1-cm quartz cells; UV spectra, with 0.2 mM solutions in 0.1-cm quartz cells. [b] Extinction coefficients were calculated per mole of Cr(III). [c] Split band–maxima of approximately equal intensity.

The two nitrogen atoms in CrEDTA have the cis configuration[15] and its absorption spectrum contains two relatively symmetrical bands at 395 and 545 nm. The violet and blue-green forms of both CrEEDTA and isomer I and the violet form of CrPMDTA all exhibit similar spectra (Table I, Figure 3). It therefore seems likely that the nitrogen atoms are cis in each of these complexes. By contrast, the spectra of both isomer II (Figure 4) and the peach-colored isomer of CrPMDTA have very broad low-energy bands and high-energy bands that are split and less intense (Table I). These spectral features are consistent with trans configuration of the nitrogen atoms in these two isomers.[26]

The UV spectrum of isomer II (Figure 5) exhibits a shoulder near 240 nm ($\epsilon \sim 10^3$) that is not present in the spectrum of isomer I, CrEDTA, or CrEEDTA. Intense ligand to metal charge-transfer bands in this vicinity have been identified in chromium(III) thiolate complexes[27,28] and the same spectral assignment has recently been given to a shoulder at 250 nm in another thioether complex in which the sulfur atom is coordinated to Cr(III).[29] A sulfur-to-chromium charge-transfer band in the spectrum of isomer II and its absence in that of isomer I are consistent with the proposed structures of these two isomers (Figure 1).

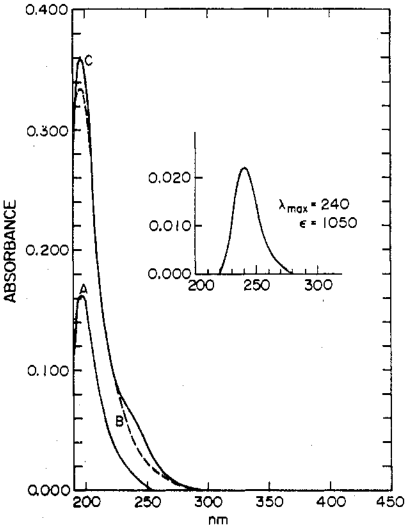


Figure 5. UV spectra of isomers I and II: (A) isomer I, pH 4.49; (B) isomer I, pH 7.13; (C) isomer II, pH 7.15. The insert is the difference between curve C and a smooth extrapolation of curve C, approximately parallel to curve B, through the region of the shoulder in the spectrum.

Ion Exchange. Attempts to determine the charges of isomers I and II from their behavior on ion-exchange resins were not successful. Isomer I behaved as a cation when loaded onto AG 50W-X8 cation-exchange resin at pH 1 but it eluted readily with dilute (0.01 M) $NaClO_4$. It seems likely that the cationic form existing at pH 1 contains two uncoordinated and protonated carboxylate groups since CrEDTA behaves similarly at low pH.[16] Isomer II showed no affinity for either AG 50W-X8 cation-exchange resin or AG 1-X8 anion-exchange resin at pH 4 in 0.1 M $NaClO_4$. The anionic CrEDTA complex behaved similarly.

Reactions with Heavy-Metal Cations. Isomer II reacted with Hg^{2+}, CH_3Hg^+, and Ag^+ to produce pink precipitates. The solids formed with Hg^{2+} and Ag^+ were insoluble in perchloric or nitric acids but dissolved readily in 1 M HCl. The solid formed with Hg^{2+} analyzed for equal molar quantities of Hg and Cr and dissolved in the presence of excess EDTA to yield solutions with spectra that matched those of the original solution of isomer II. The precipitate obtained with CH_3Hg^+ in perchloric acid solutions below pH 2 dissolved above pH 4 where the formation of CH_3HgOH is favored.[30] The Ag^+ precipitate was quite photosensitive, turning dark red unless protected from the light.[31] Unfortunately, the effect of these heavy-metal cations on the spectrum of isomer II was not observable because of the insolubility of the reaction products.

Both isomer I and free TEDTA also formed precipitates with Hg^{2+}, and isomer I precipitated with CH_3Hg^+ and Ag^+ as well. However, much higher concentrations of the heavy-metal cation were required. No reaction was observed between Hg^{2+} and CrEEDTA which contains no sulfur.

