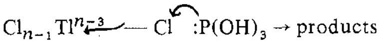
that a similar mechanism[14] operates here also as shown by



$Cl_{n-1}Tl^{n-3} \leftarrow Cl \; :P(OH)_3 \rightarrow \text{products}$

The evidence for the formation of $:P(OH)_3$ tautomer has been provided by Martin,[15] who studied the phosphonate–phosphite equilibria. Silver and Luz[16] have provided the evidence for the involvement of this tautomer in the H_3PO_3–I_2 reaction. Recently Viste et al.[17] proposed its existence to explain the results of oxidation of H_3PO_3 by silver(II). The following steps may also be considered along with (3) and (4) in order to include tautomer formation

$$H_3PO_3 + H^+ \xrightarrow{K_a} :P(OH)_3 + H^+ \quad \text{(slow)} \tag{7}$$

$$:P(OH)_3 + H^+ \xrightarrow{K_a'} H_3PO_3 + H^+ \quad \text{(rapid)} \tag{8}$$

These yield the same rate law as eq 2, with $k_{obsd} = k_n K_d K_a / K_a'$ and the assumption that $K_a'[H^+] >> k_n[Tl^{III}]$.

In the oxidations of H_3PO_2 and H_3PO_3 the reactivity of different chlorothallium(III) species follows the same order and probably the same mechanism. It is of interest to compare the rates of the two reactions. If the rate constants k_n of H_3PO_2 reactions are plotted against the corresponding rate constants of the H_3PO_3 reactions, a straight line with a slope of unity is obtained (Figure 1), although the rate constants refer to different experimental conditions. The rate constants of the two reactions are thus related by the equation

$$\log k_{n(H_3PO_2)} = \log k_{n(H_3PO_3)} + C$$

The simplest and most likely interpretation of the slope of unity is that the relative reactivities of various chlorothallium(III) complexes in the two reactions are the same. This will be true only if they react by the same mechanism in both the cases. It will be of interest to apply this equation in the reactions of different complexes of the same metal with two or more reagents believed to react by the same mechanism.

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Registry No. Tl^{3+}, 14627-67-9; H_3PO_3, 13598-36-2; Cl^-, 16887-00-6.

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Structural Trends of Tris(acetylacetonate)-, Tris(tropolonate)-, and Other Tris(bidentate ligand)-Metal Complexes. Additional Comments on the Trigonal Twist and Ligand-Ligand Repulsions in "Octahedral" D_3 Bidentate Ligand-Metal Complexes

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Since the structures of the majority of the first-row transition metal–tris(acetylacetonate) (acac) complexes are known,[1-4] it was of interest to us to examine structural trends and their correlations with some observed physical properties. Tris(tropolonate) (trop) structures were similarly scrutinized. Particular emphasis has been placed on comparisons with far-infrared spectra. The observed "trigonal twist" trends in these and other bidentate ligand complexes also have been examined.

Infrared Spectra of Neutral $(acac)_3$ and $(trop)_3$ Complexes. The determination of the $(acac)_3$ structures of most of the first-row transition metals allows a comparison of the M–O bond lengths with the positions of the metal-sensitive bands in the far-ir region. Figure 1 summarizes the far-ir data of neutral $(acac)_3$ complexes. A similar figure depicting the spectra of neutral $(trop)_3$ complexes is presented by Hulett and Thornton.[5b]

Theoretically,[6] seven metal–ligand (ML) vibration modes (2 a_2 and 5 e) are infrared active in D_3 site symmetry. Of these, three are stretching modes (a_2 and 2 e) and can be described as symmetric (e in D_3 correlating to e_g in O_h) and asymmetric (a_2 and e in D_3 correlating with t_{1u} in O_h). In practice, pure ML stretching bands are not observed in systems with ligands such as acac due to the extensive mixing of modes of the same symmetry. A number of investigators have recognized that certain bands in the far-ir region of $M(acac)_3$ and $M(trop)_3$ complexes were metal sensitive. For example, Thornton and coworkers[5] have pointed out that the pattern of frequency shifts in complexes where the metal is varied parallels the expected trends based on the crystal field stabilization energies (CFSE) of the metal ions. Analogously, we have observed the same pattern when the metal–ligand distances of the $M(acac)_3$ complexes (Table I) are plotted against the atomic number of the metal atoms. That is, the curve has the familiar "double-hump" characteristic.[7]

A comprehensive normal-coordinate analysis of $Fe(acac)_3$ by Mikami et al.[6c] identified the ML stretching bands as e_{sym} [found, 433 cm^{-1}; calcd, 446 cm^{-1} (48% pure)] and e_{asym} + a_2 [found, 298 cm^{-1} (unresolved); calcd, a_2 295 cm^{-1} (70%), e_{asym} 286 cm^{-1} (17%) and 222 cm^{-1} (40% pure)]. The proposed assignments were well supported by Nakamoto and coworkers[6d] using metal isotope shift techniques.

