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Solid State Structure and Reactivity in Solution.
II. The Crystal and Molecular Structure of (2,2,7,7-Tetramethyl-3,6-Dithiaoctane)-tetracarbonylchromium(0)

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The crystal and molecular structure of the title compound, (DTO)Cr(CO)$_4$, has been determined by single-crystal X-ray diffraction techniques. The crystals are monoclinic, a = *9.583(4),* b = *13.399(5) and* c = *14.809(8) Å, β = 101.62(4)°, space group P2$_1$/n,* d *(calc.,* z = *4) = 1.32 g/cm^3. The structure was solved by MULTAN and refined by full-matrix least-squares methods to R = 0.05 using 2274 reflections measured on a four circle diffractometer with Mo-K$_\alpha$ radiation. The coordination about the central chromium atom is a distorted octahedron, the greatest deviations from ideal geometry being the angle S1–Cr–S2, 80.6(1)°, and the angle between the two mutually* trans *carbonyls, 169.8(2)°. Mean metal–ligand bond lengths are Cr–S = 2.437(1), Cr–C(*cis*) = 1.863(5) and Cr–C(*trans*) = 1.820(5) Å. The influence of the two bulky t-butyl substituents, bonded to S, on the octahedral geometry about Cr, and the possible influence of this molecular distortion on the reactivity of the complex* via *displacement of the chelating ligand by Lewis bases are discussed.*

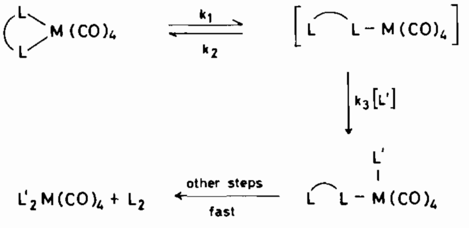
Introduction

Kinetic/mechanistic and single crystal X-ray studies are being carried out on a variety of *cis*-(L$_2$)M(CO)$_4$ complexes (L$_2$ = RS(CH$_2$)$_n$SR, R = alkyl, M = Cr, Mo, W and n = 2, 3) in order to elucidate further the influence of metal atom, substituent and chelate ring size on solid state structure, reactivity in solution, and, further, to ascertain whether the former can be correlated to the latter.

In most instances, displacement of L$_2$ by monodentate Lewis bases L′ (L′ = phosphines and phosphites),

$$(L_2)M(CO)_4 + 2L' \rightarrow L'_2M(CO)_4 + L_2 \qquad (1)$$

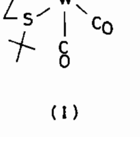
proceeds *via* initial unimolecular dissociation of one end of the chelating ligand, L$_2$ (2-k$_1$) [1–8]. A key feature of mechanisms observed for reactions (1) is competition for the intermediate, formed through unimolecular dissociation of one end of the bidentate ligand, between ring reclosure (2-k$_2$) and attack



(2)

by the incoming nucleophile L′ (2-k$_3$[L′]). The former process, but not the latter, will be strongly influenced by the nature of steric effects induced through chelate ring formation.

Significant differences in rate behavior, which may be interpreted largely in terms of the relative rates of reclosure of the chelating ring, have been observed as a function, particularly, of the identity of R and of chelate ring size [1–8]. Moreover, in the systems thus far investigated *via* X-ray crystallography (M = W, R = Bu^t, n = 2, 3) [9] (I, II), significant distortion of the octahedral environment was observed. These results prompted a continuation of the series of struc-



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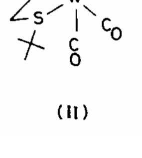

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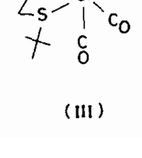


(III)

TABLE I. Crystallographically Important Data Collection and Processing Information.

