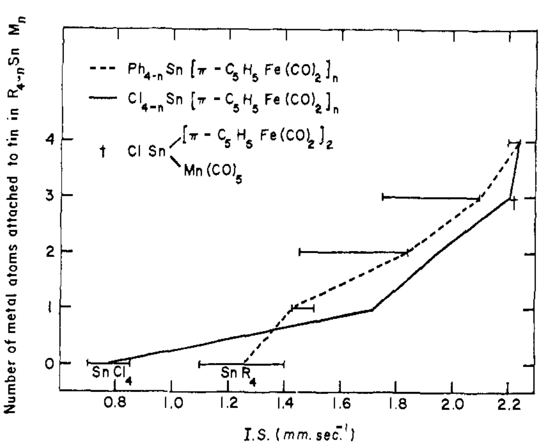
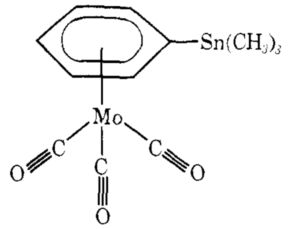


Figure 1. Sn^{119m} Mössbauer isomer shift *vs.* transition metal substitution at tin in $R_{4-n}SnM_n$ and $X_{4-n}SnM_n$. Horozontal bars represent the range of values reported.

splittings (QS) in the range 1.15–1.43 mm/sec are resolved in the Sn^{119m} Mössbauer spectra of several organotin derivatives of the type $R_{4-n}SnM_n$ (values in mm/sec): $PhSn[Co(CO)_4]_3$ (1.28 ± 0.12),[5a] $Ph_2Sn[Co(CO)_4]_2$ (1.43 ± 0.12[5a] and 1.15 ± 0.07[5b]), $Ph_2Sn[Co(CO)_4][Mn(CO)_5]$ (1.15 ± 0.07),[5b] $Ph_3Sn[Co(CO)_4]$ (1.0 ± 0.07),[5b] $(CH_3)_2Sn[Fe(CO)_4]_2Sn[Fe(CO)_4]_2Sn(CH_3)_2$ (1.24 ± 0.10),[5c] $(CH_3)_2Sn[Fe(CO)_4]_2Sn(CH_3)_2$ (1.22 ± 0.10),[5c] $(n\text{-}Bu)_2Sn[Fe(CO)_4]_2Sn(n\text{-}Bu)_2$ (1.26).[5d] According to one accepted view, resolvable QS in asymmetric organotin(IV) compounds arises only when population of empty tin 5d orbitals by electron pairs from adjacent atoms can take place.[6,7] Thus the observation of resolvable QS in these compounds is *prima facie* evidence for (d → d)-π bonding.

However, in systems of the type $R_{4-n}SnX_n$, where X = halogen or a ligand containing nitrogen, oxygen, or sulfur, $|\psi_{ns}(0)|^2$ and IS decrease generally with increasing n. The consequence of populating the tin 5d orbitals by (p → d)-π bonding in these systems would be the further reduction of $|\psi_{ns}(0)|^2$ by shielding. Thus both effects change IS in the same direction. In the tin–transition metal systems, on the other hand, IS would be expected to increase with the substitution of metal atoms in $R_{4-n}SnM_n$ or $X_{4-n}SnM_n$, but decrease as a result of the shielding introduced by π bonding with the transition metal. It is clear from the data presented in Figure 1 that if (d → d)-π interactions are present at all they do not predominate over the other factors responsible for the distribution of electrons at the tin atom.[8]

We have recently examined another type of tin-containing, transition metal compound, trimethyltinphenylmolybdenum tricarbonyl, which is monomeric [calcd for $C_{12}H_{14}O_3MoSn$: mol wt, 424; found: 431, 433 (osmometry in benzene),[9] 424 (mass spectrometry)] and which gives evidence of a small QS (<1.0 ± 0.12 mm/sec). One explanation of the appearance of this QS is based upon a (d → d)-π interaction between molybdenum and tin as has been postulated in the analogous silicon-containing ferrocenes.[10] If such an interaction led to five-coordination at the tin atom with concomitant changes in the symmetry of the trimethyltin group, these changes would be reflected in the infrared $\nu(SnC_3)$ and nmr $J(Sn^{119}\text{-}C\text{-}H^1)$.[11] However, infrared and nmr spectra show no significant differences from the trimethylphenyltin ligand itself,[12] and we conclude that the QS arises from an enhanced electric field gradient in the tin–phenyl bond brought about by the metal complexation.



