

forts to grow crystals of II. Further investigations with both pyrazolylborate and physiologically more realistic synthetic ligands are underway.²¹

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Supplementary Material Available. A listing of positional and thermal parameters will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 X 148 mm, 24X reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-7564.

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Pentagonal Bipyramidal Complexes of Nickel(II) and Copper(II). The Relative Importance of Ligand Geometry vs. Crystal Field Effects

Sir:

Pentagonal bipyramidal complexes of the first-row transition elements are relatively rare. Until recently, the only seven-coordinate complexes involved the Mn(II)¹ and Fe(III)^{2,3} ions, which have no crystal field stabilization energy. In fact, for transition metals with a nonspherical distribution of electrons, a planar pentagonal arrangement was considered unlikely because of crystal field effects.^{4,5} However, the synthesis of pentagonal bipyramidal complexes of V(III)⁶ and Fe(II), Co(II), and Zn(II)⁷ suggested that other seven-coordinate complexes of the first-row transition metals might indeed be prepared. We now wish to report the first pentagonal-bipyramidal complexes of Ni(II) and Cu(II). Our results indicate that ligand geometry may be more important than crystal field effects.

The complexes were prepared by stirring and heating a slurry of DAPSC, 2,6-diacetylpyridinebissemicarbazone, in ethanol with an ethanol-water solution of either Ni(NO₃)₂ · 6H₂O or Cu(NO₃)₂ · 3H₂O. The DAPSC slowly dissolves and after complete solution, slow evaporation of the solvent produces crystalline products. An analysis of the products suggested the stoichiometries DAPSC · Ni(NO₃)₂ · 3H₂O (I), and DAPSC · Cu(NO₃)₂ · 3H₂O (II). Since hydrolysis of the ligand could have occurred, X-ray crystal structure studies were undertaken.

Both complexes crystallize in the monoclinic system. The unit cell dimensions are $a = 11.493$ (2) Å, $b = 14.914$ (4) Å, $c = 12.154$ (4) Å, and $\beta = 104.94$ (2)° for I and $a = 10.977$ (4) Å, $b = 13.930$ (3) Å, $c = 6.977$ (3) Å, and $\beta = 104.55$ (3)° for II. The calculated densities of 1.697 g cm⁻³ for four molecules of I per unit cell and 1.669 g cm⁻³ for two molecules of II per unit cell are in good agreement with the values of 1.70 and 1.65 g cm⁻³ for I and II, respectively, measured by flotation. The systematic extinctions suggested that the space groups were $P2_1/n$ for I and either Pc or $P2/c$ for II. The intensity distribution for II favored $P2/c$, which requires the molecule to have a two-fold symmetry axis, and the successful analysis confirms this choice.

The intensity data for both complexes were measured using a Syntex P1 diffractometer with graphite monochromatized Mo K α - radiation and a variable speed θ - 2θ scan technique. The nickel atom in I was located from a Patterson function. In II, the Cu atom is required to lie on a two-fold axis and the y -coordinate was determined from a Patterson function. Subsequent Fourier syntheses for both compounds were used to locate the lighter atoms. Refinement was by least-squares techniques to an R of 0.055 for the 1623 reflections used in the analysis for I and to an R of 0.056 for the 1647 reflections used in the case of II.

The pentagonal bipyramidal nature of the two complexes is easily seen in Figures 1 and 2. In both complexes the metal atom is surrounded by an approximately planar pen-

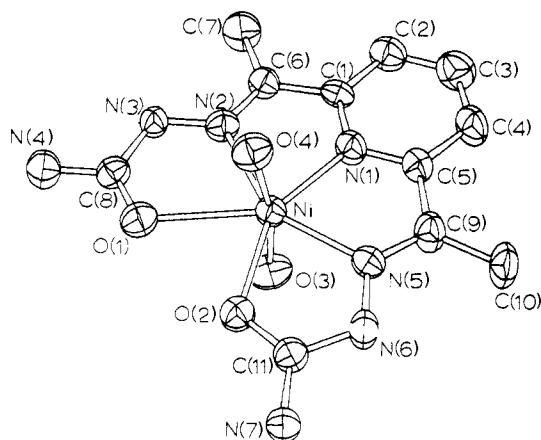


Figure 1. An ORTEP drawing of the diaqua(2,6-diacetylpyridinebis(semicarbazone))nickel(II) cation illustrating the pentagonal bipyramidal geometry of the complex. Pertinent distances are Ni-N(1) of 2.060 (6), Ni-N(2) of 2.222 (6), Ni-N(5) of 2.108 (6), Ni-O(1) of 2.478 (5) and Ni-O(2) of 2.216 (6) Å. The angles in the planar pentagon range from 66.4 (2) to 75.0 (3)° with an average of 72.0°, which is the ideal value for a plane pentagon.

