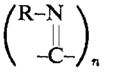
between **6** and **7** is likely to be a nickel analog of **3**. However, the tendency of nickel(II) to achieve pentacoordination facilitates the insertions resulting in **7**.

When an excess of *t*-butyl or other isocyanide was heated above room temperature (30–60°) in the presence of **7**, the isocyanide was converted into polyisocyanide with a repeating unit[6]



$$\left(\begin{array}{c}\text{R–N}\\ \|\\ \text{–C–}\end{array}\right)_n$$

The above successive insertion reactions suggest a mechanism for the catalytic polymerization of isocyanides.

---

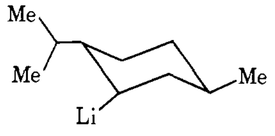
[6] Y. Yamamoto and N. Hagihara, *Bull. Chem. Soc. Jap.*, **39**, 1084 (1966).

Sei Otsuka, Akira Nakamura, Toshikatsu Yoshida
Department of Chemistry, Faculty of Engineering Science
Osaka University, Toyonaka, Osaka, Japan
Received October 6, 1969

Cyclohexylmetal Compounds. IV. The Effect of Aggregate Size on the Reactivity of Alkyllithium Compounds[1]

Sir:

Subsequent to our original investigation of menthyllithium (I)[1,2] and 4-*t*-butylcyclohexyllithium,[1-3] we have discovered that the former is an extremely reactive alkyllithium compound by all available standards. For example, I reacts with bromobenzene in *n*-pentane



I

(halogen–lithium interchange) and with 1,1-diphenylethylene (DPE) in benzene (addition) at rates too fast to measure by conventional techniques. By comparison, bromobenzene reacts with *n*-butyllithium and *sec*-butyllithium under similar conditions with half-lives of *ca.* 19 hr and 19 min, respectively.[4] Initial rates for the addition of RLi to DPE in benzene at 30° are 0.12×10^{-6} and 9.17×10^{-6} *M*/sec for *n*-butyllithium[5] and *sec*-butyllithium, respectively.[6] Under similar conditions, the addition of menthyllithium to DPE must have an initial rate greater than 625×10^{-6} *M*/sec.

Further evidence of the unusual reactivity of I is its ability to metalate toluene in the absence of basic catalysts. We have compared I to *n*-BuLi·TMEDA, *sec*-butyllithium, and cyclohexyllithium in this respect. Thus, 8.25 mmol of RLi and 47 mmol of toluene were allowed to react at 50° for 6 hr, followed by derivatization with chlorotrimethylsilane–diethyl ether. The trimethylsilylated derivatives were identified by glpc and nmr and quantitated by an internal standard. Yields of metalated products were R = cyclohexyl, 6.2%; *sec*-butyl 2.3%; *n*-butyl–TMEDA, 15.9%; and I, 35%. Under these conditions I produces approximately a 9:1 mole ratio of benzyllithium:dimetalated toluenes, the latter of as yet unspecified structures. With higher RLi:toluene ratios the yields of dimetalated and trimetalated toluenes increase significantly. Further work to determine the precise distribution of the polymetalated isomers is under way, and will be reported later.

Finally, we report that I will apparently react with tetraphenylethylene in hydrocarbon media, the first example of such a reaction involving an alkyllithium compound. Reaction of I with TPE in benzene yields a reddish brown, insoluble product. The observation of an esr signal during this reaction indicates that I transfers an electron to TPE forming the tetraphenylethylene radical anion. The fate of the latter under these conditions is probably the same as in more polar solvents, namely disproportionation to yield the dianion,[7] although proof of this is lacking at the moment.

The unusual reactivity of menthyllithium may be rationalized by an extension of ideas originally applied to a study of the rates of thermal decomposition of alkyllithium compounds.[8,9] Construction of models of the tetramer of *sec*-butyllithium suggested to us at that time that rather severe steric repulsions occur which are absent in *n*-butyllithium and *t*-butyllithium. We concluded that the tetramer structure of an alkyllithium compound would be unstable relative to the dimer if (a) the compound were a secondary or tertiary lithium compound, and (b) it were substituted at the position β to the carbon–lithium bond. If we furthermore assumed that the dimer species would be more reactive than the tetramer,[10] these considerations would predict that *sec*-butyllithium would be more reactive than *n*-butyllithium or *t*-butyllithium, as observed, but also that alkyllithium compounds with more bulky substituents in the β position would be even more reactive. That menthyllithium is branched in the β position with an isopropyl group and is, in fact, significantly more reactive than *sec*-butyllithium would seem to us to be confirmation of these ideas. In fact, we were amazed to

Table I. Molecular Association of Menthyllithium[a]

Solvent	Concn, *M*	Degree of association
Cyclohexane	0.23, 0.29	2.17, 1.95
Benzene	0.10, 0.38	1.93, 2.04

[a] Determined by depression of freezing point of solvent; solutions contained 90–96% carbon-bound lithium.

