

from both mechanistic and thermodynamic considerations.^{11,12}

Enzymic degradation of the polymer is being investigated by Dr. Elwyn T. Reese at the U. S. Army Natick Laboratories.

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(11) E. R. Ruckel and C. Schuerch, *J. Org. Chem.*, **31**, in press.

(12) NOTE ADDED IN PROOF. E. Huseman and G. J. M. Muller, *Makromol. Chem.*, **91**, 212 (1966), report the synthesis of poly- β -(1 \rightarrow 4)-anhydro-D-glucopyranose, $\overline{DP}_w = 60$.

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The Circular Dichroism of the $[\text{PtCl}_4]^{2-}$ Ion

Sir:

The weak-to-moderate intensity $d \rightarrow d$ transitions of dissymmetric metal complexes show strong circular dichroism when the transition is magnetic dipole allowed in the donor group microsymmetry of the complex.¹ This selection rule has been employed² in the assignment and the interpretation of these spectra, but, except for one reported example,³ the use of this criterion has been restricted to complexes which are dissymmetric. We wish here to draw attention to the possibility of extending this method to complexes which are formally optically inactive and, in the present example, to determining the polarization direction of the transition.

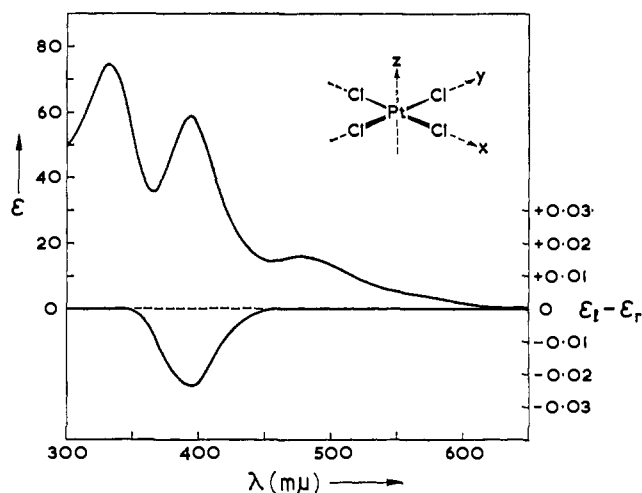


Figure 1. The visible absorption spectrum and circular dichroism of the $[\text{PtCl}_4]^{2-}$ ion in $D(-)$ -2,3-butanediol. Shown in the inset is the coordinate frame of the ion referred to in the text.

When the complex $\text{Na}_2[\text{PtCl}_4]$ is dissolved in $D(-)$ -2,3-butanediol, the unpolarized electronic absorption spectrum of a fresh solution of the ion is hardly altered in position and intensity from that found in the solid and in aqueous solution, but circular dichroism is observed at one of the $d \rightarrow d$ transitions (Figure 1).

The square-planar d^8 diamagnetic ion $[\text{PtCl}_4]^{2-}$ has

- (1) W. Moffitt, *J. Chem. Phys.*, **25**, 1189 (1956).
- (2) S. F. Mason, *Quart. Rev. (London)*, **17**, 20 (1963).
- (3) S. F. Mason and B. J. Norman, *Chem. Commun.*, 335 (1965).

three spin-allowed $d \rightarrow d$ transitions, $^1A_{1g} \rightarrow ^1B_{1g}$, $^1A_{2g}$, 1E_g , which have been assigned with some certainty.^{4,5} The $^1A_{1g} \rightarrow ^1A_{2g}$ transition has been shown⁴ by a vibronic analysis of the polarized crystal spectrum to occur at about 390 $m\mu$, and from the magnetic circular dichroism of the ion the $^1A_{1g} \rightarrow ^1E_g$ transition has been shown⁵ to occur at about 335 $m\mu$ (Figure 1). It can be shown that the $^1A_{1g} \rightarrow ^1A_{2g}$ transition is magnetic dipole allowed in z -axis polarization while the $^1A_{1g} \rightarrow ^1E_g$ transition should be allowed in the x, y plane of the axis system shown in Figure 1. The $^1A_{1g} \rightarrow ^1B_{1g}$ transition (at 480 $m\mu$) is forbidden in magnetic dipole radiation fields, and we would expect that if this band shows any circular dichroism it should be very much weaker than that exhibited by the other two.

