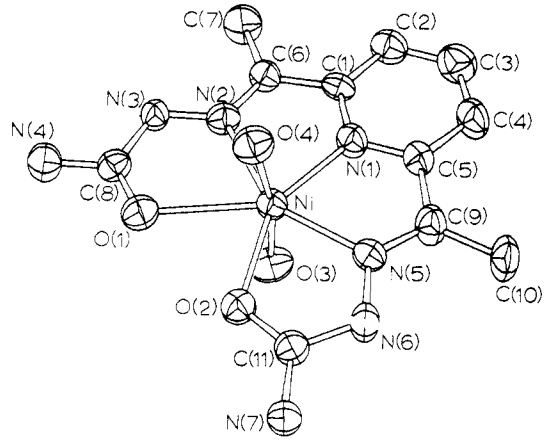

Figure 1. An ORTEP drawing of the diaqua(2,6-diacetylpyridinebis-(semicarbazone))nickel(II) cation illustrating the pentagonal bipyramidal geometry of the complex. Pertinent distances are Ni-N(1) of 2.060 (6), Ni-N(2) of 2.222 (6), Ni-N(5) of 2.108 (6), Ni-O(1) of 2.478 (5) and Ni-O(2) of 2.216 (6) Å. 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.

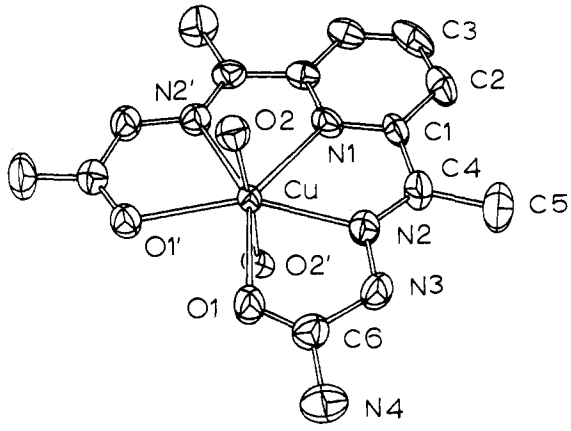

Figure 2. An ORTEP drawing of the diaqua(2,6-diacetylpyridinebis-(semicarbazone))copper(II) cation. A twofold axis passes through the Cu, N1, and C3 atoms. The pertinent bond distances are Cu-N1 of 2.265 (6), Cu-N2 of 2.258 (4), and Cu-O1 of 2.350 (4) Å. The angles are O1-Cu-N2 of 68.8 (1)°, N1-Cu-N2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

tagonal 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 × 10^3) 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-OH_2 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 $d(z^2)$ orbital is higher in energy than the $d(x^2-y^2)$, 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-OH_2 is 2.121 Å) which agrees with an increased electron density in the $d(z^2)$ 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 Complexes[1]

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 S[10] and polyamino acids,[11] and bovine serum albumin-tryptophan complexes.[12]

As shown in Table I, ^{13}C 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 ^{13}C 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).

Table I. ^{13}C Chemical Shifts of Amino Acid Salts in Diastereomeric Complexes with cyclo(Pro-Gly)$_n$ Peptides[a]

Cyclic peptides		Amino acid salt (HCl)	Salt resonances		
		D,L-Pro-OBz	124.21 (OCH_2Ph); 163.81 (C_β); 169.02 (C_γ)		
cyclo(Pro-Gly)$_3$[d]	+	L-Pro-OBz	124.71	163.55	168.87
		D-Pro-OBz	124.86	163.68	169.01
cyclo(Pro-Gly)$_4$[e]	+	L-Pro-OBz	124.56	163.50	168.91
		D-Pro-OBz	124.77	163.75	169.17
		D,L-Phe-OMe	63.04 (*o*-Ph);	63.73 (*m*);	65.00 (*p*)
cyclo(Pro-Gly)$_3$[d]	+	L-Phe-OMe	63.00	63.50	64.91
		D-Phe-OMe	63.08	63.61	64.91
cyclo(Pro-Gly)$_4$[b]	+	L-Phe-OMe	63.18	64.04	65.49
		D-Phe-OMe	63.04	64.04	65.35
		D,L-Val-OMe	174.28 (C_γ-methyl groups)		
cyclo(Pro-Gly)$_4$[c]	+	L-Val-OMe	174.17; 175.18		
		D-Val-OMe	173.84; 175.18		

