Inorg. Chem. **1992**, *31*, 1983-1985

culate $\sum\chi = 20.69$ for **1** and **3** and $\sum\chi = 17.05$ for **4**.[23] Upon application of the Rehder correlation, these values would predict chemical shifts in the −480 to −600 ppm region as is observed for **4**. Surprisingly, the single resonance of **3** at +45 ppm is a rare example of a VO^{3+} complex of oxygen and nitrogen donors with a shift *downfield* of $VOCl_3$.[24] Finally, the resonance of **1** has a downfield shift of +480 ppm.[25] A similar dependence of the chemical shift is observed when HSHED or ENSAL are substituted for SALIMH. The paramagnetic contribution to the shielding factor, σ^P, is almost certainly responsible for the extreme downfield shifts of **1** and **3**. According to Ramsey, σ^P is inversely proportional to the energy of the HOMO–LUMO gap and thus the low-energy LMCT is probably related to the large deshielding effect of the noninnocent ligands in **1** and **3**.[26] Apparently a new correlation may be required to describe chemical shifts of complexes with noninnocent type ligands. This may be an important consideration when NMR spectroscopy is applied to define the ligation of siderophore type ligands to V(V). We are currently evaluating in greater detail the relationship between the paramagnetic shielding factor and the structural and electronic properties of several homologous V(V) complexes to address this concern.[27]

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Supplementary Material Available: For **1**, Tables 1–6, listing crystallographic data, fractional atomic coordinates for non-hydrogen atoms, thermal parameters, fractional atomic coordinates for hydrogen atoms, a complete set of bond distances, and a complete set of bond angles, respectively, and Figure 3, showing a complete numbering scheme for all atoms (8 pages); Table 7, listing observed and calculated structure factors for **1** (11 pages). Ordering information is given on any current masthead page.

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[24] A downfield shift of +780 ppm has been observed for the bare vanadium(V) complex $V^V(N_3S_2)$(dtbc)(phen) (where dtbc = di-*tert*-butylcatechol and phen is phenanthroline); see ref 14b.

[25] The line width of this resonance (ca. 4000 Hz) is considerably larger than that observed for **3** and **4** (170–440 Hz). This line width may arise from a small amount of vanadium(IV) impurity which can exchange with the vanadium(V) complex or via a large quadrupolar contribution to the relaxation time (see: Rehder, D. *Bull. Magn. Reson.* **1982**, *4*, 33). We have examined several NMR samples of **1** using EPR spectroscopy to quantify the amount of vanadium(IV) present. We found that the chemical shift and the line width of the ^{51}V resonance are invariant for samples containing 4%–15% vanadium(IV). Studies are currently in progress to address the cause of the rapid relaxation for **1**.

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Gold(III) Glycyl-L-histidine Dipeptide Complexes: Preparation and X-ray Structures of Monomeric and Cyclic Tetrameric Species

Metal complexes of histidine-containing peptides have been widely used as models for interactions between metal ions and proteins.[1,2] As to the simple dipeptide glycyl-L-histidine (gly-L-his), its reactivity toward Zn(II) has been studied[3] with regard to the phenomenon of increased oxygen affinity for hemoglobin on Zn(II) binding, for example.[4] Various solution studies on binary systems have favored a binding pattern in which gly-L-his acts as a tridentate chelating ligand with the metal coordinated to the amino group of glycine, the deprotonated peptide N, and the N3 site of the his-imidazole ring.[1] In the case of Cu(II), this conclusion has been confirmed by an X-ray structure determination.[5,6] As reported by Morris and Martin,[7] mononuclear gly-L-his complexes of Cu(II), Ni(II), and Pd(II) associate into

