the cobalt. It is interesting that the Co frequencies are essentially invariant in the series $GeCl_3$, $GeBr_3$, GeI_3. In terms of a simple halogen σ effect as observed in the tin series, one would expect q_{zz} at cobalt to decrease in the order listed. The fact that this does not occur cannot, however, be accounted for in terms of d_π–d_π bonding from cobalt to germanium. In the absence of chlorine–germanium π bonding one would expect such an interaction to be greatest for $GeCl_3$, but a cobalt–germanium π interaction would lead to a *higher* q_{zz}, through depopulation of d_{xz} and d_{yz} on cobalt, contrary to the observed results. It must be concluded, therefore, that the essential constancy of q_{zz} in the halogermanium series is due to a variation in the germanium–halogen π bonding, in the order $Cl > Br > I$.

Acknowledgments.—The research at the University of California was supported by the Inorganic Materials Research Division, Lawrence Radiation Laboratory, under the auspices of the United States Atomic Energy Commission. The research at the University of Illinois was conducted with the support of the Materials Research Laboratory under the auspices of the Advanced Research Projects Agency of the Department of Defence. T. L. B. and J. L. K. wish to acknowledge the assistance of G. L. Kent and R. Anderson in the design and construction of the spectrometer.

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Organometallic Conformational Equilibria. II. The Nature of Bonding and Fluxional Character in Cycloheptatrienyl-π-cyclopentadienyldicarbonylmolybdenum[1]

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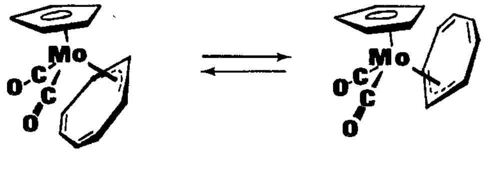
The low-temperature proton magnetic resonance spectrum and the stereochemical nonrigidity of $(C_7H_7)(C_5H_5)(CO)_2Mo$ are discussed. It is concluded that the principal pathway of rearrangement is a 1,2 shift of the metal about the cycloheptatrienyl ring. In addition to this rearrangement, a second process, the details of which are not certain, gives rise to four carbonyl stretching bands in the infrared spectrum; nevertheless, it appears that there is probably an equilibrium between two *trihapto*cycloheptatrienyl conformers.

Introduction

King[2,3] has proposed that in cycloheptatrienyl-π-cyclopentadienyldicarbonylmolybdenum the molybdenum atom is connected to the cycloheptatrienyl moiety *via* a π-allyl mode of attachment; *i.e.*, the compound contains a *trihapto*cycloheptatrienyl group.[4,5] This suggested the possibility of a conformational equilibrium analogous to that found in the π-$C_5H_5Mo(CO)_2$(π-allyl) systems.[1,6,7] Furthermore, in the room-temperature pmr spectrum, a single sharp resonance is observed for the C_7H_7 moiety. This paper describes the temperature dependence of the pmr spectrum and experiments designed to elucidate the rearrangement pathways responsible for the proton environment interchange which gives rise to the averaged single resonance.

Results and Discussion

An equilibrium between two conformers (such as Ia and Ib) manifests itself in the appearance of four carbonyl stretching modes in cyclohexane at 1966, 1960, 1911, and 1896 cm^{-1} (Figure 1), rather than the two carbonyl modes normally expected for a $Mo(CO)_2$ fragment.[8]



Ia Ib

Since the cycloheptatrienyl moiety shows a single resonance in the pmr spectrum at room temperature, it has been postulated that the compound is fluxional and rapidly rearranging on the nmr time scale.[2,3,9]

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(1) Part I: J. W. Faller and M. J. Incorvia, *Inorg. Chem.*, **7**, 840 (1968).

(2) R. B. King and A. Fronzaglia, *J. Am. Chem. Soc.*, **88**, 709 (1966).

(3) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **3**, 785 (1964).