There is little doubt that the reaction between isomers I and II and the cations of silver and mercury involves attachment of the heavy-metal cation to the sulfur atom. Monodentate binding of Ag^+, Hg^{2+}, and CH_3Hg^+ to thioether sulfur atoms in methionine[32] and *S*-methylcysteine[32b,33] has been established at low pH. The fact that higher concentrations of the heavy

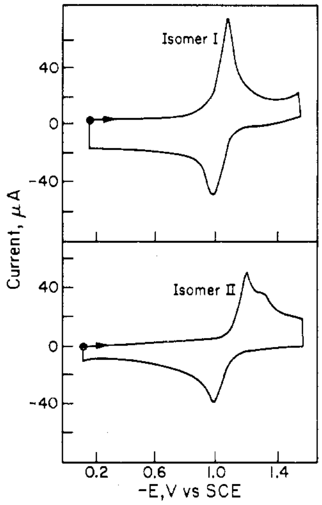


Figure 6. Cyclic voltammograms of 1 mM solutions of isomers I and II at pH 4. Scan rate was 10 V/s.

metals were required for reaction with isomer I than for isomer II adds to the evidence that the sulfur atom exhibits different coordination chemistry in the two isomers. A possible source of this difference may be an enhancement in the nucleophilicity of the sulfur atom resulting from its coordination to Cr(III) where the dπ accepting capability of the thioether moiety[34] can be expressed.

Electrochemistry. The cyclic voltammograms for isomers I and II register significant differences in their reduction potentials (Figure 6). Isomer II exhibited two reduction waves, the first of which became progressively more dominant at higher scan rates and appeared to result primarily from reduction of adsorbed molecules. The second wave may arise from the reduction of unadsorbed isomer II. At low pH, isomer I produced only a single reduction peak corresponding to the reduction of both adsorbed and diffusing complex as evidenced by the increasing deviation of the peak current from the diffusion-controlled value at higher scan rates. (The cyclic voltammogram of the CrEEDTA complex under the same conditions contained a single, reversible wave with no evidence of significant adsorption.) The adsorption of both isomers was measured by chronocoulometry. About 2×10^{-10} mol cm^{-2} of isomer II was adsorbed from a 27 μM solution at a potential of -0.4 V while only 0.3×10^{-10} mol cm^{-2} of isomer I was adsorbed under the same conditions.

The more intense adsorption of isomer II signals a stronger and more specific interaction with the mercury surface. The binding site is almost certainly the sulfur atom because the structurally very similar CrEEDTA complex is not adsorbed. The unusually strong adsorption is believed to be a result of the back-donation involved in the formation of the chromium-sulfur bond[34a] in isomer II, which may "soften" the sulfur atom, thus enhancing its adsorbability.[35]

The identical voltammograms obtained for the oxidation of the Cr(II) complex produced from both isomers indicate that the initial reduction products rapidly relax to the most stable Cr(II) complex. The product of the oxidation of the Cr(II)–TEDTA complex is apparently isomer I because the reduction wave for this isomer appears in the second cathodic scan regardless of which isomer is present in the bulk of the solution.

The voltammograms for both isomer II and CrEEDTA were unaffected by pH changes in the range from 4 to 9. By contrast, voltammograms of isomer I between pH 5 and 7 contained two new waves which grew at the expense of the original wave as the pH and, consequently, the proportion of blue-green complex (Scheme I) increased. Variation in the total concentration of isomer I produced changes in the relative magnitudes of the three waves that were approximately as expected for a dimerization reaction.[4] The reduction of the two Cr(III) centers in the dimer at slightly different potentials is in good accord with the nonequivalence of their coordination environments as proposed in Scheme II.

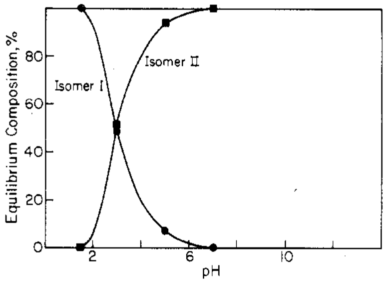


Figure 7. Influence of pH on the equilibrium composition of solutions of CrTEDTA. Solutions were equilibrated at constant pH until no further spectral changes occurred (ca. 4 months): (●) data for isomer I; (■) data for isomer II.

