region which is characteristic of low-spin five-coordinate nickel(II) complexes.[5]

These results, however, do not prove that the products contain five-coordinate metal ions with a nitrogen (or sulfur) atom bound in one axial position. We therefore studied the reaction between $Ni(TAAB)^{2+}$ and 1,5-pentanediol (which has no donor atom that can coordinate in an axial position) and obtained a complex $Ni(TAAB)L_2$ ($L = HO(CH_2)_5O$). Since only one alkoxide ion of the diol has reacted in this case, whereas both react when a nitrogen or sulfur atom is in the center of the chain, we suggest that coordination of this central atom at the axial position holds the diol in such a position that both alkoxide ions of the diol react, giving complexes of formulation M(TAAB)LN and M(TAAB)LS. We therefore suggest that addition of one dianion from bis(2-hydroxyethyl)methylamine or bis(2-hydroxyethyl) sulfide to two *trans*-azomethine linkages of $Ni(TAAB)^{2+}$ and $Cu(TAAB)^{2+}$ has occurred, with the formation of the new and unusual type of "basket-like" macrocyclic ligand III. This demonstrates a second geometry of linkage applicable to clathro chelate formation as predicted earlier.[6] The first expected form was recently reported by Boston and Rose.[7] These examples constitute the first use of coordination template effects to synthesize ligands whose donors are arrayed three dimensionally. Earlier examples all generated monocyclic, not polycyclic, ligands.

Acknowledgment. This investigation was supported by U. S. Public Health Service Grant GM-10040 from the National Institute of General Medical Science.

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Molecular Oxygen Complexes of Bis(triphenylphosphine)platinum(0)

Sir:

When the bis(triphenylphosphine)platinum(0)–ethylene complex[1] is dissolved in oxygen-saturated toluene, thin yellow plates of the complex $[P(C_6H_5)_3]_2PtO_2 \cdot C_6H_5CH_3$ are obtained,[2] the crystals being only moderately stable in air.

We have undertaken an X-ray structure analysis of this complex. Crystallographic data are: system monoclinic; $a = 9.4, b = 23.5, c = 20.5$ Å; $\beta = 113.5°$ (accuracy not determined); $Z = 4$ molecules per cell; space group, $P2_1/c$. No crystals were found which were of high enough quality for diffractometer study and so an approximate structure was obtained by photographic methods. The instability of the complex meant that several crystal specimens had to be used during data collection; 2000 independent intensity data were collected and the structure was refined by full-matrix least squares with isotropic thermal parameters to an R of 0.12. The structure could not be refined anisotropically; nonpositive definite temperature factors were observed for seven light atoms, a feature we attribute to unsatisfactory intensity data. Accordingly the bond lengths probably cannot be relied on to better than 0.05 Å.

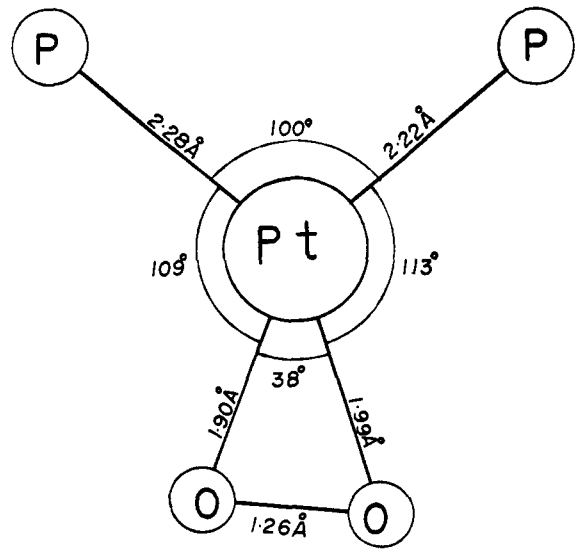

Figure 1.

Figure 1 shows the approximate configuration in the neighborhood of the Pt atom. All the atoms in this diagram are near-coplanar as evidenced by the sum of the bond angles at the Pt atom.