(4) This nomenclature has been suggested by Cotton[5] and the Greek prefix of *hapto* indicates the number of carbon atoms in the ring which are connected to the metal atom.

(5) F. A. Cotton, *J. Am. Chem. Soc.*, **90**, 6230 (1968).

(6) R. B. King, *Inorg. Chem.*, **5**, 2242 (1966).

(7) A. Davison and W. C. Rode, *ibid.*, **6**, 2124 (1967).

(8) Assuming equal molar absorptivities, the equilibrium constant obtained from the ratio of the 1896- and 1911-cm^{-1} bands was 0.35.

(9) Fluxional organometallic molecules have been reviewed by F. A. Cotton, *Accounts Chem. Res.*, **1**, 257 (1968).

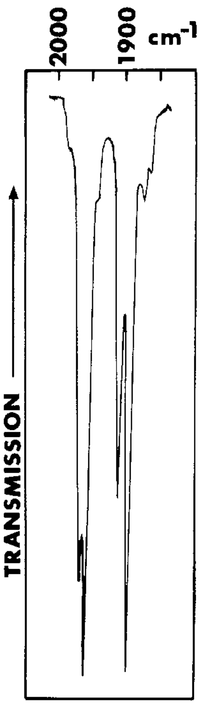
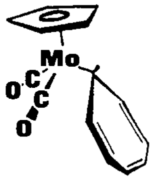


Figure 1.—The infrared spectrum of $(C_7H_7)(C_5H_5)Mo(CO)_2$ in cyclohexane in the region of the CO stretching fundamental modes.

Considering the infrared evidence above, one would anticipate that the stereochemical nonrigidity responsible for the single line in the pmr spectrum would be a combination of rapid conformational equilibrium and rapid intramolecular rearrangement of each conformer.



II

In the pmr spectrum at low temperatures (−102 to −118°) one observes what is apparently the static spectrum (Figure 2) of one of the isomers consistent with the instantaneous structure of either Ia or Ib. However, one might also argue that the spectrum is more consistent with a σ-bonded or *monohapto*-C_7H_7 moiety (II). Nevertheless, independently of bonding considerations, one may assign the resonances of the cycloheptatrienyl ring (Figure 3). Spin-decoupling experiments show that resonance (4) (from Figure 2) is strongly coupled to (3), $J_{34} = 6.6$ Hz; (3) to (1), $J_{31} = 7.0$ Hz; and (1) to (2), $J_{12} = 4.9$ Hz. Since resonance (4) must be assigned to *a* (see Figure 3) on the basis of intensities, it follows that: (3) should be assigned to the adjacent protons *b*; (1) should be attributed to the protons adjacent to *b*, *i.e.*, *c*; and (2) must therefore be due to the *d* protons. Hence, one may with certainty assign (4) to *a*, (3) to *b*, (2) to *d*, and (1) to *c*.

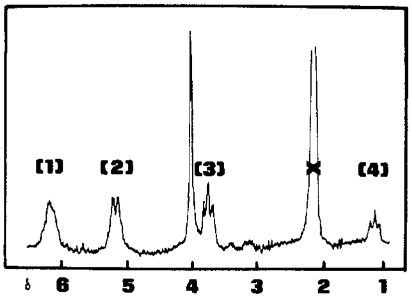


Figure 2.—The pmr spectrum of $(C_7H_7)(C_5H_5)Mo(CO)_2$ in a 2:1 mixture of CCl_2F_2 and toluene-d_8 at −107°. The resonances at δ 4.07 and 2.2 are attributed to the π-C_5H_5 group and a solvent impurity (toluene-d_7), respectively.

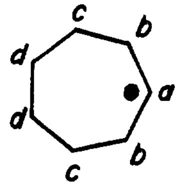


Figure 3.—A topological diagram (*i.e.*, no bond angles, bond orders, or other structural details implied) indicating labeling of the C_7H_7 ring protons relative to the position(s) of attachment of the molybdenum atom. The diagram above, as well as the structures given for I, is schematic in nature. In Ia and Ib the plane of the free diene portion of the molecule should make a sizable angle with the plane of the allyl portion.