Experiment shows that only the $^1A_{1g} \rightarrow ^1A_{2g}$ (z -polarized) band has any detectable circular dichroism, suggesting that the dissymmetric influences of the solvent are concentrated and directed at the tetragonal ($+z$ and $-z$) positions of the ion. Although this may indicate weak coordination of the solvent in these positions, the extent of covalent participation must be extremely small since the spectrum of the ion is not appreciably altered by this effect. Alternatively, it seems unlikely that the appearance of circular dichroism is due to dissymmetric distortion of the molecular framework of the ion by the solvent, because under these circumstances we would expect to see the appearance of circular dichroism in both the z - and x, y -polarized transitions and not only in the unique polarization which is observed.

(4) D. S. Martin and C. A. Lenhardt, *Inorg. Chem.*, **3**, 1368 (1964).

(5) D. S. Martin, J. G. Foss, M. E. McCarville, M. A. Tucker, and A. J. Kassmann, *ibid.*, **5**, 491 (1966).

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A New Reaction of Diborane with Carbon Monoxide Catalyzed by Sodium Borohydride. A Convenient Synthesis of Trimethylboroxine

Sir:

In 1937 it was reported by Schlesinger and Burg that diborane reacts with carbon monoxide at 100° in a sealed tube under 20 atm pressure to form a simple addition compound, borane carbonyl.¹ The product is a gas, stable at low temperatures, but largely dissociated into its components at ordinary temperatures and pressures (eq 1). This reaction and its product



have since been the subject of numerous investigations.²

We have examined the reaction of carbon monoxide with diborane in tetrahydrofuran solution, following the rate of absorption by adapting the automatic hydrogenator previously described.³ In the absence of sodium borohydride only a small quantity of carbon monoxide

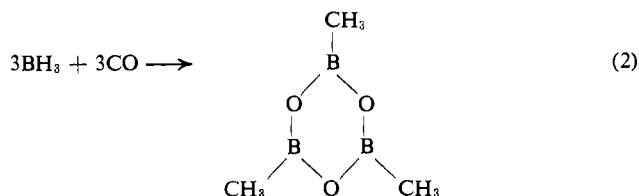
(1) A. B. Burg and H. I. Schlesinger, *J. Am. Chem. Soc.*, **59**, 780 (1947).

(2) A. B. Burg, *ibid.*, **74**, 3482 (1952); J. C. Carter and R. W. Parry, *ibid.*, **87**, 2354 (1965); T. P. Fehner and W. S. Koski, *ibid.*, **87**, 409 (1965).

(3) C. A. Brown and H. C. Brown, *ibid.*, **84**, 2829 (1962). We utilized a commercial model of the hydrogenator available from Delmar Scientific Laboratories, Maywood, Ill. 60154.

is absorbed by the solution at room temperature and atmospheric pressure, as indicated by curve A, Figure 1. Presumably this absorption is the result of the formation of a small equilibrium concentration of borane carbonyl. However, in the presence of a small catalytic quantity of sodium borohydride, the absorption of carbon monoxide is far more rapid and proceeds to the utilization of 1 mole of carbon monoxide per mole of borane present in the reaction mixture, as is evident from curve B, Figure 1.

Distillation of the reaction mixture provided trimethylboroxine⁴ in a yield of 84%.⁵ Consequently, the reaction is that shown in (2).



One mole of borane in 344 ml of tetrahydrofuran and 0.02 mole of sodium borohydride were placed in the reaction flask of the automatic hydrogenation apparatus.³ Sulfuric acid, 300 ml, maintained at 90°, was placed in the generator flask and anhydrous formic acid, 50 ml, in the buret. Carbon monoxide generated from the reaction of formic acid with the sulfuric acid was used to flush the system, and the reaction was initiated by magnetically stirring the contents of the reaction flask. (The mercury valve automatically meters the formic acid into the generator to maintain the pressure as the carbon monoxide is utilized. Consequently, a reading of the buret indicates the number of moles of carbon monoxide absorbed; 1 ml of formic acid delivers 26.6 mmoles of the gas.) Representative data for reaction in the presence and absence of sodium borohydride are shown in Figure 1. Following completion of the absorption, the tetrahydrofuran solution was carefully fractionated with an efficient column. There was obtained 35.0 g of trimethylboroxine, bp 79–80° at 745 mm (lit.^{4a} bp 79°), n_D^{20} 1.3638, trimethylamine adduct mp 67° (lit.^{4a} mp 67°). Further confirmation is provided by the proton nmr spectrum which showed only a single peak at δ 0.39 relative to TMS.