We have since obtained much better quality crystals of the oxygen complex $[P(C_6H_5)_3]_2PtO_2 \cdot 2CHCl_3$ by use of chloroform in place of toluene and these crystals, although still somewhat unstable, are satisfactory for diffractometer study. Preliminary crystal data are: system monoclinic; $a = 15.54$, $b = 13.52$, $c = 19.19$ (all ± 0.05) Å; $\beta = 98.95 \pm 0.3°$; $Z = 4$ molecules per cell; possible space group C2, Cm, Cc, C2/m, C2/c. Because the crystals last only about 1 day when exposed to X-rays, we have concentrated on the collection of intensity data and are leaving refinement of the cell parameters until the end of data collection.

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Configurational Assignment to *dl* and *meso* Sulfides, Sulfoxides, and Sulfones

Sir:

No simple method has heretofore been reported whereby absolute *dl* and *meso* assignments to sulfides, sulfoxides, and sulfones of the type $[(R_1)(R_2)(R_3)C]_2X$ have been made. Assignments to sulfide dicarboxylic acids of this type have been made *via* tedius optical resolution techniques,[1] and the first report of an unambiguous assignment to a crystalline sulfone by X-ray

(1) C. D. Cook and G. S. Jauhal, *Inorg. Nucl. Chem. Letters*, **3**, 31 (1967).
(2) S. Takahushi, K. Sonogashira, and N. Hagihara, *J. Chem. Soc. Japan*, **87**, 610 (1966); C. D. Cook and G. S. Jauhal, *J. Am. Chem. Soc.*, **90**, 1464 (1968).

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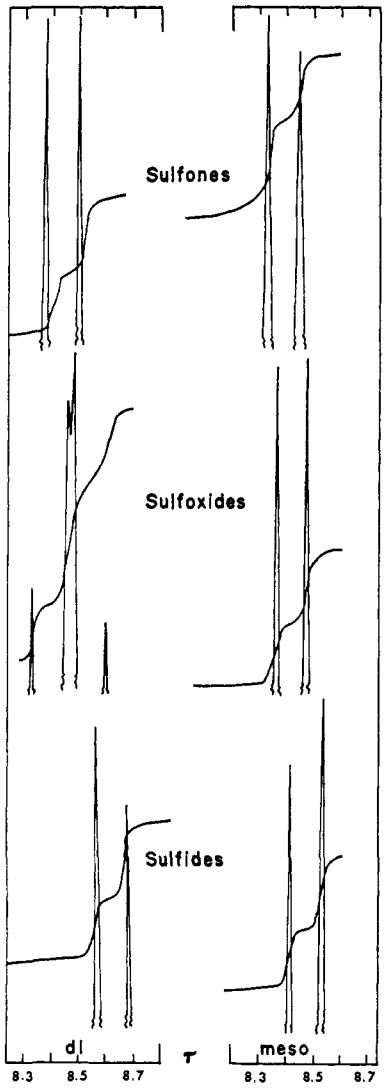
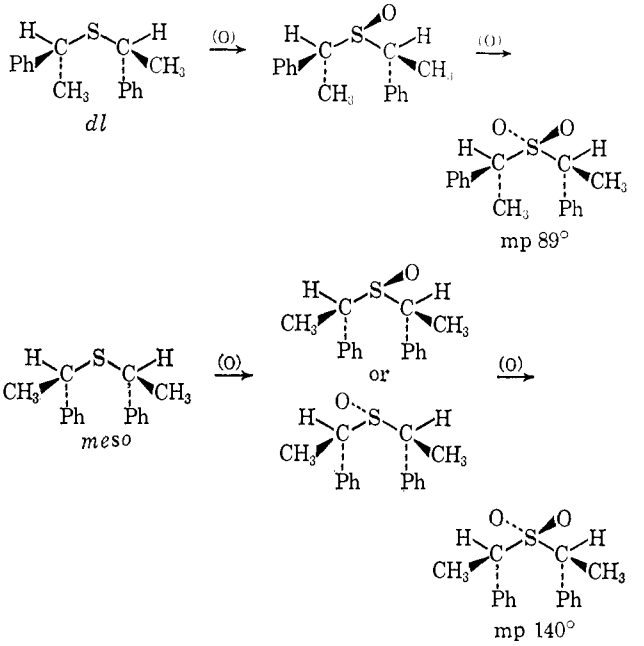


