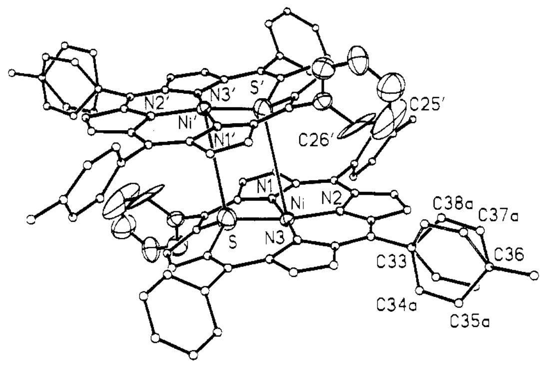

Figure 2. Drawing showing the interaction between adjacent, centrosymmetrically related Ni^{I}(SDPDTP) molecules. The disorder in one phenyl ring and large thermal parameters for C(25) and C(26), presumably due to short intermolecular contacts, are also illustrated. Atoms drawn as circles were refined with isotropic thermal parameters and are given an arbitrary size. The solid lines connecting Ni and S' and Ni' and S do not represent conventional chemical bonds.

from Ni^{II}(SDPDTP)Cl by reduction with aqueous sodium dithionite and crystallized by diffusion of acetonitrile into a benzene solution of the complex. The core structure, as determined by X-ray crystallography, is shown in Figure 1 along with that of Ni^{II}(STPP)Cl.[8] Relevant structural parameters, along with those for Ni^{II}(STPP)Cl and Cu^{II}(STPP)Cl,[8] are presented in Table I. The geometry of Ni^{I}(SDPDTP) resembles that of other thiaporphyrin complexes with the thiophene ring tipped 52.3° out of the N_3 plane and pyramidal coordination of the thiophene sulfur.

The Ni^{I} ion has nearly planar geometry and *surprisingly short* Ni–N and Ni–S bonds. Comparison of the data in Table I indicates that the Ni–N and Ni–S bond lengths decrease upon reduction of high-spin ($S = 1$), five-coordinate Ni^{II}(STTP)Cl to four-coordinate ($S = {}^{1}/_{2}$) Ni^{I}(SDPDTP). Additionally, the Ni–N and Ni–S distances in d^9 Ni^{I}(SDPDTP) are shorter than those in five-coordinate, d^9 Cu^{II}(STTP)Cl. The Ni^{I}–N distances are also shorter than the Ni^{II}–N distances (2.024, 2.052 Å) in a high-spin, six-coordinate Ni^{II} porphyrin.[11] Moreover, the Ni^{I}–N(2) distance is shorter than the Ni^{II}–N distances (1.92–1.96 Å) in four-coordinate, diamagnetic Ni^{II} porphyrins[12,13] while the Ni^{I}–N(1) and Ni^{I}–N(3) distances are longer. Similarly, the Ni^{I}–N(2) distance is shorter and the Ni^{I}–N(1) and Ni^{I}–N(3) distances are longer than the Cu^{II}–N distance (1.981 (7) Å) in the four-coordinated d^9 Cu^{II}(tetraphenylporphyrin).[14]

Comparison of the Ni^{II} and Ni^{I} structures clearly shows that reduction does not necessarily imply expansion of metal–ligand distances. In cases where the coordination number is lowered, a lack of expansion upon reduction is a fairly general phenomenon that is maintained, for example, in the following pairs: Ni^{II}(PMe$_3$)$_3$Br$_2$, Ni^{II}–P = 2.19–2.20 Å;[15] Ni^{I}(PMe$_3$)$_4^+$, Ni^{I}–P = 2.211–2.221 Å;[16] Cu(2,5-dithiahexane)$_2$(ClO$_4$)$_2$, Cu^{II}–S = 2.320–2.354 Å; Cu(2,5-dithiahexane)$_2$(ClO$_4$), Cu^{I}–S = 2.263 Å;[17] Cu(3-methoxy-1,5-dithiacyclooctane)$_2^{2+}$, Cu^{II}–S = 2.294–2.351 Å;[16] Cu(3-methoxy-1,5-dithiacyclooctane)$_2^+$, Cu^{I}–S = 2.346 Å.[18] There also are examples in which reduction without ligand loss is accompanied by a decrease in metal–ligand distances. These include the four-coordinate iron porphyrins with formal oxidation states of Fe^{II}, Fe^{I}, and Fe^{0} [19] and the corresponding cobalt complexes with formal oxidation states Co^{I} and Co^{0}.[20,21] In these cases the structures have been interpreted to indicate a significant degree of porphyrin reduction. Evidence for predominant, metal-based reduction for **2** in solution has been presented.[9] Attempts are in progress to obtain a four-coordinate Ni^{II} thiaporphyrin complex so that a comparison can be made of Ni^{II} and Ni^{I} without a change of coordination number. The dramatic shortening of the Ni–S bond that occurs upon reduction may reflect increased π back-donation as suggested previously for Cu–S bonds.[16,17] It remains to be seen whether the presence of the sulfur atom in Ni^{I}(SDPDTP) plays a role in producing the short Ni–N bonds seen here.