The abundance of reported structures of first-row transition series $M(acac)_3$ complexes prompted us to examine the assignments further. A plot of the frequencies of the three band series A, B, and C in Figure 1 against the metal–oxygen bond distances reveals high linear correlations, as shown in Figure 2. Series C bands show the steepest slope in the latter plot. Quite reasonably, these vibrations also reveal the largest metal isotope shifts, as noted by Nakamoto.[6d] Although the number of tropolonate structures reported is insufficient to warrant a similar plot, it seems that the same pattern also exists in that group of complexes.

The appearance of additional far-ir bands in the $Mn(acac)_3$ spectrum has long been attributed to distortions arising from

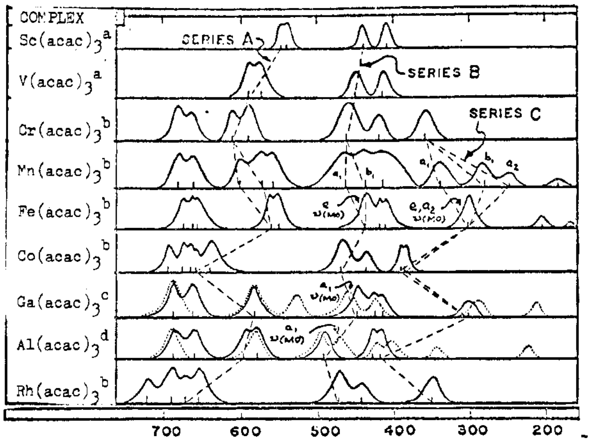

Figure 1. Far-ir bands in M(acac)$_3$ complexes. Dotted peaks refer to superimposed Raman bands. References: (a) ref 5a; (b) ref 6c; (c) ref 9 and A. W. Schlueter, R. A. Jacobson, and R. E. Rundle, *Inorg. Chem.*, 5, 277 (1966); (d) ref 9 and K. Nakamoto, P. J. McCarthy, A. Ruby, and A. E. Martell, *J. Am. Chem. Soc.*, 83, 1066 (1961).

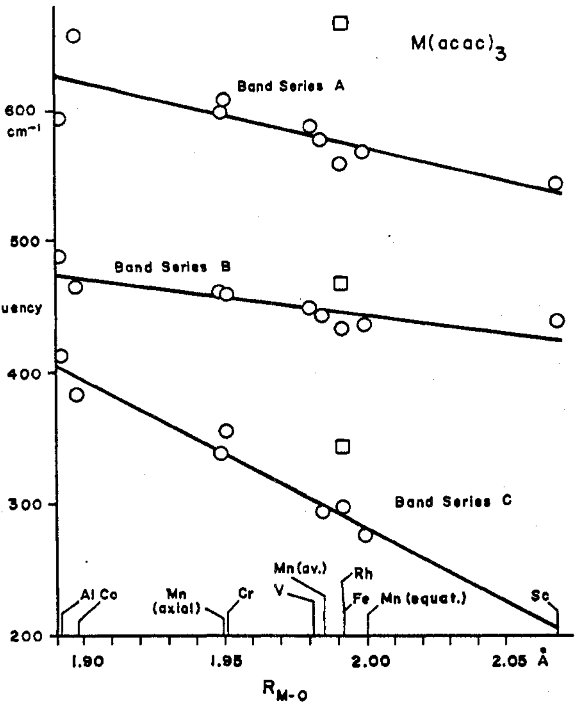

Figure 2. Plot of vibrational frequencies against the metal–oxygen distances in M(acac)$_3$ complexes. The linear correlation coefficients for band series A, B, and C are −0.82, −0.84, and −0.98, respectively. Rh(acac)$_3$, □, was not included in the fitting. Refer to Figure 1 for identification of the bands in this figure.