Acknowledgments. Some tin–transition metal compounds were donated by Professors W. A. G. Graham of the University of Alberta, Edmonton, Alberta, Canada, and B. R. Willeford of Bucknell University, Lewisburg, Pa. Mössbauer spectra were recorded with the assistance of N. W. G. Debye. This work was supported by the Advanced Research Projects Agency and the National Science Foundation under Grants GP-5025 and GP-9249.

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Received July 1, 1968

The Energetics of Dissymmetric Interactions. Differential Solubility of *d*- and *l*- and *dl*-*cis*-$[Co(en)_2Cl_2]ClO_4$ and the Enantiomerization in (−)-2,3-Butanediol

Sir:

In principle the interactions of the enantiomeric forms of a dissymmetric molecule with a dissymmetric environment must be different.[1] Provided that the dissymmetric discrimination is sufficiently large, the effects known as asymmetric transformations and asymmetric syntheses are observed.[2–10] In all these cases

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the dissymmetric interactions cause the equilibrium between d and l forms to be displaced either (homogeneously) in solution or (heterogeneously) through the preferential precipitation of one enantiomer. Fundamental to an understanding of the nature of the displacements of the $d \rightleftharpoons l$ equilibrium (a process which we call *enantiomerization*) is a quantitative knowledge of the operational thermodynamic quantities. For inorganic systems this has become possible because of two recent observations. The first relates to the fact that the racemic *cis*-$[\mathrm{Co(en)_2Cl_2}]^+$ develops strong optical activity in the solvent (−)-2,3-butanediol, and the second concerns the use of solubility data in establishing the solvent activity coefficients for transfer of isomeric complex cations.[9,11] Thus, provided the complex can be resolved into two pure enantiomers (in this case (+)- and (−)-*cis*-$[\mathrm{Co(en)_2Cl_2}]\mathrm{ClO_4}$) and the enantiomers precipitated into identical crystalline forms of the same nonoptically active anion, then the cation solvation differences in the optically active solvent, which become manifest by the process of enantiomerization, must be reflected in the solubility of these salts.

We have prepared samples of the racemic *cis*-$[\mathrm{Co(en)_2Cl_2}]\mathrm{ClO_4}$ and of both the (+)- and (−)-*cis*-$[\mathrm{Co(en)_2Cl_2}]\mathrm{ClO_4}$ by previously published methods, and finally by crystallization from water by the addition of sodium perchlorate under identical conditions of temperature and concentration.[12,13] The spectra (absorption and circular dichroism) reproduced the published data, and the optical activity of the two forms was almost (5%) equal and opposite.[14,15] By using fine crystalline solids and vigorous shaking for periods between 2 and 20 min, reproducible (±5%) solubilities in the viscous (−)-2,3-butanediol solvent were obtained. These results are shown in Table I.

Table I. Solubility Data (30°)

Compound	Solubility, mol/l.	Solubility product
dl-cis-$[\mathrm{Co(en)_2Cl_2}]\mathrm{ClO_4}$	0.6×10^{-3}	0.35×10^{-6}
(+)-*cis*-$[\mathrm{Co(en)_2Cl_2}]\mathrm{ClO_4}$	2.6×10^{-3}	7.0×10^{-6}
(−)-*cis*-$[\mathrm{Co(en)_2Cl_2}]\mathrm{ClO_4}$[a]	1.25×10^{-3}	1.5×10^{-6}

[a] (−)-*cis*-$[\mathrm{Co(en)_2Cl_2}]\mathrm{ClO_4}$ refers to the enantiomer which has a negative circular dichroism at 6200 Å and positive circular dichroism at 5350 Å, *i.e.*, the P($\mathrm{C_2}$) absolute configuration.