Figure 1. Observed nmr spectra of CH_3 protons assigned to *dl*- and *meso*-α-methylbenzyl sulfides, sulfoxides, and sulfones, in CCl_4.

analysis has recently appeared.[2] By means of nmr we have been able to assign the *dl* or *meso* configuration to a sulfoxide and thereby also unambiguously identify the corresponding sulfide and sulfone diastereomers. This technique is rapid, the compounds need not be amenable to optical resolution schemes, and crystallinity is not a requisite.

We have prepared and isolated the respective *dl* and *meso* isomers of α-methylbenzyl sulfide and sulfone. Neither the physical nor spectral characteristics provided a basis for absolute isomer identification even though the nmr chemical shifts exhibited by the respective *dl* and *meso* isomers were appreciably different.[3] Only one *dl* sulfoxide is theoretically possible, and this is related to the *dl* sulfide and sulfone. Although two *meso* sulfoxides are theoretically possible, both related to the *meso* sulfide and sulfone, one *meso* sulfoxide should be formed exclusively or predominantly (*vide infra*). Only the *dl* sulfoxide, however, should exhibit nmr nonequivalence of the protons of its two methyl as well as methine groups, in a manner similar to that exhibited by configurationally analogous *dl* sulfite esters but not the *meso* esters.[4]

Taking advantage of this concept in the transformations sulfide → sulfoxide → sulfone, using each sulfide diastereomer, we observed proton nonequivalence in



the sulfoxide from one but not the other series. In this way *dl* and *meso* assignments to the sulfoxides and, thereby, to the corresponding sulfides and sulfones were readily accomplished (Figure 1 and Table I).

Table I. Nmr Characteristics of *dl*- and *meso*-α-Methylbenzyl Sulfides, Sulfoxides, and Sulfones[a]

Protons	Sulfides *dl*	Sulfides *meso*	Sulfoxides *dl*	Sulfoxides *meso*	Sulfones[b] *dl*[d]	Sulfones[b] *meso*[e]
CH_3, doublet, 6 H, J = 7 Hz	8.63	8.48	8.40 (3 H) 8.56 (3 H)	8.42	8.44	8.40
CH, quartet, 2 H, J = 7 Hz	6.58	6.28	6.70 (1 H) 6.72 (1 H)	6.46	6.25	6.08
Ar, singlet,[c] 10 H	2.80	2.78	2.73	2.78	2.74	2.78

[a] In CCl_4, τ units. [b] Also recorded in $CDCl_3$: (*dl*) 8.36, 6.08, 2.65; (*meso*) 8.28, 5.92, 2.62 (*cf.* ref 3a). [c] The sulfoxides exhibited a more complex pattern. [d] Mp 89°. [e] Mp 140°.

A mixture of the sulfides was distilled (bp 140° (2 mm)). Both vpc[5] and nmr indicated that the distillate contained both isomers in almost equal amounts.[6]

(2) F. G. Bordwell, B. B. Jarvis, and P. W. R. Corfield, *J. Amer. Chem. Soc.*, **90**, 5298 (1968), reported the characterization of *meso*-α-bromobenzyl sulfone by three-dimensional single-crystal X-ray analysis.

(3) (a) F. G. Bordwell, D. D. Phillips, and J. M. Williams, *ibid.*, **90**, 426 (1968), also reported distinct chemical shifts for these two isomeric sulfones (mp 89 and 140°) but were unable to make definite configurational assignments. (b) Brink and Larsson[1] reported nmr spectra of configurationally known *dl* and *meso* sulfide pairs and concluded that the respective chemical shifts, while different for a *meso* and *dl* isomer, are essentially independent of the configuration.