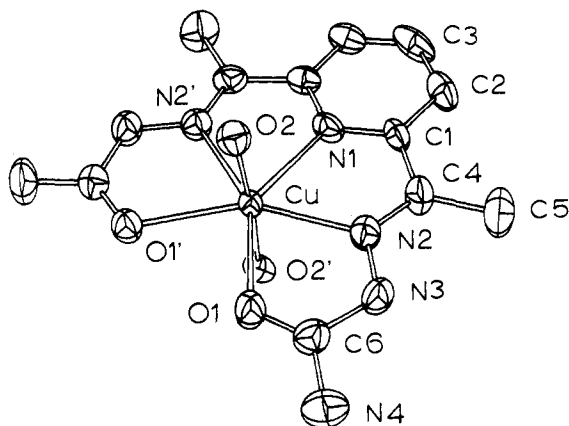


Figure 2. An ORTEP drawing of the diaqua(2,6-diacetylpyridinebis(semicarbazone))copper(II) cation. A twofold axis passes through the Cu, N1, and C3 atoms. The pertinent bond distances are Cu-N1 of 2.265 (6), Cu-N2 of 2.258 (4), and Cu-O1 of 2.350 (4) Å. The angles are O1-Cu-N2 of 68.8 (1)°, N1-Cu-N2 of 69.5 (1)°, and O1-Cu-O1' 83.5 (1)°.

agonal arrangement of three nitrogen and two oxygen atoms from the ligand. Two water molecules are bonded to the metal ion approximately normal to the plane of the ligand. The deviations from planarity are somewhat different in the two cases. The nickel complex has the smallest deviations from planarity of any of the pentagonal bipyramidal complexes prepared using DAPSC. The deviations (in Å × 10³) are N1 of -7, N2 of -2, N5 of +13, O1 of +9, and O2 of -14. In the Cu complex the deviations are large (N1 of 0, N2 of -31, and O1 of +42) although still much less than the other DAPSC complexes. The question of whether the planarity is related to the nature of the axial ligands is being explored.

A second unusual feature of the two complexes involves the M-OH₂ distances of 2.048 (6) and 2.090 (6) Å in the Ni derivative and 1.922 (3) Å in the Cu complex. These distances appear to be opposite to the expected increase in ionic radius of Cu vs. Ni. However, the in-plane distances in the Cu derivative (av Cu-N is 2.260 and Cu-O is 2.350 Å) are somewhat larger than those in the Ni complex (av Ni-N is 2.130 and Ni-O is 2.347 Å). The individual distances are given in the captions of the figure. These observations are in agreement with an energy level scheme in which the d(z²) orbital is higher in energy than the d(x²-

y²), and in going from Ni to Cu the additional electron is placed in the latter orbital. The axial distance is then a function of the in-plane distances, *via* nonbonded contacts, as well as the electronic configuration. The axial water distance increases in going from Cu to Zn (Zn-OH₂ is 2.121 Å) which agrees with an increased electron density in the d(z²) orbital. These observations are in agreement with the energy level diagram for pentagonal bipyramidal complexes.⁸

In summary, we see that the preparation and characterization of pentagonal bipyramidal complexes of Ni and Cu have demonstrated the importance of ligand geometry relative to crystal field effects. Furthermore, the preparation of these complexes reinforces the hypothesis that the use of planar pentadentate ligands will make pentagonal bipyramidal complexes of other elements readily accessible.

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Amino Acid-Cyclic Peptide Complexes¹

Sir:

We now report enantiomeric differentiation between D- and L-amino acid salts in complexes with *cyclo*(L-Pro-Gly)_n peptides (*n* = 3, 4).² Conceptually related complexes have been described in other systems, *e.g.*, the cyclodextrin inclusion complexes,³⁻⁵ chiral crown ether complexes,⁶⁻⁹ specific association complexes of copper chelates with gramicidin S¹⁰ and polyamino acids,¹¹ and bovine serum albumin-tryptophan complexes.¹²

As shown in Table I, ¹³C nmr spectra of chloroform solutions of *cyclo*(Pro-Gly)₃ or *cyclo*(Pro-Gly)₄ containing a D,L mixture of an amino acid salt display separate resonances for several carbons of the D and L enantiomers of Pro-OBz·HCl, Phe-OMe·HCl, and Val-OMe·HCl. Such spectra result from the formation of diastereomeric pairs of complexes. The present findings are exemplified by the ¹³C spectrum of the complexes of *cyclo*(Pro-Gly)₄ with D- and L-Pro-OBz·HCl (Figure 1). (It should be recalled that uncomplexed D,L-amino acid salts give one set of resonances for both enantiomers.) In addition, spectra of solutions containing 1:1 molar ratios of cyclic peptide and only one amino acid enantiomer also give single resonances for the salt (eliminating the possibility that a slow "on-off" process is responsible for the observed splitting).