Table II. Comparisons of Yields of X-Substituted Products^a from $[Cr(CN)(H_2O)_5]^{2+}$ and $[Cr(H_2O)_6]^{3+}$ under the Same Conditions

X^{n-}	$[X^{n-}]$	$[H^+]$	Time, hr	% yield from $[Cr(CN)(H_2O)_5]^{2+}$	$[Cr(H_2O)_6]^{3+}$
ClO_4^-	2.0	0.5	5	0.0	0.0
NO_3^-	2.0	0.5	5	2.5	0.7
Cl^-	2.0	0.5	5	0.7	0.0
Br^-	2.0	0.5	5	0.9	0.0
NCS^-	1.5	0.5	5	18	9
NCS^-	1.0	0.1	15	15	4
NCS^-	1.0	0.1	30	17	8
NCS^-	1.0	(pH 2)	15	24	7
NCS^-	1.0	(pH 2)	30	47	10
NCS^-	0.2	(pH 2)	30	12	9
NCS^-	0.2	(pH 3)	30	23	9
SO_4^{2-}	2.0	0.5	5	10	4
SO_4^{2-}	0.2	0.1	15	18	6
SO_4^{2-}	0.2	(pH 2)	15	30	6
			30	40	9
SO_4^{2-}	1.0	(pH 3)	13	48	14

^{a} See Table I for identities and amounts.

(III) increase with increasing pH, time, and anion concentration. Yields of anation products from hexaaquochromium-(III) under similar conditions are lower, essentially independent of pH and dependent only on time and anion concentration. The improved stability against acid-catalyzed aquation of cyanopentaaquochromium(III) at pH 2-3 ensures a longer time for the cyanide ligand to exert its influence on substitution reactions. Its effect is clearly that of labilizing coordinated water to favor an increased rate of exchange.

The experimental results do not enable a distinction to be made as to whether the cyanide ligand exerts a trans- or a cis-labilizing effect in cyanopentaaquochromium(III). It was hoped that complexes of the type $[Cr(H_2O)_4(CN)X]^{3-m}$ would be produced in sufficient yields to permit identification of their geometries, thereby revealing either cis or trans labilization. Various attempts to prepare the mixed cyano-sulfato ($X^{2-} = SO_4^{2-}$) species failed, even at ice temperatures. Apparently, loss of cyanide is greatly enhanced once sulfate ion coordination occurs. Some success in preparing the mixed-ligand complex was realized in the case of the thiocyanato (X = NCS) complex. Its presence in the different reaction mixtures was conclusively demonstrated; however, conditions for producing it in high yield were not found. The limited amounts produced were insufficient for detailed characterization and structure determination. Based on earlier studies[2-6] and lacking any new evidence to the contrary, it is believed that the cyanide ligand of cyano-pentaaquochromium(III) exerts a trans- rather than a cis-labilizing effect.

Ours is believed to be the first observation of the $[Cr(H_2O)_4(CN)(NCS)]^+$ complex ion, and further more detailed studies are planned, provided that it can be prepared in the pure form and in higher concentration. Only small amounts were found in the reaction mixtures of the present study, along with unreacted $[Cr(H_2O)_5(CN)]^{2+}$ and various other thiocyanato complexes. The order of elution of these species from the ion-exchange column was $[Cr(H_2O)_3(NCS)_3]$, $[Cr(H_2O)_4(CN)(NCS)]^+$, $[Cr(H_2O)_4(NCS)_2]^+$, $[Cr(H_2O)_5(CN)]^{2+}$, $[Cr(H_2O)_5(NCS)]^{2+}$, $[Cr(H_2O)_6]^{3+}$, using deionized water to remove the first, 0.2 M K_2SO_4 (pH 2.5) to remove the next four, and 0.6 M K_2SO_4 to remove the last of these species from the column. Identification of the red $[Cr(H_2O)_4(CN)(NCS)]^+$ complex ion in dilute solutions was by spectrophotometric determination of chromium, thiocyanate, and cyanide contents. Typical results gave molar ratios respec-

tively of 1.0:1.1:1.3, indicating some contamination. Analysis of known mixtures demonstrated that the method for determination of cyanide[13] is free of interference from either chromium or thiocyanate. Spectra of the dilute solutions, measured in a 10-cm cell, exhibited two bands in the visible region, one at approximately 530 nm of $\epsilon \sim 46$ l. mol^{-1} cm^{-1} and another at about 403 nm of $\epsilon \sim 50$ l. mol^{-1} cm^{-1}. An intense charge-transfer band appears in the near-ultraviolet spectrum.

