it been characterized spectroscopically. Our interest in the family of cyclic conjugated chlorocarbons[5] $C_nCl_n^{\pm m}$ has led us to prepare a series of solid salts: $Tl^+C_5Cl_5^-$ (**1**); $Tl^+C_5Cl_5^-\cdot 2C_6H_5CH_3$ (**2**); $R_4N^+C_5Cl_5^-$, where R = n-C_3H_7 (**3a**), n-C_4H_9 (**3b**), or n-C_7H_{15} (**3c**); $(C_2H_5)_3NH^+C_5Cl_5^-$ (**4**); $(n\text{-}C_4H_9)_4P^+C_5Cl_5^-$ (**5**); and $C_5H_5NCH_3^+C_5Cl_5^-$ (**6**). All but **6** are white or colorless salts; **6** is yellow. All are unstable at room temperature, and must consequently be handled by special techniques.

The thallium(I) salts are precipitated by adding a solution of thallium(I) ethoxide to a solution of 1,2,3,4,5-pentachlorocyclopentadiene (C_5Cl_5H) at $-78°$. If the solvent is hexane, **1** precipitates; from toluene, the adduct **2** crystallizes. The salts **3a**, **3b**, and **3c** may be precipitated at $-78°$ from methanol by (a) adding a solution of the quaternary ammonium hydroxide to C_5Cl_5H, or (b) adding lithium methoxide to a solution of the quaternary ammonium halide and C_5Cl_5H. **5** and **6** are prepared analogously. **4** may be precipitated from ether by adding triethylamine to C_5Cl_5H at $-78°$.

We also find that stable mercury(II) derivatives of the $C_5Cl_5^-$ anion can be prepared, and wish to report the following: $Hg(C_5Cl_5)_2$ (**7**); C_5Cl_5HgCl (**8**); $C_5Cl_5HgCl\cdot HgCl_2$ (**9**); and $C_6H_5HgC_5Cl_5$ (**10**). Compounds **7**, **8**, and **9** may be prepared by the action of **1** on $HgCl_2$ in THF at $-78°$ in the mole ratios 2:1, 1:1, and 1:2, respectively. The reaction of **1** with C_6H_5HgCl in ether at $-78°$ gives **10**. Unlike the salts, the mercury compounds are stable at room temperature, and have properties indicating that the $Hg-C_5Cl_5$ bond is σ in nature.

Infrared Spectra. Spectra of Nujol mulls of **3b** and **3c** were obtained between 4000 and 250 cm^{-1}. After deleting the cation bands, only two frequencies remained, 1415 (s) and 679 cm^{-1} (s). These disappeared on repeated scanning, as the salt decomposed. Similarly the spectrum of **2** in chloroform solution at $-55°$ shows bands at 1408 (m) and 659 cm^{-1} (s). For any symmetric $(CX)_n$ species, only four vibrational modes are expected to be infrared active,[6] one ring mode and three C–X modes. In hexachlorobenzene the four frequencies are reported at 1345, 694, 217, and 171 cm^{-1}.[7] Hence the spectrum is consistent with a symmetric $(CCl)_5^-$ species.

As expected for the lower symmetry in σ-bonded $C_5Cl_5^-$, the spectra of the mercury compounds contain many more frequencies. Thus the absorptions of **7** (Nujol mull) occur at 1576 (s), 1560 (sh), 1250 (vs), 1200 (m), 1126 (s), 974 (w), 950 (m), 768 (w), 724 (s), 699 (m), 654 (m), and 518 cm^{-1} (vw).

Nuclear Quadrupole Resonance (Nqr) Spectra. The ^{35}Cl nqr spectra of **2**, **5**, and **6** were recorded at 77°K. **5** shows five signals of approximately equal intensity at 35.196, 35.285, 35.334, 35.503, and 35.683 MHz. Similarly, **6** shows lines at 35.016 (intensity 3) and 35.590 MHz (intensity 2). **2** shows a very complex spectrum of about 17 lines, all within the relatively narrow range of 35.95–36.71 MHz. The patterns are consistent with chemical equivalence, but crystallographic nonequivalence, of the chlorines. The frequencies are shifted quite substantially from those in hexachlorobenzene[8] (38.381, 38.452, 38.492 MHz). Evidently the excess negative charge in the ring is repelled by the lone pairs of the five chlorines, giving a more ionic C–Cl bond and hence a lower nqr frequency. This is also consistent with the reducing nature of the anion, and leads to the prediction that, unlike quite a few chlorocarbons, the $C_5Cl_5^-$ anion should be a charge-transfer *donor*. That this is the case is indicated by the yellow color of the salt **6**, in which the cation is a charge-transfer acceptor.

