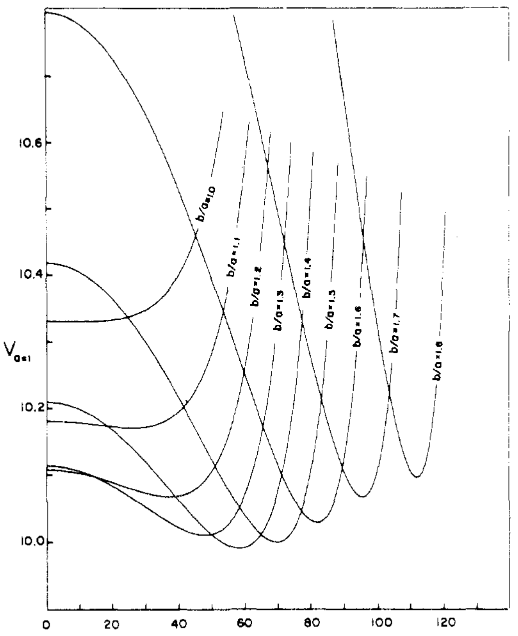

Figure 7. Plot of the relative repulsion energy against the twist angle (in degrees) at various constant values of *b*/*a*.

behavior of the 1,2-dithiolene-containing complexes.

Trigonal Twist—Inter- and Intraligand Interactions. A repulsion potential has been expressed in terms of the parameters in Table I. We assume that the six ligand atoms in the chromophore form a cage constrained to D_3 or higher symmetry and that the total repulsion energy (for one type of ligand atoms) is proportional to the sum of all the possible inverse ligand–ligand separations. The potential which results is

$$V = 3\left(\frac{1}{b} + \frac{2}{s} + \frac{1}{t} + \frac{1}{d}\right)$$

Using some of the relations derived by Stiefel and Brown[11] and those expressed in eq 1–3, the expression for the potential can be written in terms of the parameters *a*, *b*/*a*, and ϕ

$$V = \frac{3\sqrt{B + \frac{1}{4}}}{a}\left\{1 + \frac{1}{\sqrt{3}}\cos\frac{\phi}{2}\left[\frac{2}{\sqrt{B}} + \frac{1}{\sqrt{B\left(\cos\phi - \frac{1}{\sqrt{3}}\sin\phi\right) + \frac{1}{3}\cos^2\frac{\phi}{2}}} + \frac{1}{\sqrt{B\left(\cos\phi + \frac{1}{\sqrt{3}}\sin\phi\right) + \frac{1}{3}\cos^2\frac{\phi}{2}}}\right]\right\} \tag{4}$$

where

$$B \equiv \frac{1}{(b/a)^2} - \frac{1}{4}$$

In units of a^{-1} the above potential is plotted in Figure 7 as a function of the trigonal twist angle and for constant values of *b*/*a*. The minima for $\phi > 0°$ and $b/a > 1.1$ do follow the curve for group A compounds, as shown by the dashed curve in Figure 4. This had been shown by Kepert[12] using a similar repulsion model and also indirectly by Holm and coworkers[13] using an angular overlap model (to approximate the energies of the d orbitals).

An examination of the region of a minimum shows that for $\phi > \phi_{\min}$ the repulsion is dominated by interactions through the separation *t*. This is consistent with previous observations.[3] However, for $\phi < \phi_{\min}$ the repulsions are characterized by the separations *s*.

The above observations help explain the anomaly of the IDAB complexes. Figure 5 reveals that, for constant values of *b*/*a*, *s*/*a increases* with the twist angle. Clearly the group B complexes are not properly described by the repulsion model. However, since *s*/*a* decreases as ϕ approaches zero, one need only include an attractive potential V' as a function of *s*/*a* in order to shift the minima in the curves in Figure 7 toward $\phi = 0°$. One can demonstrate this by plotting $V + V'$ where $V' = \log(s/a)$ against ϕ, for example.

Suggesting that S–S attractive forces are responsible for the stereochemistry of 1,2-dithiolate-containing complexes does not explain why it occurs between the ligands in these particular complexes. Since the subject has been discussed elsewhere,[10] it is beyond the scope of this paper. To develop the concept further would necessarily involve the generation of reasonable theoretical expressions for $V + V'$, a project not to be attempted here. It seems to us, however, that such an approach could unify the descriptions of the geometries of the two apparently different groups of compounds, groups A and B, in Figure 4.

