vinyl protons of **7** (δ 2.7–3.2) and the vinyl protons of **8** (δ 6.4–6.8). One can also see the C$_7$ proton of each compound clearly: H$_7$ of **7** at δ 4.45; H$_7$ of **8** at δ 4.8; H$_7$ of **9** at δ 5.9. In addition, authentic **9** was prepared by the photoisomerization[14] of **8** and its pmr spectrum corresponded to the signals assigned in the mixture.

While the nature of the photochemical process is not known, it is clear that the appearance of quadricyclic material in both reactions probably arises from the corresponding diene,[14] the diene having been formed through photodecomplexation. The low yields of quadricyclanes may be due, in part, to valence isomerization to the norbornadiene derivative catalyzed by the transition metal complex remaining in solution.[20] Work is continuing on the photoinduced decomplexation of vinyl-substituted norbornadien-7-oneiron tricarbonyls as well as related diene–iron tricarbonyls. A more detailed report on further chemistry of **1** is forthcoming.

Acknowledgment. We gratefully acknowledge financial support by the Petroleum Research Fund, administered by the American Chemical Society (1061-G1), the Research Corporation, and the National Science Foundation (GP-7924).

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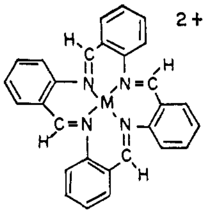
Application of the Coordination Template Effect to Prepare Five-Coordinate Nickel(II) and Copper(II) Complexes Containing a "Basket-Like" Polycyclic Ligand

Sir:

Extensive applications of the coordination template effects[1] have led to the synthesis of tridentate, many tetradentate, pentadentate, and sexadentate macrocyclic ligands. More complicated polycyclic structures should be accessible by related routes, and a novel illustration of this fact is provided by the synthesis of the compounds reported herein.

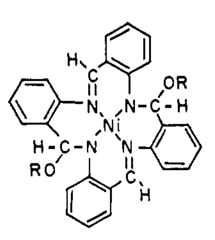
As was previously reported,[1,2] neutral compounds II containing α-amino ether linkages can be formed by the interaction of solutions of sodium alkoxide with the cyclotetrameric Schiff base metal(II) complexes derived from *o*-aminobenzaldehyde (I), hereafter abbreviated as M(TAAB)$^{2+}$.

The reactions of the Ni(TAAB)$^{2+}$ and Cu(TAAB)$^{2+}$ complexes with nucleophiles have been extended to bis(2-hydroxyethyl)methylamine and bis(2-hydroxyethyl) sulfide whose two potentially nucleophilic alkoxide ions can add to two *trans*-azomethine positions of the macrocyclic ligand. In such a product, the central nitrogen or sulfur atom is strategically positioned where it may coordinate to the metal ion in an axial position, thereby forming a square-pyramidal five-coordinate complex III. Using the reported procedure for the preparation of the simple alkoxyl adducts,[2] reaction of Ni(TAAB)(BF$_4$)$_2$ and Cu(TAAB)(NO$_3$)$_2$ with the above-mentioned nucleophiles gives the following compounds, M(TAAB)LN and M(TAAB)LS, where M = Cu^{2+} and Ni^{2+}, LN = CH$_3$N(CH$_2$CH$_2$O)$_2$, and LS = S(CH$_2$CH$_2$O)$_2$. A complete elemental analysis, excluding oxygen determination, supports these assignments. Ni(TAAB)LN and Ni(TAAB)LS are microcrystalline dark red solids which are insoluble in water but soluble in most organic solvents giving relatively stable solutions. In acid media, the alkoxide group is eliminated, leading to regeneration of Ni(TAAB)$^{2+}$. The new Ni(II) compounds are low spin at room temperature. The corresponding Cu(II) compounds, Cu(TAAB)LN and Cu(TAAB)LS, are olive green solids with similar properties. They have magnetic moments of 2.10 and 2.26 BM, respectively.