Table I

The Solvent and Temperature Dependence of the Nmr Spectrum of $(C_7H_7)Mo(C_5H_5)(CO)_2$[a]

	2:1 CCl_2F_2–toluene-d_8		1:1 CCl_2F_2–toluene-d_8		$CHCl_2F$		1:1 $CHCl_2F$–toluene-d_8	
	−107°	−17°	−102°	+10°	−118°	+10°	−118°	+9°
(1)	6.20		6.47		6.50		6.36	
(2)	5.19		5.46		5.40		5.36	
		4.66		4.69		5.02		4.84
(3)	3.76		3.84		4.59		4.37	
(4)	1.13		1.20		2.32		2.00	
C_5H_5	4.07	4.61	4.04	4.45	5.36	5.16	5.09	5.02

[a] All chemical shifts are given as parts per million downfield from tetramethylsilane.

Having the assignments at his disposal, one may confidently assert that the major pathway of rearrangement is *via* a 1,2 shift by noting that resonance (2), which was assigned to *d*, remains narrower than the other resonances as the rearrangement rate is increased by raising the temperature (see Figures 4 and 5 and Table I).[10] That is, in a sequence of 1,2 shifts the

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[10] The resonances show large variations in chemical shift with solvent (see Table I). The mixture of toluene-d_8 and CF_2Cl_2 used for the spectrum in Figure 2 allows the best compromise of acceptable solubility, minimum viscosity broadening, and good signal-to-noise ratios for the observation of all five resonances without overlapping of resonances. Since the compound was only slightly soluble in 2:1 CF_2Cl_2–toluene mixtures, other solvent mixtures were used to illustrate the collapse of the spectrum because they afforded a much greater solubility and consequently a greater signal-to-noise ratio.

TABLE II

THE EXCHANGE OF SITES FOR DIFFERENT REARRANGEMENT PATHWAYS

1, 2 Shift

$$d \text{ narrower} \quad \begin{bmatrix} a \\ b \\ c \\ d \end{bmatrix} \rightarrow \begin{bmatrix} b \\ a,\ c \\ b,\ d \\ c,\ \mathrm{d} \end{bmatrix}$$

1, 3 Shift

$$b \text{ narrower} \quad \begin{bmatrix} a \\ b \\ c \\ d \end{bmatrix} \rightarrow \begin{bmatrix} c \\ \mathrm{b},\ d \\ a,\ d \\ b,\ c \end{bmatrix}$$

1, 4 Shift

$$c \text{ narrower} \quad \begin{bmatrix} a \\ b \\ c \\ d \end{bmatrix} \rightarrow \begin{bmatrix} d \\ c,\ d \\ \mathrm{c},\ b \\ a,\ b \end{bmatrix}$$

lifetime of a proton in environment *d* is longer, and, therefore, a narrower resonance will be observed at intermediate stages of collapse of the spectrum as the temperature is raised. One may observe that pathways other than movement of the metal to the immediately adjacent carbon atom in the ring (*i.e.*, this 1,2 shift) will cause the lifetimes of the protons in other environments to be longer (see Table II). This qualitative assessment of the pathway can be further verified by a Kubo–Sack matrix calculation of the line shape as a function of rate and mechanism,[11–15] a comparison of which is shown in Figure 6.[16]

The unexpected location of a resonance between 1 and 2 ppm below TMS and the appearance of apparently only one AA'BB'CC'X spectrum for the cycloheptatrienyl moiety indicate that the possible instantaneous structures of the molecule should be examined

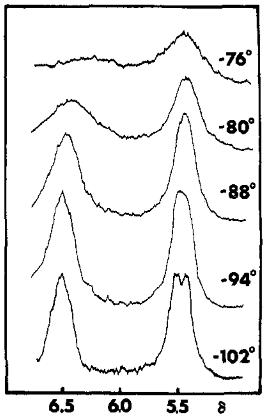

Figure 4.—The temperature dependence of resonances (1) and (2) in a mixture of CCl_2F_2 and toluene-d_8.