Equilibrium between Isomers I and II. To determine the equilibrium composition of solutions of the two isomers of CrTEDTA as a function of pH, we prepared separate 10 mM solutions of each isomer and allowed them to equilibrate at room temperature while maintaining the pH at selected values between 1.5 and 7 by periodic addition of acid or base. Equilibrium was presumed to prevail when the pH and spectrum of a solution were unchanged for at least 1 week. The total equilibration time was about 4 months. The compositions of the solutions were determined spectrophotometrically by monitoring the absorbance at 512 and 558 nm (Table I). The calculated compositions of the equilibrated solutions were the same, within the experimental error of ca. ±10%, regardless of the isomer used to prepare the original solution.

Figure 7 shows the results of these experiments. We have already expressed the view that the added base is consumed by the uncoordinated acetic acid group whose pK_a is lower in isomer II than in isomer I. Although additional factors may be involved, the enhancement of the acidity of the uncoordinated acetate group is believed to be the primary source of free energy controlling the isomerization. The trans disposition of the nitrogen atoms forces the thioether sulfur atom into close proximity with the Cr(III) center in isomer II. The formation of the sulfur–chromium bond is doubtless favored by the replacement of the large, eight-membered chelate ring in the cis isomer with two five-membered rings in the trans isomer.

Kennard and Deutsch[29] recently described thioether complexes of Cr(III) that exhibited relatively rapid aquation ($t_{1/2} \sim 14$ min) of the chromium(III)–thioether bond in the pentaaquo complex and noticeably slower aquation ($t_{1/2} \sim$ 2.3 h) when the thioether was part of a bidentate chelating ligand. The evident thermodynamic stability of the thioether–chromium(III) bond in isomer II (pH >5; Figure 7) presumably results from the maximum chelation achieved by the TEDTA ligand in this isomer.

One of our original purposes in studying the coordination chemistry of TEDTA was the hope that this ligand might serve as a general means for anchoring metal cations to the surface of mercury electrodes. This objective has certainly been achieved with the Cr(III) complex of isomer II, which is adsorbed much more strongly on mercury than most other transition-metal complexes that have been examined.[1] The ability of TEDTA to induce the adsorption of other metal cations has so far been tested only partially: The complex formed with Pb(II) is strongly adsorbed but those with Cd(II) and Tl(I) are more weakly adsorbed and the complexes with Zn(II) and La(III) are not detectably adsorbed. The behavior of additional transition-metal complexes of TEDTA is currently under study.

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Registry No. I (violet form), 70983-09-4; I (blue-green form), 71031-50-0; II, 70983-10-7; CrPMDTA (violet form), 70983-11-8; CrPMDTA (peach form), 70983-12-9; CrEEDTA (violet form), 70983-13-0; CrEEDTA (blue-green form), 70983-14-1; Hg^{2+}, 14302-87-5; CH_3Hg^+, 22967-92-6; Ag^+, 14701-21-4; azide, 14343-69-2.

