

No positive evidence is yet available to indicate whether the 4-acetyl and 4-ethylquinaldic acids, III and IV, are genuine constituents of the antibiotic, or are formed from VIII during the process of hydrolysis and isolation.

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RECEIVED AUGUST 10, 1961

PARTIAL CHROMATOGRAPHIC RESOLUTION,  
ROTATORY DISPERSION, AND ABSOLUTE  
CONFIGURATION OF OCTAHEDRAL COMPLEXES  
CONTAINING THREE IDENTICAL BIDENTATE  
LIGANDS

Sir:

We have obtained a partial resolution of the acetylacetonates of chromium(III) and cobalt(III) by chromatography<sup>1</sup> on *d*-quartz or alumina treated with *d*-tartaric acid.<sup>2</sup> The rotatory dispersion shows a strong Cotton effect associated with the spin-allowed transitions near 600  $m\mu$ . For both compounds the rotational strength<sup>3</sup>  $R$  is negative for the enantiomer less strongly adsorbed on alumina-*d*-tartaric acid. We have attempted to establish the absolute configurations of the acetylacetonates and corresponding oxalates<sup>4</sup> as well by referring them to the known absolute configuration<sup>5</sup> of the ethylenediamine derivative (+)<sub>D</sub>-Coen<sub>3</sub><sup>3+</sup> (see Fig. 1)—but first some pedagogy concerning sign conventions.

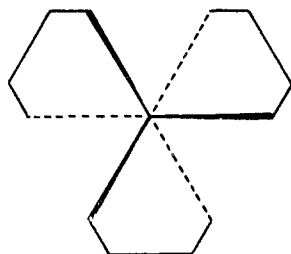


Fig. 1.—The absolute configuration of (+)<sub>D</sub>-Coen<sub>3</sub><sup>3+</sup>.

It has been customary to label the enantiomers D or L (*d* or *l*) depending on the sign of the rotation at the sodium D-line. This is unsatisfactory in that the letter designation should refer to the geometry of the molecule. If the absolute configuration is not known, then the isomers should be designated either with the sign of the rotation at some wave length, say (+)<sub>D</sub> or (+)<sub>589 mμ</sub> as is cus-

(1) These compounds also have been resolved partially on lactose. See T. Moeller and E. Gulyas, *J. Inorg. Nucl. Chem.*, **5**, 245 (1958). Our dispersion curves agree with their rotations measured at single wave lengths.

(2) G. Karagounis, E. Charbonnier and E. Flöss, *J. Chromatog.*, **2**, 84 (1959). These authors provide experimental details and a bibliography of such chromatographic separations.

(3) For a definition of this term and a summary of the theory of optical activity see W. Moffitt, *J. Chem. Phys.*, **25**, 1189 (1956).

(4) For a review of previous work on rotatory dispersion of oxalates and ethylenediamine derivatives see J. P. Mathieu, *J. chim. phys.*, **33**, 78 (1936).

(5) Y. Saito, K. Nakatsu, M. Shiro and H. Kuroya, *Acta cryst.*, **3**, 729 (1955).

tomary or alternatively with the sign of the net rotational strength associated with some excited state, say (+)<sub>T</sub>. On the other hand, if the absolute configuration is known, there is a geometrical method of identifying the enantiomers based on accepted conventions which consists in associating with the chelate ring a segment of a helix or screw. In this way the enantiomer depicted in Fig. 1 is associated with a left-handed helix. Therefore, we propose that this enantiomer be designated Λ-Coen<sub>3</sub><sup>3+</sup> rather than D-Coen<sub>3</sub><sup>3+</sup>. We use the Greek letters Λ and Δ to avoid confusion with the earlier convention.

In a study of the rotatory dispersion of these complexes Moffitt<sup>3</sup> assumed that the rotation is due to an admixture of 4p orbitals with the 3d orbitals involved in the transition under the asymmetric trigonal field in Y<sub>3</sub><sup>±3</sup>. He predicted that the rotation should take its sign from the asymmetric potential. However Sugano<sup>6</sup> has shown that this first-order theory cannot account for the rotational strength on symmetry grounds; Moffitt's error lay in the phase. While the exact mechanism of the rotation remains unknown, we may expect that the sign of the rotation should correlate to the sign of the trigonal field since this is based on symmetry.<sup>7</sup> Our studies of crystal spectra of acetylacetonates<sup>8</sup> and oxalates<sup>9</sup> have afforded values of the trigonal field parameter<sup>10</sup>  $K$ . These are recorded in Table I. Notice that for every Cr-Co pair the signs of the trigonal field parameter correlate to the signs of the rotation as expected.