Quantitative recovery of chromium was achieved without recourse to unusually large volumes or concentrations of elution agents. The efficiency of potassium sulfate solutions as a cation eluting agent is probably enhanced by the pronounced tendency of sulfate ions to form ion pairs with multivalent cations, thereby lowering their charge and promoting desorption. Use of perchloric acid as eluting agent, although noncomplexing, was precluded by the instability of the cyano complexes in strongly acidic solutions. No detectable amount of sulfate substitution occurred during the relatively short time required for chromatographic separation and analysis.

Solid samples of $[Cr(H_2O)_5(CN)]SO_4 \cdot H_2O$ (containing about 10% K_2SO_4) exposed to moist air decompose gradually, giving off hydrogen cyanide and turning dark green. The green residue contains an appreciable amount of an anionic chromate(III) species with adsorption characteristics closely resembling those reported for the disulfatotetraaquo-chromate(III) anion.[14]

Storage of the solid monocyano complex in tightly closed, dark containers, produced only partial decomposition.

Registry No. $[Cr(H_2O)_5CN]SO_4 \cdot H_2O$, 38782-96-6; $[Cr(H_2O)_5(CN)](ClO_4)_2$, 38782-97-7; $[Cr(H_2O)_6](ClO_4)_3$, 27535-70-2; LiClO$_4$, 7791-03-9; LiNO$_3$, 7790-69-4; LiCl, 7447-41-8; LiBr, 7550-35-8; LiNCS, 556-65-0; Li$_2$SO$_4$, 10377-48-7.

(14) N. Fogel, J. M. J. Tai, and J. Yarborough, *J. Amer. Chem. Soc.*, **84**, 1145 (1962).

Studies of Hydroxy Acid Complexes. II. Lactatobis((R)-1,2-propanediamine)cobalt(III) Complexes

Roland A. Haines* and Anthony A. Smith

We have previously reported[1] the optical activity associated with complexes of the type $[Co(en)_2ha]^+$ where en is ethylenediamine and ha is an optically active hydroxy acid. The configurational and vicinal effects associated with those complexes were separated out and it was found that both effects had very significant contributions to the net circular dichroism. This was contrary to results obtained for other related systems containing amino acids,[2,3] and this was surprising since hydroxy acids are the oxygen analogs of amino acids and one would anticipate that there should have been a great deal of similarity between the two systems. In an

(1) E. B. Kipp and R. A. Haines, *Inorg. Chem.*, **11**, 271 (1972).
(2) C. T. Liu and B. E. Douglas, *Inorg. Chem.*, **3**, 1356 (1964).
(3) S. K. Hall and B. E. Douglas, *Inorg. Chem.*, **8**, 372 (1969).

attempt to gain further information concerning the changes produced by hydroxy acids we have examined complexes of the type $[Co(R\text{-}pn)_2(lactate)]^+$ where R-pn is (R)-1,2-propanediamine and lactate is the anion of optically active lactic acid. Since the R-pn ligands favor coordination with a preferred conformation, certain restrictions could be placed on the conformation of the hydroxy acid ring. The results of our study are reported here.

Experimental Section

All chemicals were used without further purification. $(R(-))$-lactic acid ($[\alpha]_{589}$ $-1.76°$) and $(S(+))$-lactic acid ($[\alpha]_{589}$ $+2.58°$) were obtained as 30% aqueous solutions from Miles Laboratories. $[Co(R\text{-}pn)_2CO_3]ClO_4$ was prepared as described previously.[4]

Preparation of Lactatobis((R)-1,2-propanediamine)cobalt(III) Perchlorate. $[Co(R\text{-}pn)_2CO_3]ClO_4$ (0.5 g) and one optical isomer of lactic acid (0.27 g) were weighed into a flask and dissolved in ~20 ml of water. The mixture was refluxed for 4 hr on a steam bath and was then transferred to an evaporating dish and taken to dryness on the steam bath.

Separation of isomers from the crude reaction product was a-chieved using thin-layer chromatography. A concentrated solution of the reaction product in water was spotted in 10 × 20 cm plates of Camag DS-O silica gel 1 mm in thickness and developed with water. Some minor components were separated in this way and a dark red band formed the major part of the chromatogram. This product was washed off the silica gel with water and a solid product was obtained by evaporating the filtered solution to dryness at room temperature in an air stream. The product was then re-chromatographed and recovered as before.