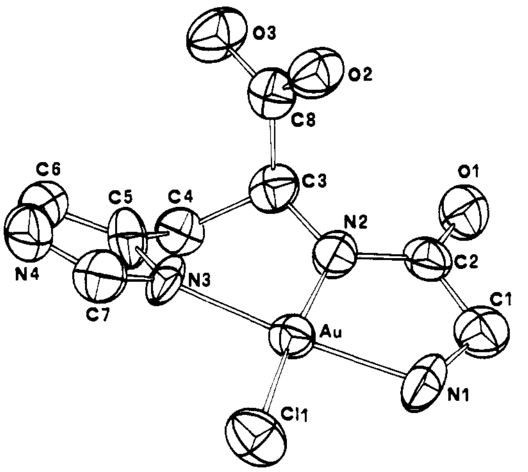

Figure 1. ORTEP drawing (50% probability thermal ellipsoids) of the cation of **1**, Au(gly-L-his)Cl⁺. Selected bond lengths (Å) angles (deg) are as follows: Au–Cl1 = 2.273 (3), Au–N1 = 2.002 (9), Au–N2 = 1.94 (1), Au–N3 = 1.991 (8); Cl1–Au–N1 = 89.54, Cl1–Au–N2 = 174.5 (3), Cl1–Au–N3 = 94.9 (3), N1–Au–N2 = 84.9 (5), N1–Au–N3 = 175.5 (6), N2–Au–N3 = 90.7 (4).

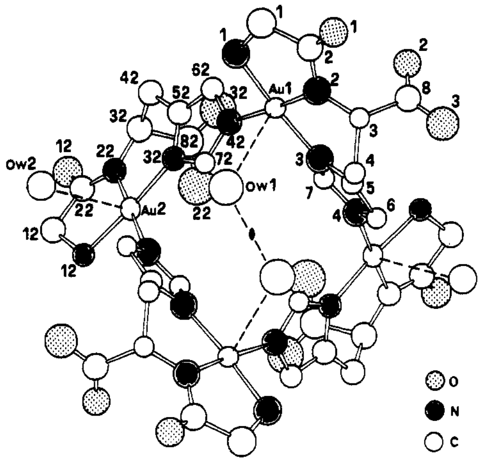

Figure 2. ORTEP drawing (50% probability thermal ellipsoids) of [Au(gly-L-his)]$_4$ (**2**) with the numbering scheme of crystallographically independent species. Coordination bond lengths (Å) are as follows: Au1–N1 = 2.018 (8), Au1–N2 = 1.993 (9), Au1–N3 = 1.981 (8), Au1–N42 = 1.987 (7), Au2–N12 = 1.993 (6), Au2–N22 = 1.999 (7), Au2–N32 = 1.985 (6), Au2–N4′ = 2.038 (8). The symbol of the crystallographic C_2 axis is also indicated.

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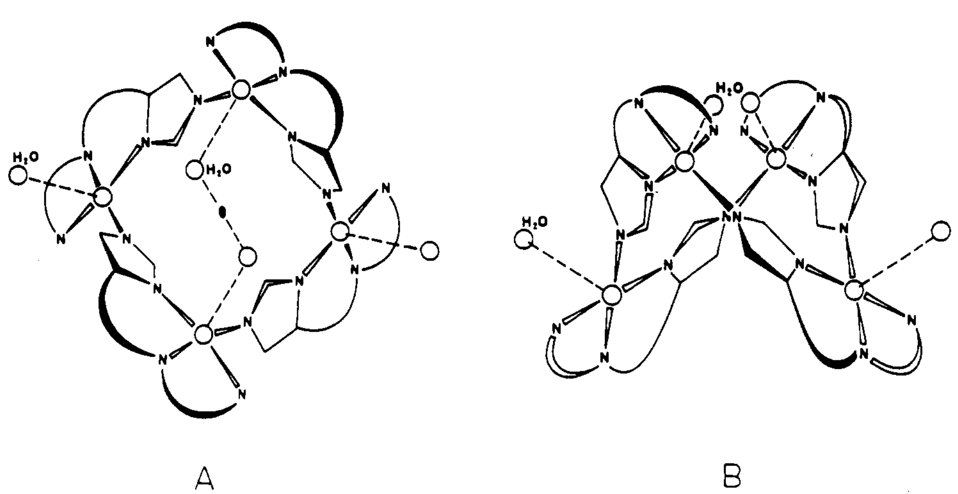

Figure 3. Sketches of the tetramer [Au(Gly-L-His)]$_4$ (**2**) viewed along (A) and perpendicular (B) the C_2 axis.

larger aggregates at pH 9–10 with the deprotonated imidazole ring of his being the bridging entity. Specifically, the authors postulated the preferential formation of a cyclic tetramer. We have now been able to unambiguously confirm the conclusions of these authors in the case of Au(III). As a consequence of the strong polarizing power of Au(III), formation of the mononuclear complex occurs in moderately acidic solution (pH 1.5–2) already, and the tetramer forms at pH 6–7.