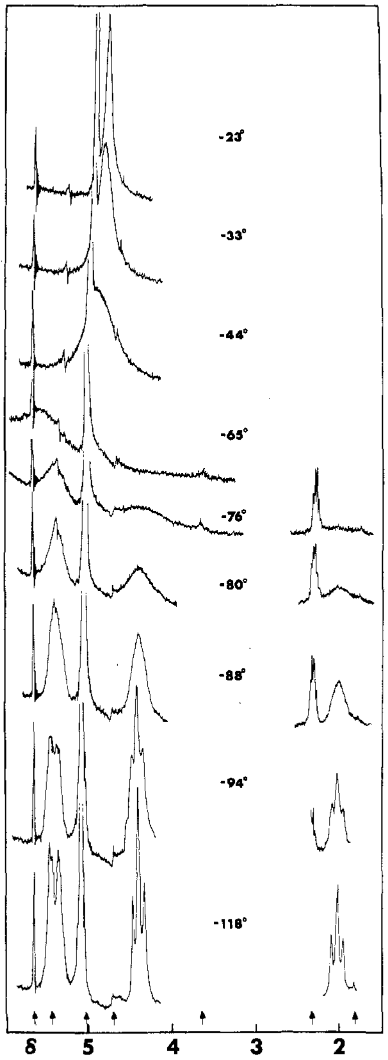

Figure 5.—The temperature dependence of the pmr spectrum in a 1:1 mixture of $CHCl_2F$ and toluene-d_8. The resonances of interest are: (2), δ 5.36[2]; (π-C_5H_5), δ 5.09; (3), δ 4.37; (4), δ 2.00. Extraneous resonances are indicated by arrows and are due to solvent impurities at δ 1.8, 3.6, and 5.0; toluene-d_7 at δ 2.3; $C^{13}HCl_2F$ at δ 5.6; and spinning side bands at δ 4.7 and 5.5.

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[11] The qualitative determination of the rearrangement mechanism on the basis of lifetimes in environments has been outlined in previous papers.[12,13] The Kubo–Sack matrix approach has been used several times before in dealing with fluxional organometallic molecules.[12,13] I am indebted to Professor Martin Saunders for supplying a program which carried out the matrix manipulations.

[12] M. J. Bennett, F. A. Cotton, A. Davison, J. W. Faller, S. J. Lippard, and S. M. Morehouse, *J. Am. Chem. Soc.*, **88,** 4371 (1966).

[13] W. K. Bratton, F. A. Cotton, A. Davison, and A. Musco, and J. W. Faller, *Proc. Natl. Acad. Sci. U. S.*, **58,** 1324 (1967).

[14] G. M. Whitesides and J. S. Fleming, *J. Am. Chem. Soc.*, **90,** 2855 (1967).

[15] F. A. Cotton, J. W. Faller, and A. Musco, *ibid,*. **90,** 1438 (1968).

[16] The determination of the mechanism should be reliable, regardless of the interpretation of the bonding; however, determination of rates will depend upon the nature of the equilibria between the isomers. Assuming that there are two isomers with the resonances superposed, the quantitative value of the rates may be slightly different for each isomer, even though the qualitative aspects of the rearrangement pathways are the same. One can attempt to determine the rates as a function of temperature using the Kubo–Sack matrix method and matching calculated and observed line shapes. Obviously the rates obtained will have to be interpreted with caution particularly with the large systematic errors which are likely to be introduced by the great dependence of chemical shifts on solvent. The following approximate rate constants for the molybdenum atom leaving site *a* (in sec^{-1}) were determined: −88°, 20; −80°, 45; −76.4°, 80; −44°, 18,200; −33°, 34,000; −22.5°, 83,800. The activation energy of 12.5 ± 0.6 kcal/mol and log *A* of 16.0 ± 0.6, which one obtains from a least-squares fit to the Arrhenius equation, should be regarded with some suspicion because of the possibility of systematic error and the rather high value of log *A*. Using absolute rate theory, the free energy of activation varies between 8.8 and 9.7 kcal/mol, if calculated from the above rates.