Anal. Calcd for $[Co(R\text{-}pn)_2(lactate)]ClO_4$: C, 27.39; H, 6.13; N, 14.19; Cl, 8.98. Found for $R(-)$-lactate: C, 27.55; H, 6.04; N, 14.01; Cl, 8.79. Found for $S(+)$-lactate: C, 27.18; H, 6.22, N, 14.08; Cl, 8.88. Molar conductivity: for $R(-)$-lactate, 88 mhos cm² mol⁻¹; for $S(+)$-lactate, 93 mhos cm² mol⁻¹.

Microanalyses were performed by Alfred Bernhardt, Elbach, West Germany. Absorption spectra were recorded on a Beckman DK-1 spectrophotometer and circular dichroism spectra were obtained using a Durrum–Jasco ORD/UV-5/CD-1 spectropolarimeter. Nmr spectra were recorded on Varian T-60 or HA-100 spectrometers using deuterium oxide as solvent with sodium 2,2-dimethyl-2-silapentanesulfonate (NaDSS) as an internal reference.

Results and Discussion

The starting material $[Co(R\text{-}pn)_2CO_3]^+$ is capable of existing in three geometrical arrangements. However, CD and nmr data have revealed[4] that one isomer is formed preferentially and this has the Δ configuration.[5] The particular geometric isomer formed is cis(N_2),trans(N_1) where N_1 and N_2 refer to the amino groups attached to the 1 and 2 positions, respectively, on the propane chain. On reaction with lactic acid this particular configuration would be expected to be maintained since the removal of carbonate is known[6] to occur with retention of configuration in $[Co(en)_2$-$CO_3]^+$ and this retention should be even more favored here. This is due to the fact that coordination of R-pn with the λ conformation is strongly favored since the methyl group is then in an equatorial position and the complex has added stability.[7] Consequently the Δ arrangement of R-pn rings would be expected to be maintained upon reaction with lactic acid. Thus the CD spectra of the two isomers isolated, $[Co(R\text{-}pn)_2(R(-)\text{-lactate})]^+$ and $[Co(R\text{-}pn)_2(S(+)\text{-lactate})]$, would be anticipated to be rather similar, the chief difference being that the vicinal effect of the lactate ion would be of opposite sign in the two isomers. As shown in Figure 1, this
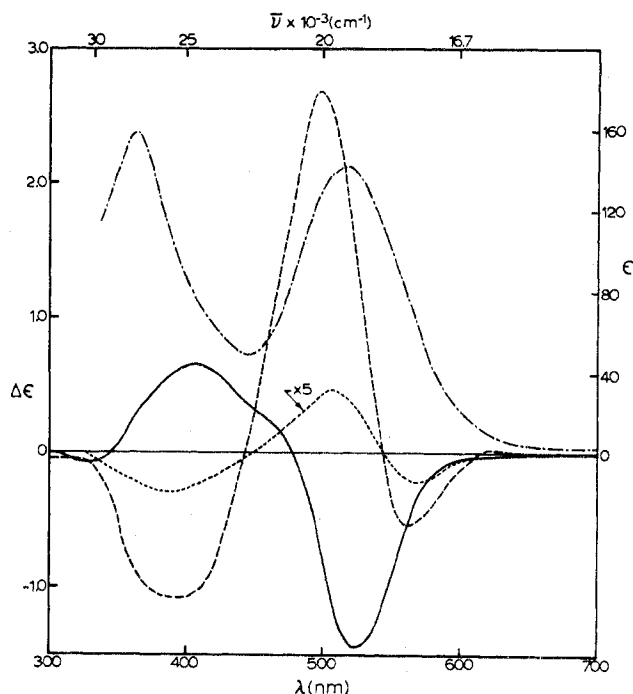

Figure 1. Circular dichroism spectra of Δ-$[Co(R\text{-}pn)_2(S(+)\text{-lactate})]ClO_4$ (———), Δ-$[Co(R\text{-}pn)_2(R(-)\text{-lactate})]ClO_4$ (— — —), and (from ref 1) $[Co(NH_3)_4(R(-)lactate)]Cl$ (— — — — —). Absorption spectrum of $[Co(R\text{-}pn)_2(R(-)lactate)]ClO_4$ (— · — · —).

was not found to be the case. The CD spectra are completely different and the predominant bands are of opposite sign. The $[Co(R\text{-}pn)_2(R(-)\text{-lactate})]ClO_4$ species had peaks at 561 nm ($\Delta\epsilon = -0.55$) and 498 nm ($\Delta\epsilon = 2.66$) while the compound $[Co(R\text{-}pn)_2(S(+)\text{-lactate})]ClO_4$ had one peak at 524 nm ($\Delta\epsilon = -1.40$). Both species had absorption maxima at 516 nm (ϵ 148 for $R(-)$-lactate, ϵ 139 for $S(+)$-lactate) and 363 nm (ϵ 163 for $R(-)$-lactate, ϵ 156 for $S(+)$-lactate). These results could be indicative of two possibilities: (i) there has been an inversion of configuration about the cobalt or (ii) the vicinal effect due to the coordinated lactate ion has become quite pronounced and is severely altering the shapes of the curves.