Empirical Formula	$CrS_2C_{14}O_4H_{22}$
Molecular Weight	370.45
Cell Constants	a = 9.583(4) Å
	b = 13.399(5)
	c = 14.809(8)
	β = 101.62(4)°
Unit Cell Volume	V = 1862.5 $Å^3$
Space Group	$P2_1/n$
Density (calculated)	1.32 g cm^{-3}
Absorption Coefficient	8.3 cm^{-1}
Radiation Used for Data collection	MoK_α (λ = 0.71069 Å)
Scanning Range for 2θ	$4° \leqslant 2\theta \leqslant 52°$
Crystal along	[0,0,1] approx.
Standard for Intensity Control	(0, 4, 6 and $\bar{1}$,5,7)
Scan Width	$\Delta\theta = (1.10 + 0.35 \tan\theta)$
Maximum Scan Time	180 sec
Scan Technique	ω: 2θ
Total Number of Reflections Collected	3293
Number of Contributing Reflections in the Last Cycle of Least-Squares	2274
Number of Variables	278
Weighting Scheme	$[\sigma(F_o)]^{-2}$
Absorption Corrections	Not applied
Final R(F)	0.051
Final R_w(F)	0.044

tural investigations. Here are reported results for the substrate in which M = Cr, R = Bu^t and n = 2, (III) to investigate the influence of atomic number of the metal atom on molecular distortions.

Experimental

The crystal used for the study was prismatic and had well developed faces. Maximum edge dimensions were *ca.* 0.35 × 0.35 × 0.15 mm. Intensity measurements were carried out on an ENRAF-NONIUS CAD-4 computer-controlled diffractometer. A summary of the crystallographically important parameters for data collection and processing are given in Table I. Accurate cell constants determination and data collection were similar to those described elsewhere [9] and are thus not repeated here.

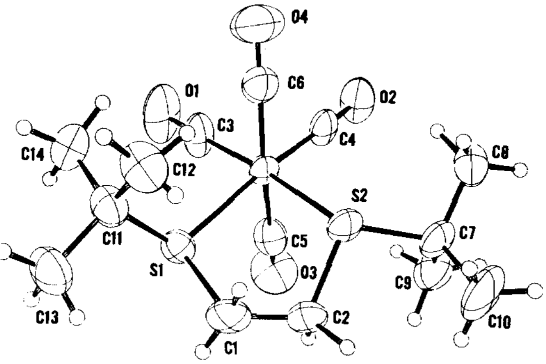


Fig. 1. A general view of the molecule showing the numbering scheme used in the crystallographic study. The thermal ellipsoids are 50% probability envelopes for the heavy atoms and of convenient size for the hydrogen atoms.

Solution and Refinement

Data decoding was accomplished using a locally written program. Lorentz and polarization factors were applied in converting the intensities to structure factors amplitudes, $|F_o|$. No corrections for absorption were made due to the low value of the absorption coefficient (μ = 8.3 cm^{-1}). Standard deviations of the intensities, $\sigma(I)$, were estimated as $\sigma^2(I) = I_{TOT} + 2\Sigma I_{BG}$. Standard deviations in the structure factors amplitudes, $\sigma(|F_o|)$, were estimated as $\sigma(|F_o|) = \sigma(I)/2Lp|F_o|$. The structure was solved by MULTAN [10]. All the subsequent calculations were carried out using the SHELX 76 [11] system of programs. Successive difference Fourier syntheses revealed all the 21 non-hydrogen atoms, which were refined isotropically to convergence at R = 0.14. Conversion to anisotropic thermal parameters was then accomplished (R = 0.08). At this stage, hydrogen atoms were added at theoretically calculated positions (C–H = 0.95 Å). Further anisotropic refinement of the non-hydrogen atoms yielded the following final unweighted and weighted agreement factors: R = 0.051 and R_w = 0.044. The function minimized during all the least-squares refinements was $\Sigma w(|F_o|-|F_c|)^2$. Corrections for the real term of the anomalous dispersion for Cr and S were applied. The values used for these corrections were those given in the International Tables of X-Ray Crystallography [12]. The estimated standard deviations were computed from the inverse matrix of the final, full matrix, least squares cycle. No unusually high correlations were noted between any variables in the final cycle. Final positional and thermal parameters are presented in Table II, based on the numbering scheme shown in Fig. 1. Interatomic distances and angles are given in Table III. The equations of the least squares planes through selected groups of atoms are given in Table IV. The stereo drawings (Fig. 1, 2 and 3) were obtained by using Johnson's ORTEP 2 [13].

