However, it will be recalled from the earlier discussion that a mixed alkali metal uranate was also obtained in the absence of BrO_3^- simply by raising the temperature of the nitrate melt above 300°. In this case, one can envision a direct (Lewis) acid reaction of a U(VI) complex with an O^{2-} species formed by the dissociation of NO_3^-

$$NO_3^- = NO_2^+ + O^{2-}$$

In order to determine whether the actinate formation resulted from a mixed BrO_3–NO_3^- mechanism in the 220–270° range, or was due entirely to BrO_3^- decomposition, we examined the infrared spectrum of the liberated gases. No oxides of nitrogen were detected. Thus the evidence indicated that the nitrate melt served only as an inert solvent for the reaction.

Summarizing our results, we see that the reaction of BrO_3^- and U(VI) in the nitrate melt gave rise to a new complex alkali metal uranate containing both lithium and sodium. A product of the same structure was then synthesized from a mixture of alkali metal carbonates and UO_3. The X-ray diffraction pattern and infrared spectrum of the complex uranate were similar to, but distinct from, those of $Na_2U_2O_7$. Reaction of Np(VI) or of Np(V) with BrO_3^- gave one product only. It contained Np(VI) and was analytically essentially the counterpart of the complex uranate. There was, however, a much closer relationship between the cell constants (determined from X-ray powder patterns) and the infrared spectra of the complex neptunate and $Na_2Np_2O_7$ than was found with the corresponding uranium compounds. We were able to offer an interpretation of some of the infrared absorption bands both in the complex actinates and the pure sodium diactinates. The U–O_I and Np–O_I bond distances in all four of the sodium compounds studied was calculated to be approximately 1.78 Å.

This result is of particular interest since some authors have been tempted to assume that the similarity, for example, in the uranium positions in $Na_2U_2O_7$ with those in $CaUO_4$, as established by X-ray diffraction data, implies a similarity in U–O_I bond distances in the two compounds. The present findings argue strongly against this being the case.

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Notes

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Configurational and Vicinal Contributions to the Optical Activity of Tris(*l*-propylenediamine)cobalt(III) Ion[1]

BY BODIE E. DOUGLAS

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Corey and Bailar[2] have provided an explanation of stereospecific effects in terms of the conformations of chelate rings and the resulting interactions of substituents. It has been suggested[3,4] that $[Co(en)_3]^{3+}$ exists in solution as an equilibrium mixture of the lel and less stable ob forms. Mason favors this explanation for the relative intensities of the A_2 and E_a circular dichroism (CD) bands.

Vicinal and configurational effects have been shown to be separable and additive in $[Co(en)_2am]^{2+}$ (am = optically active amino acid anion)[5] and in $[Co(am)_3]$.[6] The stereospecific effects are expected to be smaller for α-amino acids than for substituted ethylenediamines because the chelate ring formed by the amino acid can assume a planar configuration with little or no strain.

In order to test the additivity of these effects for 1,2-propanediamine (pn), the CD was measured for a series of Co(III) complexes containing en and pn. Measurements were made for 0.005–0.01 *M* solutions in 1-cm. cells on a Roussel-Jouan Dichrograph.

The CD curves for (+)- and (−)-$[Co(l\text{-pn})_3en]^{3+}$ are shown in Figure 1 for the first absorption band region. The complexes show one and two CD peaks, respectively, as reported for the tris(propylenediamine) complexes.[4] These curves were added to give the summation curve shown. If one assumes that the optical activity is the result of additive configurational and vicinal effects, then the configurational effects (for right and left spirals) should cancel to leave four times the vicinal effect of *l*-pn. The vicinal effect for two *l*-pn (taken as one-half the summation curve at each wave length) was subtracted from the experimental curves to give the curves shown in Figure 2. These curves are mirror images and are very similar to the curve for (+)-$[Co(en)_3]^{3+}$ where there is no vicinal effect. The peaks (E_a, lower frequency, and A_2) have the same relative height as for $[Co(en)_3]^{3+}$.

In order to press the test for additivity further, the vicinal effect for one *l*-pn (taken as one-fourth the value at each λ from the summation curve in Figure 1)

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[1] This work was supported by a research grant (GM 10829-07) from the Division of General Medical Studies, Public Health Service.

[2] E. J. Corey and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 2620 (1959).

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[4] A. J. McCaffery, S. F. Mason, and B. J. Norman, *Chem. Commun.* (London), 49 (1965).

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[6] B. E. Douglas and S. Yamada, *ibid.*, **4**, 1561 (1965).