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Reduction of Cobalt(III) Complex Ions by Copper Metal

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Heterogeneous oxidation–reduction reactions between transition metal ions and metal surfaces have received little attention, only a few detailed studies having been reported.[1] We describe herein the kinetics of reduction of aquopentaamminecobalt(III) ion ($\mathrm{RoOH_2}^{3+}$) by zerovalent copper and briefly survey the reactivity toward copper of other ions (RoL)

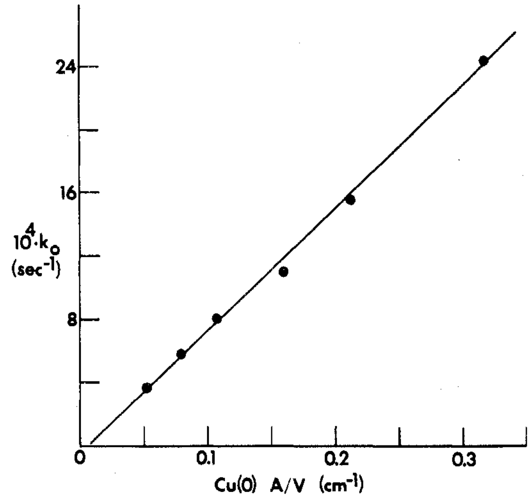

Figure 1. Copper dependence of the rate constant for apparent first-order $RoOH_2^{3+}$ ion decomposition. Reaction conditions: $(RoOH_2) = 5$ m*M*, $(HClO_4) = 0.1$ *M*, $(CH_2{=}CHCH_2OH) = 0.1$ *M*, 23°. The copper surface area (*A*) was calculated assuming spherical granules with 0.20-mm radii. The line drawn through the data points, determined by linear regression analysis, has a slope (k) of 7.8×10^{-3} cm sec^{-1} and intercept of -5.5×10^{-5} sec^{-1}.

in the pentaamminecobalt(III) series. We first observed these reactions during the course of study of ligand-bridged cobalt(III)–copper(I) ions; attempts at generating the binuclear ions in situ by forming Cu(I) from equilibration of cupric ion with copper metal[3] were met with extensive reduction of the cobalt(III) complex ions. This reaction was unanticipated since the driving forces for electron transfer from Cu(0) and Cu(I) are comparable, e.g.: Ro–fum + $Cu^0 \rightleftarrows (NH_3)_5Co^{II}$–fum–$Cu^I$, $\Delta G° \simeq -0.5$ kcal/mol;[4] Ro–fum–$Cu^I \rightleftarrows (NH_3)_5Co^{II}$–fum + Cu^{II}, $\Delta G° \simeq 0.8$ kcal/mol[2] (fum = fumarato); electron transfer rates in the RoL–Cu^I binuclear ions are immeasurably slow.[2]

In the present studies 0.1 *M* perchloric acid solutions of RoL ions, generally containing as well 0.1 *M* allyl alcohol, were placed in a flat-bottomed vessel and purged of oxygen with a stream of O_2-free nitrogen. Reaction was initiated by adding copper granules (0.35-mm mesh, previously washed successively with nitric and hydrochloric acids). The particles were approximately spherical, with average radii of 0.20 mm measured on a Zeiss research metallograph. Solutions were vigorously stirred with a magnetic bar to agitate the copper continuously. Disappearance of cobalt(III) was monitored spectophotometrically by measuring absorbancy decreases in the L_1 ligand field bands (λ_{max} 480–580 nm) of periodically withdrawn aliquots; Cu(I) formation, which is quantitative under the reaction conditions,[5] was similarly determined from the increase in absorbance at 270 nm arising from charge-transfer excitation of the copper(I)–allyl alcohol π complex (ϵ_{270} 1.5×10^3 cm^{-1} M^{-1}).[2] Allyl alcohol also provided an essential function in maintaining well-behaved kinetics; reaction in the absence of ligands that form Cu(I) π complexes exhibited variously induction periods, incomplete reaction, and generally irreproducible rates.