the Jahn–Teller effect.[8] Apparently, the splitting of bands in Mn(trop)$_3$ is also due to the same phenomenon.[5] Knowing the structure of Mn(acac)$_3$, one can extend the ir assignments of Mikami et al.[6c] to the distorted complex. Each Mn(acac)$_3$ band in series A and B is split into two components. It is proposed that a threefold split exists in series C (Figure 1). If the splitting arises from tetragonal distortion of the ideally D_3 symmetry molecule, then the higher energy band may be "assigned" to the 1.948-Å Mn–O bond[4] vibrations while the lower energy band may be "assigned" to the 2.000-Å Mn–O bond[4] vibration. The actual labeling of a$_1$ and b$_1$ bands in Mn(acac)$_3$ in Figure 1 is based on choices which minimize the deviations from linearity in the plots in Figure 2. Thus the third band in series C in Mn(acac)$_3$ is thought to be a$_2$, which in Fe(acac)$_3$ is unresolved from the e$_{\mathrm{asym}}$ band. At best these assignments are just educated guesses. It is hoped that they may be of use in further studies of the ir spectra of Jahn–Teller molecules.

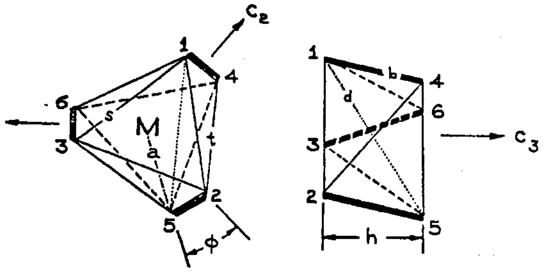

Figure 3. Parameters describing the shape of the ML$_6$ octahedron of D_3 symmetry.

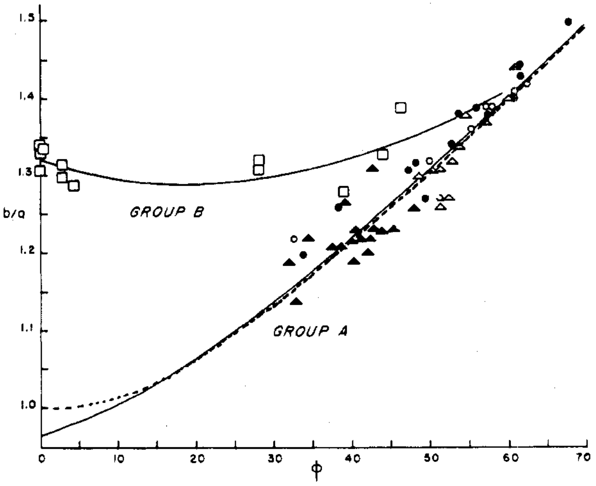

Figure 4. Plot of b/a vs. ϕ (in degrees) for the complexes in Table I. Group A: nitrogen ligands (△), oxygen ligands (○), sulfur and selenium ligands (▲); acac and trop ligands (●). Group B: 1,2-dithiolenes and selenium analogs (□). Solid lines are deduced from geometrical considerations. The dashed line includes electrostatic terms.

In order to discuss[4] the tetragonal structure of Mn(acac)$_3$ in terms of the Jahn–Teller theory, the normal-coordinate vibrational analysis of Fe(acac)$_3$ was of considerable value. It was necessary to know the force constants for hypothetical octahedral e$_g$ and a$_{1g}$ vibrations. In Fe(acac)$_3$ the diagonal element in the force constant matrix corresponding to the vibration at 433 cm^{-1} is 1.584 mdyn/Å. Using the scaling information deduced from Figure 2, the corresponding value for Mn(acac)$_3$ would be ~1.69 mdyn/Å. The Raman studies[9] of Ga(acac)$_3$ and Al(acac)$_3$ indicate that the a$_{1g}$ band is approximately in the same position as the band series B. Using this information the force constants were assigned[4] as $k_{\mathrm{a_{1g}}} \sim k_{\mathrm{e_g}} \sim 1.69$ mdyn/Å in Mn(acac)$_3$.

