

fins.²⁴ The yield of azoxyalkane is thus limited, but variation of reaction conditions may permit augmented N-alkylation and better yields. Note that alkylation of the diazotates' other nitrogen (yielding *N*-alkyl-*N*-nitrosoamines) is a minor process. Synthesis of the authentic *N*-nitrosoamines, followed by gc analysis of the crude reaction mixtures accompanying 1 and 6, limit *N*-nitrosoalkane formation to less than 5%.

By uv^{9a,b} and nmr,^{9,12} our azoxyalkanes are *trans* (see eq 1 and 2).²⁵ Because the diazotates from which they come are probably of *syn* configuration,²⁶ reactions 1 and 2 could lead directly to *trans*-azoxyalkanes by nucleophilic attack of the diazotate on RX, with retention of the N=N configuration.

The new azoxyalkane synthesis meets generality requirements 1-3. Our synthesis of (*S*)-4 from (*S*)-butane-2-diazotate (method 1) shows that it can partly meet the chirality requirement, 4. The CD spectrum of (*S*)-4 closely resembled those of (*S*)-ONN-1-cyclohexylazoxyethane²¹ and elaiomycin.^{5b} We are studying stereospecific synthetic routes to azoxyalkanes in which the chiral center is bonded at the =N(O) position.

Our synthesis generates primary and secondary *trans*-azoxyalkanes of varied structure. Superior syntheses of *tert*-azoxyalkanes¹⁵ complement our work. Coupled with photoisomerization,^{8,9} we can gain access to new O-position isomers, *cis*-azoxyalkanes, and oxadiaziridines as well. The potential for the synthesis of naturally occurring azoxyalkanes is patent, and we are exploring such possibilities.

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(24) R. A. Moss and M. J. Landon, *J. Amer. Chem. Soc.*, **92**, 5755 (1970).

(25) This is true for 4 and 6 whether their isolation involves gc or tlc.²⁰

(26) E. H. White, T. J. Ryan, and K. W. Field, *J. Amer. Chem. Soc.*, **94**, 1360 (1972).

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Robert A. Moss,*²⁷ Mildred J. Landon²⁸
Karen M. Luchter, Andrew Mamantov
Wright Laboratory, School of Chemistry
Rutgers, The State University of New Jersey
New Brunswick, New Jersey 08903

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Geometry of Nickel(II) Complexes

Sir:

Nickel(II) forms many complexes with octahedral, square-planar, and tetrahedral geometries and a smaller number of five-coordinate compounds¹ with other stereochemical arrangements. It is generally considered that a combination of steric and electronic factors determines which of the three common geometries is assumed by a given compound. Steric factors clearly operate in the sense that bulky ligands are most favorable to tetrahedral geometry and least favorable to octahedral geometry. The mode of operation of the electronic effects is much less clear in spite of ex-

(1) E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem. Soc.*, **20**, 245 (1966).

tensive discussion of the subject.²⁻⁴ We wish to present some new data on the structure of thiourea (tu) complexes of nickel(II) in solution and to suggest a simple rationale for their geometries.

Measurements of visible spectra, magnetic moments, conductivity, and molecular weights of nickel(II) complexes of thiourea and substituted thiourea at room temperature have been reported^{2,3} and have provided evidence for all three geometries. We have undertaken nmr and other studies of a number of these complexes over a wide range of temperature primarily to elucidate ligand exchange mechanisms. We report here data on four complexes chosen to illustrate the geometric possibilities. Ni(tu)₆(ClO₄)₂ gives conducting solutions in acetone and has a magnetic moment ranging from 2.3 (+27°) to 3.2 BM (-90°), and the nmr spectrum indicates fast ligand exchange involving a paramagnetic complex at room temperature. In the presence of excess ligand the exchange is barely frozen out at -90°. (The dimethylthiourea complex is similar but the ligand exchange is slow at -90° giving complexed resonances at -101.4, -19.9, and -12.1 ppm from TMS.) All data are consistent with octahedral Ni(tu)₆²⁺ being the only species present at -90° with some dissociation to square-planar Ni(tu)₄²⁺ at higher temperatures. Solutions of Ni(tu)₂Cl₂ in acetone are nonconducting at all temperatures and the magnetic moment varies from 3.5 (+27°) to 3.8 BM (-90°). The nmr of this complex shows fast exchange with dissociated ligand at +27°, but at -90° one of the two complexed tu protons (chemical shift -104.8 ppm) which result from restricted rotation about the C-N bond is no longer exchanging with free ligand. Free ligand and the second complexed ligand proton give an averaged resonance at -11.3 ppm. The species present is tetrahedral Ni(tu)₂Cl₂ at all temperatures. Ni(tu)₆Br₂ in acetone has a moment varying from 3.6 BM at +27° to 1.2 BM at -94°. It has a small conductivity at room temperature which increases at low temperature. The nmr spectrum at -90° has four resonances. Two show contact shifts (-110.3 and -20.2 ppm) and are attributed to tetrahedral Ni(tu)₂Br₂. One arises from free ligand (-8.9 ppm) and the fourth at -9.3 ppm is assigned to a diamagnetic complex. This latter compound must be ionic since its formation is accompanied by an increase in conductivity. The concentration of the analogous iodide complex is decreased by addition of (CH₃)₄NI (experiment carried out at -50° in the fast exchange region). On the other hand it cannot be Ni(tu)₄²⁺ since at -90° in the presence of excess ligand this species is completely converted to Ni(tu)₆²⁺. It must therefore be square-planar Ni(tu)₃Br⁺.⁶ Ni(tu)₆I₂ has a

(2) S. L. Holt and R. L. Carlin, *J. Amer. Chem. Soc.*, **86**, 3017 (1964).

(3) L. Venanzi, *J. Inorg. Nucl. Chem.*, **8**, 137 (1958).

(4) L. Sacconi, *Transition Metal Chem.*, **4**, 199 (1968).

(5) S. Basso, J. A. Costamagna, and R. Levitus, *J. Inorg. Nucl. Chem.*, **31**, 1797 (1969).

(6) A referee has suggested that the species formulated as Ni(tu)₃²⁺ or Ni(tu)₃X⁺ may be diamagnetic, five-coordinated Ni(tu)₃²⁺ or Ni(tu)₃X⁺. We consider these assignments less likely for several reasons. At room temperature optical spectra consistent with square-planar Ni(tu)₄²⁺ have been reported. The susceptibility and nmr data show that diamagnetic Ni(tu)₃²⁺ is not formed at low temperatures in the perchlorate solutions. At -90° the relative intensities of the "free ligand" and "diamagnetic complex" nmr peaks agree better with the ratios expected for Ni(tu)₃X⁺ than they do for Ni(tu)₃X⁺. We also find that this complex exchanges ligands by an associative process. A dissociative mechanism might have been expected for a five-coordinate compound. Although not conclusive these arguments incline us against postulating five-coordinate complexes.

