find that I apparently exists in hydrocarbon solutions predominantly as the dimer, as evidenced by molecular weight measurements shown in Table I. Thus, the unusual reactivity of menthyllithium apparently is a reflection of its low state of aggregation, lending credence to the often expressed notion that smaller aggregates of alkyllithium compounds are indeed more reactive.[10]

We shall report soon in more detail concerning the reactions described above, as well as others involving menthyllithium and related compounds.

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The Absolute Configuration of Tris(biguanide)chromium(III)

Sir:

In a recent report of the electronic and circular dichroism spectra of the tris(biguanide hydrochloride)cobalt(III) and tris(biguanide hydrochloride)chromium(III) complexes, Michelsen[1] noted an anomaly in the circular dichroism spectra in the region of the internal ligand electronic transitions; the signs of the Cotton effects are inverted, though all other evidence indicated that the complexes have the same absolute configuration. We have determined the structure and absolute configuration of $(-)_D$-tris(biguanide)chromium(III) by X-ray analysis of the least soluble *d*-10-camphorsulfonic acid salt. We have applied this and other results to the reassignment of the CD spectra of the cobalt(III) and chromium(III) trisbiguanide complexes.

Orange needlelike crystals of $(-)_D$-tris(biguanide)chromium(III) *d*-10-camphorsulfonic acid trihydrate were grown from aqueous solution. The crystals are monoclinic, space group $P2_1$, with $a = 16.393$ (0.006), $b = 10.753$ (0.004), $c = 16.666$ (0.006) Å, $\beta = 117.68°$ (0.02), $Z = 2$, $D_c = 1.418$, $D_m = 1.428$ (flotation). The unit cell parameters and standard deviations were determined by least-squares treatment of 2θ angles measured with a Picker four-circle diffractometer. The intensities of 2249 independent reflections in the range $2\theta < 90°$ were measured manually with the Picker diffractometer using nickel-filtered copper radiation and the stationary-crystal–stationary-counter technique. Absorption corrections ($\mu = 36.8_8$ cm^{-1}) for the 2158 nonzero intensities were calculated with a program based on the method of Busing and Levy.[2] The structure obtained by the heavy-atom method was refined by blocked diagonal least squares including anomalous scattering terms and anisotropic temperature factors for the chromium and sulfur atoms. The present conventional R factor including the 91 unobservable structure factors is 0.159.

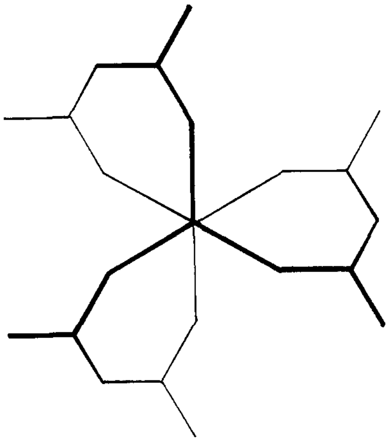

Figure 1. $\Lambda(C_3)$ $(-)_D$-tris(biguanide)chromium(III).

More data will be needed to reduce the present 0.03–0.05 Å estimated standard deviations of the bond lengths, but it is apparent that the tris(biguanide)chromium(III) complex conforms closely to D_3 symmetry. The biguanide chelate rings appear to be planar, and at the present stage of analysis, the carbon–nitrogen bond lengths do not differ significantly from the 1.34-Å length found in pyridine.[3] The N–Cr–N angles are all 90° within experimental error.

The CD curves of *d*-10-camphorsulfonic acid show that it has the same absolute configuration as that already established by X-ray methods for *d*-3-bromocamphor-9-sulfonic acid[4] and *d*-3-bromocamphor.[5] Selection of the known absolute configuration of the camphor group in the crystal structure specifies the $\Lambda(C_3)$ configuration of the $(-)_D$-tris(biguanide)chromium(III) complex, shown in Figure 1. The Λ configuration is in agreement with the absolute configuration determined by the method of Bijvoet, *et al.*,[6] using the anomalous scattering of the chromium and sulfur atoms.