Trigonal Twist. Based on empirical correlation studies, it was proposed[3] that for a wide variety of tris(bidentate ligand)–metal complexes, excluding those containing 1,2-dithiolate ligands, the trigonal twist angle, ϕ, due to electron–electron repulsions, was highly correlated to the ratio of the ligand bite distance to the metal–ligand bond distance, b/a. Stiefel and Brown[11] recognized the importance of this ratio in the context of the twist angle.

Kepert[12] shortly thereafter formalized the relationship in terms of a semiquantitative electrostatic model. A more detailed examination of the subject is presented here.

A sampling of tris(bidentate ligand)–metal complexes whose structures are known is presented in the table. Figure 3 identifies the parameters appearing in the table. Some useful relations between the parameters, not given by Stiefel and

Table I. Structural Parameters (See Figure 3) for a Sampling of Tris(bidentate ligand) Complexes

Complexes[zz,aaa]	a	b	s	h	t	d	s/h	ϕ	b/a	s/a	Ref
$[Cu(HOCH_2CH_2OH)_3SO_4$	2.11	2.69	3.12	2.19	3.01	4.12	1.42	51.4	1.27	1.48	*a*
$[Cu(IPCP)_3](ClO_4)_2$	2.09	2.97	2.98	2.37	2.89	4.21	1.26	62.5	1.42	1.43	*b*
$[Co(OMPA)_3](ClO_4)_2$	2.08	2.89	2.97	2.37	2.99	4.15	1.25	57.6	1.39	1.43	*c*
$[Cu(PCP)_3](ClO_4)_2$	2.09	2.95	2.97	2.38	2.91	4.18	1.25	61.1	1.41	1.42	*d*
$[Cu(OMPA)_3](ClO_4)_2$	2.07	2.88	2.93	2.37	2.94	4.11	1.24	58.0	1.39	1.42	*c*
$[Mg(OMPA)_3](ClO_4)_2$	2.06	2.81	2.95	2.33	2.95	4.08	1.27	55.4	1.36	1.43	*c*
$[Fe(CNN(O)Ph)_3]$	2.00	2.45	2.85	2.27	3.22	3.91	1.26	32.5	1.22	1.43	*e*
$(NH_4)_3[Cr(Ox)_3]$	1.96	2.59	2.83	2.18	2.88	3.84	1.30	50.0	1.32	1.44	*f*
$[Cu(en)_3]SO_4$	2.15	2.80	3.11	2.36	3.15	4.18	1.32	48.9	1.30	1.45	*g*
$[Cu(phen)_3](ClO_4)_2$	2.13	2.71	3.19	2.17	3.00	4.18	1.47	52.3	1.27	1.50	*h*
$[Cu(bipy)_3](ClO_4)_2$	2.13	2.68	3.20	2.15	3.00	4.17	1.49	51.4	1.26	1.50	*i*
$[Ni(en)_3]SO_4$	2.12	2.79	3.07	2.29	3.10	4.14	1.34	52.8	1.32	1.45	*j*
$[Cr(en)_3][Co(CN)_6]$	2.08	2.73	3.01	2.29	3.03	4.06	1.31	50.4	1.31	1.45	*k*
$[Cr(en)_3][Ni(CN)_5]$	2.08	2.73	3.00	2.29	3.00	4.06	1.31	51.3	1.31	1.44	*l*
$[Co(pn)_3]Br_3$	2.00	2.74	2.88	2.23	2.90	3.97	1.29	57.3	1.37	1.44	*m*
$[Co(en)_3]Br_3$	2.00	2.80	2.87	2.25	2.80	4.01	1.28	59.9	1.40	1.44	*n*
$[Co(cptn)_3]Cl_3$	2.00	2.75	2.82	2.32	2.93	3.94	1.22	54.5	1.38	1.41	*o*
$[Co(en)_3]_2[Cu_2Cl_8]Cl_2$	1.97	2.63	2.84	2.17	2.91	3.87	1.31	53.6	1.34	1.44	*p*
$(DMANH)[Cu(hfacac)_3]$	2.07	2.86	2.95	2.35	2.94	4.11	1.26	57.5	1.38	1.43	*q*
$(DMANH)[Mg(hfacac)_3]$	2.06	2.77	2.94	2.32	2.98	4.04	1.27	52.8	1.34	1.43	*q*
$Sc(acac)_3$	2.07	2.72	2.96	2.34	2.72	4.02	1.26	47.4	1.31	1.43	*r*
$V(acac)_3$	1.98	2.75	2.79	2.30	2.83	3.92	1.21	56.0	1.39	1.41	*s*
$Cr(acac)_3$	1.95	2.79	2.76	2.26	2.75	3.92	1.22	61.6	1.43	1.42	*t*
$Mn(acac)_3$	1.99	2.79	2.81	2.26	2.78	3.96	1.24	60.2	1.40	1.41	*u*
$Fe(acac)_3$	1.99	2.74	2.80	2.32	2.92	3.92	1.21	54.0	1.38	1.41	*v*
$Co(acac)_3$	1.90	2.85	2.62	2.30	2.65	3.87	1.14	67.9	1.50	1.38	*w*