TABLE II. Positional and Thermal Parameters and Their Estimated Standard Deviations given in Parentheses*.

Atoms	x/a	y/b	c/z	U11, B	U22	U33	U23	U13	U12
Cr	37453(7)	75065(6)	30959(4)	426(4)	577(5)	330(4)	017(4)	–066(3)	–070(4)
S1	3699(1)	6357(1)	4372(1)	609(7)	549(7)	428(7)	033(6)	069(6)	001(6)
S2	5536(1)	8291(1)	4277(1)	453(6)	650(8)	418(7)	–025(6)	–083(5)	–036(6)
C1	5287(7)	6636(6)	5269(4)	75(4)	82(6)	48(4)	10(4)	–22(3)	04(4)
C2	6361(6)	7218(5)	4887(4)	61(4)	75(4)	51(4)	12(3)	–15(3)	03(3)
C3	2269(5)	6835(4)	2370(3)	79(4)	94(4)	52(3)	07(3)	–09(3)	–41(3)
C4	3959(4)	8252(3)	2114(3)	51(3)	77(3)	47(3)	05(3)	–08(2)	–23(3)
C5	4961(5)	6603(3)	2686(3)	81(4)	71(4)	56(3)	01(3)	18(3)	–09(3)
C6	2414(5)	8458(4)	3285(3)	59(3)	78(4)	67(3)	12(3)	07(3)	–01(3)
C7	7018(5)	8960(4)	3920(3)	49(3)	83(4)	59(3)	–02(3)	–16(3)	–16(3)
C8	6373(8)	9912(6)	3467(6)	79(5)	78(5)	113(6)	21(5)	–02(5)	–24(4)
C9	7677(7)	8339(7)	3235(6)	61(4)	121(7)	109(6)	17(5)	31(4)	–05(5)
C10	8138(9)	9211(9)	4803(6)	78(5)	155(9)	104(6)	–03(6)	–38(5)	–53(6)
C11	2242(5)	6472(3)	5030(3)	76(3)	57(3)	67(3)	05(3)	26(3)	01(3)
C12	2197(10)	7478(6)	5473(6)	106(7)	76(5)	77(5)	–05(4)	36(5)	03(5)
C13	2423(9)	5639(6)	5742(5)	107(6)	88(6)	90(5)	30(4)	48(5)	09(5)
C14	0864(6)	6287(6)	4295(5)	63(4)	96(6)	98(5)	–01(5)	23(4)	–13(4)
O1	1332(4)	6431(3)	1894(2)	125(3)	169(4)	76(3)	00(3)	–31(2)	–88(3)
O2	4036(4)	8711(3)	1449(2)	96(3)	117(3)	51(2)	24(2)	–04(2)	34(2)
O3	5655(4)	6053(3)	2362(3)	132(4)	107(3)	113(3)	–25(3)	53(3)	19(3)
O4	1523(4)	9049(3)	3288(3)	85(3)	123(4)	140(4)	27(3)	22(3)	40(3)
H11	548(5)	600(3)	534(3)	7(1)					
H12	499(5)	716(3)	550(3)	7(2)					
H21	717(5)	756(3)	535(3)	9(2)					
H22	680(4)	682(3)	456(3)	5(1)					
H81	584(7)	1017(5)	386(4)	14(4)					
H82	550(6)	974(4)	293(4)	12(2)					
H83	714(5)	1030(4)	326(3)	9(2)					
H91	698(9)	795(6)	279(6)	23(5)					
H92	819(7)	769(6)	353(5)	20(4)					
H93	832(5)	880(4)	298(3)	10(2)					
H101	742(7)	949(6)	528(5)	19(4)					
H102	874(6)	973(5)	475(4)	13(3)					
H103	859(6)	858(4)	490(5)	13(3)					
H121	294(5)	760(5)	568(4)	10(3)					
H122	138(5)	755(4)	575(3)	09(2)					
H123	226(5)	804(4)	513(3)	08(2)					
H131	337(5)	556(4)	599(3)	08(2)					
H132	255(6)	497(4)	554(4)	10(2)					
H133	163(4)	560(3)	603(3)	06(1)					
H141	062(5)	688(3)	387(3)	06(1)					
H142	007(4)	622(3)	462(3)	06(1)					
H143	098(5)	557(4)	407(3)	09(2)					