---

[1] Part III: W. H. Glaze, C. M. Selman, A. L. Ball, Jr., and L. E. Bray, *J. Org. Chem.*, **34**, 641 (1969).

[2] W. H. Glaze and C. M. Selman, *ibid.*, **33**, 1987 (1968).

[3] W. H. Glaze and C. M. Selman, *J. Organometal. Chem.*, **11**, P3 (1968).

[4] Kinetic data for bromobenzene–RLi reactions were obtained by monitoring bromobenzene and alkyl bromide by glpc. Aliquots were removed with a microliter syringe from reaction vessels fitted with syringe caps. An internal standard was employed. The identity of the alkyl bromide was established by spiking with known material and observing the glpc pattern.

[5] A. G. Evans and D. B. George, *J. Chem. Soc.*, 4653 (1961).

[6] Initial rates for RLi–DPE reactions were measured spectrophotometrically at or near the absorption maximum of the adduct $CH_2RC(Li)Ph_2$ (440 mμ for *sec*-butyllithium and menthyllithium). The initial rates referred to above were measured at initial concentrations of RLi and DPE of 2.46×10^{-2} and 8.88×10^{-3} *M*, respectively. The initial rate for *n*-butyllithium was calculated from the data of Evans and George[5] under identical conditions.

[7] A. G. Evans, J. C. Evans, E. D. Owens, B. J. Tabner, and J. E. Bennett, *Proc. Chem. Soc.*, 226 (1962).

[8] W. H. Glaze, J. Lin, and E. G. Felton, *J. Org. Chem.*, **31**, 2643 (1966).

[9] W. H. Glaze and G. M. Adams, *J. Amer. Chem. Soc.*, **88**, 4653 (1966).

[10] T. L. Brown, *J. Organometal. Chem.*, **5**, 191 (1966).

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.

Acknowledgment. We are grateful to The Robert A. Welch Foundation and the N. T. S. U. Faculty Research Fund for generous support of this work.

William H. Glaze, Charles H. Freeman
Department of Chemistry, North Texas State University
Denton, Texas 76203

Received August 28, 1969

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.

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.

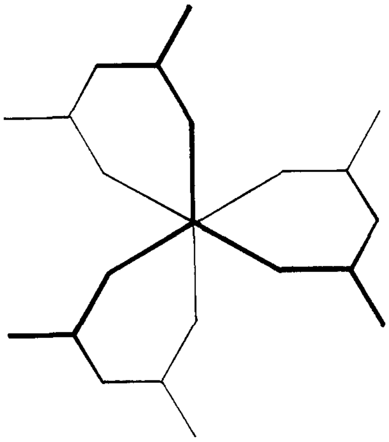


Figure 1. $\Lambda(C_3)$ $(-)_D$-tris(biguanide)chromium(III).

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.

---

(1) K. Michelsen, *Acta Chem. Scand.*, **19**, 1175 (1965).
(2) W. R. Busing and H. A. Levy, *Acta Cryst.*, 10, 180 (1957).
(3) B. Bak, L. Hansen, and J. Rastrup-Andersen, *J. Chem. Phys.*, **22**, 2013 (1954).
(4) J. A. Wunderlich, *Acta Cryst.*, **23**, 846 (1967).
(5) F. H. Allen and D. Rogers, *Chem. Commun.*, 846 (1966).
(6) J. M. Bijvoet, A. F. Peerdeman, and A. J. van Bommel, *Nature*, **168**, 271 (1951).
(7) P. G. Beddoe and S. F. Mason, *Inorg. Nucl. Chem. Lett.*, **4**, 433 (1968).
(8) A. J. McCaffery, S. F. Mason, and R. E. Ballard, *J. Chem. Soc.*, 2883 (1965).