The first possibility does not appear to obtain here and this is particularly evident from the nmr spectrum. For $[Co(R\text{-}pn)_2(R(-)\text{-lactate})]^+$ the methyl resonances due to the R-pn and lactate ion overlap and peaks are seen at 1.26 and 1.33 ppm downfield from NaDSS. For $[Co(R\text{-}pn)_2$-$(S(+)\text{-lactate})]^+$ the methyl resonances due to the lactate ion are separate and occur at 1.36 and 1.30 ppm while the methyl resonances of R-pn again occur at 1.26 and 1.33 ppm. Previous studies[1] on the analogous ethylenediamine series have shown the usefulness of nmr in determining the stereochemistry of these diastereoisomers and other systems have similarly been examined.[8-14] Since the methyl

(4) R. A. Haines and A. A. Smith, *Can. J. Chem.*, **49**, 3907 (1971).

(5) The nomenclature is that proposed by the IUPAC, *Inorg. Chem.*, **9**, 1 (1970).

(6) F. P. Dwyer, A. M. Sargeson, and I. K. Reid, *J. Amer. Chem. Soc.*, **85**, 1215 (1963).

(7) E. J. Corey and J. C. Bailar, *J. Amer. Chem. Soc.*, **81**, 2620 (1959).

(8) J. I. Legg, D. W. Cooke, and B. E. Douglas, *Inorg. Chem.*, **6**, 700 (1967).

(9) D. A. Buckingham, L. Durham, and A. M. Sargeson, *Aust. J. Chem.*, **20**, 257 (1967).

(10) J. G. Brushmiller and L. G. Stadtherr, *Inorg. Nucl. Chem. Lett.*, **3**, 525 (1967).

(11) E. A. Berends and J. G. Brushmiller, *Inorg. Nucl. Chem. Lett.*, **6**, 847 (1970).

(12) L. G. Stadtherr and J. G. Brushmiller, *Inorg. Nucl. Chem. Lett.*, **6**, 907 (1970).

(13) L. N. Shoenberg, D. W. Cooke, and C. F. Liu, *Inorg. Chem.*, **7**, 2386 (1968).

(14) J. C. Dabrowiak and D. W. Cooke, *J. Amer. Chem. Soc.*, **92**, 1097 (1970).

resonances of the R-pn group are constant for the two species, it is reasonable to assign the same overall configuration to both. On the basis of arguments presented above concerning the starting carbonate complex, this should be the Δ configuration. Further support for the Δ configuration can be derived from the relative positions of the methyl protons of the lactic acid. For the Δ configuration, molecular models indicate that more steric compression of the methyl protons is experienced for coordinated $S(+)$-lactate. Hence these should have resonances at lower field[14] as was found to be the case.

Further evidence for the Δ configuration comes from the CD spectrum. The $S(+)$-lactate complex has a large negative band in the region of the $A_{1g} \rightarrow T_{1g}$ transition and is similar to that of Δ-$[Co(R\text{-}pn)_2CO_3]^+$ reported earlier[4] and that of Δ-$[Co(en)_2(S(+)\text{-}lactate)]^{+}$.[1] The R-lactate compound has a CD sign pattern similar to that found earlier[1] for Δ-$[Co(en)_2(R(-)\text{-}lactate)]^+$ but the relative intensities differ quite markedly. However, since the sign patterns of the individual transitions are identical, it would appear that both of the isolated lactate species indeed have the Δ configuration.

The difference in CD spectra therefore appears to arise from a very significant contribution from the vicinal effect, and as is shown for the $R(-)$-lactate complex, the vicinal effect predominates over the configurational effect in its contribution to the observed CD spectrum. The contribution from vicinal effects should exhibit CD spectra similar in shape to those determined for the analogous ethylenediamine systems.[1] However, there will be differences, other than sign for the two acids since the conformational preferences of the other rings present have a very marked effect on the vicinal CD intensity. This was quite evident for the $[Co(en)_2(lactate)]^+$ complexes where the vicinal CD intensity was an order of magnitude greater than that of $[Co(NH_3)_4(lactate)]^+$. The coordinated R-pn ligands have an even greater conformational preference and hence the enhanced vicinal effect could be related to this. Moreover, the two acids would not necessarily have the same vicinal effect in terms of absolute magnitude since the relationship of the coordinated acid to the other ligands is not enantiomeric as it is in other systems studied. The vicinal CD appears to be strongest for the R-lactate ion and this is consistent with predictions from conformational arguments. For Δ-$[Co(R\text{-}pn)_2(R(-)\text{-}lactate)]^+$ all three chelate rings would have the same configuration and would be coordinated with the λ conformation. The C–C bonds of the chelate would thus have the lel arrangement[7] and the CD due to the vicinal effect of all ligands would enhance each other.

