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]

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

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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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$_2$Se$_{13}^{2-}$,[3] W$_2$Se$_4$(Se$_2$)(Se$_3$)$^{2-}$,[4,5] W$_2$Se$_4$(Se$_3$)$_2^{2-}$,[4,5] Ni(Se$_2$)(WSe$_4$)$^{2-}$,[6] In$_2$(Se$_4$)$_4$(Se$_5$)$^{4-}$,[7] Au$_2$Se$_2$(Se$_4$)$_2^{2-}$,[8] Cr$_3$Q$_{24}^{3-}$[9] (Q = Se, Te), and NbTe$_{10}^{3-}$.[10]

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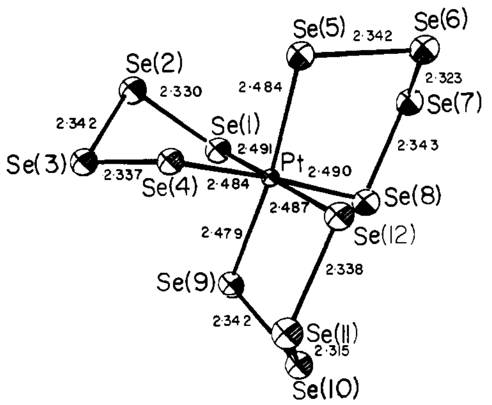

Figure 1. Drawing of the $Pt(Se_4)_3^{2-}$ ion, showing the labeling scheme and principal distances. Estimated standard deviations are as follows: Pt–Se, 0.004 Å; Se–Se, 0.005 Å.

The $Pt(S_5)_3^{2-}$ ion is one of the earliest known of the metal polysulfide ions.[11] It may be synthesized by the reaction of $PtCl_6^{2-}$ or $PtCl_4^{2-}$ with a saturated alkaline aqueous polysulfide solution.[12,13] In our exploration of the chemistry of transition-metal polyselenide ions we have not succeeded in synthesizing the analogous $Pt(Se_5)_3^{2-}$ ion but rather have synthesized the $Pt(Se_4)_3^{2-}$ anion, for which there is no known sulfur analogue. In fact, no anion of the type $M(Q_4)_3^{n-}$ is known, where M is a transition metal and Q = S, Se, or Te. We report here the synthesis and characterization of the $Pt(Se_4)_3^{2-}$ ion.

"Li_2Se_5" was generated in situ by the reaction of Li_2Se (279 mg, 0.3 mmol) with Se (948 mg, 1.2 mmol) in DMF (50 mL) and Et_3N (5 mL). To this solution was added $Pt(xan)_2$ (490 mg, 0.1 mmol) in the presence of PPh_4Cl (750 mg, 0.2 mmol) (xan = xanthate,[14] S_2COEt^-). The resulting solution was stirred for 1 h and filtered, and then the filtrate was diluted with 50 mL of diethyl ether to afford $[PPh_4]_2[Pt(Se_4)_3]$ as a red microcrystalline product in 75% yield.[15] Crystals marginally suitable for diffraction studies were grown by cooling a DMF solution saturated with $[PPh_4]_2[Pt(Se_4)_3]$ over a period of 5 days.

The ^{77}Se NMR spectrum of a DMF solution of $[PPh_4]_2[Pt(Se_4)_3]$ showed only two resonances and provided the first indication that the material prepared did not contain the expected $Pt(Se_5)_3^{2-}$ ion (which would show three resonances). Both peaks in the NMR spectrum are in the range for ring selenium.[5,6,16] The resonance at δ 680 ppm is assigned to Pt-bound Se, because of the presence of a satellite, and the second resonance at δ 790 ppm is attributed to ring Se not bound to Pt.

The presence of $PtSe_4$ rings deduced from the NMR spectrum is confirmed in the crystal structure determination.[17] Figure 1 shows the $Pt(Se_4)_3^{2-}$ ion. The anion features a six-coordinated Pt^{IV} center in a pseudooctahedral geometry chelated to three Se_4^{2-} units. Each five-membered $PtSe_4$ ring is in the envelope configuration with a Se atom occupying the "flap" position. The ion is chiral, and presumably optical isomers could be resolved, as was done for $Pt(S_5)_3^{2-}$.[18] Pt–Se distances vary from 2.479 (4) to 2.491 (4) Å. There is no alternation of Se–Se distances: average Se(internal)–Se(internal) = 2.327 (8) Å; average Se(external)–Se(internal) = 2.339 (2) Å. In $Zn(Se_4)_2^{2-}$ [19,20] such alternation occurs with the internal–internal distances being shorter, while in $[PPN]_2[Se_4]$[21] alternation occurs in the other direction. The Se–Pt–Se angles in $Pt(Se_4)_3^{2-}$ are 99.9 (1), 99.1 (1), and 99.1 (1)°; these differ significantly from the S–Pt–S angles of 92.0 (3), 92.7 (3), and 92.3 (3)° in $[NH_4]_2[Pt(S_5)_3]$.[22]

In an attempt to isolate the possible $Pt(Se_4)_2^{2-}$ and $Pt(Se_5)_2^{2-}$ ions, $Pt(xan)_2$ was reacted with 2 equiv of Li_2Se_4 and Li_2Se_5, respectively, but only $Pt(Se_4)_3^{2-}$ was obtained. As observed for sulfides[1,23] and more recently for the higher chalcogenides,[10,24] the size of the chalcogenide ring in the product does not seem to depend on the starting polychalcogenide; it is the metal that chooses the appropriate component of what must be a complex polychalcogenide mixture. Note also that the synthesis of the $Pt(Se_4)_3^{2-}$ ion, as described above, involves the oxidation of a Pt^{II} to a Pt^{IV} center, presumably by an Se_n^{2-} species. The reaction chemistry of this new ion, which contains the highest selenium-to-metal ratio known to date, is being probed.

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Supplementary Material Available: A listing of positional parameters (2 pages). Ordering information is given on any current masthead page.

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