TABLE I

Complex ion or compound	Method of resolution	Sign of $R$ (600 $m\mu$ band)	$K$ (cm. <sup>-1</sup> )	$\Delta b$
Cren <sub>3</sub> <sup>3+</sup>	Less soluble	+	+ 67 <sup>b</sup>	< -2.6 <sup>o/</sup>
Coen <sub>3</sub> <sup>3+</sup>	Chlorotartrate <sup>c</sup>	+	+ 45 <sup>b</sup>	-2.6 <sup>o/</sup>
Cr(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> <sup>-3</sup>	Less soluble	+	+270 <sup>c</sup>	-8 <sup>o/</sup>
Co(C <sub>2</sub> O <sub>4</sub> ) <sub>3</sub> <sup>-3</sup>	Strychnine salt <sup>c</sup>	-	-100 <sup>c</sup>	> -8 <sup>o/</sup>
Cr(O <sub>2</sub> C <sub>6</sub> H <sub>9</sub> ) <sub>3</sub>	Less readily adsorbed	-	+600 <sup>d</sup>	+3 <sup>o/</sup>
Co(O <sub>2</sub> C <sub>6</sub> H <sub>9</sub> ) <sub>3</sub>	On Al <sub>2</sub> O <sub>3</sub> -C <sub>4</sub> O <sub>6</sub> H <sub>6</sub>	-	+600 <sup>e</sup>	> +3 <sup>o/</sup>

<sup>a</sup> See reference 4. <sup>b</sup> Calculated from spectra reported by S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Japan*, **33**, 98 (1960). <sup>c</sup> From reference 9. <sup>d</sup> From reference 8. <sup>e</sup> T. S. Piper, *J. Chem. Phys.*, in press. <sup>f</sup> These values have been inferred from the fact that the radius of Cr(III) is larger than that of Co(III). <sup>g</sup> From reference 5. <sup>h</sup> J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.*, **5**, 196, 499 (1952). <sup>i</sup> L. M. Shkolnikova and E. A. Shugam, *Kristallografiya*, **5**, 32 (1960).

Of course there is no necessary correlation between the sign of  $K$  and the absolute configuration. This is readily understood in terms of the ionic model. An asymmetric potential (point group D<sub>3</sub>) may be generated by representing the ligands

(8) S. Sugano, *J. Chem. Phys.*, **33**, 1883 (1960).

(7) In this note we suppress the splittings of the excited states in the trigonal field since they are considerably smaller than the width of the rotational dispersion curves. In some cases the components are known to have opposite signs (see ref. 3). Indeed our dispersion curves for the cobalt acetylacetonate become slightly positive at longer wave lengths, indicating the A<sub>1</sub> component of  $R$  is positive while the E component is negative. We will deal with this in a later publication.

(8) R. L. Carlin and T. S. Piper, to be published in *Inorg. Chem.*

(9) T. S. Piper and R. L. Carlin, *J. Chem. Phys.*, in press.

(10) T. S. Piper and R. L. Carlin, *ibid.*, **33**, 1006 (1959).

with six point charges at the corners of an octahedron and distorting the ligand-metal-ligand angle ( $b$ ) within the chelate plane.<sup>11</sup> Thus a geometrically right-handed molecule may have a trigonal potential (as well as all odd potentials) and rotational strength of either sign depending on the change of this angle,  $\Delta b$ , from  $90^\circ$ . For this reason it is not safe to conclude that two enantiomers with the same sign of  $R$  but with different ligands have the same configuration unless the ligands are very little different from one another.

From Table I it may be seen that the ionic model fails to account for the sign of  $K$  since there is no consistent correlation to  $\Delta b$ . Our studies of the acetylacetonate spectra indicate that the very anomalous intensities observed probably are due to the effects of  $\pi$ -covalency. These effects should be absent in the more ionic oxalates and indeed the signs of  $K$  and  $\Delta b$  for the chromium oxalate and ethylenediamine complexes do correlate. Thus we can say nothing for certain about the acetylacetonates, but we are led to the tentative conclusion that the trisoxalates which form the less soluble strychnine salts have the same absolute configuration as the (+)-D-Coen<sub>3</sub><sup>+3</sup> enantiomer.

NOTE ADDED IN PROOF.—Andrew D. Liehr has recently described (Sixth Int. Conf. Coord. Chem.) a covalent bond model which can account for the optical rotations. The sign depends primarily on an angle,  $\alpha$ , which the  $\sigma$ -bonding orbital makes with the metal-ligand bond axis. To apply this model, if we assume that the orbital is intermediate between  $sp^2$  and  $sp^3$ , then its angle to the O-C bond axis is  $115^\circ$ . Since the angles Cr-O-C are  $107^\circ$  and  $131^\circ$  in the oxalate and acetylacetonate, respectively, this model apparently makes the same incorrect prediction as the ionic model, namely, that in these compounds K (as well as R) should have opposite signs. However the model also contains  $\pi$ -bonding and overlap parameters which will have to be included in a complete calculation since they may affect the sign.