The solution obtained from the racemic compound showed no detectable circular dichroism attributable to the *cis*-$[\mathrm{Co(en)_2Cl_2}]\mathrm{ClO_4}$ complex, and thus the solubility is that of the racemic complex. The results for the (+)- and (−)-*cis*-$[\mathrm{Co(en)_2Cl_2}]\mathrm{ClO_4}$ leave no doubt that enantiomerization of *cis*-$[\mathrm{Co(en)_2Cl_2}]^+$ will occur in (−)-2,3-butanediol provided there is no competing isomerization or solvolysis. We calculate that the establishment of the enantiomerization equilibrium

$$(-)\text{-}cis\text{-}[\mathrm{Co(en)_2Cl_2}]^+ \rightleftharpoons (+)\text{-}cis\text{-}[\mathrm{Co(en)_2Cl_2}]^+$$

in (−)-2,3-butanediol involves a free-energy change (ΔF°) of −0.9 kcal mol^{-1}.[16] In other words, provided there are no complicating reactions, an equilibrated solution of racemic *cis*-$[\mathrm{Co(en)_2Cl_2}]^+$ in (−)-2,3-butanediol will contain approximately 80% (+)-*cis*-$[\mathrm{Co(en)_2Cl_2}]^+$ and 20% (−)-*cis*-$[\mathrm{Co(en)_2Cl_2}]^+$. These results have been confirmed by the solutions formed from equilibrating an equal mixture of (+)- and (−)-*cis*-$[\mathrm{Co(en)_2Cl_2}]\mathrm{ClO_4}$ solids in (−)-2,3-butanediol. It was found, after an analysis of the circular dichroism spectra, that the equilibrated solutions contained (+)-*cis*-$[\mathrm{Co(en)_2Cl_2}]\mathrm{ClO_4}$ and (−)-*cis*-$[\mathrm{Co(en)_2Cl_2}]\mathrm{ClO_4}$ in the ratio of 4:1. This observation leads us to conclude that in all these experiments solubility saturation under reversible conditions has been achieved.

These results, which show that (+)-*cis*-$[\mathrm{Co(en)_2Cl_2}]^+$ is more stable, are contrary to a previous report on this system, and we have investigated this discrepancy more closely at lower temperatures where the details of the spectral changes can be more precisely studied.[9] By using racemic *cis*-$[\mathrm{Co(en)_2Cl_2}]\mathrm{B(C_6H_5)_4}$ we confirm that an enantiomerization occurs after the establishment of spectrophotometric equilibrium, but, when the reaction is carried out at room temperature, the spectrophotometric results clearly show that the initial reaction of the *cis* complex is predominantly solvolysis (note the initial isobestic at ~5200 Å), and that isomerization only occurs following this initiation which produces free chloride ions. The features of similar reactions where solvent intermediates are isolatable are well established.[17,18]

The eventual equilibrium mixture contains *trans*-$[\mathrm{Co(en)_2Cl_2}]^+$ and the solvolysis product which probably contains (−)-2,3-butanediol coordinated as a unidentate ligand and which, because of the magnitude of the circular dichroism spectrum, is most probably one form of the asymmetric ion *cis*-$[\mathrm{Co(en)_2Cl}$((−)-2,3-butanediol)$]^{2+}$. It is this last species which undergoes the enantiomerization reaction. That the enantiomerizing species cannot be *cis*-$[\mathrm{Co(en)_2Cl_2}]^+$ and is the *cis*-$[\mathrm{Co(en)_2Cl}$((−)-2,3-butanediol)$]^{2+}$ is strongly suggested by comparing the circular dichroism spectra of the reacting solutions and of the final equilibrium mixture with those of the freshly prepared enantiomers (+)- and (−)-*cis*-$[\mathrm{Co(en)_2Cl_2}]^+$. It was found that circular dichroism showed little solvent shift in (−)-2,3-butanediol compared with water solutions (Figure 1), and the observed displacements of the circular dichroism maxima (Figure 1) must be due to a new species.[15] These conclusions are further reinforced by a study of