$Al(acac)_3$	1.89	2.73	2.65	2.23	2.71	3.80	1.19	61.6	1.44	1.40	*w*
$Sc(trop)_3$	2.10	2.52	3.05	2.31	3.33	4.13	1.32	33.9	1.20	1.45	*x*
$Mn(trop)_3$	2.00	2.55	3.01	2.16	2.90	3.94	1.39	49.4	1.27	1.51	*y*
$Fe(trop)_3$	2.01	2.52	2.87	2.27	3.13	3.82	1.26	38.5	1.26	1.43	*yy*
$Al(trop)_3$	1.89	2.49	2.70	2.13	2.80	3.67	1.27	48.1	1.32	1.43	*z*
$[Me_4N]_2[Zr(S_2C_6H_4)_3]$	2.54	3.26	3.59	2.96	4.00	4.85	1.21	39.0	1.28	1.41	*aa*
$[Ph_4As]_2[Mo(mnt)_3]$	2.37	3.13	3.19	3.00	3.99	4.47	1.06	28.3	1.32	1.35	*bb*
$[Ph_4As]_2[W(mnt)_3]$	2.37	3.11	3.19	2.98	4.00	4.46	1.07	28.1	1.31	1.35	*bb*
$[Me_4N]_2[V(mnt)_3]$	2.36	3.13	3.31	2.78	2.98	4.55	1.19	44.5	1.33	1.40	*cc*
$[Ph_4As]_2[Fe(mnt)_3]$	2.26	3.15	3.07	2.82	3.43	4.40	1.09	46.5	1.39	1.36	*dd*
$[Ph_4As][Nb(S_2C_6H_4)_3]$	2.44	3.15	3.23	3.15	4.46	4.51	1.03	4.2	1.29	1.32	*aa*
$Mo(S_2C_2H_2)_3$	2.33	3.10	3.11	3.10	4.39	4.39	1.00	0.0	1.33	1.33	*ee*
$Mo(S_2C_6H_4)_3$	2.37	3.11	3.09	3.11	4.38	4.38	0.99	0.0	1.31	1.30	*aa*
$V(S_2C_2Ph_2)_3$	2.34	3.06	3.07	3.05	4.30	4.33	1.01	3.0	1.31	1.31	*ff*
$Re(S_2C_2Ph_2)_3$	2.33	3.03	3.05	3.03	4.26	4.30	1.01	3.0	1.30	1.31	*gg*
$(NH_4)_2[Pt(S_5)_3]$	2.39	3.45	3.33	2.85	3.44	4.79	1.17	60.9	1.44	1.39	*hh*
$V(Et_2DTP)_3$	2.45	3.21	3.45	2.86	3.46	4.71	1.21	42.8	1.31	1.41	*ii*
$Co(Et(txan))_3$	2.40	2.89	3.55	2.49	3.50	4.58	1.43	42.1	1.20	1.48	*jj*
$Fe(n\text{-}Bu(txan))_3$	2.30	2.80	3.38	2.42	3.45	4.39	1.40	42.2	1.22	1.47	*kk*
$Fe(Et(xan))_3$	2.32	2.84	3.40	2.48	3.51	4.43	1.37	41.2	1.22	1.47	*ll*
$Co(Et(xan))_3$	2.28	2.81	3.34	2.42	3.41	4.36	1.38	43.2	1.23	1.46	*mm*
$In(Pm(dtc))_3$	2.59	2.95	3.84	2.66	4.06	4.84	1.44	33.0	1.14	1.48	*nn*
$Mn(Et_2dtc)_3$	2.45	2.91	3.64	2.52	3.70	4.66	1.44	40.3	1.19	1.49	*oo*
$Fe((n\text{-}Bu)_2dtc)_3$	2.42	2.87	3.51	2.64	3.86	4.53	1.33	32.0	1.19	1.45	*pp*
$Fe(pyrr(dtc))_3$	2.41	2.91	3.52	2.58	3.70	4.56	1.36	38.6	1.21	1.46	*qq*
$Fe(Et_2dtc)_3$	2.36	2.85	3.44	2.54	3.65	4.47	1.35	37.6	1.21	1.46	*rr*
$Fe(MePh(dtc))_3$	2.31	2.82	3.38	2.48	3.52	4.40	1.36	40.4	1.22	1.46	*qq*
$Fe(Et_2dtc)_3$, 79° K	2.31	2.84	3.36	2.50	3.52	4.40	1.34	40.5	1.23	1.45	*rr*
$[Fe(pyrr(dtc))_3]ClO_4$	2.30	2.81	3.30	2.57	3.65	4.34	1.20	34.5	1.22	1.43	*ss*
$Fe(Et_2dtc)_2(tfd)$	2.27	2.88	3.19	2.67	3.62	4.30	1.19	38.3	1.27	1.41	*tt*
$Co(Et_2dtc)_3$	2.26	2.79	3.32	2.40	3.37	4.34	1.38	43.6	1.23	1.47	*uu*
$[Ni((n\text{-}Bu)_2dtc)_3]Br$	2.26	2.79	3.34	2.37	3.33	4.34	1.41	45.3	1.23	1.48	*vv*
$Mo(Se_2C_2Ph_2)_3$	2.49	3.32	3.22	3.32	4.63	4.63	0.97	0.0	1.33	1.29	*ww*
$Mo(sfd)_3$	2.49	3.32	3.22	3.32	4.52	4.52	0.97	0.0	1.33	1.29	*ww*
$[Ni((n\text{-}Bu)_2dsc)_3]Br$	2.39	3.00	3.53	2.50	3.46	4.63	1.41	48.0	1.26	1.48	*xx*
Regular octahedron	a	$\sqrt{2}a$	$\sqrt{2}a$	$2a/\sqrt{3}$	$\sqrt{2}a$	$2a$	$\sqrt{3/2}$	60	$\sqrt{2}$	$\sqrt{2}$	
Trigonal prism (containing square faces)	a	$2a\sqrt{3}/\sqrt{7}$	$2a\sqrt{3}/\sqrt{7}$	$2a\sqrt{3}/\sqrt{7}$	$2a\sqrt{6}/\sqrt{7}$	$2a\sqrt{6}/\sqrt{7}$	1	0	$2a\sqrt{3}/\sqrt{7}$	$2a\sqrt{3}/\sqrt{7}$	