The nqr spectra of the mercury compounds **7–10** span a much larger frequency range, consistent with the nonequivalence of the chlorines. As an example, **7** shows seven absorptions in the range 36.26–37.06 MHz, assignable to the vinylic chlorines, and two frequencies at 38.86 and 39.06 MHz, assignable to the allylic chlorines. Compounds **8–10** show more complex spectra, but all have resonances in both the vinyl and allyl ranges with relative intensity 4:1.

Acknowledgment. The authors thank the National Institutes of Health for partial financial support of this work.

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Circular Dichroism Induced in Symmetric Cations by Dissymmetric Anions in the Solid State

Sir:

Recently we described a number of effects which were observed when symmetric molecules or racemic molecules were placed in an optically active medium. It was found that the symmetric ion $[PtCl_4]^{2-}$ showed circular dichroism when dissolved in optically active 2,3-butanediol,[1] and similar effects were seen with certain organic ketones and transition metal complexes.[2] Moreover, for the inorganic systems, not only was optical activity induced in the symmetric or racemic systems, presumably through dissymmetric solvation, but the equilibrium constant for the *d* and *l* forms was displaced from unity in the optically active medium.[3] We wish to describe here yet another related phenomenon which is observed in the solid state and which has a significance over and above its observation for the first time.

If the ammine groups freely rotate in the ion $[Co(NH_3)_6]^{3+}$, it is incapable of resolution into optical isomers. However, when the cation is precipitated as the tri[(+)-α-bromocamphor-π-sulfonate] [(+)BCS] salt, $[Co(NH_3)_6]((+)BCS)_3$, the solid dispersed in pressed KBr disks displays clearly detectable circular dichroism in the regions of the first magnetic-dipole-allowed transitions, $^1A_{1g} \rightarrow {}^1T_{1g}$, of the central cobalt(III) ion (Figure 1). Similar effects are observed for the *trans*-$[Co(en)_2Cl_2]$(+)BCS, and *meso-trans*-$[Co(2,3,2\text{-tet})Cl_2]$(+)-BCS salts (Figure 2) (where en = ethylenediamine and 2,3,2-tet = $NH_2(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$). In all cases no detectable circular dichroism was observed

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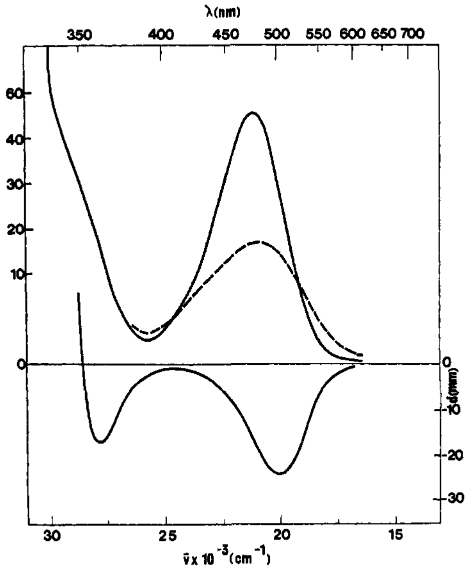

Figure 1. The aqueous-solution (——) and diffuse-reflectance (- - -) absorption spectra and the KBr disk (2%) circular dichroism spectrum of the $[Co(NH_3)_6]((+)BCS)_3$ complex.

when these salts were dissolved in water solutions at about 1×10^{-2} *M*. Furthermore, the compounds pressed in the preparation of the disks gave identical solution electronic spectra with those of the unpressed compounds. This last observation establishes that neither the Br^- ion nor the (+)BCS ion was substituted into the coordination sphere during the KBr disk preparation process and that the induced circular dichroism originates from the uncoordinated counteranions.

Figure 1 shows the aqueous visible absorption spectrum, the corresponding diffuse-reflectance spectrum, and the associated solid circular dichroism spectrum of the $[Co(NH_3)_6]((+)BCS)_3$ salt. It will be seen that unlike the solution spectrum both solid spectra show evidence of splitting. This is particularly evident in the circular dichroism band which has a maximum of absorption displaced some 1000 cm^{-1} from that shown by the solution spectrum. Both solid spectra are more unsymmetrical than the solution spectrum and both have shoulders to higher energies of their absorption manifolds. It is probable that these splittings are due to distortions of the $[Co(NH_3)_6]^{3+}$ ions in the solid. If this is so, the observation elicits caution in the interpretation of the small splittings observed in solid-state circular dichroism spectra in weakly perturbed metal chromophores. Thus, in the case of the active $[Co(en)_3]^{3+}$ ion the small splittings *ca.* 500 cm^{-1} deduced for the $^1A_2$ and ^1E components of the $^1T_{1g}$ manifold were ascribed to the trigonal perturbations of the three chelate rings.[4] Our results show, however, that splittings of this order of magnitude can occur in the solid state in a molecule which apparently has O_h symmetry. It is possible, of course, to interpret the splittings in terms of Jahn–Teller distortions generated by the triply degenerate excited state, but this argument is difficult to sustain since the splitting is not evident in solution where the molecule is less constrained.