(4) (a) R. E. Lack and L. Tarasoff, *Chem. Commun.*, 609 (1968); (b) M. K. Hargreaves, P. G. Modi, and J. G. Pritchard, *Chem. Commun.*, 1306 (1968); (c) P. C. Lauterbur, J. G. Pritchard, and R. L. Vollmer, *J. Chem. Soc.*, 5307 (1963).

(5) Varian Aerograph 1526-C, Gow-Mac gas density detector, Carbowax 20, 5-ft column, 275°. T. J. Wallace, H. Pobiner, F. A. Baron, and A. Schriesheim, *J. Org. Chem.*, **30**, 3147 (1965), determined the purity of a commercial sample by glpc, but neither detection nor separation of the isomers was reported.

(6) Commercial sulfide (Wateree Chemical Co.) and our preparation (α-bromoethylbenzene, sodium sulfide, in ethanol) provided similar results. The isomers could not be separated by fractional distillation.

The purified mixed sulfides were transformed (H_2O_2–HOAc) into the mixed sulfones. Pure sulfone isomers (mp 88–89 and 139–140°; *cf.* ref 3a) were isolated by fractional crystallization (1:3 Et_2O–pentane). The SO_2 bands were identical (in CS_2: 1312, 1135 cm^{-1}), as were their other ir bands, but their nmr chemical shifts were sufficiently different to allow isomer distinguishability but not configurational assignment.[3a]

From another portion of distillate each sulfide was isolated by vpc[5] but their respective configurations were not obvious even though their chemical shifts also were quite different.[3b] Each sulfide was cautiously oxidized to its sulfoxide (1 equiv of H_2O_2 in HOAc, 0–5°)[7] as well as sulfone. The sulfide of lower retention time provided the sulfoxide (S–O, neat, 1040 cm^{-1}) that clearly exhibited proton nonequivalence[8] and the sulfone that was identical with that melting at 89°. This series was assigned the *dl* configuration. The other sulfide yielded the sulfoxide (S–O, neat, 1033 cm^{-1}) exhibiting equivalent signals for both methyl groups as well as methine protons, respectively, and the sulfone identical with that melting at 140°. This series was assigned the *meso* configuration.[9]

We have observed striking differences in the reactivity of the two sulfones which now can be directly related to their respective configurations.[13] This is especially important in light of the opposite tentative assignments recently reported.[3a] Assignments to other diastereomers by this method are now being investigated.

Acknowledgment. We are grateful to the Southern Illinois University Foundation for a postdoctoral fellowship and to the University for providing maximum research support.

(7) The absence of sulfide was verified by vpc and nmr, and of sulfone by ir and nmr.

(8) As would be expected from nonequivalent dimethyl substituents their shifts were different but their areas were equal. It is highly unlikely that the nonequivalence represented the two *meso* sulfoxides formed in exactly equal amounts.[9] If this were so, moreover, the sulfoxide exhibiting proton equivalence would be the *dl* isomer, also highly unlikely.

(9) It is strongly suspected that the less hindered of the two possible *meso* sulfoxides was formed preferentially: (1) *cf.* the exclusive formation of one *meso*-2-butene episulfoxide (depicted as *anti*)[10] and the 24:1 selectivity in *meso* sulfite esters.[4c] (2) The *meso* sulfoxide was unchanged when treated with polyphosphoric acid, a rapid sulfoxide epimerization agent.[11] (3) No sulfoxide resulted when the *meso* sulfide was treated with *t*-BuOCl in *t*-BuOH, a sulfide oxidation agent whose two-step mechanism for S–O bond formation apparently requires a minimum approach barrier from *both* sides of the sulfur atom.[12]

(10) G. E. Hartzell and J. N. Paige, *J. Org. Chem.*, 32, 459 (1967).

(11) J. Day and D. J. Cram, *J. Amer. Chem. Soc.*, 87, 4398 (1965).