The findings of our study are significant in that an example has been found in which the vicinal contribution to the optical activity outweighs the configurational contribution. Further studies are now in progress to determine reasons for such a situation.

Molecular Orbital Descriptions of the Bonding in Bis(amino)diborane(4) and (Amino)vinylborane as Theoretical Models for Photochemical Reactivity
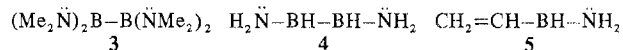
Anthony K. Uriarte and Kenneth G. Hancock*

We recently reported that the photochemistry of 1,2-bis-(dimethylamino)-1,2-diphenyldiborane(4) (1) was best rationalized in terms of photolytic boron–boron homolysis as the primary process.[1] The contrast between this reaction and the photochemical electrocyclic ring closure of the isoelectronic 2,3-diphenyl-1,3-butadiene[2] (2), while thermodynamically reasonable, is nevertheless striking. In order to gain further insight into the causes for the diverging excited-state properties of the bis(amino)diborane(4) and butadiene
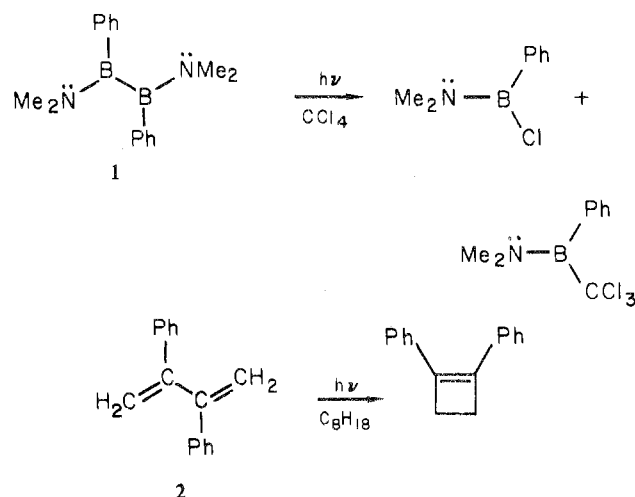
systems, a theoretical investigation of the electronic structure of the $>$N–B–B–N$<$ chromophore seemed desirable. Several theoretical studies of the closely related tetrakis(amino)-diborane(4) (3) system have appeared,[3] but these are not sufficient since the photochemistry of tetrakis(dimethylamino)diborane(4) and bis(amino)diborane(4) systems are significantly different.[4]

$$(Me_2\ddot{N})_2B–B(\ddot{N}Me_2)_2 \quad H_2\ddot{N}–BH–BH–\ddot{N}H_2 \quad CH_2=CH–BH–\ddot{N}H_2$$
$$\quad\quad\quad\; 3 \quad\quad\quad\quad\quad\quad 4 \quad\quad\quad\quad\quad\quad\quad 5$$

Accordingly, two systems—bis(amino)diborane(4) (4) and (amino)vinylborane (5)—were chosen so as to note any trends in the electronic redistribution as one and then two aminoboryl moieties are substituted for the vinyl linkages in butadiene. Two all-valence-electron semiempirical solutions to the Schrodinger equation were employed: (a) extended Huckel theory, iterated to self-consistent charge (EHT–SCC);[5] and (b) the intermediate neglect of differential overlap (INDO) approximation.[6] Although both offer economic advantages over *ab initio* methods, INDO in particular has

(1) K. G. Hancock and A. K. Uriarte, *J. Amer. Chem. Soc.*, 92, 6374 (1970).
(2) E. H. White and J. P. Anhalt, *Tetrahedron Lett.*, 3937 (1965).
(3) (a) P. G. Perkins and D. H. Wall, *J. Chem. Soc. A*, 1207 (1966); (b) N. C. Baird and M. A. Whitehead, *Can. J. Chem.*, 45, 2059 (1967).
(4) K. G. Hancock, A. K. Uriarte, and D. A. Dickinson, submitted for publication.
(5) R. Hoffmann, *J. Chem. Phys.*, 39, 1397 (1963).
(6) J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *J. Chem. Phys.*, 47, 2026 (1967).