We may regard the induced optical activity in the solid state as arising by three different mechanisms.

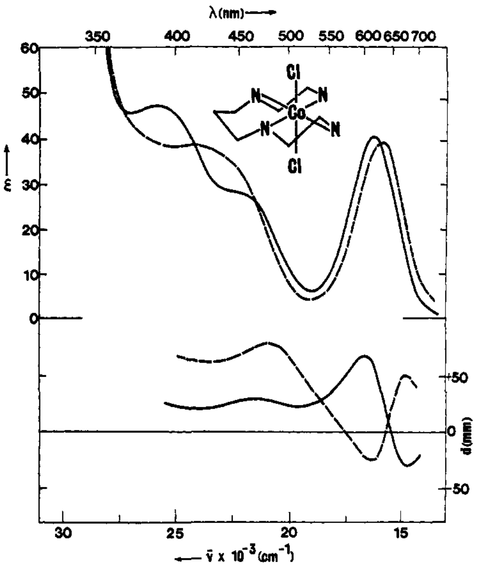

Figure 2. The aqueous-solution absorption spectra and the corresponding KBr disk (2%) circular dichroism spectra of the *trans*-$[Co(en)_2Cl_2](+)BCS$ (—) and *trans-meso*-$[Co(2,3,2\text{-tet})Cl_2](+)BCS$ (- - - -) complexes. The structure in the inset is that of the *trans-meso*-$[Co(2,3,2\text{-tet})Cl_2]^+$ ion.

The first is connected with the dissymmetric perturbation exerted by the electrons and nuclei of the dissymmetric anion on the d electrons of the central cobalt ion of the symmetric cation. This effect is expected to be small since the pseudoscalar potential[5] is acting at distances outside the first coordination sphere. The second effect is related to the ability of the dissymmetric anion to distort the metal–ligand bonds dissymmetrically in order to minimize the crystal interactions between the symmetric cation and the dissymmetric anion. Under these circumstances the cation would belong to an optically active point group (C_n or D_n). Since such distortions involve the first coordination sphere, the optical activity induced by this effect is expected to be much stronger than the first type of dissymmetric perturbation. The third effect is a dissymmetric transformation whereby, in conformationally or rotamerically labile systems, one preferred dissymmetric conformer or rotamer is stabilized in the solid state by the dissymmetric anion. The magnitude of this effect will depend on the particular complex, but generally it is expected to be of the same order of magnitude as the second (distortion) effect. The rotamerically labile $[Co(NH_3)_6]^{3+}$ ion, the conformationally labile *trans*-$[Co(en)_2Cl_2]^+$ ion, and the rotamerically and conformationally rigid *trans-meso*-$[Co(2,3,2\text{-tet})Cl_2]^+$ ion all show activity of a similar magnitude, which suggests a common origin for the induced activity.

These observations are important in another respect which is related to the measurement of circular dichroism of optically active molecules in the solid state. In an optically active crystal, any given molecule is surrounded by other optically active molecules of the same absolute configuration, and it is important to know how much of the observed circular dichroism is due to the dissymmetric molecule itself (hypothetical gas) and how much is due to that induced by its dissymmetric neighbors. This is particularly critical in conforma-

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tionally induced circular dichroism which is generally weaker than the configurational optical activity. We have found in most cases studied that the neighbor-induced optical activity is at least an order of magnitude less than the conformational (or vicinal) optical activity.[6]

It is possible that the present technique may be useful in identifying magnetic dipole transitions of metal complexes which are optically inactive. Thus we have found that the distrychnine salt of the $[PtCl_4]^{2-}$ ion gives appreciable circular dichroism in the regions of the spin-allowed magnetic dipole transitions of the anion.

The CD spectra were recorded on a Durrum-Jasco SS20 modified CD instrument at a sensitivity of 1 mdeg/cm.

Acknowledgment. We thank the National Research Council of Canada for financial support.

(6) B. Bosnich and J. MacB. Harrowfield, unpublished results.

