

A projection view of the structure is shown in Figure 1A and bond distances and angles are shown in 1B. The dimeric cation has a crystallographic center of symmetry coincident with the central nitrogen atom of the bridging azide ion. The set of nitrogen donor configurations is the same as that determined previously for the trans-dichloro complex of **2** and that inferred from pmr studies on **3** and **4**.² No significant steric interactions involving the methyl groups are apparent. A unique feature of the structure reported here is the single end-to-end azide bridge between the two nickel complex moieties. To our knowledge, an azide bridge of this type has not previously been demonstrated by structural methods.⁹ The dimeric cation does not exist as a detectable species in solution. Dissociation to the planar form and to a pentacoordinate form takes place in water and nitromethane, respectively.

The structure determined for **5** is the one having the most favorable set of ring conformations. It seems reasonable to assume that the same set of nitrogen configurations is present in **6** and **7**. The extreme inertness of these complexes is due to their resistance toward folding along a N-Ni-N direction which is required as a preliminary step to ligand dissociation.¹⁰ Although kinetic and thermodynamic factors cannot be separated on the basis of the available data, clearly, the complex obtained from **1** and nickel ion has a kinetically controlled stereochemistry and it is probably thermodynamically less stable than **5**.

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Supplementary Material Available. A listing of atomic coordinates and structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-2625.

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F. Wagner, M. T. Mocella, M. J. D'Aniello, Jr.
A. H.-J. Wang, E. Kent Barefield*

W. A. Noyes Laboratory, School of Chemical Sciences
University of Illinois
Urbana, Illinois 61801

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Determination of Optical Purity Using Circular Polarization of Luminescence

Sir:

The method of circular dichroism (CD) is based on the property of optically active compounds to absorb

left and right circularly polarized light unequally. Both Samoilov¹ and Emeis and Oosterhoff^{2,3} independently showed this phenomenon of CD to have an analog in emission: an optically active molecule in solution^{2,3} or an optically active crystal of an optically inactive compound,¹ when excited, may preferentially emit left or right circularly polarized light. Their experiments¹⁻³ led to the introduction of the method of circular polarization of luminescence (CPL).

The method of CPL has many potential applications.^{2,4,5} One of them, the determination of optical purity, has been proposed by Eaton.⁶ The suggested procedure⁶ requires the measurement of CPL of the mixture of enantiomers of which the optical purity has to be determined and of the corresponding racemic mixture. However, this racemate may not always be at hand, e.g., if the mixture of enantiomers has resulted from the conversion of a natural product. Moreover, the effect in CPL of a racemate might be too small for measurement because it is a factor 0.5g smaller than the effect of the corresponding optically pure compound.^{4,7} It will be shown that the use of a racemate can be avoided.

Let us consider a homogeneous mixture of enantiomers, L and R, containing n_L molecules of L and n_R molecules of R. L is assumed to be the main component of this mixture. A quantity, p , related to the optical purity ($= 100p(\%)$) can then be introduced

$$p = \frac{n_L - n_R}{n_L + n_R}; \quad (p > 0) \quad (1)$$

Irradiation of the mixture with left circularly polarized (l) light gives rise to excited-state populations of L and R, n_L^* and n_R^*

$$\begin{aligned} n_L^* &= a_1 n_L \\ n_R^* &= a_2 n_R \end{aligned} \quad (2)$$

whereas irradiation with right circularly polarized (r) light of the same wavelength and intensity results in

$$\begin{aligned} n_L^* &= a_2 n_L \\ n_R^* &= a_1 n_R \end{aligned} \quad (3)$$

The coefficient a_1 is proportional to the intensity of the exciting light and to the molar extinction coefficient ϵ_1 pertaining to molecules of L absorbing l-light or to molecules of R absorbing r-light.⁹

The g factor⁷ can be expressed in our symbols

$$g = \frac{a_1 - a_2}{\frac{1}{2}(a_1 + a_2)} = \frac{\epsilon_1 - \epsilon_2}{\frac{1}{2}(\epsilon_1 + \epsilon_2)} \quad (4)$$

If e is defined as the fraction of the intensity of the light emitted by L which is l-light at the wavelength of

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(7) g has the conventional meaning of the ratio of the effects in CD ($\Delta\epsilon(\lambda)$) and in absorption ($\epsilon(\lambda)$) of the optically pure compound.⁸

(8) Irradiation takes place at wavelength λ , measurement of the emission phenomena at wavelength λ' . In order to keep the formulas as simple as possible both λ and λ' have been omitted from (1-10).