Reduction of $RoOH_2^{3+}$ ion obeyed simple first-order kinetics—measured rate constants (k_0) were independent of ($RoOH_2^{3+}$), varied over the range 1.0–40 m*M*, but were linearly dependent upon the total surface area of copper particles (Figure 1). Rate constants for copper(I)–allyl alcohol ion formation and $RoOH_2^{3+}$ ion disappearance were identical in individual runs to within ±5%. Rates were independent within experimental error of the presence of oxygen or the product ion, Co(II), added to the initial reaction solution at concentrations of 1–10 m*M*, and of allyl alcohol from 2 to 500 m*M*. If $(CH_2{=}CHCH_2OH) \leq 1$ m*M*, rate behavior was erratic and irreproducible; under these conditions appreciable concentrations of Cu(II) ion appear in the reaction product solutions.[5]

Table I. Rate Constants for RoL Ion Reductions by Copper Metal

Ion	$10^3 k_{Cu(O)}$,[a,b] cm sec^{-1}	$k_{Cu(I)}$,[b] M^{-1} sec^{-1}
RoF^{2+}	1.3 ± 0.1 (0.2)	1.1^c (10^3)
$RoCl^{2+}$	25 ± 3 (3.8)	$4.8 \times 10^{4\ c}$ (5×10^7)
$RoBr^{2+}$	23 ± 6 (3.5)	$4.4 \times 10^{5\ c}$ (4×10^8)
RoI^{2+}	21 ± 4 (3.2)	
RoN_3^{2+}	12 ± 3 (1.8)	$1.5 \times 10^{3\ c}$ (1.5×10^6)
$RoOH_2^{3+}$	6.6 ± 0.8 (1.0)	$1.0 \times 10^{-3\ c}$ (1.0)
$RoNH_3^{3+}$	2.3 ± 0.3 (0.3)	
$RoO_2CCH_3^{2+}$	1.8 ± 0.3 (0.3)	$\leqslant 4 \times 10^{-3\ d}$ ($\leqslant$4)
$RoO_2CCH{=}CH_2^{2+}$	0.006 ± 0.002 (0.001)	$\leqslant 3 \times 10^{-9\ e,g}$ ($\leqslant 3 \times 10^{-6}$)
$RoO_2CCH{=}CH$-CO_2H^{2+} (trans)	0.8 ± 0.09 (0.1)	$\leqslant 3 \times 10^{-9\ e,g}$ ($\leqslant 3 \times 10^{-6}$)
$RoO_2CCH_2CH{=}CH_2^{2+}$	0.04 ± 0.005 (0.006)	$\leqslant 3 \times 10^{-9\ e,g}$ ($\leqslant 3 \times 10^{-6}$)
$RoO_2C(CH_2)_2$-$CH{=}CH_2^{2+}$	0.4 ± 0.3 (0.06)	$\leqslant 3 \times 10^{-9\ e,g}$ ($\leqslant 3 \times 10^{-6}$)
$RoNH_2CH_2CH{=}CH_2^{3+}$	0.03 ± 0.003 (0.005)	$\leqslant 10^{-8\ f,g}$ ($\leqslant 10^{-5}$)
$RoNH_2(CH_2)_2$-$CH{=}CH_2^{3+}$	0.04 ± 0.009 (0.006)	$\leqslant 10^{-8\ f,g}$ ($\leqslant 10^{-5}$)

[a] This work: $(HClO_4) = 0.1$ *M*; $(CH_2{=}CHCH_2OH) = 0.1$ *M*; (RoL) = 2.0 m*M*, except ($RoOH_2^{3+}$) which varied from 1.0 to 40 m*M*; temperature 23°. Rates were first order in (RoL); rate constants were calculated from $k_0 = k(A/V)$ with the copper surface area (*A*) calculated assuming spherical particles; radii 0.20 mm. For the first eight entries, $A/V = 0.107$ cm^{-1}; for the remainder, $A/V = 2.14$ cm^{-1}. Error limits are average deviations for duplicate runs, except $RoOH_2^{3+}$ (nine runs). [b] Relative rate constants normalized to values for the $RoOH_2^{3+}$ ion are given in parentheses. [c] O. J. Parker and J. H. Espenson, *J. Am. Chem. Soc.*, **91**, 1968 (1969); $(HClO_4) = 0.2$ *M*; temperature 25°. [d] E. R. Dockal, E. T. Everhart, and E. S. Gould, *ibid.*, **93**, 5661 (1971); $(HClO_4) = 1.1$ *M*; temperature 25°. [e] Reference 2; $(HClO_4) = 1.0$ *M*; temperature 23°. [f] J. K. Hurst, unpublished observations; $(HClO_4) = 0.1$ *M*; temperature 23°. [g] First-order rate constants for electron transfer in $RoLCu^I$ binuclear ions.

