

CHEMISTRY

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ABSTRACTS

Why Square Planar Complexes Exist. LINDA S. HILL and ERWIN BOSCHMANN, Department of Chemistry, Indiana University-Purdue University at Indianapolis, Indiana 46202.—An important characteristic of coordination complexes (AB_x) is the coordination geometry. Symmetry considerations, steric factors, and electronic repulsions alone can often correctly predict the geometry of a complex, *i.e.*, AB_2 and AB_3 systems are expected to be of linear and trigonal planar geometries, respectively. But the AB_4 system is different in that two configurations, tetrahedral and square planar, are possible. Based on steric or electronic repulsions, only tetrahedral complexes should exist. However, a number of transition metals prefer the planar configuration. For these cases, barring steric limitations, crystal field stabilization energy (CFSE) becomes the important feature in structure determination. This aspect of theoretical inorganic chemistry is all too often dismissed with brief statements such as 'd⁸ electronic configurations are more likely to form planar complexes', or 'the scale is tipped in favor of a square configuration at d⁸ due to large CFSEs'. These vague arguments do not adequately explain for instance why $NiCl_4^{2-}$, a d⁸ system, is tetrahedral while $Ni(CN)_4^{2-}$ is planar, or why some d⁷ and d⁹ systems also have planar configurations. We have found it instructive to treat this point by preparing carefully chosen plots of CFSE *differences vs.* 'd' electron population. Not only can the structures of existing AB_4 complexes be clearly understood, but the structures of as yet unknown AB_4 species can be predicted as well.

Rhenium (I) Complexes of 2-Cyanophenyldiphenylphosphine. BRUCE N. STORHOFF and ANTHONY J. INFANTE, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—Novel, Re(I) derivatives of 2-cyanophenyldiphenylphosphine (L) have been isolated in good yields from the reactions of $Re(CO)_5X$ (X=Cl, Br) with L in refluxing benzene. These derivatives are stable and colorless, but, unfortunately, nearly insoluble in all organic solvents. The stoichiometries have been established as $(Re(CO)_3LX)_n$ from elemental analyses. Thorough infrared and Raman spectroscopic studies of these molecules indicate that for both, the CO groups are in a *fac* arrangement around the metal center. In addition, these studies indicate that L functions as a bidentate bridging ligand rather than as a bidentate chelating ligand.

The Stereochemistry of Reactions at Carbon Transition Metal σ -Bonds. P. L. BOCK, Department of Chemistry, Ball State University, Muncie, Indiana 47306, and G. M. WHITESIDES, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139.—The use of the stereospecifically 1,2-dideuterated 3,3-dimethylbutyl grouping as a stereochemical probe is discussed. Convenient syntheses of the parent compounds *threo*- and *erythro*-3,3-dimethylbutan-1-ol-1,2- d_2 (1) are described. Reactions of the *p*-bromobenzene sulfonate esters of 1 with $C_5H_5Fe(CO)_2$ yields alkyliron compounds with >95% inversion of configuration at carbon. The stereochemical results for halogenation, oxidation, thermal decomposition and insertion reactions of the alkyliron species are presented.

Synthesis and Catalytic Properties of a Cyclic Octapeptide. MARJORIE SVOBODA and R. W. ROESKE, Department of Biochemistry, Indiana University Medical Center, Indianapolis, Indiana 46202.—The cyclic octapeptide, cyclo lysyl glycyl *p*-aminobenzoyl glycyl histidyl glycyl *p*-aminobenzoyl glycyl, has been synthesized by the solution technique. This peptide was designed to have some of the characteristics of an enzyme: a hydrophobic cavity for substrate binding, a histidine residue as a catalytic site and a charged group, the protonated ϵ amino group of lysine, to enhance solubility in water.

To ascertain the catalytic properties of this peptide, a number of substrates were synthesized; the nitrophenyl esters of *t*-butoxycarbonyl glycyl *p*-aminobenzyl glycine, *t*-butoxycarbonyl glycyl (valyl) gamma amino butyryl glycine, *N* succinyl 11 aminoundecanoic acid, 2,4 dinitrophenyl lysyl glycine, and carbobenzoxy glutamyl glycine. These esters were designed to fit the hydrophobic cavity of the cyclic peptide to properly position the ester carbonyl with respect to the histidine imidazole nitrogen.