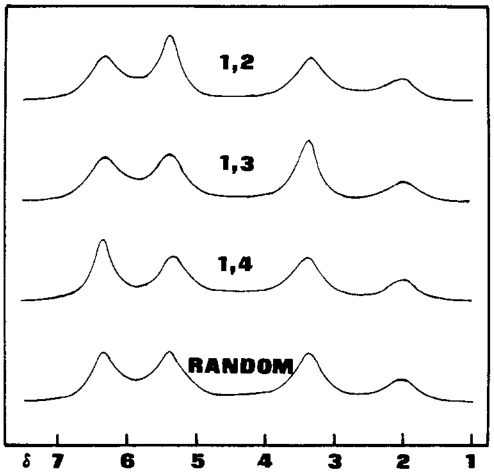

Figure 6.—Calculated spectra for different modes of rearrangement assuming a first-order rate constant of 100 sec^{-1} for the molybdenum atom leaving site *a*.

carefully. Hence, we wish to determine if the spectrum is consistent with the most plausible structures—Ia, Ib, II, or a mixture of them.[17] Specifically, upon weighing the evidence, one must choose between the alternatives: an equilibrium mixture of Ia and Ib or an equilibrium mixture of conformers of II.

The similarity of the infrared spectrum of the cycloheptatrienyl derivative to that of the π-allyl derivative strongly suggests an equilibrium between Ia and Ib. However, all attempts to resolve the pmr spectrum into two superimposed spectra consistent with a mixture of Ia and Ib proved fruitless.[18] Furthermore, the equilibrium constant does not appear to vary significantly with solvent or temperature;[19] hence, to rationalize the low-temperature pmr spectrum, one may ascribe the simplicity of the spectrum to accidental overlapping of all of the resonances. Furthermore, the appearance of the resonance of the single proton at high field might be attributed to shielding of the proton by the proximity of the uncoordinated double bonds.

A *monohapto*cycloheptatrienyl moiety is more consistent with the nmr on the basis of chemical shifts, for which one would expect a single resonance at high field for the proton at the carbon atom attached to the metal. Hindered rotation around the metal–carbon bond could give rise to the infrared spectrum as observed in iron derivatives, such as π-$C_5H_5Fe(CO)_2SO_2CH_3$,[20] which should bear some structural similarities to the molybdenum compound. These barriers to rotation are generally quite low and do not give rise to temperature-dependent pmr spectra.[21] The major objection to a structure containing the *monohapto*cycloheptatrienyl ligand (II) is that it violates the inert-gas rule for molybdenum. However, violations of this rule in molybdenum complexes have been reported in trispyrazolylborate[22] and indenyl[23] derivatives. To test this possibility, a solution of $(C_7H_7)(C_5H_5)Mo(CO)_2$ was treated with carbon monoxide and pyridine, but the appearance of the carbonyl region of the infrared spectrum was not altered. An electron-deficient molybdenum atom would be expected to coordinate these donors readily if it were sterically possible; hence, one tends to favor an inert-gas structure. Attempts to determine the nature of the equilibrium by preventing the 1,2 shift rearrangement *via* a "fixing" of the diene fragment by Diels–Alder addition were inconclusive.[24] Nevertheless, although improbable, it still appears possible that the instantaneous configuration of the molecule may be that of structure II.