[a] Chemical shifts (estimated uncertainty ±0.03 ppm) given in ppm upfield from external CS_2; solvent, $CDCl_3$; concentration, 30–50 mg/ml of cyclic peptide. Molar ratio of amino acid–cyclic peptide = 1/1. Molar ratio of L/D in amino acid salts = 1/1 except where indicated. Bracketed salts were studied together in one solution. [b] Ratio of L/D amino acid = 1/2. [c] Ratio of L/D amino acid = 2. [d] Assignments to D or L enantiomers are tentative. [e] The ^{13}C nmr spectrum of this sample is shown in Figure 1.

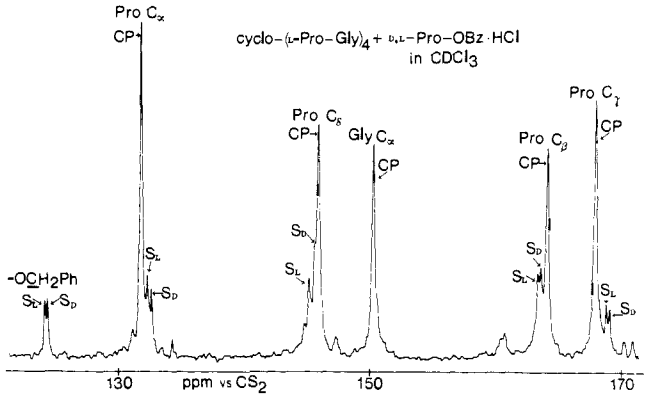

Figure 1. ^{13}C nmr spectrum (20 MHz) in chloroform-*d* of the upfield region (122–172 ppm *vs.* external CS_2) of *cyclo*(L-Pro-Gly)$_4$ complexed with D,L-Pro-OBz · HCl. Concentration of cyclic peptide is 50 mg/ml. The solution contains 0.5 equiv each of L-Pro-OBz · HCl and D-Pro-OBz · HCl per equivalent of *cyclo*(Pro-Gly)$_4$. Assignments of resonances (CP = cyclic peptide, S = salt) were made by comparison with related peptides.[13-17] The following chemical shifts were obtained for the complete spectrum: for the C_4-symmetric *cyclo*(Pro-Gly)$_4$, Pro C=O, 21.05; Gly C=O, 23.74; Pro C_α, 132.30; Pro C_δ, 146.17; Gly C_α, 150.54; Pro C_β, 164.25; Pro C_γ, 168.08; for D,L-Pro-OBz · HCl, Pro C=O, 22.86; Ph ring, 57.85 (C_{quat}), 64.05, (o, m), 64.45 (p); OCH_2Ph, 124.56 (L), 124.77 (D); Pro C_α, 132.67, 132.96; Pro C_δ, 145.41, 145.88; Pro C_β, 163.50, 163.75; Pro C_γ, 168.91, 169.17. Other small resonances correspond to minor populations of cis peptide bond containing conformations of *cyclo*(Pro-Gly)$_4$.

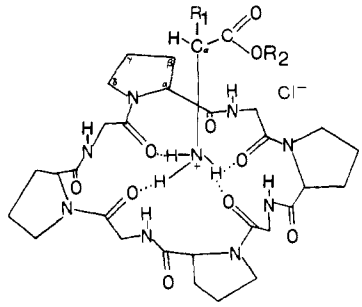

Figure 2. A possible binding scheme of an amino acid salt to *cyclo*(L-Pro-Gly)$_4$. All eight peptide bonds of the cyclic peptide are trans. The N–C_α bond of the salt is elongated for clarity of presentation. For Phe-OMe · HCl, R_1 = CH_2Ph and R_2 = CH_3. For Val-OMe · HCl, R_1 = $CH(CH_3)_2$ and R_2 = CH_3. For Pro-OBz · HCl, the side chain R_1 is a pyrrolidine ring (and eliminates one of the ammonium NH protons) and R_2 = CH_2Ph. A second binding site on the opposite face of the peptide can be formed by inward rotation of the four Pro carbonyl groups.