*Positional Parameters for Co × 10^5; S, C and O × 10^4 and for H × 10^3. Thermal Parameters for Co and S × 10^4; for C and O × 10^3 and for H × 10^2.

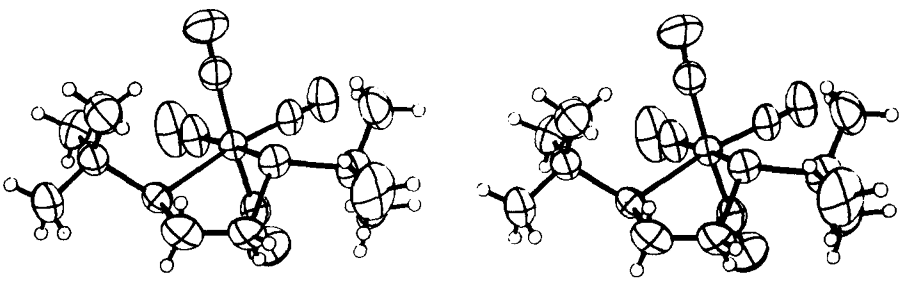


Fig. 2. A stereo pair of the molecule. Note the *anti* conformation of the t-butyl groups.

TABLE III. Molecular Geometry with Estimated Standard Deviations given in Parentheses.

(a) Bond Lengths (Å)

Cr–S1	2.445(1)	C1–H11	0.87(4)
Cr–S2	2.429(1)	C1–H12	0.85(5)
Cr–C3	1.831(5)	C2–H21	1.04(4)
Cr–C4	1.810(4)	C2–H22	0.89(4)
Cr–C5	1.862(5)	C8–H81	0.92(7)
Cr–C6	1.864(5)	C8–H82	1.06(5)
S1–C1	1.845(6)	C8–H83	1.00(5)
S1–C11	1.863(5)	C9–H91	0.99(8)
S2–C2	1.794(6)	C9–H92	1.05(7)
S2–C7	1.845(5)	C9–H93	1.01(5)
C3–O1	1.157(6)	C10–H101	1.14(8)
C4–O2	1.175(5)	C10–H102	0.91(6)
C5–O3	1.162(7)	C10–H103	0.95(6)
C6–O4	1.166(6)	C12–H121	0.73(5)
C7–C8	1.514(9)	C12–H122	0.96(5)
C7–C9	1.542(10)	C12–H123	0.93(5)
C11–C12	1.503(10)	C13–H131	0.92(4)
C11–C13	1.522(9)	C13–H132	0.97(6)
C11–C14	1.553(7)	C13–H133	0.94(5)
C1–C2	1.490(9)	C14–H141	1.01(4)
C7–C10	1.553(9)	C14–H142	0.98(4)
		C14–H143)	1.04(5)

(b) Angles (°)

