Scheme I

$$(C_6H_5)_2C\overset{+}{=}\overset{\bar{O}}{N}\diagdown_{CH(C_6H_5)_2} \longrightarrow \begin{array}{c}(C_6H_5)_2C=N\overset{O\cdot}{\diagup} \\ + \\ (C_6H_5)_2\dot{C}H\end{array}$$

$$\begin{array}{c}(C_6H_5)_2C=N\overset{O\cdot}{\diagdown} \\ + \\ (C_6H_5)_2\dot{C}H\end{array} \overset{?}{\diagdown} \longrightarrow (C_6H_5)_2C=N\overset{OCH(C_6H_5)_2}{\diagup}$$

$$2(C_6H_5)_2\dot{C}H \longrightarrow (C_6H_5)_2CHCH(C_6H_5)_2$$

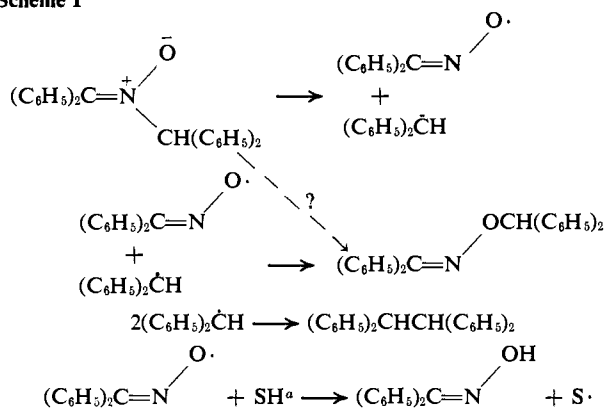$$(C_6H_5)_2C=N\overset{O\cdot}{\diagup} + SH^a \longrightarrow (C_6H_5)_2C=N\overset{OH}{\diagup} + S\cdot$$

a SH represents the solvent, bis(β-ethoxyethyl) ether (diethyl Carbitol). The products derived from the solvent following hydrogen atom abstraction have not yet been characterized.

O-ethers obtained by thermal rearrangement of the pure nitrones (in the absence of solvent) is not entirely clear. It may indicate an increase in product formation *via* radical-cage recombination in a viscous medium.[8] Experiments in progress will determine the effects of solvent (of varying polarity, viscosity, and hydrogen atom donating ability) on rates and product distribution.

Finally, the possibility that some of the nitrone (Ia) is converted to the oxime O-ether (IIa) in diethyl Carbitol directly by a concerted intramolecular nucleophilic displacement cannot be excluded. A study of the geometric stereochemical course of this isomerization currently in progress may provide an answer to this question.

In connection with our observations, it is of interest to note that Schöllkopf, *et al.*,[9] have recently detected radical intermediates by epr in the rearrangement of benzylmethylaniline oxide to O-benzyl-N-methyl-N-phenylhydroxylamine. Furthermore, these workers have found that the rearrangement of N,N-dimethylbenzylamine oxide to N,N-dimethyl-O-benzylhydroxylamine proceeds with net retention of configuration at the benzyl carbon atom, but accompanied by extensive racemization.[10] The kinetic data of Shulman, *et al.*,[11] for this rearrangement tend to support the conclusion[10] that a radical dissociation–recombination mechanism[12] is operative.

ment was obtained in the thermal rearrangement of Ib to IIb and amounted to 82%.[3]

(8) Of interest in this regard is the recent study by R. Hiatt and T. G. Traylor [*J. Am. Chem. Soc.*, **87**, 3766 (1965)] which reveals the dependence of *t*-butoxy radical cage recombination on solvent viscosity.

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(10) U. Schöllkopf and H. Schäfer, *Ann.*, **683**, 42 (1965).

(11) G. P. Shulman, P. Ellgen, and M. Connor, *Can. J. Chem.*, **43**, 3459 (1965).

(12) Evidence in support of a similar radical dissociation–recombination mechanism for the thermal rearrangement of benzyl *p*-toluenesulfenate to benzyl *p*-tolyl sulfoxide has been offered by E. G. Miller, D. R. Rayner, and K. Mislow, *J. Am. Chem. Soc.*, **88**, 3139 (1966).

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Five-Coordinate Nickel(II) Complexes with Nitrogen–Phosphorus and Nitrogen–Arsenic Tetradentate Ligands

Sir:

A considerable number of five-coordinate complexes of nickel(II) have already been synthesized and characterized. They have been found to be either of the low-spin[1] or high-spin[2] type. The polyfunctional ligands which induce a low-spin ground state have been found to always contain the atoms P and/or As and never O or N as donor atoms. The reverse is true for complexes of high spin.