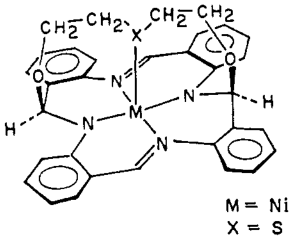
M = Ni and Cu

(I)



R = CH$_3$ and C$_2$H$_5$

(II)



M = Ni and Cu
X = S and NCH$_3$

(III)

Infrared spectra of these compounds are very similar with the following significant features: (a) the absence of peaks due to NO$_3^-$ and BF$_4^-$; (b) the absence of absorptions due to N–H and O–H vibrational modes, confirming that both hydroxyl groups have reacted; (c) the disappearance of the band at 1650 cm^{-1} originally present in Ni(TAAB)$^{2+}$ and Cu(TAAB)$^{2+}$ (previously assigned as the C=N stretching vibrational mode[3]) and the appearance of a new band at 1529 cm^{-1} which has been assigned as a stretching vibration of the two remaining azomethine linkages; and (d) the presence of bands in the 2950-cm^{-1} region, at 1465 and 1350 cm^{-1}, which can be attributed to aliphatic C–H stretching and bending vibrations.[4] Molecular weight determinations (osmometric in 1,2-dichloroethane) confirm that Ni(TAAB)LN (calcd 588; found 584, 600), Cu(TAAB)LN (calcd 593; found 610), and Cu(TAAB)LS (calcd 596; found 580) are monomeric in solution. The electronic spectra of Ni(TAAB)LN and Ni(TAAB)LS are similar to the spectra of the simple alkoxyl adducts except for the presence of an additional band in the visible region. Bands at 18,200, 19,200, 27,000, and 38,500 cm^{-1} are found in all solvolyzed products of Ni(TAAB)$^{2+}$ and have been attributed to charge-transfer transitions. The spectra of Ni(TAAB)LN and Ni(TAAB)LS display a new band in the 16,000-cm^{-1}

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[1] D. H. Busch, "Fasciculus Extraordinarius Alfred Werner 1866–1919," Verlag Helvetica Chimica Acta, Basel, 1967, p 174.

[2] L. T. Taylor, F. L. Urbach, and D. H. Busch, *J. Am. Chem. Soc.*, **91**, 1072 (1969).

[3] G. A. Melson, F. L. Urbach, and D. H. Busch, unpublished results.

[4] R. T. Conley, "Infrared Spectroscopy," Allyn and Bacon, Inc., Boston, Mass., 1966.

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$_2$)$_5$O). 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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[6] D. H. Busch, *Record Chem. Progr.*, **25**, 107 (1964).
[7] D. R. Boston and N. J. Rose, *J. Am. Chem. Soc.*, **90**, 6859 (1968).
[8] On leave from the University and Institute "R. Bošković," Zagreb, Yugoslavia.

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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$_6$H$_5$)$_3$]$_2$PtO$_2$·C$_6$H$_5$CH$_3$ 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.

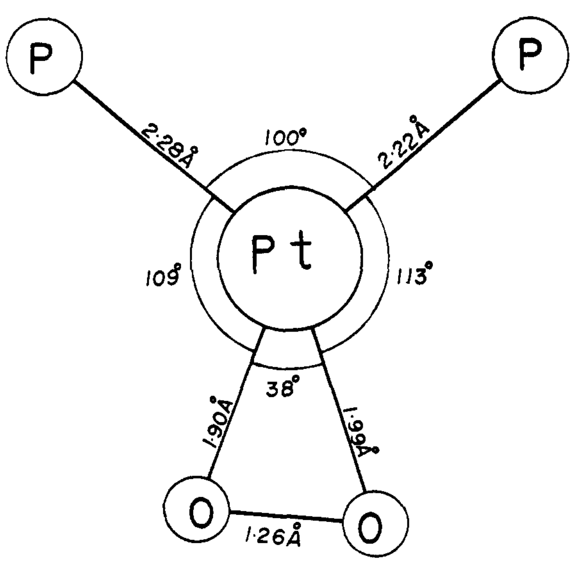

Figure 1.

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$_6$H$_5$)$_3$]$_2$PtO$_2$·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.

[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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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]$_2$X 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] Pertinent references are given by A. M. Brink and E. Larsson, *Acta Univ. Lund*, (II) No. 10 (1967); No. 29 (1966).