Figure 2 shows the interaction of a pair of Ni^{I}(SDPDTP) molecules within the crystal. The intermolecular Ni–S' contacts (shown as solid lines) are quite long (4.106 (6) Å), and the nickel ions lie on the side of the thiaporphyrin plane that is opposite the neighboring sulfur. Consequently, the Ni$\cdots$S interaction is weak and is of minor importance to the geometry of the molecule. However, it probably is a major component involved in the antiferromagnetic behavior of the solid ($\mu = 2.28\ \mu_B$ (per Ni) at 295 K and 0.71 μ_B at 2 K). Contact between molecules also leads to disorder in the positions of two phenyl rings. Notice that in Figure 2 the phenyl ring involving C(21)–C(26) is close to the *p*-tolyl ring containing C(33)–C(38). These contacts lead to two alternate positions for the *p*-tolyl ring and large amplitudes for thermal parameters for the phenyl ring C(21)–C(26).

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Supplementary Material Available: A table of crystal data, a fully labeled drawing, and tables of positional parameters, bond lengths, bond angles, anisotropic thermal parameters, and hydrogen atom positions (8 pages); a table of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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(10) Dark-brown plates of Ni^{I}(SDPDTP)·CH$_3$CN belong to the space group $P2_1/c$ with $a = 15.746$ (6) Å, $b = 15.944$ (4) Å, $c = 15.472$ (6) Å, $\beta = 113.25$ (3)°, and $Z = 4$ at 130 K. Refinement yielded $R = 0.077$ for 1585 reflections with $I > 3\sigma(I)$ and 273 parameters. There is disorder in the carbon atoms of two phenyl rings. In one case (C(33)–C(38)) the disorder could be modeled by the assignment of two equally probable positions of the phenyl ring, one rotated with respect to the other. In the other case (C(21)–C(26)) it could be only modeled by assuming anisotropic thermal motion.

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Aromatic Ring Stacking in Ternary Copper(II) Complexes [Cu(histamine)(L-AA)(ClO$_4$)] (AA = Phenylalaninate, Tyrosinate). Structural Evidence for Intramolecular Stacking Involving a Coordinated Imidazole Ring

Biological molecular recognition is achieved by combination of various noncovalent interactions.[1] Aromatic ring stacking has

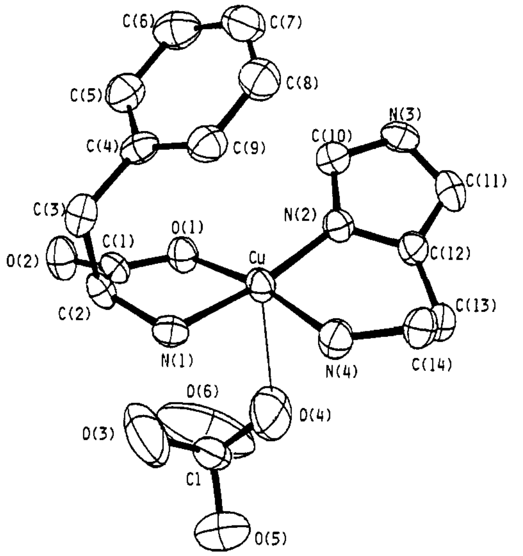

Figure 1. Structure of [Cu(hista)(L-Phe)(ClO_4)] (**1**), showing the 50% probability thermal ellipsoids and the atom-labeling scheme. Selected bond lengths (Å) and angles (deg): Cu–N(1) = 1.991 (6); Cu–N(2) = 1.942(7); Cu–N(4) = 2.002 (6); Cu–O(1) = 1.983 (5); Cu–O(4) = 2.705 (8); N(1)–Cu–N(2) = 170.9 (2); N(1)–Cu–N(4) = 90.9 (3); N(1)–Cu–O(1) = 83.7 (2); N(2)–Cu–N(4) = 93.9 (3); N(2)–Cu–O(1) = 92.8 (2); N(4)–Cu–O(1) = 169.3 (3).