We have prepared two new ligands which contain donor atoms of both low and high crystal field splitting strength. They are tris(2-diphenylphosphinoethyl)-amine, $N(CH_2-CH_2-PPh_2)_3$ (TPN, set NP_3) and tris-(2-diphenylarsinoethyl)amine, $N(CH_2-CH_2-AsPh_2)_3$ (TAN, set NAs_3). With nickel(II) salts these tetradentate ligands form compounds of the types $Ni(TPN)X_2$ and $Ni(TPN)XBPh_4$ (X = Cl, Br, I) and $Ni(TAN)XBPh_4$, where X = Br, I. These crystalline compounds are stable and are intensely colored (dark blue, dark green, violet). The analyses for C, H, P, Ni, and halogen are in good agreement with calculated theoretical values.

These complexes are all diamagnetic. The spectra of the complexes in the solid state and in solution in dichloroethane and nitroethane are identical. In these solvents they behave as 1:1 electrolytes. Their spectra in the range 5000–22,000 cm^{-1} exhibit two bands in the range at 13,200–13,900 cm^{-1} (ϵ 2800–3100) and 18,200–20,000 cm^{-1} (ϵ 800–1450) for the TPN complexes and 12,650–13,150 cm^{-1} (ϵ 1000–2620) and 17,100–18,100 cm^{-1} (ϵ 600–1400) for the two TAN derivatives (Figure 1). These spectra are very similar to those of the diamagnetic trigonal bipyramidal nickel(II) complexes.[1c,d] Thus these complexes can be assigned a five-coordinate structure with formulas [Ni(TPN)X]X, [Ni(TPN)X]BPh$_4$, and [Ni(TAN)X]-BPh$_4$. The frequencies of the bands are in agreement with the respective positions of the halogen, phosphorus, and arsenic atoms in the spectrochemical series. The two bands can be assigned[3] to the transitions from the $^1A_1$ state to the two ^1E states, arising from the ^1D state of the free ion, in symmetry field C_{3v}. This symmetry is the highest possible consistent with the geometry of the two tetradentate ligands TPN and TAN. Also the relative intensity of the two bands is consistent with this symmetry.[3b]

All of the five-coordinate complexes of nickel(II) described to date containing tetradentate ligands with

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(2) (a) L. Sacconi, P. Nannelli, N. Nardi, and U. Campigli, *ibid.*, **4**, 943 (1965); L. Sacconi, P. L. Orioli, and M. DiVaira, *J. Am. Chem. Soc.*, **87**, 2059 (1965); L. Sacconi, M. Ciampolini, and G. P. Speroni, *ibid.*, **87**, 3102 (1965); L. Sacconi and I. Bertini, *ibid.*, **88**, 5182 (1966); (b) M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966); M. Ciampolini and G. P. Speroni *ibid.*, **5**, 45 (1966); M. Ciampolini and N. Nardi, *ibid.*, **6**, 445 (1967).

(3) (a) M. Ciampolini, *ibid.*, **5**, 35 (1966); (b) M. J. Norgett, J. H. M. Thornley, and L. M. Venanzi, *J. Chem. Soc.*, in press.
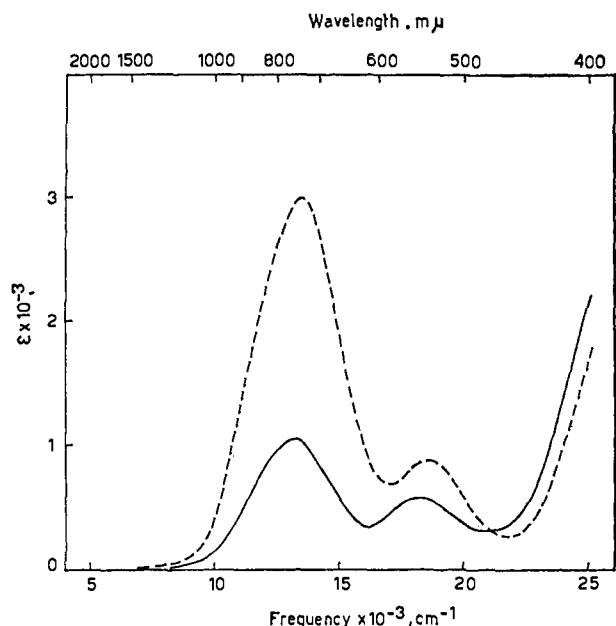
Figure 1. Absorption spectra of TPN and TAN nickel(II) complexes in dichloroethane: ----, [Ni(TPN)Br]BPh$_4$; ———, [Ni(TAN)Br]BPh$_4$.

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$_4$)$_3$W$_2$Cl$_9$ 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$_9$H$_6$NO)$_4$: 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 coworkers[3] only isolated the reduced, partially substituted [W^{II}(diars)$_2$I$_2$] 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$_2$WCl$_6$,[5] WCl$_6$,[4] and K$_3$W$_2$Cl$_9$[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$_9$H$_6$NO)$_2$] 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$_9$H$_6$NO)$_3$·C$_9$H$_6$NOH, 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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