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(16) $-RT \ln (K_{\mathrm{SP}(-)}/K_{\mathrm{SP}(+)}) = -\bar{\mu}^\circ_{\mathrm{S}(+)} + \bar{\mu}^\circ_{(-)} + \bar{\mu}^\circ_{\mathrm{ClO_4^-}} + \bar{\mu}^\circ_{\mathrm{S}(-)} - \bar{\mu}^\circ_{(+)} - \mu^\circ_{\mathrm{ClO_4^-}} = \bar{\mu}^\circ_{(-)} - \bar{\mu}_{(+)} = -RT \ln K = \Delta F^\circ$, where K_{SP^-} is the solubility product of (−)-*cis*-$[\mathrm{Co(en)_2Cl_2}]\mathrm{ClO_4}$ and $\bar{\mu}^\circ$ is the standard chemical potential. These equations hold provided the chemical potentials for the solids $\bar{\mu}^\circ_{\mathrm{S}(+)}$ and $\bar{\mu}^\circ_{\mathrm{S}(-)}$ refer to identical crystalline materials. K is the enantiomerization constant.

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(18) W. R. Fitzgerald and D. W. Watts, *Australian J. Chem.*, **19**, 935 (1966).

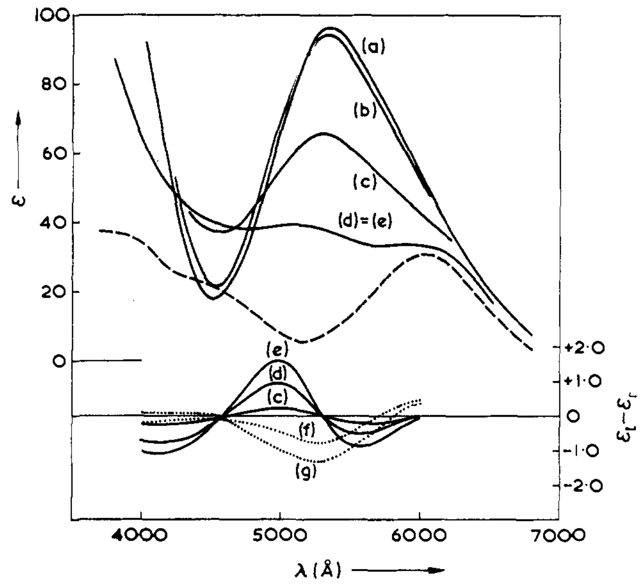

Figure 1. The changes in absorption and associated circular dichroism spectra (solid lines) of solutions of racemic *cis*-[Co(en)$_2$Cl$_2$]B(C$_6$H$_5$)$_4$ in (−)-2,3-butanediol at 30°. The time intervals are t = 0 (a); t = 0.33 hr (b); t = 4.00 hr (c); t = 19.00 hr (d); t = 96.00 hr (e). Also shown is the absorption spectrum of *trans*-[Co(en)$_2$Cl$_2$]$^+$ in (−)-2,3-butanediol (− − −) and the circular dichroism spectra (· · · · ·) of (+)-*cis*-[Co(en)$_2$Cl$_2$]$^+$ in water (f) and (−)-2,3-butanediol (g). The circular dichroism spectrum of (−)-*cis*-[Co(en)$_2$Cl$_2$]$^+$ in (−)-2,3-butanediol is enantiomorphic (±5%) to (g). The circular dichroism spectra c, d, and e were computed on the basis of unit concentration of *cis* species as calculated from ε(*cis* species at 5200 Å) = 90 and ε(*trans*-[Co(en)$_2$Cl$_2$]$^+$ at 5200 Å) = 6.0.