The binary complex [Au(gly-L-his$^-$)Cl]Cl·3H$_2$O (**1**) was prepared as follows: Solutions of H[AuCl$_4$] (0.9 mmol in 10 mL of H$_2$O) and gly-L-his·HCl (0.9 mmol in 10 mL of H$_2$O) were combined. A yellow precipitate that formed initially redissolved gradually, when the mixture was stirred in the dark at 22 °C for 10 d. During this time, the pH was kept between 1.5 and 2 by means of 1 N KOH. Then Au^0 particles were filtered off, and the resulting clear solution was concentrated to a 5-mL volume by rotary evaporation and allowed to slowly evaporate at 22 °C. Yellow, transparent plates of **1** were harvested after several days (43% yield) and dried in air.[8] The cation of **1** is depicted in Figure 1.[9] It presents, to the best of our knowledge, the first Au(III) dipeptide complex characterized by X-ray analysis.[10]

The coordination geometry of Au in **1** is square-planar, with the metal coordinated by the amino group of gly (N1), the deprotonated peptide nitrogen (N2), and the imidazole nitrogen (N3) of his, as well as a chlorine. The Au–N1 (2.002 (9) Å) and Au–N3 (1.991 (8) Å) bond lengths are comparable and slightly longer than the Au–N2 bond (1.94 (1) Å). The difference in metal–N bond lengths thus follows the trend seen in di- and tripeptide complexes of Cu(II) with the metal–peptide nitrogen bond shorter than the others.[11–13] The values of the Au–N2–C2 and Au–N2–C3 bond angles of 117.7 (8) and 124.4 (7)°, respectively, should reflect the difference in strain between the five- and six-membered rings. Similar differences were found in the Cu analogue.[5] The Au–Cl bond length of 2.272 (3) Å is normal.[14,15] The peptide linkage, the imidazole ring, and the carboxylate group are planar within experimental error. The dihedral angle between the imidazole ring and the Au coordination plane is 25.0 (6)°.

The cyclic tetramer [Au(gly-L-his^{3-})]$_4$·10H$_2$O (**2**) was obtained by dissolving **1** (0.5 mmol) in water (5 mL) and maintaining the solution at pH 6–7 (KOH) for 3 d in the dark. Au^0 particles were removed by centrifugation several times during this period. The resulting reddish-brown solution was evaporated to dryness and redissolved in a minimum of water. Reddish-brown, transparent plates of **2** appeared within several hours and were isolated (10% isolated yield).[16] A ^{1}H NMR experiment carried out in D$_2$O under identical conditions showed the formation of **2** to be quantitative. **2** gives rise to two sets of imidazole C2H and C5H resonances of identical intensities each.[17] This is a consequence of the C_2 symmetry of the cyclic tetramer (vide infra).

The cyclic tetramer **2** is depicted in Figure 2.[18] As can be seen, each Au(III) is surrounded by a three nitrogen donor set as in **1** and in addition by a fourth nitrogen of the deprotonated imidazole ring.[19] Thus, the imidazole acts as a bridging ligand between pairs of Au(III). Consequently, each of the four Au ions, arranged at the vertices of a distorted tetrahedron, possesses four nitrogen donors in an approximately square-planar arrangement with two imidazole groups in cis positions. The four N donors are coplanar within ±0.02 (3) Å in the Au1 unit and ±0.05 (2) Å in the other. The imidazole rings, bridging pairs of Au ions, are roughly parallel to the coordination plane of the metal center of the same unit and roughly perpendicular to the coordination plane of the other bridged metal ion. On the basis of charge consideration, the carboxylate terminus of his is, unlike in **1**, deprotonated in **3**. As correctly predicted,[7] the cyclic tetramer, with metals adopting a square-planar N$_4$ coordination geometry, is of C_2 symmetry. As a consequence, pairs of Au^{III} entities are equivalent. Figure 3 provides two schematic views of the folded tetramer and depicts the saddlelike shape of the molecule. Owing to the asymmetric C atom on each dipeptide ligand, the carboxylate groups have different orientations. On one side of the saddle, they are directed far away from the C_2 axis, while on the opposite side they point toward that axis.