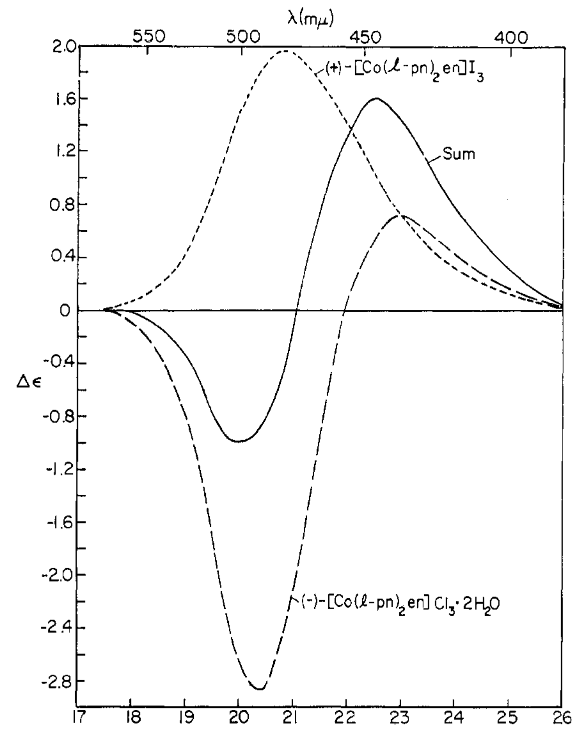

Figure 1.—The CD curves for (+)- and (−)-$[Co(l\text{-}pn)_2en]^{3+}$ and the sum curve.

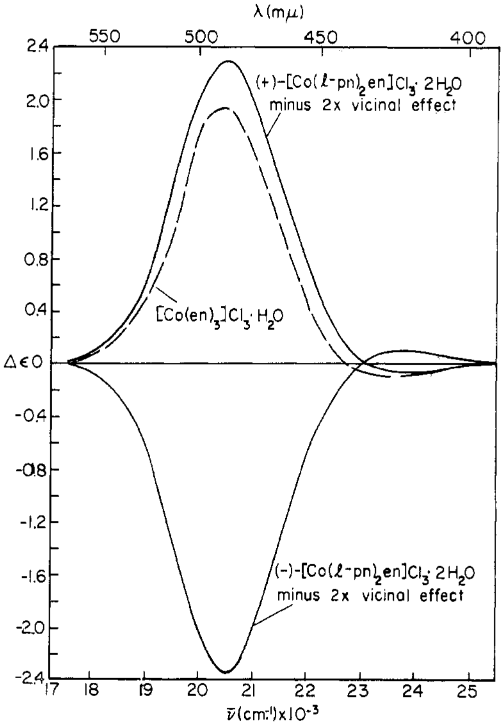

Figure 2.—Configurational effect curves for (+)- and (−)-$[Co(l\text{-}pn)_2en]^{3+}$ obtained from the curves in Figure 1; the CD curve for (+)-$[Co(en)_3]Cl_3 \cdot H_2O$.

was subtracted from the CD curve for (−)-$[Co(l\text{-}pn)(en)_2]Cl_3 \cdot H_2O$ with the result shown in Figure 3. The resultant curve is more similar in relative peak heights to that for $[Co(en)_3]^{3+}$ than is the experimental curve.

The CD curve for (+)-$[Co(l\text{-}pn)_3]Cl_3 \cdot 1.5H_2O$ shows a single peak (Figure 4), but the subtraction of the vicinal effect for three pn ($^3/_4$ × summation curve) gives a resultant curve very similar to that of $[Co(en)_3]^{3+}$. If six times the vicinal effect of one l-pn is subtracted from the CD curve for (+)-$[Co(l\text{-}pn)_3]^{3+}$ one obtains a curve with a very intense A_2 peak as reported[4] for (+)-$[Co(d\text{-}pn)_3]^{3+}$, to which this calculated curve should correspond.