The selection between the two alternatives may be aided by the report of Cotton and Reich[25] that upon irradiation in the presence of iron carbonyl one obtains $(C_5H_5)Mo(CO)_2(C_7H_7)Fe(CO)_3$. The infrared spectrum and low-temperature nmr spectrum of this iron tricarbonyl derivative are consistent with a single isomer, similar to Ia or Ib with the diene fragment of the cycloheptatrienyl ligand coordinated to the $Fe(CO)_3$ group. Of particular note is that the resonance attributed to *a* now appears at more than 5 ppm below TMS. These results could be construed to favor either alternative by: (1) implying that steric factors have forced the equilibrium between Ia and Ib toward the predominance of a single isomer and that the conformation of the ring has been altered to remove the *a* proton from the shielding region of the diene fragment; or (2) suggesting that coordination of the diene fragment has so altered the structure of the C_7H_7 ring that *trihapto* coordination is favored when the diene is coordinated and *monohapto* coordination is favored when the diene is free.

Therefore, in addition to the 1,2 shift rearrangement, the data generally favor an equilibrium between

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(17) Other less likely possibilities, such as norcaradienyl valence isomers, were considered but dismissed on the basis of chemical shift or energetic grounds.

(18) Large chemical shift differences between the resonances of Ia and Ib are not expected. Assuming the analogous resonances in the different isomers of π-allyl-π-cyclopentadienyldicarbonylmolybdenum would be approximately the same in the cycloheptatrienyl derivative, one would expect the following magnitude of chemical shift differences: *a*, 0.00; *b*, 0.07; π-C_5H_5, 0.04. Many solvent mixtures were used and in none was it feasible to observe any additional splitting of either the π-C_5H_5 resonance or resonance (3). Assuming activation energies of isomer interconversion ($Ia \rightleftharpoons Ib$) to be of approximately the same magnitude as those in the π-allyl and π-methallyl derivatives, one would expect to resolve separate sets of resonances for each conformer below a temperature of 5°. In particular, the infrared spectrum of the cycloheptatrienyl compound shows four carbonyl stretching bands in methylcyclohexane. In this solvent at −25° a half-height resonance width of the cyclopentadienyl group of 0.4 Hz at 100 MHz was obtained and no indication of two superimposed cyclopentadienyl resonances was observed.

(19) The equilibrium constant does not vary significantly over a range of −10 to +60° as determined by comparing the intensity ratios of the infrared carbonyl stretching bands in *n*-octane solution. The polarity of solvents can alter the equilibrium constant and it is difficult to assess the size of this effect. A solution of more than 5% methylene chloride in cyclohexane broadens the carbonyl bands so that the bands of the individual isomers are not observed; however, there is no significant variation in the band intensities between 5% methylene chloride and pure cyclohexane. In the corresponding allyl derivatives solvent effects appear capable of altering the equilibrium constant by as much as a factor of 2.

(20) J. P. Bibler and A. Wojcicki, *J. Am. Chem. Soc.*, **88**, 4862 (1966).

(21) J. W. Faller and A. S. Anderson, unpublished observations.

(22) S. Trofimenko, *J. Am. Chem. Soc.*, **90**, 4754 (1968).

(23) R. B. King and M. B. Bisnette, *Inorg. Chem.*, **4**, 475 (1965).

(24) Although addition products were formed with dienophiles, the formation of chemically similar isomers (presumably *endo* and *exo*) makes separation difficult and any position based on the nmr interpretation of the mixtures precarious.

(25) F. A. Cotton and C. R. Reich, *J. Am. Chem. Soc.* **91**, 847 (1969).

two isomers containing h^3-C_7H_7 moieties (Ia and Ib); however, on the evidence at hand one cannot eliminate the possibility of an equilibrium between conformers of an h^1-C_7H_7 derivative. It appears that a crystal structure determination may be necessary to distinguish between these alternatives.

Experimental Section

The compound was prepared by the method of King and Bisnette.[3] The solvents were commercially available: $CHCl_2F$, CCl_2F_2, Matheson; toluene-d_8, Merck and Co. The Freons were purified by trap-to-trap distillation before use. Particular attention must be paid to this purification to avoid impurities which have nmr spectra surprisingly similar to some of the resonances observed in metal–olefin derivatives. Especially poor in this respect is $CHCl_2F$, which has impurities giving resonances at δ 0.89, 1.33, 4.19, and 5.23 at 0°. All of these impurity resonances except that at δ 5.23 can be efficiently removed by trap-to-trap distillation.