References and Notes

(1) Anson, F. C. *Acc. Chem. Res.* **1975**, *8*, 400.
(2) Reference 1 and references cited therein.
(3) Anson, F. C. *Anal. Chem.* **1964**, *36*, 932.
(4) Peerce, P. J.; Anson, F. C. *J. Electroanal. Chem.*, in press.
(5) Sawyer, D. T.; Roberts, J. L. "Experimental Electrochemistry for Chemists"; Wiley: New York, 1974; Chapter 5.
(6) Altman, C.; King, E. L. *J. Am. Chem. Soc.* **1961**, *83*, 2825.
(7) Haupt, G. W. *J. Res. Natl. Bur. Stand.* **1952**, *48*, 414.
(8) Smolin, D. D.; Kazbitnaya, L. M.; Viktovov, Yu. M. *J. Gen. Chem. USSR* **1964**, *34*, 3762.
(9) Peerce, P. J. Ph.D. Thesis, California Institute of Technology, 1978.
(10) Kaufman, S.; Keyes, L. S. *Anal. Chem.* **1964**, *36*, 1777.
(11) The spectrum of the oxo-bridged species in acid differs from that of isomer I by the presence of a shoulder at 309 nm and a much more intense absorption in the UV.
(12) Hamm, R. E. *J. Am. Chem. Soc.* **1953**, *75*, 5670.
(13) Schwarzenbach, G.; Biedermann, H. *Helv. Chim. Acta* **1948**, *31*, 459.
(14) Dwyer, F. P.; Garvan, F. L. *J. Am. Chem. Soc.* **1960**, *82*, 4823.
(15) Hoard, J. L.; Kennard, C. H. L.; Smith, G. S. *Inorg. Chem.* **1963**, *2*, 1316.
(16) Thorneley, R. N. F.; Sykes, A. G.; Gans, P. *J. Chem. Soc. A* **1971**, 1494.
(17) Ogino, H.; Tsukahara, K.; Tanaka, N. *Inorg. Chem.* **1977**, *16*, 1215.
(18) Ogino, H.; Watanabe, T.; Tanaka, N. *Chem. Lett.* **1974**, 91.
(19) Ogino, H.; Watanabe, T.; Tanaka, N. *Inorg. Chem.* **1975**, *14*, 2093.
(20) Sulfab, Y.; Taylor, R. S.; Sykes, A. G. *Inorg. Chem.* **1976**, *15*, 2388.
(21) Finn, M. G.; Anson, F. C., unpublished experiments.
(22) Schwarzenbach, G.; Senn, H.; Anderegg, G. *Helv. Chim. Acta* **1957**, *40*, 1886.
(23) Pavkovic, S. F.; Meek, D. W. *Inorg. Chem.* **1965**, *4*, 20. Legg, J. I.; Cooke, D. W. *Ibid.* **1965**, *4*, 1576; **1966**, *5*, 594. Hamilton, H. G., Jr.; Alexander, M. D. *J. Am. Chem. Soc.* **1967**, *89*, 5065.
(24) Wilkins, R G.; Williams, M. J. P. "Modern Coordination Chemistry. Principles and Methods", Lewis, J., Wilkins, R. G., Eds.; Interscience: New York, 1960; pp 187–91.
(25) Garner, C. S.; House, D. A. *Transition Met. Chem.* **1970**, *6*, 59.
(26) None of the complexes assigned cis configurations for the nitrogen atoms exhibited appreciable affinity for Selectacel anion-exchange resin, whereas the two isomers assigned trans configurations, isomer II and the peach isomer of CrPMDTA, were bound strongly by this resin.
(27) Weschler, C. J.; Deutsch, E. *Inorg. Chem.* **1973**, *12*, 2682.
(28) Lane, R. H.; Sedor, F. A.; Gilroy, M. J.; Bennett, L. E. *Inorg. Chem.* **1977**, *16*, 102.
(29) Kennard, G. J.; Deutsch, E. *Inorg. Chem.* **1978**, *17*, 2225.
(30) Schwarzenbach, G.; Schellenberg, M. *Helv. Chim. Acta* **1965**, *48*, 28.
(31) Complexes containing Ag–S bonds are often photosensitive: McAuliffe, C. A.; Quagliano, J. V.; Vallarino, L. M. *Inorg. Chem.* **1966**, *5*, 2000.
(32) (a) McAuliffe, C. A.; Quagliano, J. V.; Vallarino, L. M. *Inorg. Chem.* **1966**, *5*, 1996. (b) Natusch, D. F. S.; Porter, L. J. *J. Chem. Soc., Chem. Commun.* **1970**, 596. (c) Fairhurst, M. T.; Rabenstein, D. L. *Inorg. Chem.* **1975**, *14*, 1413.
(33) McAuliffe, C. A. *Inorg. Chem.* **1973**, *12*, 1699. Livingstone, S. E.; Nolan, J. D. *Ibid.* **1968**, *7*, 1447.
(34) (a) Williams, R. J. P. *Annu. Rep. Prog. Chem.* **1959**, *56*, 87. (b) Cotton, F. A.; Zingales, F. A. *Chem. Ind.* (*London*) **1960**, 1219. (c) Livingstone, S. E. *Q. Rev., Chem. Soc.* **1965**, *19*, 386.
(35) Barclay, D. J. *J. Electroanal. Chem.* **1968**, *19*, 318. Barclay, D. J.; Caja, J. *Croat. Chem. Acta* **1971**, *43*, 221.