The splitting observed in resonances of the enantiomeric amino acid salts (*ca.* 0.2 ppm) may be due to differences in binding constants of the D and L salt to the cyclic peptide and/or to conformational and electronic differences between the resulting pair of diastereomeric complexes. Resonances of the cyclic peptides are not split in the complexes, a result which may be attributable, in part, to the fact that these differences must be averaged over three or four magnetically equivalent Pro-Gly units.

The consistent location of Pro C_γ resonances of the cyclic peptides near 168 ppm in the complexes indicates that they contain only trans peptide bonds, in accord with observations for trans X-Pro peptide bonds in a variety of proline peptides.[13-17] The downfield movement (*ca.* 1–2 ppm) observed for cyclic peptide carbonyl chemical shifts upon complex formation reflects changes in *cyclo*(Pro-Gly)$_n$ conformations, as well as relative involvement of Gly and Pro C=O's in binding.[18,19] Based upon the ^{13}C data, model building, and upon analogy with studies on *cyclo*(Pro-Gly)$_3$ conformations,[18,23] a structure may be suggested for *cyclo*-(Pro-Gly)$_4$–amino acid salt complexes as shown schematically in Figure 2. The alkylammonium NH protons of the salt can be positioned into a peptide binding cavity consisting of four Gly carbonyl groups.

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(19) Two cyclic peptides which were not expected to bind amino acid salts *specifically* were studied under similar conditions. In *cyclo*(Pro)$_3$, the three rigid Pro C=O groups are oriented away from the center of the peptide in a manner unfavorable for cooperative cation binding.[20] Valinomycin, a naturally occurring cyclic depsipeptide, has a binding site in the interior of the molecule which would not be accessible to bulky amino acid cations.[21,22] Upon addition of D,L-Phe-OMe · HCl up to a twofold molar excess in chloroform solutions, no chemical shift changes in spectra of either of the cyclic peptides (or in the salt) were noted, suggesting that the observed changes in spectra of *cyclo*(Pro-Gly)$_n$ peptides and added salts result from specific, cooperative binding. Note that nonspecific binding of an alkylammonium group to an individual peptide carbonyl group, which may occur in chloroform, was also not manifested by any ^{13}C chemical shift changes.
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End-to-End Bridging by the Thiocarbonyl Ligand. Complexes of the Type MC≡SM′

Sir:

Only a small number of oxygen-bonded adducts of terminal metal carbonyl derivatives have been isolated,[1] and there is spectroscopic evidence for only a few additional such adducts.[2] It is apparent from these few examples that a high electron density on the carbonyl ligand, indicated by a low carbonyl stretching frequency, is a prerequisite for adduct formation. In all cases the adducted carbonyl exhibits a lowered CO stretching frequency, while any other carbonyl groups in the complex have absorptions shifted to higher frequency.

Based on a comparison of organic carbonyl and thiocarbonyl compounds,[3] the thiocarbonyl ligand may be expected to be more polar and reactive than analogous carbonyl ligands. Evidence supporting this idea derives from the observed ease with which thiocarbonyls undergo nucleophilic attack at the carbon,[4] as in eq 1. However, until now there

$$(CO)_5WC{\equiv}S + RNH_2 \longrightarrow (CO)_5WC{\equiv}NR + H_2S \quad (1)$$

has been no chemical evidence for high electron density on the sulfur. In view of the larger anticipated negative charge on the sulfur atom and its lower electronegativity as compared to oxygen, Lewis acids may form sulfur-bonded adducts of suitable metal thiocarbonyls even under circumstances where the carbonyl ligand does not. We now report the first examples of such complexes.