An interesting aspect of the structure of **2** is the location of four of the water molecules. Although not strongly bound to Au (Au1–Ow1 = 2.985 (9) Å; Au2–Ow2 = 2.973 (8) Å), their

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(8) Anal. Calcd for C$_8$H$_{14}$N$_4$O$_{4.5}$Cl$_2$Au: C, 19.0; H, 2.8; N, 11.1. Found: C, 18.8; H, 2.1; N, 10.6. X-ray analysis of freshly prepared **1** indicates a trihydrate.

(9) Crystal data for **1**: a = 11.505 (1) Å, b = 6.879 (2) Å, c = 11.606 (1) Å, β = 116.94 (1)°, V = 818.9 (3) Å^3, space group $P2_1$, Z = 2, ρ(calcd) = 2.16 g cm^{-3}. Of the 2232 measured reflections, 1694 with $I \geq 3\sigma(I)$ were used. R = 0.044, and R_w = 0.055.

(10) In the Cambridge Crystallographic Data Base (Version 4.3, July 1990), two structures of gold(I)–amino acids derivatives have been retrieved as follows. [Au$_2$Ni$_2$(penicillaminato)$_4$]$^{2-}$: Birker, P. J. M. W. L.; Verschoor, G. C. *Inorg. Chem.* **1982**, *21*, 990. Ph$_3$PAu(hippurato): Jones, P. G.; Schelbach, R. *J. Chem. Soc., Chem. Commun.* **1988**, 1338.

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(16) Elemental analysis data (C, H, N) were consistent with a higher content of water of crystallization, ca. 20 H$_2$O per tetramer. Anal. Found: C, 19.2; H, 3.5; N, 11.2.

(17) ^{1}H NMR chemical shifts for **2** in D$_2$O, pD 5: Two sets of aromatic protons at 7.38 ppm (H2), 7.14 ppm (H5) and 7.20 ppm (H2), 6.79 ppm (H5).

(18) Crystal data for **2**: a = 12.335 (3) Å, b = 21.542 (8) Å, c = 22.484 (7) Å, V = 5975 (2) Å^3, space group $C222_1$, Z = 16, ρ(calcd) = 2.01. Of the 3915 measured reflections, 2424 with $I \geq 3\sigma(I)$ were used. R = 0.055, and R_w = 0.065. Only Au atoms were refined anisotropically.

(19) The imidazole nitrogens N4 and N42 correspond to N1 used in the IUPAC convention.

positions reflect the tendency of Au(III) to extend its coordination sphere beyond four.[20] As is to be seen from Figure 3, the Au-water interactions occur inside and outside the saddle, respectively, with Ow1 hydrogen bonded to that related by the C_2 axis at a distance of 2.88 (2) Å.

The mean coordination Au–N1 (2.005 (7) Å) and Au–N3 (1.983 (7) Å) bond lengths do not differ from the corresponding ones found in **1**. The mean values are obtained by averaging the values relative to the two crystallographically independent Au(gly-L-his) units. However, the mean Au–N2 distance of 1.995 (8) Å appears slightly longer than the corresponding one in **1** (1.94 (1) Å). This difference could be ascribed to the trans influence of the deprotonated imidazole N donor being greater than that of Cl. The Au1–N42 bond length of 1.987 (7) Å appears shorter than the corresponding Au2–N4 one (2.083 (8) Å). The difference, if significant, may be due to the steric requirements for closing the tetramer structure.

The overall geometry of the Au(gly-L-his) fragments in **2** is similar to that of **1**. The dihedral angles between the mean planes of the imidazole ring and of the metal coordination plane, belonging to the same dipeptide ligand, amount to 24 (2) and 9 (4)° in the two crystallographically independent units of **2**. Comparison with **1** (25.0 (6)°) suggests that the closure of the tetramer slightly alters the conformation of the Au(gly-L-his) units.

