Wavelength, mμ

Figure 1. Absorption spectra of TPN and TAN nickel(II) complexes in dichloroethane: - - - -, [Ni(TPN)Br]BPh₄; ———, [Ni(TAN)Br]BPh₄.

sets of donor atoms P_4, PAs_3, and As_4 are of the low-spin type.[1c,d] This research shows that the substitution of the central P or As atom with N maintains the singlet ground state in the five-coordinate complexes. Subsequent experiments in this laboratory have moreover shown that the complexes of cobalt(II) with TPN are five-coordinate but high spin.

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A Completely Chelated Spin-Paired Eight-Coordinate Tungsten(IV) Complex

Sir:

Tetrakis(8-quinolinolato)tungsten(IV), isolated in our laboratory from the products of a sealed-tube reaction between $(NH_4)_3W_2Cl_9$ and 8-quinolinol, is believed to be the first completely chelated eight-coordinate complex of tungsten. This inner (noncharged) coordination compound is diamagnetic, slightly soluble in solvents of low polarity such as benzene, and insoluble in water. Rigorous exclusion of both air and water are essential during and after the sealed-tube reaction between the ammonium salt and a twofold excess of ligand (95°, 2 days). Extraction of other products and unreacted ligand with acetonitrile and extraction of the desired product with benzene give a 33% yield of aqua plates.[1]

Anal. Calcd for $W(C_9H_6NO)_4$: C, 56.84; H, 3.16; N, 7.37; W, 24.21. Found: C, 56.92; H, 3.15; N, 7.30; W, 23.84.[2]

(1) The flat, square plates appear aqua by transmitted light and violet by reflected light.
(2) Analyses by Huffman Laboratories, Wheatridge, Colo. The C, H, and N analyses have been checked with a second sample. Molecular weight determinations have been attempted in benzene, camphor, carbon tetrabromide, camphoquinone, chlorobenzene, and dimethyl sulfoxide. Low solubility in all of these solvents, even at elevated

Previously, substitution of ligands for halide ions in tungsten halides and halo complexes had given only mixed complexes. To illustrate, Nyholm and co-workers[3] only isolated the reduced, partially substituted $[W^{II}(diars)_2I_2]$ species from a sealed-tube reaction between tungsten(III) iodide and diars [*o*-phenylenebis-(dimethylarsine)] at 165°. Earlier attempts to substitute pyridine for the chloro ligands of WCl_4,[4] K_2WCl_6,[5] WCl_6,[4] and $K_3W_2Cl_9$[6] also resulted in only mixed complexes.

The 8-quinolinol ligand is ideal for obtaining electronically stable complexes, even if a change in the oxidation state of the metallic ion is necessary, since the ligand is easily oxidized or reduced.[7] For example, both chromium(II) and chromium(VI), as well as chromium(III), give the tris(8-quinolinolato)chromium-(III) chelate.[7] Therefore, the attainment of eight-coordinate tungsten(IV) is not surprising. Fortunately, oxidation to tungsten(VI) did not occur under the reaction conditions used in our laboratories. The $[WO_2(C_9H_6NO)_2]$ complex is also known.[7]

The solid 8-quinolinol complex appears to be reasonably stable. For example, one sample was heated in air to 200° and then held at 170° for 8 hr. Microscopic examination of the sample after the heat treatment revealed no detectable decomposition. On the other hand, reagent-grade benzene solutions of the complex slowly decompose unless the solvent is dry and oxygen-free.

The current interest in the stereochemistry of eight-coordinate complexes[8] makes this synthesis particularly timely. The relative positions of the oxygen donors and the σ-donor, π-acceptor nitrogen atoms are particularly important. According to Orgel,[9] the π acceptors should be in the foreshortened tetrahedron and the others in the elongated tetrahedron of the dodecahedral structure for d^2 systems. However, the possibility of an antiprismatic structure cannot be ruled out.[10] A single crystal X-ray determination, currently in progress, should clarify this important aspect.

Intense ($\epsilon > 10^3$) absorption bands are observed in the visible and near-ultraviolet region at 14,300, 15,300, and 25,600 cm⁻¹. All appear too strong to be simple d–d transitions. More quantitative spectral measurements and a band analysis are being carried out.

temperatures, has precluded meaningful results; *e.g.*, <50 mg dissolves in 1 l. of benzene. The analyses are within experimental error of $W(C_9H_6NO)_3 \cdot C_9H_6NOH$, the tungsten(III) complex with an extra mole of 8-quinolinol. The diamagnetism of the complex, the extraction of excess 8-quinolinol with acetonitrile with the duplication of analyses within experimental error, and the absence of an OH stretch in the infrared spectrum of the complex convinces us that the tungsten-(IV) designation is appropriate. Inability to obtain a molecular weight does allow the possibility of nine- or ten-coordinate bridged dimers or polymers.