S1–Cr–S1	80.60(4)	C2–S2–C7	104.3(3)
C3–Cr–C4	89.9(2)	S1–C1–C2	111.4(4)
S1–Cr–C3	90.7(2)	C1–C2–S2	110.0(4)
S2–Cr–C3	170.2(2)	S1–C11–C12	113.1(5)
S1–Cr–C4	172.5(1)	S1–C11–C13	108.0(4)
S2–Cr–C4	99.3(1)	S1–C11–C14	104.0(4)
S1–Cr–C5	87.3(2)	C12–C11–C13	111.3(5)
S2–Cr–C5	96.7(1)	C12–C11–C14	110.8(5)
S1–Cr–C6	101.3(2)	C13–C11–C14	109.3(5)
S2–Cr–C6	90.1(1)	S2–C7–C8	105.5(4)
C3–Cr–C5	87.1(2)	S2–C7–C9	111.5(4)
C3–Cr–C6	87.3(2)	S2–C7–C10	107.8(5)
C4–Cr–C5	85.2(2)	C8–C7–C9	110.3(6)
C4–Cr–C6	86.3(2)	C8–C7–C10	110.0(6)
C5–Cr–C6	169.8(2)	C9–C7–C10	115.5(5)
Cr–S1–C1	106.7(2)	Cr–C3–O1	178.1(5)
Cr–S1–C11	118.9(1)	Cr–C4–O2	176.5(4)
C1–S1–C11	104.7(3)	Cr–C5–O3	174.7(4)
Cr–S2–C2	101.1(2)	Cr–C6–O4	171.7(4)
Cr–S2–C7	118.5(2)		

Final observed and calculated structure factors are available.

Results and Discussion

The structure of (DTO)Cr(CO)$_4$

Compound III exists in the crystal as discrete molecules in which the DTO group functions as a bidentate ligand with the two sulfurs as donor atoms.

TABLE IV. Least Squares Planes[a] through Selected Groups of Atoms and Their Deviations from the Planes (Å).

(1) Plane through S1, S2, C3 and C4
$0.7526x - 0.6045y - 0.2612z = -5.214$

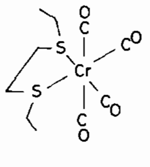
S1	0.095	C3	−0.1158
S2	−0.089	C4	0.1098
Cr	−0.033	C5	1.820
C6	−1.877		

(2) Plane through Cr, S1, S2 and C1
$0.7570x - 0.5259y - 0.3827z = -5.111$

Cr	0.099	S1	−0.131
S2	−0.085	C1	0.117
C2	0.787	C7	0.799
C11	−1.788		

[a] Planes are expressed as $px + qy + rz = s$ in orthogonal (Å) space.

The two Cr–S bonds have lengths of 2.445(1) and 2.429(1) Å (mean 2.437(1) Å). Similar bond lengths, 2.425(1) and 2.412(1) Å were obtained by Baker and Larsen for (3,6-dithiaoctane)tetracarbonylchromium(0) (IV) [14]. These values are about 0.1 Å shorter than the expected length of 2.52 Å for a Cr–S single bond (based on the covalent radii of 1.48 Å for Cr and 1.04 Å for sulfur) [14]. This shortening is consistent with a significant π component to the bond.



(IV)

The coordination about the central chromium atom is a distorted octahedron, the equatorial plane being formed by two carbonyl groups and by two sulfur atoms. The deviation of the Cr atom from the equatorial plane is 0.033 Å. Similar deviations of 0.013, 0.023 and 0.016 Å were found in compounds I, II, IV, respectively. The two Cr–C(0) bonds *trans* to the sulfur atoms (1.831(5) and 1.810(4) Å) are significantly shorter than the two *cis* Cr–C(0) bonds (1.862(5) and 1.864(5) Å). Concomitantly, the average C–O distance of the two mutually *trans* carbonyl ligands should be shorter than the respective distance of the other two carbonyl groups. However, such a difference, although found in compound IV, was not observed in complex III, the avearage C–O distance being 1.164(6) and 1.166(6) Å.