The configurational and vicinal effects are not perfectly additive for all three types of pn–en complexes examined here, but they were not generally expected to be additive at all. One would not expect the vicinal contribution of a pn to be exactly the same in the three cases because of the crowding caused by the methyl

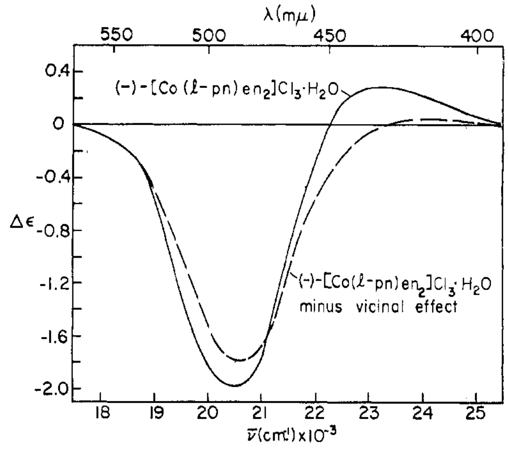

Figure 3.—The CD curve for (−)-$[Co(l\text{-}pn)(en)_2]Cl_3 \cdot H_2O$ and the configurational effect curve obtained using the vicinal effect (sum) curve from Figure 1.

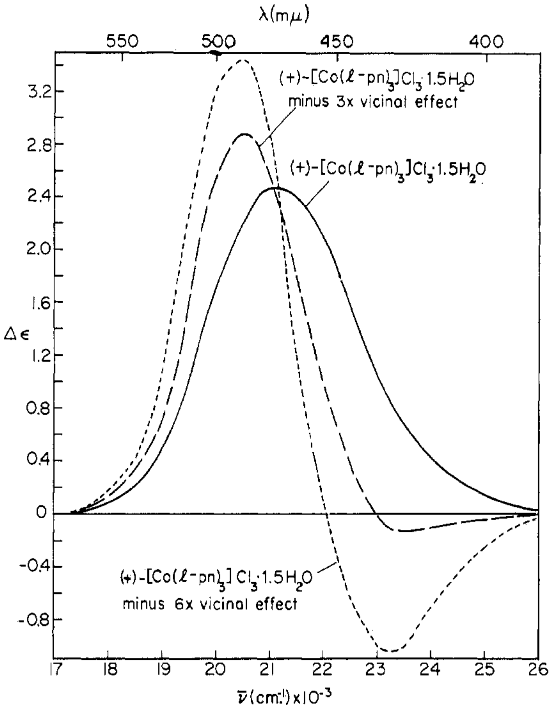

Figure 4.—The CD curve for (+)-$[Co(l\text{-}pn)_3]Cl_3 \cdot 1.5H_2O$ and the configurational effect curve obtained using the vicinal effect (sum) curve from Figure 1. The curve with six times the vicinal effect subtracted should correspond to (+)-$[Co(d\text{-}pn)_3]^{3+}$.

groups. However, it is clear that one does not have to assume an equilibrium between the ob and lel forms in order to explain the presence of sometimes one and sometimes two peaks for the mixed en–pn complexes. It must be largely the result of the fact that the configurational effect contributes most strongly to the E_a peak and the vicinal effect contributes most strongly to the A_2 peak, as observed for amino acids.[6] The observed curve is the sum of the two effects which contribute differently in magnitude and in sign so that A_2 can be quite strong (Figures 1 and 4) or completely covered by E_a (Figures 1 and 4).

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Facile Polyhedral Rearrangement of Icosahedral Silylcarboranes

BY RUDOLF M. SALINGER AND CECIL L. FRYE

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The thermal rearrangement of carborane ($C_2H_2B_{10}H_{10}$) to neocarborane has been reported[1,2] to take place at 465–500°, a change which moves the carbon atoms in the icosahedral cage from an *ortho* (1,2) to a *meta* (1,7) position. 1-Methylcarborane is isomerized to 1-methylneocarborane at 400° and is the only carborane derivative previously reported[1] to undergo this rearrangement.

A mechanism for this rearrangement (involving a cubeoctahedral intermediate) has been suggested,[3] and the prediction has been made that $B_{12}H_{10}X_2^{2-}$ would undergo polyhedral rearrangement by the same mechanism. A comprehensive study[4] of polyhedral rearrangements in $B_{12}H_{12}^{2-}$ and $B_{10}H_{10}^{2-}$ derivatives showed isomerizations in the $B_{12}H_{12}^{2-}$ series to be higher energy processes than those in the $B_{10}H_{10}^{2-}$ series. One of the most facile polyhedral rearrangements in the $B_{10}H_{10}^{2-}$ series involves 2,3-$B_{10}H_8[N(CH_3)_3]_2$, in which both steric interactions and electronic repulsions would be reduced by the isomerization. This reaction was reported to have an activation energy of only 37 kcal., with rearrangement exclusively to the 1,6 isomer being complete after 30 min. at 230° in solution. Attempts to observe such rearrangements in 1,2-$B_{12}H_{10}[N(CH_3)_3]_2$ (a member of the $B_{12}H_{12}^{2-}$ series which is analogous in structure and electronic configuration to the carboranes) failed because of decomposition of the compound at its melting point. Similar negative results were reported for 1,2-$B_{12}H_{10}[N(CH_3)_3]_2$ in Dowtherm A solution at 325°.