Analysis for metal ions in the product solutions showed that the amounts of $RoOH_2^{3+}$ ion consumed (determined spectrally), Co(II) formed (determined as the chloro[6] or thiocyanato[7] complex ions) and Cu(I) formed (determined spectrally or determined after oxidation with O_2, as the thiocyanatocupric ion[7]) were identical to within 5%. Net oxidation–reduction is therefore consistent with the stoichiometric equation

$$RoOH_2^{3+} + Cu^0 + 5H^+ + CH_2{=}CHCH_2OH \rightarrow$$
$$Co^{2+} + Cu(CH_2{=}CHCH_2OH)^+ + 5NH_4^+ + H_2O$$

Because the disproportionation equilibrium $2Cu(I) \rightleftarrows Cu(II) + Cu(0)$ is rapidly established, it is impossible from these experiments to identify the immediate copper ion product arising from cobalt(III) reduction.

Mechanisms involving electron transfer to adsorbed $RoOH_2^{3+}$ ion, e.g.

$$RoOH_2^{3+} + Cu^0 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} RoOH_2Cu^0 \xrightarrow{k_2} \text{products}$$

are consistent with the observed rate law, $-d(RoOH_2^{3+})/dt = k(A/V)(RoOH_2^{3+})$, with $k = k_1k_2/(k_{-1} + k_2)$ in the steady state and the effective concentration of copper metal given by A/V, its surface area per unit volume of reaction solution. Rates can in principle be limited by either chemical reaction or hydrodynamic processes,[8] i.e., transport of RoL ions to the copper surface, surface diffusion to reactive sites,[1b] or desorption of product ions. Since electron transfer to cobalt(III) is rapidly followed by release of coordinated ammonia[9] in steps that are strongly exergonic in acidic media[1d] and since activation energies for desorption must be small,[1i] it is highly unlikely that any of the present reactions could be desorption controlled. Rate constants for transport-limited reduction (k_1) can be calculated from $k_1 = D_{\mathrm{Ro}}/\delta$, where D_{Ro} is the diffusion coefficient for the RoL ion and δ is the diffusion layer thickness. Taking as reasonable values for the latter parameters, $D_{\mathrm{Ro}} \simeq 7 \times 10^{-6}$ cm²/sec and $\delta \approx 10^{-3}$ cm,[1d] we estimate $k_1 \approx 7 \times 10^{-3}$ cm/sec, which is the same order of magnitude as that measured for the halogen-containing RoL ions, excepting the fluoro complex (Table I). Transport-limiting reduction is also suggested by the comparable reaction rates of other RoL ions; e.g., the $RoOH_2^{3+}$ ion is only threefold less reactive toward Cu^0, despite being as much as 10^8-fold less reactive toward cuprous ion in homogeneous solution (Table I). Transport of the $RoOH_2^{3+}$ ion is probably also partially rate limiting; i.e., a significant diffusion layer develops during reaction. Similar arguments have been advanced in support of transport-limited reduction of $RoBr^{2+}$ and $RoCl^{2+}$ ions by silver metal.[1d]

With RoL ions containing alkenoic acid or aminoalkene ligands, measured rate constants are too low to be accounted for by variations in transport rates; cf. $RoO_2CCH_3^{2+}$ and $RoO_2CCH{=}CH_2^{2+}$. Preferential adsorption to copper by π coordination to the olefin bond might account for the low reactivity as electron transfer does not occur by this pathway in cobalt(III)–copper(I) binuclear ions (Table I). From this perspective, the marked enhancement of reduction by copper metal over cuprous ion might be attributed to increased probabilities for electron transfer through the π-bridging system resulting from geometrical distortions of adsorbed RoL ions, to relaxation of spin restrictions[10] through spin–orbit interactions involving the copper lattice, or to the availability of other pathways. Facile reaction by "outer-sphere"-type pathways is evident from the relatively rapid reduction of the hexaamminecobalt(III) complex ion by copper metal.