The carbonyl groups are slightly non-linear, the

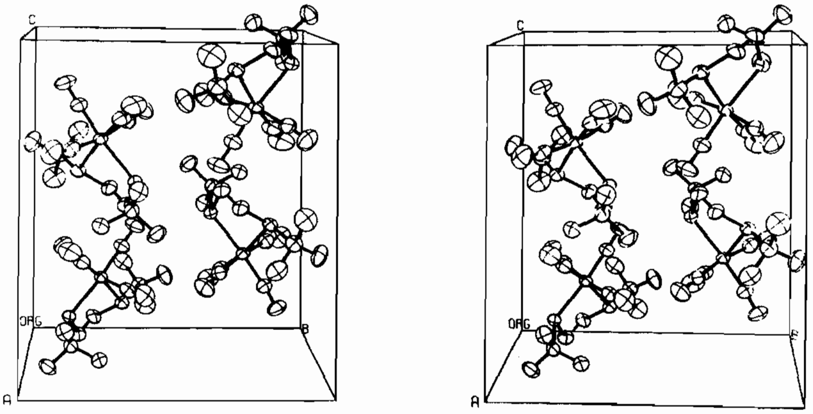


Fig. 3. A packing diagram of the molecule.

Cr–C–O angles being 174.7(4) and 171.7(4)° for the *cis*-carbonyl groups and 178.1(5) and 176.5(4)° for the carbonyls *trans* to the sulfurs. The angle between the mutually *trans* coordinated carbonyl groups is 169.8(2)°. The same trend was observed also by Brown [15] for other substituted complexes of chromium. Similar displacement of the mutually *trans* carbonyls from their ideal octahedral positions, leading to angles of 173.5(7) and 174.2(2)° was found by Kruger *et al.* [16], whereas others reported angles as low as 167.0(2)° [17]. Baker and Larsen [14] report an angle of 174.7(1)° and suggest that the bending of the carbonyl atoms may be influenced by repulsion from the lone pair electrons of the sulfur atoms.

A large deviation from the ideal octahedral environment is also observed for the S–Cr–S angle, where a contraction from 90° to 80.60(4)° occurs. This value is close to the angles found for compounds I and II but is significantly smaller than the value of 85.05(3)° observed for complex IV. As in the case of the W compounds, the contraction of the S–Cr–S angle is compensated for by an increase in *only one* of the S–Cr–C(*cis*) angles (S2–Cr–C4 being 99.3(1)°) while the other angle S1–Cr–C3, remains close to 90° (90.7(2)°). In complex IV, however, the contraction of the S–Cr–S angle is compensated equally between the two S–Cr–C(*cis*), angles, their values being 93.0(1) and 92.7(1)°. Since these deviations from the regular octahedral geometry are almost identical for the t-butyl substituents of both complexes (chromium and tungsten) but differ significantly from the slighter distortions observed for the ethyl chromium compound, it seems reasonable to assume that these variations are metal-independent and are mainly caused by the bulk of the ligand substituents. Shortest intra- and intermolecular distances between the t-butyl substituents and the carbonyl groups of compound III are presented in Table V (since the structure determinations of compounds I and II are less accurate, we refrain from presenting a similar table for these compounds). No short intramolecular distances were observed for compound IV [10]. It is noted that the steric interactions between the t-butyl substituent of S2 and carbonyls C4–O2 and C5–O3 are greater than those between the second t-butyl substituent and the other two carbonyls. Thus, it is probable that this strain is released by a greater displacement of the S2 atom resulting in a lowering of the S1–Cr–S2 angle and a corresponding increase of the C4–Cr–S2 angle. In view of this, it seems that the greater deviations from octahedral symmetry observed for the t-butyl substituent complexes of chromium and tungsten are due to the flexibility of the dithiaoctane ligand which can undergo slight conformational changes in order to minimize the steric interactions between the bulky t-butyl substituents and the carbonyl groups.

TABLE V. Shortest (up to 2.90 Å) Intra and Intermolecular Distances between the Carbonyl Groups and the t-Butyl Substituents (Å)[a].