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Structural Studies of Some Multiply Bonded Diruthenium Tetracarboxylate Compounds

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Five compounds, three of types not previously described, containing the $Ru_2(O_2CR)_4^+$ unit have been structurally characterized by X-ray crystallography. These compounds and their crystallographic parameters are as follows: (**1**) $Ru_2(O_2CCH_3)_4Cl \cdot 2H_2O$, space group $C2/m$ with $a = 13.963\ (1)$ Å, $b = 7.399\ (1)$ Å, $c = 11.143\ (1)$ Å, $\beta = 138.88\ (2)°$, and $Z = 2$; (**2**) $[Ru_2(O_2CCH_3)_4(H_2O)_2]BF_4$, space group Cc with $a = 14.246\ (2)$ Å, $b = 6.904\ (1)$ Å, $c = 17.687\ (2)$ Å, $\beta = 97.19\ (1)°$, and $Z = 4$; (**3**) $Cs[Ru_2(O_2CCH_3)_4Cl_2]$, space group $P4_2/n$ with $a = 12.061\ (3)$ Å, $c = 11.335\ (2)$ Å, and $Z = 4$; (**4**) $Ru(O_2CCH_2CH_3)_4Cl$, space group $I\bar{4}$ with $a = 11.049\ (2)$ Å, $c = 7.423\ (1)$ Å, and $Z = 2$; (**5**) $K[Ru_2(O_2CH)_4Cl_2]$, space group $P4_2/n$ with $a = 11.483\ (2)$ Å, $c = 9.571\ (1)$ Å, and $Z = 4$. In **1** the $Ru_2(O_2CCH_3)_4^+$ ion has $2/m$ (C_{2h}) symmetry, with Ru–Ru = 2.267 (1) Å, and the Cl^- ions form perfectly linear symmetrical bridges between them. In **2** all atoms are on general positions. The $[Ru_2(O_2CCH_3)_4(OH_2)_2]^+$ ion has virtual D_{4h} symmetry with Ru–Ru = 2.248 (1) Å. In **3** the $[Ru_2(O_2CCH_3)_4Cl_2]^-$ ion has a crystallographic inversion center, and Ru–Ru = 2.286 (2) Å. In **4** the $[Ru_2(O_2CCH_2CH_3)_4]^+$ ion has $\bar{4}$ symmetry with Ru–Ru = 2.297 (7) Å. The Cl bridges are perfectly linear and symmetrical. In **5** the $[Ru_2(O_2CH)_4Cl_2]^-$ ion resides on a crystallographic inversion center with Ru–Ru = 2.290 (1) Å.

Introduction

The first report[1] of purportedly dinuclear complexes of ruthenium appeared in 1930. In 1966, Stephenson and Wilkinson[2a] published a study in which they found that this work could not be reproduced, but by different reactions they obtained other dinuclear diruthenium complexes, such as $Ru_2(O_2CR)_4Cl$. They suggested, however, that "the metal–metal distance in these systems is large enough to prevent direct orbital overlap." Independently, Japanese workers[2b,c] reported the preparation of the formato and acetato compounds $Ru_2(O_2CR)_4X$ (R = CH_3, H; X = Cl, Br, I). They described[2b] these substances as "the first spin-free complexes of ruthenium" and did not mention the possibility of Ru–Ru bonding. A few years[3] later it was suggested, and proven by an X-ray study of the compound with R = $CH_3CH_2CH_2$, that, on the contrary, a great deal of direct Ru–Ru overlap exists, since the Ru–Ru distance is 2.281 (4) Å. However, the reason for the ready formation of these particular systems with their odd-electron $Ru_2(O_2CR)_4^+$ unit was not at all obvious.

In an effort to account for the reported[2a] presence of three unpaired electrons, it was proposed[3] that in addition to eight electrons forming a $\sigma^2\pi^4\delta^2$ quadruple bond configuration, three more electrons with parallel spins occupy three orbitals of very similar but not equal energy, which were suggested to be the