We observed that $W(CO)_5(CS)$[4] and *trans*-$W(CO)_4(PPh_3)(CS)$,[4] having relatively high CS stretching frequencies (Table I), do not react with mercuric halides or BCl_3 at 25° in CH_2Cl_2 solvent. The complex *mer*-$W(CO)_3(CS)(DPE)$ (DPE = ethylenebis(diphenylphosphine)), prepared by refluxing equimolar amounts of $W(CO)_5(CS)$ and DPE in xylene for 2 hr, has a lower CS absorption but also does not react with these reagents. However, $W(CO)(CS)(DPE)_2$ (**1**), having the lowest CS stretching frequency (1161 cm^{-1}) yet reported for a metal thiocarbonyl ligand, does react with a variety of Lewis acids. This complex was prepared in good yield (>80%) by heating equimolar $W(CO)_3(CS)(DPE)$ and molten DPE under N_2 at 195° for 1 hr. The crude product could be recrystallized from CH_2Cl_2 or CS_2. The carbonyl and thiocarbonyl groups are presumed to be cis in this complex, based on the geometry of its precursor, *mer*-$W(CO)_3(CS)(DPE)$.

Table I. Infrared Data

Compound	ν(CO),[a] cm^{-1}	ν(CS),[a] cm^{-1}
$W(CO)_5(CS)$	2096 (w), 2007 (m), 1989 (vs)[b]	1258 (vs)[b]
trans-$W(CO)_4(PPh_3)(CS)$	2052 (w), 1981 (vw), 1956 (vs)[b]	1247 (vs)[b]
mer-$W(CO)_3(CS)(DPE)$	2013 (w), 1925 (vs)	1215[c]
$W(CO)(CS)(DPE)_2$	1838 (s)	1161 (s)
$W(CO)(DPE)_2CSW(CO)_5$	2062 (w), 1925 (vs), 1878 (m)	*d*
$W(CO)(DPE)_2CSHgCl_2$	1885	*d*
$W(CO)(DPE)_2CSHgI_2$	1872	*d*
$\{[W(CO)(DPE)_2CS]_2Ag\}BF_4$	1869 (s)[e]	1106 (s)[e]

[a] Recorded in CH_2Cl_2 unless specified otherwise. [b] *n*-Hexane solution. [c] CS_2 solution. [d] Absorption is partially obscured by a ligand absorption and an exact value could not be obtained. [e] Nujol mull.

When stirred in CH_2Cl_2 with an equimolar amount of the reactive $W(CO)_5$(acetone),[5] **1** forms an orange complex (>80% yield), which was recrystallized from CH_2Cl_2–hexane or CS_2. Elemental analyses indicate a composition of

$$W(CO)(CS)(DPE)_2 + (Me_2CO)W(CO)_5 \longrightarrow (DPE)_2(CO)WC{\equiv}SW(CO)_5 + Me_2CO \quad (2)$$

$(DPE)_2(CO)W(CS)W(CO)_5$ for this compound (Calcd: C, 51.45; H, 2.87; S, 2.32. Found: C, 51.76; H, 3.54; S, 1.75). The complex shows evidence of some decomposition in acetone solution in minutes but is stable in the solid state for several days. This is the first complex known to contain a bridging thiocarbonyl ligand; its end-to-end bridging (*via* C and S) structure contrasts with the carbon-bridging form (*via* only the carbon) observed for CO bridging of transition metals. The infrared spectrum (Table I) of the product shows the three expected carbonyl absorptions of the $W(CO)_5$ moiety, and the lowest of these apparently overlaps the lone carbonyl absorption of the $W(CO)(CS)(DPE)_2$ fragment. This carbonyl band has therefore shifted to higher frequency as compared to its position in the starting complex, **1**. The thiocarbonyl absorption, however, has not shifted to higher frequency since no new bands appear in the ir spectrum from 1160 to 1400 cm^{-1}, and the CS band originally near 1160 cm^{-1} has disappeared. It is apparently overlapped by a strong, broad DPE ligand absorption near 1095 cm^{-1} since this absorption has become more intense.

This novel binuclear complex, bridged only by the CS ligand, reacts with PPh_3 in CH_2Cl_2 solution at 25° to yield, within several minutes, **1** and $W(CO)_5PPh_3$.[7] It was hoped that W–C cleavage might occur in this reaction to give the isothiocarbonyl complex $(C{\equiv}S)W(CO)_5$; this was not observed, however.

The reaction of **1** with an equimolar amount of $HgCl_2$ or HgI_2 in CH_2Cl_2 (eq 3) gives orange[8] or red crystals,[9] respectively (>80% yield), when hexane is added to the solu-