C4---H82	2.62
C5---H91	2.62
C6---H123	2.81
O1---H81(54503)[b]	2.73
O2---H143(55503)	2.60
O2---H82	2.73
O2---H133(56404)	2.84
O3---H83(64503)	2.67
O3---H91	2.85

[a] Estimated standard deviation of the distances is about 0.07 Å. [b] The codes of the various moieties are those used in ORTEP [13]. The reference molecules (those whose coordinates are given in Table II) are denoted as 555, translations along the axes are specified by adding or subtracting integers from the reference code. The sequence of the symmetry elements is that given in the International Tables. Codes for the various hydrogens are 55501 unless otherwise specified.

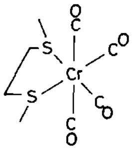
The chelate plane is defined by the Cr, S1, S2 and C2 atoms; the deviation of C1 from this plane being 0.787 Å. A distance of 0.771 Å was found for compound I. The angles at the carbon atoms within the chelate ring are approximately tetrahedral (111.4(4)) and 111.0(4)°). The angles about the sulfur atoms vary considerably, from 101.1(2) to 118.9(2)°, The Cr–S–C (t-butyl) angles being considerably greater than the others. This distortion may arise mainly from a bending of the bulky t-butyl substituents away from the neighboring carbonyl groups. A similar behavior was observed also by Baker and Larsen [14].

Since it is suggested that the variations in the deviations from ideal octahedral symmetry are metal-independent and are due mainly to the size of the substituents at the sulfur atoms additional structure determination of complexes of Cr, Mo and W having substituents with various degrees of bulkiness seems warranted. It also seems desirable to determine the size of torsional barriers in thes substances *via* ^{1}H and ^{13}C NMR measurements to determine whether or not they correlate with ligand bulk.

Structure and Mechanism

A key feature of the kinetics of chelate ligand displacement in these systems is competition between ring-reclosure and attack by L′ at a five-coordinate 'ring-opened' intermediate (governed by k_2 and k_3, Eqn. 2). As a consequence of a high 'effective concentration' [18] of the free end of the bidentate ligand the unimolecular rate of ring reclosure is often found to be much greater than the bimolecular rate of attack at the intermediate by L′ [19]. In the three complexes thus far studied by our group (I–III), significant distortion from octahedral geometry – smaller S–M–S angles and the unsymmetrical influence of this effect and of R on the equatorial plane containing the two sulfur atoms – can reasonably be interpreted as being responsible for the kinetically-observed inhibition of ring-reclosure.

Thus, it is of great significance that these distortions are smaller and more symmetrically disposed in $(EtSCH_2CH_2SEt)Cr(CO)_4$ [14]. It might be expected that unimolecular ring-closure would be more facile in this complex relative to that in (I–III). Unfortunately, the kinetics of ligand-displacement in this system has not been studied. For the very similar compound $(MeSCH_2CH_2SMe)Cr(CO)_4$ (V), which might be expected to be structurally-analogous to the ethyl analogue, the kinetics results for ring displacement suggest more facile ring reclosure [1].



(V)

Infrared evidence is consistent with geometrical differences between (III) and (V), and their tungsten analogues; real differences in the positions of carbonyl stretching absorptions due to carbonyls in the equatorial planes for these pairs have been noted. These differences are not observed for the motion of axial carbonyls [20].

The observation that in all three systems which have been studied (I, II and III) $k_2 \sim k_3$ (eqn. 2) suggests that the identity of the metal atom, whether Cr or W, has little influence on the observed distortion from octahedral geometry if the kinetics results may be considered a criterion for the extent of this distortion. Of course, the crystallographic data also support this conclusion in that they indicate that distortions are similar for these complexes in the solid state.

It will be of interest to extend further both kinetics and crystallographic studies to delineate more fully possible relationships between solid state structure and reactivity in solution in these complexes.

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