The hydrolysis of the esters in phosphate buffer at pH 7 was followed by the change in absorbance at 400 nanometers with the Cary 14 Spectrophotometer. K_{cat} values for the cyclic peptide catalyzed hydrolyses were compared with those obtained for imidazole and a small histidine peptide. It will be attempted to correlate the kinetic results with interactions between the cyclic peptide and substrate molecules.

Syntheses and Binding Properties of Cyclic Hexapeptides Containing *CIS*-4-Aminocyclohexane Carboxylic Acid. S. M. KALBAG and R. W. ROESKE, Department of Biochemistry, Indiana University Medical Center, Indianapolis, Indiana 46202.—Cyclohexaamylose has been studied extensively as a model for a hydrophobic binding site of an enzyme, by M. Bender, F. Cramer and others. Attempts to modify cyclohexaamylose by replacing one or more of the hydroxyls by amino, sulfhydryl or imidazole groups have not been very successful. We synthesized a series of cyclic peptides that resemble the cycloamyloses in size and shape. The peptides consist of four or five residues of *cis*-4-aminocyclohexane carboxylic acid (Acc) or *cis*-4-hydroxycyclohexane carboxylic acid (Hcc).

The following cyclic peptides have already been synthesized (I through III), and synthesis of IV is in progress.

Lys (Acc) ₅	I
Lys Acc Acc Gly Acc Acc	II
Lys Acc Hcc Gly Acc Hcc	III
Lys Gly (Acc) ₄	IV

The following intermediates have been synthesized and used in synthesizing above peptides.

Boc	
Z-Lys (Acc) ₅ -OBz	V
Z	
Boc-Gly-Acc-Acc-Lys-Acc-Acc-OBz	VI
Boc	
Z-Lys (Acc) ₄ Gly-OBz	VII
Boc-Acc-Hcc-Gly-Acc-Hcc-OBz	VIII
Boc	
Z-Lys-Acc-Acc-Gly-Acc-Hcc-OBz	IX

Interesting problems were involved in the synthesis of II and IV, which were presented.

For binding studies 1-(p-bromophenyl)-1-cyanoacetic acid is synthesized and its rate of decarboxylation is planned to be studied in the presence and in the absence of the above cyclic peptides (I through IV).

Reaction Mechanism of Benzylpenicillin with 2-Mercaptoethylamine.

DAVID R. HOGUE and EUGENE S. WAGNER, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—Penicillin is known to be inactivated by cysteine and related 2-mercaptoamines. An earlier study, using polarimetric methods, proposed that 2-mercaptoamines with a free sulphhydryl and amino group on adjacent carbon atoms formed an intermediate thioester with the carbonyl group of the β -lactam of penicillin. It was proposed that the thioester had been formed by an intramolecular rearrangement via a S \rightarrow N acyl transfer to give penicilloyl-amide. This study re-examines the reaction of benzylpenicillin with 2-mercaptoethylamine at 30°Centigrade and pH 7.5. The progress of the reaction was followed using nuclear magnetic resonance. The spectra obtained indicate that benzylpenicillin reacts directly with 2-mercaptoethylamine, with no evidence of a thioester intermediate or S \rightarrow N acyl transfer.

Synthesis and Cope Elimination of N-(2-Deuteroethyl)-N-ethyl aniline oxide.

WILLIAM E. GROVES and TERRY L. KRUGER, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—The title compound was prepared by lithium aluminum hydride reduction of N-ethyl-N-trideuteroacetanilide followed by peracid oxidation. Good yields were obtained in each step. Analysis by nuclear magnetic resonance and infrared was used to verify the structures. A value for k_H/k_D in the Cope Elimination was presented.



The Polonovski Reaction of Substituted-N,N-diethylaniline Oxides. TERRY L. KRUGER and HARRY F. BANEY, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—The reaction of acetic anhydrid with substituted-N, N-diethylaniline oxides yields: N,N-diethylanilines, N-ethylanilines, and N,N-diethyl-*o*-acetoxyanilines. The reaction is very rapid—occurring in seconds even at low temperatures. The ratios of products are dramatically solvent dependent. The products have been successfully analyzed by glpc and the progress of the reaction monitored by nuclear magnetic resonance. No evidence (chemically induced dynamic nuclear polarization CIDNP) for free radical pathways to the major products can be found. Product ratios and their solvent dependence can be interpreted by present polar and electrocyclic mechanisms.