The spectra were recorded at 100 MHz using a Varian Associates HA-100 instrument with a variable-temperature probe. The temperature was measured with a thermocouple placed in an nmr tube at the level of the receiver coil. Variable-temperature infrared spectra were obtained with a modified Barnes Engineering temperature cell and a Perkin-Elmer 421 spectrometer.

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Absolute Configurations of 1,10-Phenanthroline and 2,2′-Bipyridine Metal Complexes

BY J. FERGUSON, C. J. HAWKINS, N. A. P. KANE-MAGUIRE, AND H. LIP

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The nonempirical circular dichroism method for determining the distribution of chelate rings in dissymmetric metal complexes, which is based on long-axis-polarized $\pi \rightarrow \pi^*$ ligand transitions, is reviewed and applied to some cobalt(III), chromium(III), and nickel(II) 1,10-phenanthroline and 2,2′-bipyridine complexes. It is found that the relative energies of the split components of these transitions for the bis and tris complexes are dependent on the metal ion and cannot be determined by the simple dipole–dipole interaction theory. However, the sign of the splitting was determined experimentally by comparing the centers of gravity of the absorption bands for the bis and tris complexes with those of the equivalent mono complexes. The absolute configurations determined in this way are compared with those from the empirical method based on the d–d transitions and are found to be in good agreement.

The chirality of the distribution of chelate rings in dissymmetric metal complexes has been determined by circular dichroism studies using two fundamentally different approaches. The most general method is an empirical one which has been developed on the assumption that the signs of the Cotton effects of magnetic dipole allowed d–d transitions are dependent upon the distribution of chelates and independent of the ligand atoms and the chelate ring parameters such as the angle between the coordinate bonds.[1,2] Mason and his coworkers have developed an alternative nonempirical approach based on ligand transitions and have applied it to tris complexes of 1,10-phenanthroline,[3,4] 2,2′-bipyridine,[4] acetylacetonate,[5] and catecholate.[6] Bosnich has extended the application to the bis complex *cis*-bis(pyridine)bis(1,10-phenanthroline)ruthenium(II).[7] Recently Mason and Norman have attempted[8] to correlate the two approaches for d-$Co(phen)_3^{3+}$ and also have studied mixed phenanthroline and bipyridine complexes of osmium.[9]

The crucial issue in the application of the nonempirical method lies in the assignment of the components of the ligand absorption bands for which the circular dichroism has been measured. For the tris complexes, electrostatic interactions between the three ligands remove the threefold degeneracy associated with electronic excitation energy on one of the ligands. As a result, there are two excited states, an A_2 state and a twofold degenerate E state, within the D_3 symmetry of the complex. For the bis complexes, the corresponding states are A and B for the C_2 symmetry of the

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(1) A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, 2883 (1965).

(2) C. J. Hawkins and E. Larsen, *Acta Chem. Scand.*, **19**, 1969 (1965).

(3) A. J. McCaffery and S. F. Mason, *Proc. Chem. Soc.*, 211 (1963).

(4) A. J. McCaffery, S. F. Mason, and B. J. Norman, *ibid.*, 259 (1964).

(5) E. Larsen, S. F. Mason, and G. H. Searle, *Acta Chem. Scand.*, **20**, 191 (1966).

(6) J. Mason and S. F. Mason, *Tetrahedron*, **23**, 1919 (1967).

(7) B. Bosnich, *Inorg. Chem.*, **7**, 178 (1968).

(8) S. F. Mason and B. J. Norman, *Inorg. Nucl. Chem. Letters*, **3**, 285 (1967).

(9) S. F. Mason and B. J. Norman, *Chem. Phys. Letters*, **2**, 22 (1968).