**Acknowledgment.**—The author thanks the National Science Foundation for a grant and Mr. Ki Chang Oh and Mr. Lee Brecker for assistance in the experimental work.

(11) H. Hartmann, C. Furlani and A. Buerger, *Z. physik. Chem. (Frankfurt)*, **9**, 62 (1956).

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RECEIVED JULY 20, 1961

## ELECTROLYTIC GENERATION OF RADICAL IONS IN AQUEOUS SOLUTION

Sir:

The electrolytic generation of radical ions directly in the microwave cavity of an EPR spectrometer was introduced in 1959 by Maki and Geske.<sup>1</sup> A great deal of interest has developed in this technique and already a considerable body of information has been obtained on both anion and cation radicals.<sup>2-4</sup>

Such generations have not been attempted in aqueous solution, probably because the prevailing theories of voltammetry imply that especially nega-

- (1) A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **30**, 1356 (1959).
- (2) D. H. Geske and A. H. Maki, *J. Am. Chem. Soc.*, **82**, 2671 (1960).
- (3) A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **33**, 825 (1960); *J. Am. Chem. Soc.*, **83**, 1852 (1961).
- (4) M. T. Melchior and D. H. Geske, *ibid.*, **34**, 471 (1961).

tive ion radicals cannot be generated in proton rich solvents since a rapid, irreversible protonation followed by further electrochemical reduction occurs.<sup>5,6</sup> We wish to report the successful generation of both cation and anion radicals and especially negative ions from *aliphatic* nitro compounds in ordinary aqueous solutions.

The electrolysis vessel consisted of a rectangular aqueous cell inserted in the cavity of a standard Varian V-4500 EPR spectrometer using 100 Kc. field modulation. The supporting electrolyte was 0.1 *M* lithium perchlorate or 0.5 *M* potassium chloride or acetate buffer. In some cases 10-30% 1-propanol was added to improve solubility.

The mono-negative ions of *o*-, *m*- and *p*-nitroaniline; *o*-, *m*- and *p*-nitrophenol, *p*-nitroanisole, *p*-nitrodimethylaniline and nitrobenzene itself were generated and detected at a mercury pool electrode. The e.p.r. spectra were all well resolved and the hyperfine structure interpreted in terms of the molecular structure. The e.p.r. spectra of the *para* and *meta* isomers of nitroaniline, *p*-nitroanisole and nitrobenzene have been reported in acetonitrile very recently.<sup>3</sup> In water the N<sup>14</sup> coupling constants are some 3-4 gauss larger than in acetonitrile. It was observed that the radical ions decayed by a first order reaction (with a half-life of *ca.* 2 sec.) when the current was turned off. Such a decay strongly suggests reaction with the solvent and not with another ion.

The spectra of the mono negative ions of aliphatic nitro compounds show a very strong N<sup>14</sup> coupling and, in addition, coupling of the unpaired electron with protons on the carbon adjacent to the nitrogen. The N<sup>14</sup> coupling constants are summarized in Table 1. Figure 1 shows a typical spectrum. It is very interesting that these aliphatic anions exhibit such

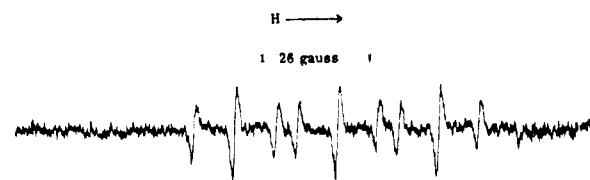


Fig. 1.—E.p.r. spectrum of 1-nitropropane negative ion in aqueous solution.

stability, especially in aqueous media. Only in the case of nitromethane was it not possible to obtain a spectrum with satisfactory signal/noise, although evidence of the radical ion was obtained. The widespread feeling that radical anions are too unstable *per se* to be observed by electrogeneration in aqueous media is rendered untenable by the present studies.

The stability of radical cations in aqueous solution has been known for years but electrogenerations of such species again have only been reported in acetonitrile.<sup>4</sup> Satisfactory generation and detection of the positive ions of *p*-phenylenediamine, *N,N*-dimethyl-*p*-phenylenediamine (Wurster's red), *o*-tolidine, *N,N'*-tetramethylbenzidine, *p*-amino-

- (5) G. J. Hoijtink, J. van Schooten, E. de Boer and W. Y. Aalbersberg, *Rec. trav. chim.*, **73**, 355 (1954).
- (6) P. H. Given and M. E. Peover, *Advances in Polarography (Proc. 2nd Intn'l. Polarog. Cong., Cambridge)*, Vol. 3, p. 948 (1959).