attracted much attention because of its significance such as in DNA–intercalator interactions leading to denaturation of DNA.[2] The imidazole group of histidine (His) is the most important metal binding site[3] and at the same time a potential partner of stacking interactions for other aromatic rings in biological systems.[4] Solution chemical studies on the ternary Cu(II)–histidine–amino acid complexes[5,6] indicated the existence of intramolecular stacking between the imidazole ring and the side-chain aromatic rings of phenylalanine (Phe), tyrosine (Tyr), and tryptophan (Trp), which was supported by circular dichroism spectral magnitude anomaly.[6] It is interesting to note in this connection that enkephalin and other endogenous analgesic peptides (opioid peptides) have essential N-terminal tyrosyl and phenylalanyl residues[7] and that the receptor was reported to have an imidazole group at the binding site.[8] This raised the possibility that the peptide–receptor bonding might be achieved at least partly by the imidazole–tyrosine phenol stacking. On the basis of the solution equilibria of ternary Cu(II)–aromatic diamine–aromatic amino acid systems, it was concluded that the stacking interactions occur between the aromatic rings of amino acids and coordinated diamines such as histamine (hista) and 1,10-phenanthroline (phen).[9] We have now established the stacking interactions in two Cu(II) complexes, [Cu(hista)(L-Phe)(ClO_4)] (**1**) and [Cu(hista)(L-Tyr)(ClO_4)] (**2**), in the solid state by X-ray crystal structure analysis. To our knowledge these are the first examples of intramolecular aromatic ring stacking involving imidazole and aromatic amino acids and serve as evidence for similar stacking interactions hitherto proposed in solution[5,6,9] and in biological systems.[4]

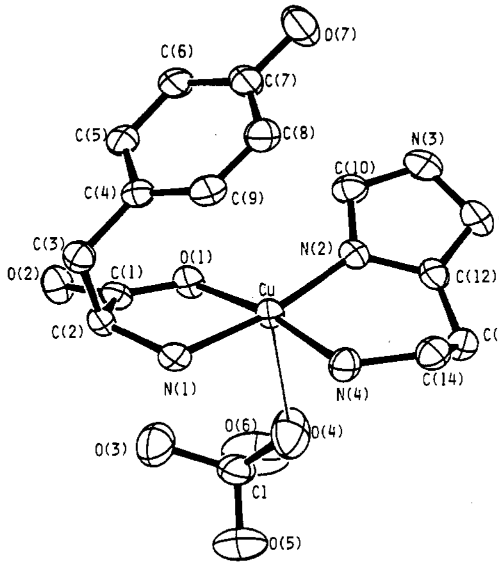

Figure 2. Structure of [Cu(hista)(L-Tyr)(ClO_4)] (**2**), showing the 50% probability thermal ellipsoids and the atom-labeling scheme. Selected bond lengths (Å) and angles (deg): Cu–N(1) = 1.982 (3); Cu–N(2) = 1.948 (2); Cu–N(4) = 2.020 (2); Cu–O(1) = 1.982 (2); Cu–O(4) = 2.682 (3); N(1)–Cu–N(2) = 170.1 (1); N(1)–Cu–N(4) = 91.4 (1); N(1)–Cu–O(1) = 83.09 (9); N(2)–Cu–N(4) = 93.6 (1); N(2)–Cu–O(1) = 93.40 (9); N(4)–Cu–O(1) = 168.6 (1).

Complex **1** was isolated as deep blue crystals from an aqueous solution containing $Cu(ClO_4)_2$, histamine hydrochloride, and L-Phe in the molar ratio of 1:1:1 at pH 8. Crystals suitable for X-ray studies were obtained by recrystallization from water.[10] The crystals of **2** were obtained in a similar manner by using L-Tyr in place of L-Phe.[11] The molecular structures of **1** and **2** are respectively shown in Figures 1 and 2, which indicate a remarkable structural similarity between the two complexes. In both cases the Cu(II) ion has a five-coordinate square-pyramidal structure with the two nitrogen atoms of hista and the nitrogen and the oxygen atom of Phe or Tyr coordinated in the equatorial plane, a perchlorate oxygen occupying a remote axial position (Cu–O(4) distances: 2.705 (8) Å for **1** and 2.682 (3) Å for **2**) to complete the square pyramid. The amino groups from hista and Phe or Tyr occupy equatorial cis positions. The equatorial Cu–N and Cu–O bond lengths agree well with those reported for Cu(L-Phe)$_2$,[12] Cu(L-Tyr)$_2$,[13] and Cu(L-asparaginate)(L-His).[14]