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Table I (*Footnotes Continued*)

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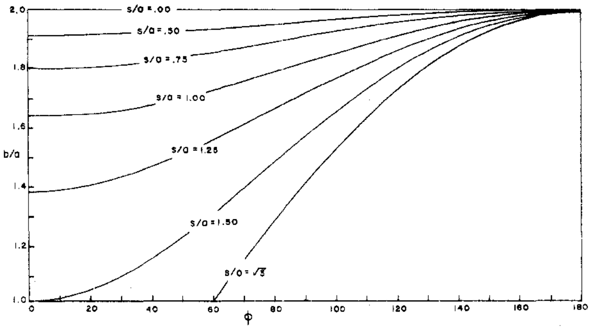

Figure 5. Precise relation between b/a and ϕ (in degrees) as a function of the parameter s/a for tris(bidentate ligand) complexes with D_3 symmetry at the metal.

Brown,[11] are given by eq 1–3.

$$(b/a)^2 = 4\left[1 - \frac{1}{3}(s/a)^2 \cos^2(\phi/2)\right] \tag{1}$$

$$t^2 = b^2 + s^2 \left(\cos\phi - \frac{1}{\sqrt{3}}\sin\phi\right) \tag{2}$$

$$d^2 = b^2 + s^2 \left(\cos\phi + \frac{1}{\sqrt{3}}\sin\phi\right) \tag{3}$$

By plotting the ratio b/a vs. the twist angle ϕ one notes that the compounds fall into either of two groups, as is shown in Figure 4. The "trigonal prism" complexes, group B in the figure, are composed of 1,2-dithiolene or 1,2-diselenolene ligands. Such ligands are considered to participate in "interligand donor atom bonding" (IDAB), where it has been proposed[10] that the attraction between adjacent ligands overcomes to a significant degree the electronic repulsions. A number of examples exist which appear to support this hypothesis.[10]

The structures of the complexes in group A in Figure 4 are thought to be determined primarily by electronic repulsions. In attempting to understand better how an attractive potential could stabilize the trigonal-prismatic configuration, we chose to examine the Kepert[12] electrostatic model in more detail than reported to date.