(9) (2) and (3) hold only if the Lambert-Beer law is valid.

observation, then the intensities of l-light and r-light, I_l and I_r , in the luminescence excited by l-light or r-light depend on the excited state populations according to

$$I_l \sim \{en_L^* + (1 - e)n_R^*\} \quad (5a)$$

and

$$I_r \sim \{(1 - e)n_L^* + en_R^*\} \quad (5b)$$

As a measure for the magnitude of optical activity in emission, g_{lum}^{10} has been introduced.^{2,3} For our mixture of enantiomers we define χ analogous to g_{lum}

$$\chi = (I_l - I_r)/\frac{1}{2}(I_l + I_r) \quad (6)$$

For an optically impure compound, χ must be dependent on the ellipticity of the exciting light. This follows from symmetry arguments. Thus χ for excitation with l-light (χ_l) will be unequal to χ for excitation with r-light (χ_r). The method proposed in this paper is based on this property. One derives

$$\chi_l = 2(2e - 1) \frac{a_1 n_L - a_2 n_R}{a_1 n_L + a_2 n_R} = g_{lum} \frac{p + \frac{1}{2}g}{1 + \frac{1}{2}pg} \quad (7)^{11}$$

and

$$\chi_r = g_{lum} \frac{p - \frac{1}{2}g}{1 - \frac{1}{2}pg} \quad (8)^{12}$$

Numerical values for χ_l and χ_r follow from CPL measurements.

There are three unknown quantities in (7) and (8). Thus in order to determine p we need a third equation. This equation is obtained by measuring CD and absorption of the mixture at the same wavelength as used for excitation. It is obvious that the ratio $\equiv \Phi$ of these effects is equal to pg

$$\Phi = pg \quad (9)$$

Combining (7), (8), and (9) yields an equation from which p can be solved

$$p^2 = \frac{\frac{1}{2}\Phi\chi_l + \chi_r + \frac{1}{2}\Phi(\chi_l - \chi_r)}{\chi_l - \chi_r + \frac{1}{2}\Phi(\chi_l + \chi_r)} \quad (10)$$

Once p is known it is also possible, of course, to determine the anisotropy factors g and g_{lum} which characterize the optical activity of a molecule in its ground state and in its excited state.

It must be emphasized that the measuring light in the determination of absorbance and CD should have the same band width and intensity distribution as the excitation light in the two luminescence experiments. This condition can be rather influential because in order to get a measurable signal-to-noise ratio in an actual CPL measurement, the slit width of the excitation monochromator is made much larger than in a usual absorption measurement.

The maximum accuracy in the determination of CPL, and thus in the determination of optical purity using the method presented in this paper, is obtained when the compound studied has both a large value of g_{lum} and a

(10) $g_{lum}(\lambda')$, the effect in CPL of the optically pure compound, has been defined as $g_{lum}(\lambda') = (I_l(\lambda') - I_r(\lambda'))/\frac{1}{2}(I_l(\lambda') + I_r(\lambda'))$, where $I_l(\lambda')$ is the intensity of the left circularly polarized component of the emitted light of wavelength λ' .

(11) To see the simple relation between $2(2e - 1)$ and g_{lum} one might consider the case of optical purity ($p = 1$: 100% L).

(12) Note that $100|(p + \frac{1}{2}g)/(1 + \frac{1}{2}pg)|$ and $100|(p - \frac{1}{2}g)/(1 - \frac{1}{2}pg)|$ have the meaning of optical purity in the excited state (in %).

high quantum yield in the luminescence. We suggest an application of this method to transition metal complexes where these requirements can be expected to be frequently met.

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W. C. M. C. Kokke

Department of Theoretical Organic Chemistry, University of Leiden
Leiden, The Netherlands

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Synthesis of "Superstoichiometric" Poly(carbon monofluoride)

Sir:

Poly(carbon monofluoride), $(CF_x)_n$, has been known since 1934 when Ruff and coworkers¹ prepared a gray compound of composition $CF_{0.92}$. In 1947 W. and G. Rudorff² reported a series of compositions $CF_{0.68}$ to $CF_{0.99}$, varying in color from black in the case of $CF_{0.68}$ through gray to white in the case of $CF_{0.99}$. Reviews of this chemistry have been published by Rudorff³ and Hennig,⁴ and it is perhaps due to the widespread review of these syntheses that the difficulty of preparing samples of stoichiometry higher than $CF_{0.8}$ is not generally appreciated even by fluorine chemists.

Poly(carbon monofluoride) (Figure 1) is a white compound, often reported to be explosive and unstable but found in this work to be stable in air to temperatures up to at least 600°. In fact, poly(carbon monofluoride) is the most thermally stable fluorocarbon polymer known. It decomposes upon heating at 800° or under a high vacuum at 580° to form a series of polyolefinic-fluorocarbons.⁵ The compounds with compositions in the range of $CF_{0.68}$ to $CF_{0.8}$ are nearly black. The $CF_{0.8}$ to $CF_{0.95}$ compounds become gray and the $CF_{0.95}$ to $CF_{1.12}$ develop into a snow white solid. The earlier syntheses^{1,2} report that poly(carbon monofluoride) may be prepared by passing fluorine over graphite at 450–600° for several hours. In some cases hydrogen fluoride is used as a catalyst.² Using these methods, a gray material of stoichiometry $CF_{0.68}$ to $CF_{0.8}$ is normally obtained.

Careful control of the reaction temperature at higher temperatures than previously reported was necessary to reproducibly obtain a completely fluorinated pure white material. One to one and a half grams of graphite were spread uniformly over the bottom of a 6-in. boat. The boat was placed in a 1-in. nickel tube heated by a resistance furnace and the furnace was allowed to warm to 200° for about 1 hr while helium was passed over the sample at a rate of 4 cm³/min to drive oxygen and moisture from the sample and reaction chamber. At the end of this period the furnace was

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