(12) C. Y. Meyers and W. S. Matthews (unpublished) have also observed that oxidation of a *trans* alkenyl sulfide compared with the more hindered *cis* isomer was favored 2:1 with H_2O_2–HOAc, and more than 20:1 with *t*-BuOCl in *t*-BuOH. Steric effects in sulfoxide formation are briefly reviewed by G. Barbieri, M. Cinquini, S. Colonna, and F. Montanari, *J. Chem. Soc., C*, 659 (1968).

(13) C. Y. Meyers and A. M. Malte, submitted for publication.

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Received January 13, 1969

The Acetylpyridinium Ion Intermediate in Pyridine-Catalyzed Acyl Transfer[1]

Sir:

We wish to report the direct observation of the formation and disappearance of an acetylpyridinium ion intermediate in the course of the pyridine-catalyzed hydrolysis of acetic anhydride in aqueous solution (eq 1). It has been generally believed that this intermediate is too unstable to permit its accumulation in easily detectable concentrations,[2,3] although the inhibition of the over-all reaction by acetate ion, the rapid reaction rate, and the even faster pyridine-catalyzed exchange of labeled acetate into acetic anhydride provide strong kinetic evidence for such an intermediate.[4] Similarly, inhibition of the pyridine-catalyzed hydrolysis of substituted phenyl acetates by low concentrations of the leaving phenolate ion provides evidence for the same intermediate in these reactions.[5] Estimates of the expected kinetic and thermodynamic stability of the acetylpyridinium ion, based on equilibrium and rate constants for reactions of acetylimidazolium and phosphorylpyridinium ions,[6] led us to search for direct evidence for its formation.

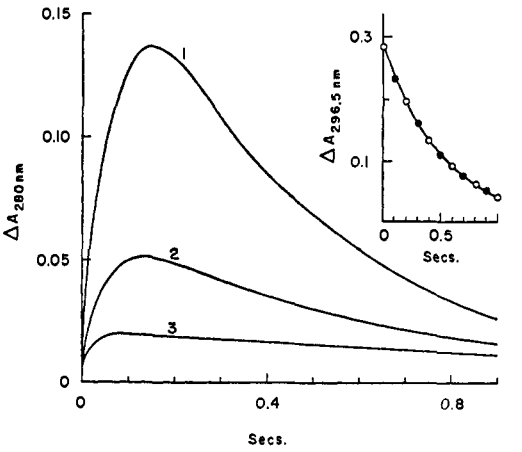

Figure 1. The formation and hydrolysis of acetylpyridinium ion, followed at 280 nm, during the hydrolysis of 2×10^{-4} *M* acetic anhydride catalyzed by pyridine buffer (0.06 *M* free base, pH 5.5) at 25°, ionic strength 1.0, maintained with potassium chloride. Added sodium acetate: curve 1, 4×10^{-3} *M*; curve 2, 10^{-2} *M*; curve 3, 5×10^{-2} *M*. Inset: the disappearance of 10^{-3} *M* (open circles) and 5×10^{-4} *M* (closed circles) *p*-anisidine in the presence of 10^{-4} *M* acetic anhydride and pyridine buffer (0.02 *M* free base, pH 6.5), followed at 296.5 nm, ionic strength 1.0, 25°.

$$\mathrm{Pyr} + \mathrm{Ac_2O} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{AcPyr^+} + \mathrm{AcO^-} \xrightarrow{k_2} \mathrm{Pyr} + \mathrm{AcOH} \qquad (1)$$

The formation and subsequent disappearance of this intermediate may be followed spectrophotometrically at 280–290 mμ after mixing aqueous solutions of pyridine and acetic anhydride in a stopped-flow apparatus (Figure 1). Increasing concentrations of acetate ion decrease the amount of acetylpyridinium ion formation by increasing the rate of the back reaction (k_{-1}, eq 1). Increasing pyridine concentration was found to increase

(1) Publication No. 634 of the Graduate Department of Biochemistry, Brandeis University, Waltham, Mass. Supported by grants from the National Science Foundation and the National Institute of Child Health and Human Development of the National Institutes of Health (HD-1247).

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(3) D. E. Koshland, Jr., *J. Am. Chem. Soc.*, 74, 2286 (1952).

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