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(10) The complex was isolated from an aqueous solution (10 mL) containing $Cu(ClO_4)_2 \cdot 6H_2O$ (3.70 g, 10 mmol) and recrystallized from water in ca. 50% yield. *The perchlorate salt is stable at room temperature but should be handled with care* (see for example: *J. Chem. Educ.* **1973**, *50*, A335). *It may decompose when irradiated by a laser beam.* Crystal data for **1**: $C_{14}H_{19}N_4O_6ClCu$, M_r = 438.31, monoclinic, space group $P2_1$, a = 9.142 (1) Å, b = 16.469 (2) Å, c = 5.889 (1) Å, β = 92.55 (2)°, V = 885.8 Å^3, Z = 2, ρ_{calcd} = 1.643 g cm^{-3}, ρ_{obsd} = 1.641 g cm^{-3}, μ(Cu Kα) = 34.95 cm^{-1}, crystal dimensions 0.20 × 0.20 × 0.10 mm. The structure was solved by the heavy-atom method and refined anisotropically for non-hydrogen atoms by block-diagonal least-squares calculations using the program KPPXRAY (Taga, T.; Higashi, T.; Iizuka, H. "KPPXRAY, Kyoto Program Package for X-Ray Crystal Structure Analysis", Kyoto University, 1985). The final R and R_w factors were 0.0398 and 0.0460, respectively, for 1337 unique reflections with $|F_o| \geq 3\sigma|F_o|$.

(11) This complex was prepared in ca. 60% yield in the same way as above. *The precautions for the perchlorate salt should also be taken.* Crystal data for **2**: $C_{14}H_{19}N_4O_7ClCu$, M_r = 454.31, monoclinic, space group $P2_1$, a = 9.186 (1) Å, b = 16.394 (2) Å, c = 5.976 (1) Å, β = 90.35 (1)°, V = 899.9 Å^3, Z = 2, ρ_{calcd} = 1.676 g cm^{-3}, ρ_{obsd} = 1.676 g cm^{-3}, μ(Mo Kα) = 14.09 cm^{-1}, crystal dimensions 0.50 × 0.16 × 0.10 mm. The structure was solved by a method similar to that used for **1** by using the program UNICS III. The final R and R_w factors were 0.0252 and 0.0322, respectively, for 2130 unique reflections with $|F_o| \geq 3\sigma|F_o|$.

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Interestingly, the side-chain aromatic rings of Phe and Tyr are located above the coordination plane to be involved in the stacking with the coordinated imidazole, which in turn deviates from the plane toward the aromatic side chain probably through the distortion of the N(1)–Cu–N(2) angle (170–171°) from 180°.[15] The shortest distances between the two rings (C(7)···C(10)) are 3.49 and 3.45 Å for **1** and **2**, respectively. The stacking seems to be less effective than that detected in Cu(phen)(L-Trp),[16] because the ring overlapping is limited and the dihedral angle between the rings in **1** is 38.5° (38.1° in **2**) with the distance of 4.15 Å (4.20 Å in **2**) between the centers of the mean planes of the benzene and imidazole rings. The side-chain conformation of L-Tyr in **2** is similar to that reported for Cu(L-Tyr)$_2$,[13] where one of the two phenol rings approaches the Cu(II) ion form above the coordination plane. While Cu(L-phenylalaninamide)$_2$ with the two amino and two deprotonated nitrogens coordinated in the plane has a similar bent conformation,[17] Cu(L-Phe)$_2$ has the two Phe side chains directed outward from the Cu(II) center,[12] so that the bent conformation in **1** may reflect the effect of the stacking interaction. The Cu(II) coordination planes formed by Cu, N(1), N(2), N(3), and O(1) atoms are planar only to within 0.17 and 0.15 Å for **1** and **2**, respectively, and Cu(L-Tyr)$_2$ with a similar bent conformation also exhibits a large distortion (0.10 Å).[13] These deviations are in contrast with the planarity revealed for Cu(L-Phe)$_2$ with a very small distortion (0.012 Å)[12] and are indicative of the effects of the intramolecular stacking.