We now wish to report the *facile* rearrangement of suitably substituted icosahedral carboranes at relatively low temperatures. When the C-hydrogen atoms of carborane are replaced by the bulky methyldiphenylsilyl groups to give 1,2-bis(methyldiphenylsilyl)carborane (**1**), rearrangement to the neo isomer (**2**) is observed at 260°. Evidence for the rearranged species consists of a lower melting point, a shift in the methyl proton magnetic resonance signal from τ 9.45 to 9.23, and a change in the 9.3 μ region of the infrared spectrum. An authentic sample of **2** was synthesized from neocarborane and methyldiphenylchlorosilane *via* dilithioneocarborane and was found to be identical (infrared, n.m.r., mixture melting point, elemental analyses) with the above rearrangement product. Several related compounds were also examined; the results are summarized in Table I.

TABLE I
THERMAL REARRANGEMENT OF CARBORANES[a,b] TO NEOCARBORANES

$$1,2\text{-}R_2(C_2B_{10}H_{10}) \xrightarrow{\Delta} 1,7\text{-}R_2(C_2B_{10}H_{10})$$

	Reaction conditions		Compound designation and m.p., °C.	
R	Temp., °C.	Time, days	1,2-	1,7-
$CH_3(C_6H_5)_2Si$	260	2	**1**, 241–243	**2**, 138–140
$Cl(C_6H_5)_2Si$	260	2	**3**, 249–251[c]	**4**, 121–122[d]
$C_6H_5(CH_3)_2Si$	300[e]	4	**5**, 138–139	**6**, 82–85
$(CH_3)_3Si$	300[e]	10	**7**, 141–142	...
H	425	2	...[f]	...[f]

[a] Rearrangements of **1**, **3**, **5**, and **7** were followed qualitatively by infrared; of **1**, **5**, and **7** by n.m.r.; and of carborane by g.l.p.c. [b] Analytical results: **1**. Calcd. for $C_{28}H_{36}Si_2B_{10}$: C, 62.7; H, 6.76; Si, 10.45. Found: C, 62.8; H, 6.70; Si, 10.23. **2**. Calcd. for $C_{28}H_{36}Si_2B_{10}$: C, 62.7; H, 6.76; Si, 10.45. Found: C, 62.8; H, 7.17; Si, 10.84. **5**. Calcd. for $C_{18}H_{32}Si_2B_{10}$: C, 52.4; H, 7.82; Si, 13.6. Found: C, 53.3; H, 8.15; Si, 13.6. **6**. Calcd. for $C_{18}H_{32}Si_2B_{10}$: C, 52.4; H, 7.82; CH_3/C_6H_5, 6/5. Found: C, 53.2; H, 8.03; CH_3/C_6H_5, 6.1/5.0 (n.m.r.). **7**. Calcd. for $C_8H_{28}Si_2B_{10}$: C, 33.3; H, 9.79; Si, 19.5; B, 37.5. Found: C, 33.8; H, 9.70; Si, 19.3; B, 37.3. [c] Lit. 244–245° [S. Papetti and T. L. Heying, *Inorg. Chem.*, **2**, 1105 (1963)]. [d] Lit. 131–133° [ref. *c*]. [e] At 260° no evidence for rearrangement is observed for 5 days. [f] Infrared spectra of these compounds are identical with those published.[1]

The greater ease with which **1** rearranges is reasonably ascribed to the resulting relief of strain arising from juxtaposition of such large groups in the *ortho* isomer. 1,2-Bis(phenyldimethylsilyl)carborane (**5**), with presumably less internal strain, required a somewhat higher temperature for rearrangement. Even at this higher temperature, 1,2-bis(trimethylsilyl)carborane (**7**) rearranged considerably more slowly than did **5**. The fact that 1,2-bis(chlorodiphenylsilyl)carborane (**3**) undergoes rearrangement at nearly the same rate as **1** argues against the importance of electronic effects; while chlorine is approximately isosteric with methyl

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(1) D. Grafstein and J. Dvorak, *Inorg. Chem.*, **2**, 1128 (1963).

(2) (a) S. Papetti, B. B. Schaeffer, H. J. Troscianiec, and T. L. Heying, *ibid.*, **3**, 1444 (1964); (b) H. Schroeder and G. D. Vickers, *ibid.*, **2**, 1317 (1963).

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