Temperature Dependence of the Surface Tensions of Aqueous n-Heptanol Solutions. EUGENE SCHWARTZ and SPENCER K. PORTER,¹ Department of Chemistry, DePauw University, Greencastle, Indiana 46135.—A Du Nouy tensiometer was modified for precise temperature control and used to measure surface tensions of aqueous n-heptanol solutions. The temperature range was 10° to 30° Centigrade, and the concentration range was very dilute to saturated. Each set of surface tension *vs.* temperature data was fitted to a second order virial equation by least squares.

A thermodynamic analysis using the Gibbs-Helmholtz equation gave ΔG , ΔS , and ΔH for the virtual process of transferring material from the bulk of the solution to its surface. It was found that ΔS for this process was positive and independent of concentration, and that ΔH decreased with increasing concentration at constant temperature.

The Gibbs adsorption isotherm was used to calculate surface excesses and to estimate the area of the surface per heptanol molecule. These ranged between 24.5 and 69. square Angstroms. The former value is slightly above the minimum of 21.5 square Angstroms found by Langmuir and others in their studies of insoluble monomolecular films.

The Comparison of Calcium Hydroxide and Sodium Hydroxide for Chemical Processing Liquid Wastes Control and Purification. ROBERT H. L. HOWE, Eli Lilly and Company, Tippecanoe Laboratories, Lafayette, Indiana 47902.—The physical and chemical advantages and disadvantages of calcium hydroxide and sodium hydroxide for chemical and biochemical processing liquid wastes control and purifications were compared and discussed.

Physical and Chemical Evaluation of Used Motor Oil. ROSS C. KOILE and ROBERT E. VAN ATTA, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—Crankcase oil samples were removed at intervals from a test vehicle during extensive urban and highway driving and subjected to various physical and chemical tests. The mechanical

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condition of the vehicle was inspected and monitored throughout the study, which was designed to develop a simple and inexpensive, though scientifically accurate, method for evaluating the condition of crankcase oil so that the necessity for an oil change could be reliably determined. Viscosity, refractive index, acidity, infrared spectrophotometric and gas chromatographic data were reported. Correlations were drawn between the test results and the type of traffic, normal engine function, mechanical condition of the test vehicle, and the operational life of the oil. Possible applications of the tests to fleet scale operations were discussed.

Diffusion of Ca^{++} , Mg^{++} , and Pb^{++} and their Interaction with Precipitated Amino Acid Barriers. ANN C. WORTHINGTON and JOHN H. MEISER, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—Diffusion coefficients of Ca^{++} , Mg^{++} , and Pb^{++} were determined in agar solutions at room temperature. Precipitate bands similar to those observed in Liesegang phenomena were formed by each of the above ions with various amino acids or their derivatives. The motion of the two ions not included in the band were studied in relation to their interaction with the band. A brief discussion of the techniques and of the results was given.

High Resolution Mass Spectrum of Non-Vicinal $^{13}\text{C}_2$ Labeled Tropylium Iodide. ALAN SIEGEL, Department of Chemistry, Indiana State University, Terre Haute, Indiana 47809.—One of the most intriguing and important findings in the field of mass spectrometry has been the discovery by Meyerson and co-workers that the C_7H_7^+ ion derived from toluene and related species is not the familiar benzyl ion but rather a more symmetrical species, *viz.*, the tropylium ion. C-13 and deuterium labeling data have established thus far that the C_7H_7^+ ion formed is best represented by a tropylium ion in which the carbon atoms have all lost positional identity with respect to their toluene origin. In an effort to determine whether the observed rearrangement in toluene occurs before or during the primary cleavage (loss of hydrogen) or whether skeletal reorganization also occurs in the tropylium ion itself, a non-vicinal $^{13}\text{C}_2$ tropylium salt was synthesized and its high-resolution mass spectrum recorded.