We explored the amount of sodium borohydride necessary to achieve this reaction. As little as 0.3 mole % proved to be effective, although we adopted 2 mole % for the synthetic procedure described above. Since sodium borohydride does not react with carbon monoxide under these conditions, it is probable that it functions by reducing borane carbonyl, and the intermediate thus produced reacts with diborane to regenerate sodium borohydride and a species which then undergoes transformation into the product. We shall elaborate on a proposed mechanism in a later publication.

Sodium borohydride also catalyzes the reaction of trialkylboranes with carbon monoxide,⁶ and we are currently exploring this reaction.

(4) (a) A. B. Burg, *J. Am. Chem. Soc.*, **62**, 2228 (1940); (b) P. A. McCusker, E. C. Ashby, and H. S. Makowski, *ibid.*, **79**, 5179 (1957).

(5) Trimethylboroxine has been obtained previously in an over-all yield of 12% by the dehydration of methylboronic acid, synthesized from methyl borate and methylmagnesium halide.⁴

(6) M. E. D. Hillman, *J. Am. Chem. Soc.*, **84**, 4715 (1962); **85**, 982 (1963).

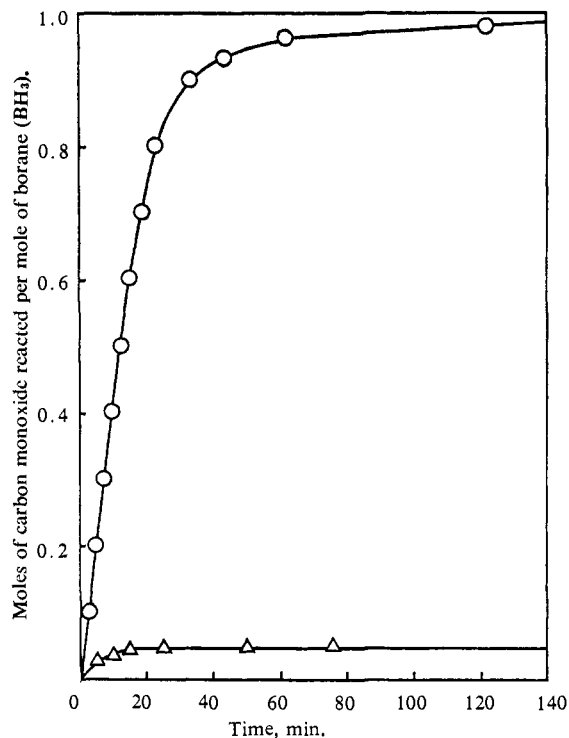


Figure 1. Reaction of carbon monoxide at atmospheric pressure with borane in tetrahydrofuran (0.5 M) at 25°: Δ, curve A, no sodium borohydride; O, curve B, 2 mole % sodium borohydride added.

Finally, we wish to call attention to the fact that tri-*n*-butylboroxine has proven to be a highly useful reagent for the identification and separation of isomeric *cis-trans* diols.⁷ Trimethylboroxine possesses obvious advantages for this application, such as greater volatility of the cyclic esters and greater stability to atmospheric oxygen. Consequently, the ready synthesis of trimethylboroxine *via* the present synthesis should greatly facilitate its availability for this application.

(7) H. C. Brown and G. Zweifel, *J. Org. Chem.*, **27**, 4708 (1962).

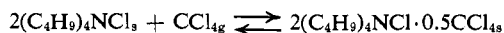
(8) National Science Foundation Fellow, 1964–1966.

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The CCl₃⁻ Species

Sir:

Preliminary studies have revealed evidence of compound formation between carbon tetrachloride and tetrabutylammonium chloride. Figure 1 shows the 0° pressure-composition isotherm for the system CCl₄-(C₄H₉)₄NCl and shows evidence of solid phases having CCl₄/(C₄H₉)₄NCl mole ratios of 0.5, 0.93 (currently interpreted as 1.0), and 4.8. We suggest that (C₄H₉)₄NCl·0.5CCl₄ is a mixed salt containing Cl⁻ and CCl₃⁻ ions. The approximate enthalpy of the reaction



calculated using the van't Hoff equation and decomposition pressures over the temperature range 0° to 70° is -9 ± 2 kcal. (C₄H₉)₄NCl·0.5CCl₄ melts at approximately 80° to give a pale yellow liquid. The re-