We have reexamined the CD spectra of the least soluble *d*-10-camphorsulfonic acid salts of tris(biguanide)cobalt(III) and -chromium(III) to determine the effect of added phosphate; the least soluble *d*-10-camphorsulfonic acid salts are spectroscopically identical with the least soluble *d*-3-bromocamphor-9-sulfonic acid salts prepared by Michelsen.[1] Mason, *et al.*,[7,8] have shown that the phosphate anion, among others, serves to enhance the intensity of the $^1A_1 \rightarrow {}^1A_2$ (or $^4A_1 \rightarrow {}^4A_2$, for the chromium(III) ion) CD band at the expense of the intensity of the $^1A_1 \rightarrow {}^1E_a$ (or $^4A_1 \rightarrow {}^4E_a$) band. Application of this criterion to the data in Table I shows that the low-energy CD band of

Table I. The Effect of Added Phosphate on the Ratios of the Intensities of the Low-Energy Circular Dichroism Bands of Tris(biguanide)cobalt(III) and Tris(biguanide)chromium(III)

Compound	I^+/I^-, aqueous[a]	I^+/I^-, phosphate
Cobalt(III)	0.86	2.27
Chromium(III)	0.79	1.28

[a] Integrated intensities.

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(7) P. G. Beddoe and S. F. Mason, *Inorg. Nucl. Chem. Lett.*, **4**, 433 (1968).

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negative sign for both complexes corresponds to the $A_1 \rightarrow E_a$ electronic transition. Our structural data clearly show that $(-)_D$-tris(biguanide)chromium(III) has the same absolute configuration as the $(+)_D$-tris(ethylenediamine)cobalt(III) ion; Λ with respect to the threefold axis.[9,10] Thus, in contrast with the cobalt(III) system, the *negative* E_a component of the CD spectrum of trigonal chromium(III) corresponds to the $\Lambda(C_3)$ configuration.

Turning our attention to the anomaly reported by Michelsen[1] in the CD spectra in the region of the ligand internal transitions, we believe that the enantiomeric character of the tris(biguanide)cobalt(III) and -chromium(III) CD spectra arises from the opposite absolute configurations of these complexes. We note that the chelate rings in the biguanide complexes are planar, and that the bond lengths suggest a high degree of electronic delocalization. We suggest, therefore, that the CD spectra in the region of the ligand electronic transitions be interpreted using the exciton model recently described by Bosnich and by Mason.[11] The exciton theory predicts that complexes with the $\Lambda(C_3)$ configuration will exhibit a positive (E) CD band followed, at higher energy, by a negative (A_2) band in the region of the internal ligand electronic transitions. Our experimental results verify this relationship for the chromium(III) ion and for the biguanide ion, which is among the few ligands which forms resolvable complexes and has isolable electronic transitions within the range of practical instrumentation.

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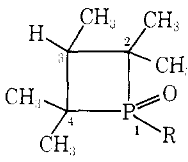
Stereochemistry of Nucleophilic Attack on a Cyclic Phosphinate Ester[1]

Sir:

Nucleophilic displacement reactions at a phosphoryl center generally proceed with inversion of configuration at phosphorus.[2] We wish to report a noteworthy exception to this: namely, attack of methoxide ion on either the *cis* or *trans* isomers of 1-methoxy-2,2,3,4,4-pentamethylphosphetane 1-oxide (**1**) takes place with retention of configuration.



1, R = CH_3O
2, R = Cl
3, R = OH

The pure *trans* (1-Cl and 3-CH_3) isomer[3] of the acid chloride **2** was prepared by treatment of 2,4,4-trimethyl-2-pentene with PCl_3–$AlCl_3$ according to the procedure of McBride.[4] Subsequent reaction of the recrystallized product with sodium methoxide–methanol[4] or triethylamine–methanol gave a single isomer of **1** (*trans*).[5] A predominance (3:2) of the *cis* ester was obtained by heating the acid **3** with thionyl chloride in benzene (5 hr at reflux temperature) followed by esterification with triethylamine–methanol.[6] Use of deuteriomethanol–triethylamine gave the labeled ester (R = CD_3O) in each case above.