Radiocarbon Dating of Indian Site Remains of Indiana. R. JACK BINNION and JOHN H. MEISER, Department of Chemistry, and DAVID E. KOLTENBAH, Department of Physics, Ball State University, Muncie, Indiana 47306.—A sample of charcoal from an Indian pit site of Indiana was used to demonstrate the method of determining the age of a sample through radiocarbon dating. This paper concentrated on the calculation of data once liquid scintillation counting gives a measure of the radioactivity in the sample. Included in this discussion was the use of a "modern" carbon sample to determine a reference date, thus eliminating the effects of atomic atmospheric testing. Details of the experimental procedure were given in a paper presented by Lepera, Koltensbah and Meiser (see the Physics Division). Findings concerning the age of the sample were presented.

Computer Simulation of Titration Curves. CLAUDE EDWIN WILSON, Department of Chemistry, Indiana-Purdue University at Indianapolis, Indiana 46205.—The theory used to generate the titration curves makes no approximations except that equilibrium is obtained and that activity corrections can be neglected. The method yields an algorithm that is easily incorporated into a program to calculate the points. The output consists of the calculated points and an approximate plot using the line printer. Examples were given for the titration of simple acids, polyfunctional acids, edta and acids titrated with sodium hydroxide contaminated with carbon dioxide. The use of such curves in the teaching of analytical chemistry was discussed.

Titration Errors Arising from the Use of Gran Plots with Experimentally Obtained Data from a Strong Acid-Strong Base Titration. STANLEY L. BURDEN and DAVID E. EULER, Chemistry Department, Taylor University, Upland, Indiana 46989.—Endpoints for six titrations of 100.00 milliliters of 0.01 normal HCl with 0.09956 normal NaOH were determined both by phenolphthalein color change and by Gran plots and compared. The pH was measured at 1.00-milliliter increments of added titrant until 17.00 milliliters of titrant had been added. Several techniques were investigated to optimize the precision and accuracy of the endpoints obtained from the Gran plots. The best results were obtained when only data taken after the endpoint were used and when the parameter $2.303RT/nF$ was varied until the best linear fit using the least squares method was achieved. Agreement with phenolphthalein endpoints ranged from -0.31 per cent when seven data points were used to $+1.15$ per cent when three data points taken immediately following the endpoint were used. The relative average deviation among the six endpoints in each set of data ranged from $+0.54$ per cent to $+0.67$ per cent. A $+0.18$ per cent relative average deviation among the corresponding phenolphthalein endpoints was observed. When data preceding the endpoint were used in the Gran analysis the effects on the titration error arising from the number and spacing of data points were found to agree with predictions reported in an earlier theoretical study. These effects were reduced when data taken after the endpoint were used in the Gran analysis.

An Experiment in Practical Polarography—Determination of Zinc and/or Manganese in Magnesium Alloys. GLENN A. SHERWOOD and ROBERT E. VAN ATTA, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—An experiment was described which introduces the student to polarography via the usual qualitative measurements and direct comparison, pilot ion, and standard addition quantitative methods, as well as the effects of maximum suppressors, buffer-electrolytes, and most other conventional direct current voltammetric techniques. The experiment involves the analysis of an industrial magnesium-base alloy (such as Dowmetals) for its zinc and/or manganese content in the range of 0.25 to 1.06 per cent, with an average accuracy of ± 5 relative per cent. The experiment may be completed in approximately 2 hours with easily constructed manual apparatus or with any commercially available instrumentation.

Synthesis and Characterization of Penicilloyl-Poly-L-Cysteine: A Possible Skin Test Reagent for Penicillin Allergy. DIANA F. STORHOFF and EUGENE S. WAGNER, Department of Chemistry, Ball State University, Muncie, Indiana 47306.—Penicilloyl-poly-L-lysine is the most commonly used skin test reagent for penicillin allergy, but varies markedly in its reliability. We believe that penicillin, or the more reactive derivative penicillenic acid formed *in vivo*, reacts with thiol groups of proteins rather than amino groups to elicit the major/minor allergic response. Kinetic and spectral studies indicate that the synthesis of penicilloyl-poly-L-cysteine was accomplished by the reaction of benzylpenicillenic acid with poly-L-cysteine under physiological conditions and could serve as a skin test reagent for penicillin allergy.