In conclusion, $[AuCl_4]^-$ reacts with the dipeptide gly-L-his under acidic conditions to give the mononuclear complex **1**, which displays the expected ligation pattern. **1** readily forms the cyclic tetramer **2** at pH 6–7, which makes Au(III) different from Cu(II), Ni(II), and Pd(II), which reportedly[7] form a cyclic tetramer under alkaline conditions only. The isolation of **1** and **2** is somewhat unexpected considering the instability of Au(III) complexes with amino acids and peptides other than gly-L-his.[21]

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and MURST (Rome) for financial support of this work. We are grateful to Prof. Dr. Braga (Bologna, Italy) for the data collection of compound **1**.

Supplementary Material Available: For **1** and **2**, tables listing crystallographic data and details of refinement, atomic positional and displacement parameters, and bond lengths and angles (9 pages); listings of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

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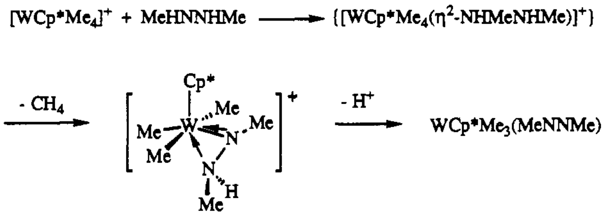
Synthesis and Structure of a Tungsten(IV) η^2-Dimethyldiazene Complex in Which the Diazene Ligand Behaves as a Four-Electron Donor

We have been interested for several years in the chemistry of high-oxidation-state molybdenum and tungsten complexes that is relevant to the reduction of dinitrogen to ammonia, in particular compounds in which N_2H_x ligands are bound to a WCp^*Me_3 core; examples are $WCp^*Me_3(\eta^1\text{-}NNH_2)$,[1] $[WCp^*Me_3(\eta^2\text{-}NHNH_2)]^+$,[1] and $[WCp^*Me_3(\eta^2\text{-}NH_2NH_2)]^+$.[2] A key feature of compounds of this type is the availability of three bonding orbitals on the WCp^*Me_3 fragment, a σ type hybrid orbital, and two orbitals that can be used for either σ or π bonding, the d_{xy} orbital (which lies parallel to the plane of the Cp* ligand between the four basal ligands) and the d_{z^2} orbital.[3] All of the N_2H_x species can be reduced in the presence of protons to give ammonia in high yield and have been shown to reduce hydrazine catalytically to ammonia in high yield in the presence of protons.[2] A type of monomeric complex that is relatively rare in this "high-oxidation-state" chemistry, as well as in the much more extensively studied "low-oxidation-state" chemistry,[4,5] is one that contains a diazene ligand. (*Free* diazene is a relatively high-energy unstable species and therefore an unlikely intermediate in dinitrogen reduction.) In the vast majority of diazene or substituted diazene complexes, the ligand is bound to more than one metal[6–9] or is monodentate.[10] The only structurally characterized examples of monometallic η^2-diazene complexes are diphenyldiazene (azobenzene) complexes[11–17] in which the azobenzene behaves as a two-electron "olefin-like" donor ligand. We report here an example of a monometallic η^2-dimethyldiazene complex in which the diazene behaves as a *four*-electron donor ligand or, alternatively, as a *six*-electron η^2-1,2-dimethylhydrazido(2−) ligand.

Addition of 1,2-dimethylhydrazine to $[WCp^*Me_4]PF_6$[18] in dichloromethane at 25 °C yields lemon yellow, crystalline $[WCp^*Me_3(\eta^2\text{-}NMeNHMe)]PF_6$ (eq 1).[19] We speculate that



(1)

$[WCp^*Me_4(\eta^2\text{-}NHMeNHMe)]PF_6$ is formed first and that it then decomposes rapidly by losing methane. The structure of $[WCp^*Me_3(\eta^2\text{-}NMeNHMe)]PF_6$ is believed to be analogous to that found for $[WCp^*Me_3(\eta^2\text{-}NHNH_2)]^+$ (as shown in eq 1), in which the d_{xy} orbital is used to form the W–N dative π bond and the d_{z^2} orbital the W–N dative σ bond. Unlike the case of $[WCp^*Me_3(\eta^2\text{-}NHNH_2)]^+$, which is deprotonated readily by

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