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Registry No. RoF^{2+}, 15392-06-0; $RoCl^{2+}$, 14970-14-0; $RoBr^{2+}$, 14970-15-1; RoI^{2+}, 15392-08-2; RoN_3^{2+}, 14403-83-9; $RoOH_2^{3+}$, 14403-82-8; $RoO_2CCH_3^{2+}$, 16632-78-3; $RoO_2CCH{=}CH_2^{2+}$, 44982-34-5; $RoO_2CCH{=}CHCO_2H^{2+}$ (trans), 17712-85-5; $RoO_2CCH_2CH{=}CH_2^{2+}$, 45017-98-9; $RoO_2C(CH_2)_2CH{=}CH_2^{2+}$, 45095-56-5; $RoNH_2CH_2CH{=}CH_2^{3+}$, 55012-62-9; $RoNH_3^{3+}$, 14695-95-5; $RoNH_2(CH_2)_2CH{=}CH_2^{3+}$, 55012-63-0; Cu, 7440-50-8.

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Dinuclear Rhenium Carbonyl Diketonate Complexes

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The preparation of a number of group 6 metal tetracarbonyl diketonate anions has been previously described.[1] The study of these materials is often complicated by the presence of the bulky cations. The isoelectronic group 7 metal complexes, being neutral, avoid this problem and could provide interesting comparisons with the anionic derivatives of the group 6 metals. The manganese complex $Mn(CO)_4(hfacac)$[2] and several rhenium pentacarbonyl carboxylate complexes[3] had previously been prepared by methods similar to that used for the group 6 metal anionic derivatives. It therefore seemed likely that under these mild conditions, complexes of the type $Re(CO)_4(diket)$ (where diket = a β-diketonate anion) could also be easily prepared. Barrick and coworkers[4] were able to prepare dimeric complexes of the type $Re_2(CO)_6(diket)_2$; however rather forcing conditions were used. Nevertheless under identical conditions an analogous manganese compound yielded $Mn(CO)_4(hfacac)$ indicating a distinct difference in behavior between the two metals.

Results and Discussion

The reaction between various thallium diketonates and rhenium pentacarbonyl chloride in the usual solvents, chloroform and tetrahydrofuran, proved to be very sluggish. After refluxing for several days only partial conversion of the reactants had occurred and the resultant products were very difficult to separate from the starting materials. In order to facilitate the reaction, the higher boiling solvent 1,2-dimethoxyethane was chosen. Using this solvent, complete reaction was observed after refluxing for 72 hr as evidenced by the weight of TlCl formed. The products isolated from the reaction mixtures were not the expected $Re(CO)_4(diket)$ complexes but rather complexes which analyzed for $[Re(CO)_3(diket)]_2 \cdot CH_3OCH_2CH_2OCH_3$. The dimethoxyethane appears to be strongly held since it could not be removed by warming to 40° under a reasonably good vacuum ($<10^{-3}$ mm). The products are yellow to red crystalline solids (the color depending on the specific ligand) which are stable indefinitely at room temperature under a nitrogen atmosphere. Other solvents such as acetonitrile, dimethyl sulfoxide, and diglyme were tried but in each case decomposition seemed to take place and no identifiable products could be isolated.

Infrared and NMR data have proven helpful in establishing the geometry of the complexes, but the exact configuration of all the groups cannot be determined from the available data. A bridged structure similar to that determined for $Re_2(CO)_6(dbzm)_2$[4] with dimethoxyethane solvent molecules held in the crystal lattice appears to be quite likely. Alternately a structure with dimethoxyethane bridging two octahedral $Re(CO)_3(diket)$ groups also seems possible and satisfies the 18-electron rule as does the structure with bridged diketonate groups.

When prepared as Nujol mulls, all the $[Re(CO)_3(diket)]_2(dme)$ complexes give infrared spectra which consist of a relatively sharp, strong band at around 2030–2040 cm^{-1} and a very intense broad band centered around 1900 cm^{-1}. In CH_2Cl_2 solution this broad band is often resolved (although poorly) to two bands of approximately equal intensity. (See Table I.) The position of the two lower frequency bands is very uncertain since the bands are still very broad and poorly resolved. Although these complexes deviate somewhat in local symmetry, their infrared patterns are reminiscent of M-