the solvent interchange reaction on the previously prepared complex *cis*-[Co(en)$_2$Cl(DMF)](ClO$_4$)$_2$ (DMF = dimethylformamide).[19] In all analogous solvent-interchange reactions, this complex reacts to an equilibrium of *cis*-solvent-containing species.[19] Furthermore, this complex in (−)-2,3-butanediol reacts to give an identical circular dichroism with that found for the *cis*-dichloro reaction and a visible absorption spectrum which is consistent with that found for the *cis*-dichloro reaction after the spectral contribution of *trans*-[Co(en)$_2$Cl$_2$]$^+$ has been subtracted.

The solubility measurements reported here and the consideration of the thermodynamic terms involved allow us to draw certain conclusions about the problem of attempting to resolve compounds through fractional crystallization from an optically active solvent.[16,7,8] We wish to make the following observations.

(i) Attempts at resolution through fractional crystallization from a solution containing equal numbers of *d* and *l* forms in an optically active solvent will only be successful under thermodynamically reversible conditions if the chemical potential of crystals containing equal numbers of *d* and *l* forms (racemic compound) is greater than that of crystals which contain exclusively only one hand. This is evident from the equation given in footnote 16 and is clearly not the case here because the less soluble form is the racemic compound (Table I). It might be possible in unfavorable thermodynamic circumstances to achieve resolution through kinetic differences which may become manifest by "seeding" one enantiomer.

(ii) In the absence of other complicating factors, allowing the enantiomerization to occur before the crystallization is attempted will tend to decrease the possibility of the racemic compound precipitating, but the chances of fractionally crystallizing the enantiomers are not greatly improved because the solution-stabilized form is also more soluble.

Acknowledgment. One of us (D. W. W.) wishes to acknowledge a Fulbright-Hays Australian-American Government Educational Committee Travel Grant and the invitation of Professor J. Lewis to work at University College, London.

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Received August 5, 1968

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Proposed Nomenclature for Olefin-Metal and Other Organometallic Complexes

Sir:

Hundreds of molecules containing polyolefins and other organic molecules bound to metal atoms are now known. More are being prepared every day, and both the olefins themselves and the manner of their attachment to the metal atom (or atoms) are becoming increasingly complex. Existing nomenclature is, in general, inadequate.

I wish to propose the following scheme for *all* compounds containing organic residues bound to metal atoms.[1] It is applicable whether bonding occurs through σ or π electrons or both. Indeed, one of its chief advantages is that it *avoids* implications and, hence, subjective judgments about bonding details; it simply gives a topological description of the structure by indicating the connexity of atoms. The rules are as follows.

(1) The olefin or other organic moiety is named and, if necessary, numbered as it would be when unattached to the metal atom(s). Hence, existing nomenclature and notation are employed as fully as possible. While the olefin whose name is chosen should be the one most similar in structure to that known or assumed to exist in the organometallic compound (usually, it will be the one from which the compound is prepared), the use of the name is not necessarily intended as a literal specification of the arrangement of multiple bonds in the organic moiety after it is part of the organometallic molecule.

(2) The adjectival prefix *hapto* (from the Greek *haptein*, ηαπτειν, to fasten, denoting contact or combination[2a]) is placed before the name of the olefin.[2b]

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(1) Unsaturated compounds which contain heteroatoms may also be accommodated (*cf.* example **10**), and the emphasis here on olefins is not intended to exclude such other cases as the scheme may appropriately and conveniently be applied to. The system is applicable to olefinic ligands of great complexity (*cf.* examples **9** and **16**) and heterocyclic ligands without modification so long as a name and numbering scheme are established for the ligand. It is indeed possible that the principle of using the *hapto* prefix with numerical modifiers may be applicable to more conventional polydentate ligands where the points of attachment to a metal atom need to be specified. For example, a compound where only the first, second, and fourth nitrogen atoms of a tetradentate tetramine ligand are coordinated could be so described.