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The infrared spectrum of the compound, as determined on Beckman Models IR-5A and IR-10 spectrometers, has absorptions at the following wavenumbers (cm^{-1}) with the relative intensities given in parentheses: 1580 (7), 1540 (9), 1495 (7), 1450 (5), 1415 (2), 1385 (shoulder, 1), 1370 (10), 1310 (8), 1270 (9), 1210 (1), 1168 (2), 1129 (2), 1104 (8), 1052 (1), 1030 (3), 905 (7), 812 (8), 805 (7), 770 (8), 738 (5), 615 (8), 580 (2), 520 (6), 510 (3). This spectrum is similar to that reported between 4000 and 650 cm^{-1} for the thorium(IV) complex,[11] except near 3400 cm^{-1}, the OH stretch, and between 700 and 850 cm^{-1}, the CH deformation region.[12] No OH stretch was observed for the tungsten complex in the 3400-cm^{-1} region when the spectrum of a KBr pellet containing the complex was measured vs. a blank KBr disk of appropriate thickness. Traces of water in the KBr usually give bands in the 3400-cm^{-1} region if the pellets are measured single beam or against air; cf. ref 11. The differences in multiplicities and positions in the CH deformation region suggest different interactions in the solid state, such as might be obtained in going from antiprismatic to dodecahedral coordination, the two favored configurations for eight-coordination,[10] but a change in crystal structure might produce a similar effect. Since the sizes of central cations are different, no definite conclusions as to geometry can be drawn from the infrared spectrum alone.

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(12) L. J. Bellamy, "The Infra-red Spectra of Complex Molecules," 2nd ed, Methuen, London, 1958, pp 280–281.
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The Structure of B_2H_6–Base Complexes. Molecular Electron Deficiency and Acidity

Sir:

In a recent communication Shore and Hall reported[1] that trimethylamine and diborane at low temperature can form a specific complex whose stoichiometry was established as B_2H_6–NR_3 by titrimetry. With the only additional structural characterization being a boron-11 nmr spectrum, the authors report that this complex has the structure of a "singly hydrogen bridged borane," i.e., R_3N–BH_2–H–BH_3. The spectrum shown for this unsymmetrical structure is a symmetrical multiplet. The two chemically different boron-11 atoms were assumed to give a seven-line nmr pattern, a superimposed triplet and quartet.[2]

Actually, the spectrum shown by Shore and Hall for

(1) S. G. Shore and C. L. Hall, J. Am. Chem. Soc., **88**, 5346 (1966).
(2) These seven lines were said to generate a symmetrical spectrum which "established the presence of a BH_2 (triplet) and BH_3 (quartet) unit."[1] Our initial observations were that the structure reported by Shore and Hall could not be established by such a spectrum, for a variety of reasons. For example, if the assumption of a superimposed BH_2 triplet and BH_3 quartet were correct, a remarkable rearrangement

the diborane–amine complex is that of a nine-line pattern, i.e., the triplet of triplets expected of B_2H_6 itself. Their spectrum is, in fact, virtually superimposable on the first boron-11 nmr spectrum published for diborane 12 years ago by Ogg.[3,4] Each boron in the diborane unit is split by two proton pairs. The two J_{BH} values in the low-temperature diborane–amine spectrum (136 ± 2 and 44 ± 2 cps) are within the same experimental error that Gaines has found[5] with diborane etherate at low temperature. In short, the nmr spectrum of B_2H_6–NR_3 cannot be that of a "singly hydrogen-bridged borane."[6]

We propose that trimethylamine coordinates the electron-deficient borane dimer intact to yield a complex represented by **1**. In general, a Lewis base reacts with the intact dimer as represented in eq 1; additional base may or may not dissociate the complex, e.g., as in eq 2. In addition to being consistent with the observed nmr spectrum, complex **1** is analogous to coordination complexes we have found for intact alkyllithium dimers with Lewis bases, i.e., ethers and tertiary amines.[7] Ethers also may be seen to coordinate the intact borane dimer. Thus, as with the elec-

1
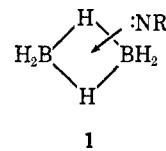
tron-deficient lithium reagents, ethereal solvents (relative to hydrocarbons or no solvent) effect the nmr chemical shift of diborane without at the same time interrupting the multicenter splitting of the dimer. With increasing temperature, this splitting pattern of boron-11 in ethereal diborane is modified, as first reported by Gaines.[5] From the usual triplet of triplets (each boron split by two distinct proton pairs), an intramolecular exchange process causes the pattern to become a regular septet, both borons equivalently split by all six protons.[6]

$$B_2H_6 + base \rightleftharpoons B_2H_6\text{-base} \quad (1)$$

$$B_2H_6 + 2\,base \rightleftharpoons 2\,base\text{-}BH_3 \quad (2)$$
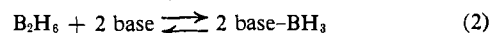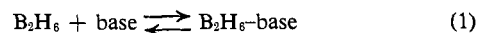
The boron-11 splitting observed by Gaines[5] demonstrates the absence of fast intermolecular exchange of borane units from its dimer etherate in ethereal solvents, including the very basic glycol dimethyl ether, and thus demonstrates that the excess Lewis base

mechanism must average out the chemical shift between two protonic environments but not at the same time cause equivalent splitting by these protons. The point here is, considering the large chemical shifts observed between boron-11 atoms in subtly different environments, that one could certainly not expect such different B atoms as assumed[1] would show superimposed absorption unless their signals were averaged; cf., J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Pergamon Press Inc., New York, N. Y., 1966, p 970 ff.
(3) R. A. Ogg, J. Chem. Phys., **22**, 1933 (1954).
(4) The third and seventh lines in a triplet of triplets can be difficult to resolve and therefore easy to miss. For some reason, resolution of those two particular lines requires precise phasing adjustment of the spectrometer. Also, excess amine beyond that required to form the complexed dimer causes line broadening of the dimer nmr signals, presumably by some exchange process; we have observed the same effect with trialkyl-aluminum dimers complexed by amines at low temperature (unpublished work with S. C. Watson).
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(6) Certainly a singly bridged species might exist as a metastable intermediate, e.g., in allowing intramolecular exchange processes, as Gaines has pointed out.[5]
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