Clear distinction between the isomers was apparent in the nmr[7] spectra (60 MHz, benzene, TMS): **1** (*trans*) τ 8.86 (d, 6 H, J_{PCCH_3} = 18.5 Hz), 8.92 (d, 6 H, J_{PCCH_3} = 18.0 Hz), 6.37 (d, 3 H, J_{POCH_3} = 10.1 Hz); **1** (*cis*) τ 8.75 (d, 6 H, J_{PCCH_3} = 18.3 Hz), 8.97 (d, 6 H, J_{PCCH_3} = 18.0 Hz), 6.42 (d, 3 H, J_{POCH_3} = 10.1 Hz); **2** (*trans*) τ 9.32 (dd, 3 H, J_{HCCH_3} = 7.0 Hz, J_{PCCCH_3} = 1.5 Hz), 8.83 (d, 6 H, J_{PCCH_3} = 21.4 Hz), 8.88 (d, 6 H, J_{PCCH_3} = 23.0 Hz); **2** (*cis*) τ 9.28 (dd, 3 H, J_{HCCH_3} = 7.0 Hz, J_{PCCCH_3} = 1.0 Hz), 8.77 (d, 6 H, J_{PCCH_3} = 21.5 Hz), 8.97 (d, 6 H, J_{PCCH_3} = 23.8 Hz).

An aliquot from a solution of 400 mg of *trans*-**1** (R = CD_3O) in 1.0 ml of 0.65 *N* $NaOCH_3$–CH_3OH was placed in a sealed, evacuated nmr tube; a similar aliquot was prepared from a mixture of **1** (*trans*:*cis*, 2:3; R = CD_3O). Exchange of CD_3O by CH_3O took place in each isomer; for example, after 3 hr at 25° the *trans*–*cis* mixture (2:3) had undergone about 30 and 70% exchange, respectively. After 48 hr, exchange (under these conditions) for both isomers was about 90% complete. The pure sample of **1** (*trans*) showed 80% exchange after 11 hr at 50°. Control runs in each of the above cases were performed under identical conditions using **1** (*trans*) and **1** (*trans*:*cis*, 2:3) in which R = CH_3O; no isomer interconversion was

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[1] We wish to thank the National Institutes of Health for support of this research under Grant CA-11631.

[2] M. J. Gallagher and I. D. Jenkins in "Topics in Stereochemistry," Vol. 3, N. L. Allinger and E. L. Eliel, Ed., John Wiley & Sons, Inc., New York, N. Y., 1968, pp 31–38 and 82–85.

[3] The stereochemistry and detailed geometrical structure of **2** (*trans*) has been determined by X-ray work by Dr. M. Haque of Montana State University, Department of Chemistry (unpublished results).

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[5] Since this communication was submitted, W. Hawes and S. Trippett, *J. Chem. Soc., C*, 1455 (1969), showed that treatment of the acid chloride with sodium methoxide proceeds with retention.

[6] There is some confusion in the literature on the preparation of the isomers of **2** and **3**. McBride[4] has implied that thionyl chloride treatment of **3** (from aqueous hydrolysis of **2**) gave back the starting isomeric acid chloride; repetition of this work in our laboratory revealed that both *cis*- and *trans*-**2** are formed and that each is clearly distinguishable in the nmr (see text). Moreover, K. Bergesen, *Acta Chem. Scand.*, **21**, 1587 (1967), claimed to have isolated *cis*- and *trans*-**3**; there is obvious uncertainty concerning this point [see W. H. Hawes and S. Trippett, *Chem. Commun.*, 577 (1968); P. Haake, R. D. Cook, W. Schwarz, and R. D. McCoy, *Tetrahedron Lett.*, 5251 (1968)].

[7] The interpretation of chemical shifts and coupling constants for these compounds is parallel to that of analogs whose spectra have been discussed elsewhere [S. E. Cremer, and R. J. Chorvat, *J. Org. Chem.*, **32**, 4066 (1967)]. The ^{31}P–^{1}H coupling constants were verified by decoupling experiments. The nmr of pure **1** (*trans*) and **2** (*trans*) enabled the assignment of peaks for **1** (*cis*) and **2** (*cis*) in which each was the predominant component in an isomeric mixture.