Close contacts between a metal ion and aromatic rings have been reported for a number of complexes in the solid state, such as Cu(phen)(L-Trp),[16] Cu(L-Tyr)$_2$,[13] Pd(L-Tyr)$_2$,[18] Cu(glycyl-L-tryptophanate),[19] and Cu(glycyl-L-leucyl-L-tyrosinate),[20] where the Cu(II)···aromatic ring separations are 3.04–3.34 Å. Complexes **1** and **2** also exhibit such a contact with the shortest distances of 3.14 and 3.20 Å, respectively, for Cu(II)···C(9), but the central Cu(II) ion is not appreciably moved toward the aromatic ring from the mean plane, the deviation being negligibly small (0.007 and 0.005 Å in **1** and **2**, respectively).

The stability enhancement due to intramolecular ligand–ligand stacking interactions is evaluated by the constant *K* for the following hypothetical equilibrium:[6,9,21]

$$\mathrm{Cu(en)(L\text{-}Phe) + Cu(hista)(L\text{-}Ala)} \overset{K}{\rightleftharpoons} \mathrm{Cu(hista)(L\text{-}Phe) + Cu(en)(L\text{-}Ala)}$$

where en is ethylenediamine and stacking is possible in Cu(hista)(L-Phe) only. The log *K* values for **1** (0.26) and **2** (0.51) indicate stabilization due to aromatic ring stacking, although they are smaller than those for Cu(phen)(L-Trp) (1.39), Cu(phen)(L-Phe) (0.64), and Cu(phen)(L-Tyr) (1.05).[9] They reasonably explain the extent of stacking among various aromatic rings, because Cu(phen)(L-Trp) with perfect stacking[16] shows the highest stabilization. The ESR parameters for both complexes at 77 K,[22] which are exactly the same ($g_\parallel = 2.228$; $g_\perp = 2.054$; $|A_\parallel| = 195 \times 10^{-4}$ cm^{-1}; $|A_{N_\perp}| = 14.4 \times 10^{-4}$ cm^{-1}), show that the Cu(II) environment is of axial symmetry. On the other hand, Fischer and Sigel[5] concluded the presence of stacking in ternary Cu(II)–amino acid complexes containing His by careful examination of the stability constants: The complexes Cu(L- or D-His)(L-AA) (AA = Trp, Phe) in solution were calculated to be mostly in the stacked form (28–90%) depending on the aromatic ring size and the combination of enantiomers around the central Cu(II) ion. On the assumption that the amino groups occupy cis positions, higher stabilization of the meso form Cu(D-His)(L-AA) as compared with the active form Cu(L-His)(L-AA) has been interpreted as due to the interference of stacking in the active form by the carboxylate group probably coordinated and located on the same side of the coordination plane as that for the aromatic ring.[5,6]

The present structural studies support the previous conclusions that the stacking interactions involving imidazole exist in aqueous solution and in biological systems. They may further add to evidence for the cis configuration in His-containing ternary Cu(II)–amino acid complexes.

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Supplementary Material Available: Tables of atomic parameters for non-hydrogen atoms, fractional coordinates and isotropic thermal parameters for hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, bond lengths and valence angles, and torsion angles (6 pages); listings of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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(15) In contrast with this the imidazole ring in Cu(Tyr·His) (Tyr·His = L-tyrosyl-L-histidinate) does not interact with the Tyr phenol ring with the result that the former faces the outside of the coordination sphere and that the N(1)–Cu–N(2) angle is close to 180° (177.0°): Masuda, H.; Odani, A.; Yamauchi, O. *Inorg. Chem.* **1989**, *28*, 624–625.

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Synthesis and Characterization of the New Soluble Selenide Anion $Pt(Se_4)_3^{2-}$

The chemistry of soluble metal sulfides has been studied extensively over the past two decades.[1] Quite recently, studies of the chemistry of the soluble anions of the higher chalcogenides have been initiated.[2] This chemistry generally differs significantly from that of the corresponding sulfides. Examples of species that have no known sulfur analogues include $V_2Se_{13}^{2-}$,[3] $W_2Se_4(Se_2)(Se_3)^{2-}$,[4,5] $W_2Se_4(Se_3)_2^{2-}$,[4,5] $Ni(Se_2)(WSe_4)^{2-}$,[6] $In_2(Se_4)_4(Se_5)^{4-}$,[7] $Au_2Se_2(Se_4)_2^{2-}$,[8] $Cr_3Q_{24}^{3-}$[9] (Q = Se, Te), and $NbTe_{10}^{3-}$.[10]

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