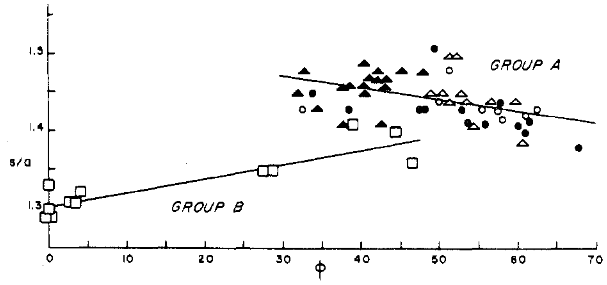

Figure 6. Linear description of the dependence of s/a on ϕ (in degrees). Group A and B compounds are those included in Figure 5: group A, $s/a = 1.52 - 0.0015\phi$; group B, $s/a = 1.30 + 0.0019\phi$.

Trigonal Twist—Geometrical Considerations. Of the various parameters tabulated in the table, three are needed to specify uniquely the shape of the chromophore of a complex possessing local D_3 symmetry. Thus it surprised us that the plot of b/a vs. ϕ exhibited a high linear correlation for so many different compounds, exclusive of the IDAB group. A further examination of the geometrical relations seemed fruitful.

Figure 5 shows the exact geometrical relationship between b/a and ϕ (eq 1) for constant values of s/a. The latter parameter is considered important in IDAB complexes. Each curve (constant s/a) contains approximately linear portions in the 30–70° region in ϕ. It appears as though only two such curves are needed to fit the data for the complexes reported. The two groups of compounds in Figure 4 can be described by two unique values of s/a.

A plot of s/a vs. ϕ, Figure 6, shows only a nominal linear dependence on ϕ. The two groups of s/a values are 1.35 ± 0.05 and 1.45 ± 0.05. By using the geometric relationship which connects b/a and ϕ (eq 1) and including the slight linear dependence of ϕ on s/a, the two solid curves in Figure 4 are produced.

The fit produced is excellent. It is also noted that the curves proposed by Kepert[12] (based on a repulsion model) can be duplicated considering only geometrical factors. Since the exponential term in Kepert's expression for the repulsion, Xr^{-n}, is "not critically dependent on the assumed repulsive law", it correlates with the parameter s/a ($n = 1$). In order to come to a closer understanding of why there are two classes of compounds, the repulsion model was examined in more detail. Kepert[12] did not propose an explanation for the "anomalous"

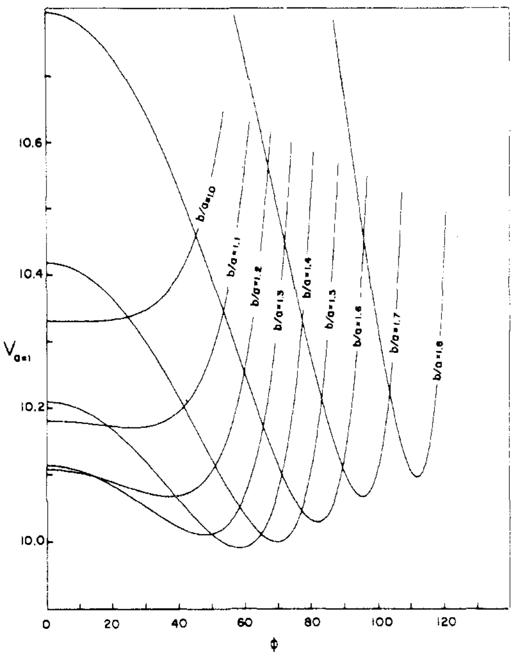

Figure 7. Plot of the relative repulsion energy against the twist angle (in degrees) at various constant values of b/a.

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 ($RoOH_2^{3+}$) by zerovalent copper and briefly survey the reactivity toward copper of other ions (RoL)