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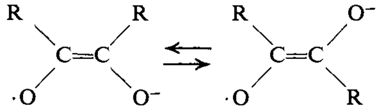
Ion Pairing in Alkali Metal Salts of Biacetyl and Perfluorobiacetyl. Mechanism of the Homogeneous Reduction of an α-Diketone by Lithium Metal and an Example of a Remarkably Slow Equilibration between Paramagnetic Lithium Salts in Tetrahydrofuran Solution[1,2]

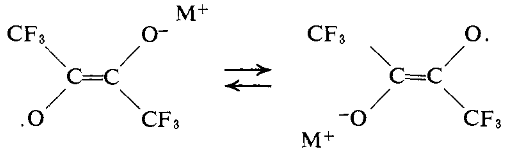
Sir:

Biacetyl semidone (10^{-5} *M*, 25°) exists as a mixture of cis (a^H = 7.0 G, DMSO) and trans (a^H = 5.6 G, DMSO) isomers.[3] In the presence of tetraalkylammonium alkoxides the ratio of trans–cis isomers is 35 in DMSO solution at 25°. We presume this reflects the stability of the free anions because the cis–trans ratio observed in the presence of R_4N^+ is not particularly solvent dependent. Rubidium and cesium cations (0.1 *M*) favor the trans isomer by preferential association since trans–cis ratios of 40 and >200, respectively, were observed in DMSO. Smaller alkali metal cations such as potassium, and, to a much greater extent, sodium and lithium gegenions favor the cis structure; trans/cis = 18, 1.8, <0.01 for 0.1 *M* K^+, Na^+, Li^+, DMSO, 25°.[4] Changes in solvent had a large effect on these cis–trans ratios.[3] The lithium salt (cis) exists as a tight ion pair with hyperfine splitting (hfs) by a single lithium atom, a^{Li} = 0.58 G (DMSO, 25°). The cis sodium salt shows a sodium hfs, a^{Na} = 0.23 G, DMSO, 25°. However, the sodium hfs consists of much broader lines than the lithium hfs, presumably the result of exchange with free sodium ions. Addition of dibenzo-18-crown-6 ether[5] (0.1 *M*) to a DMSO solution causes the sodium hfs to become quite sharp, apparently because the free sodium ions are now complexed by the cyclic ether and no longer exchange readily with the ion pair. The ether (0.1 *M*) also had an appreciable effect on the trans–cis ratio in DMSO increasing it from 18 to 40 for 0.1 *M* K^+ and from 1.8 to 7.2 for 0.1 *M* Na^+. In the presence of the ether the trans–cis ratios approach more closely those expected for the free anions. No alkali metal splittings have been observed for any of the trans isomers.



Perfluorobiacetyl[6] radical anion gave additional evidence for the formation of several kinds of ion pairs. Electrolytic reduction in THF (R_4N^+ cation) gave a trans (a^F = 8.30 G, a^C = 4.5, 1.8 G)–cis (a^F = 10.92 G) ratio of 170, whereas in DMSO the ratio was 120. Again Cs^+ or Rb^+ seemed to favor the trans structure since trans/cis = 150 (DMSO, Rb^+), >200 (THF, Cs^+).

In THF, perfluorobiacetyl was readily reduced by the group Ia and certain group IIa metals, a process which does not yield reasonable spectra for biacetyl itself. In THF the equilibrium trans–cis ratios at 25° were 1.5, 0.4, and 1.2 for Li^+, Na^+, and K^+, respectively. Hyperfine splitting from Li^+ and Na^+ was well resolved in the cis structure while the trans isomers showed pronounced broadening of certain lines, a phenomenon interpreted as the result of magnetic nonequivalence of the CF_3 groups because of movement of the gegenion in **1**.[7] For Na^+ the trans isomer spectrum consisted of four sharp lines in the ratio 1:9:9:1 separated by 2(8.05) G, apparently the result of extensive alternate line broadening in the fast exchange mode. The line-width alternation was more pronounced for Na^+ than for K^+. With Li^+, ten lines were observed which were consistent with a^F = 10.38 (3), 5.38 (3) G (8.11 G av) and with the broadening expected for the slow exchange mode (Figure 1a). The rate constant for interconversion of the isomeric structures of **1** is $\sim 10^7$ sec^{-1}.



1

The esr spectra of the lithium salts of perfluorobiacetyl radical anion showed an unexpected variation with time following reduction by lithium metal. Immediately after reduction at 25° the spectrum of Figure 1a was observed. This spectrum slowly changed to 1b. Spectrum 1a is interpreted as being a mixture of **1** (with line broadening), a tight ion pair **2** with a^{Li} = 0.48 G, and another species, **3**, with sharp lines the result of hfs by six equivalent fluorine atoms (without lithium splitting), a^F = 10.67 G. Spectrum 1b contains only **1** and **2** without a trace of **3**. The hfs of **3** strongly suggests a cis structure for the perfluorobiacetyl fragment(s).

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(1) Application of Electron Spin Resonance Spectroscopy to Problems of Structure and Conformation. XXIII

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