Pro, 1.01. The crude product when rechromatographed on a PA-35 column or on a C-18 reverse phase column eluted with CH_3CN–0.1% phosphoric acid gradient (0.4 × 30 cm) in LC showed a symmetrical peak (Figure 3). This product also eluted as a single peak in both systems when cochromatographed with standard, biologically active [Val^5]angiotensin II.

Cyanide and photolytic cleavage gave 60 and 61% yields, respectively. When both products were further deprotected in HF and applied to the Dowex 50 × 4 ion-exchange column, each showed a major peak at 309 min (86.2 and 89.5% of ninhydrin-positive materials) corresponding to angiotensin. The photolytic cleavage product gave a mixture of about 2:1 of angiotensinyl-OMPA and protected angiotensin, indicating an incomplete conversion of resin 11 to $BrCH_2$-Pop-resin before the esterification step of Boc-Phe. This would account also for the low yield of the HF cleavage. All reactions were not optimized.

Reattachment of Boc-Leu-Ala-Gly-Val-OMPA and Boc-[Leu^5]Enkephalin-OMPA to Aminomethyl-Resin. Boc-Leu-Ala-Gly-Val-OMPA and Boc-[Leu^5]enkephalin-OMPA were each obtained from the photolysis of 200-mg resin samples of Boc-Leu-Ala-Gly-Val-OCH_2-Pop-resin and Boc-[Leu^5]enkephalin-OCH_2-Pop-resin. After the evaporation of the photolysate DMF filtrate both samples were used for the reattachment experiments. After a single precipitation from EtOAc–hexane as slightly yellowish waxy solids, both samples gave one major ninhydrin-positive spot on TLC (CMA, CA). Boc-Leu-Ala-Gly-Val-OMPA (20 mg, 33 μmol) was activated by DCC (10 mg, 48 μmol) and HOBt (7 mg, 48 μmol) at 0 °C in 2 mL of CH_2Cl_2/DMF (1:1 v/v) for 1 h and followed by addition of aminomethyl resin[41] (200 mg, 0.25 mmol/g). The coupling was conducted for 1 day. The resin was then washed five times each with 5 mL of DMF and CH_3CN, dried, and analyzed as follows.

(1) Amino acid analysis (25 mg) gave 81% coupling yield based on Leu ($Leu_{1.00}Ala_{0.95}Gly_{1.07}Val_{0.98}$).

(2) HF cleavage (70 mg) gave 84% yield of LAGV based on the chromatographic analysis of the product on a Beckman 120B[45] and the amino acid analysis of the resin. Similarly, Boc-[Leu^5]enkephalin-OMPA (18 mg, 22 μmol) was coupled to aminomethyl-resin (200 mg, 0.25 mmol/g). Amino acid analysis (28 mg of resin) gave 95% coupling yield based on Tyr ($Tyr_{1.00}Gly_{2.18}Phe_{0.98}Leu_{0.95}$) and 82% yield based on amino acid analysis of the resulting resin, HF cleavage Boc-[Leu^5]-enkephalin-OCH_2-Pam-resin.

Acknowledgments. We wish to thank Drs. S. B. H. Kent and S. Wolff for helpful discussions during the course of this work. We also thank Ms. N. Wu and A. McNichol for technical assistance, and Ms. M. LeDoux for the amino acid analyses. This work was supported in part by Grant AM 01260 from the U.S. Public Health Service and by a grant from the Hoffmann-La Roche Foundation.

2,5-Diphenyl-2,5-norbornyl Dications[1]

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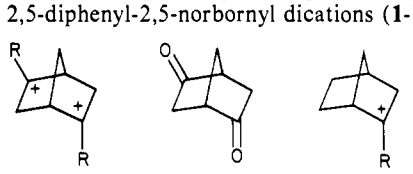
Abstract: Preparation and ^{13}C NMR spectroscopic study of the parent and a series of substituted 2,5-diphenyl-2,5-norbornyl dications **1**-R with both electron-releasing and electron-withdrawing substituents were carried out to determine the effect of dipositive charge on the norbornyl skeleton. A plot of C-1 vs. C-3 carbon chemical shifts shows an excellent linear fit with a wide variety of substituents, indicating the regular phenylcarbenium ion nature of dications **1**-R in contrast to 2-phenyl-2-norbornyl monocations **3**-R, where significant deviation from linearity was observed in the case of electron-withdrawing substituents due to the onset of nonclassical σ delocalization. The observed behavior of dications can be rationalized by charge–charge repulsion resulting in increased charge delocalization into the phenyl rings.

Introduction

Experimental and theoretical studies on carbodications are extremely sparse as compared to those on carbomonocations.[2] In the early 1960s the first carbodications were reported by Hart[3] and subsequently by Volz.[4] In these studies the two carbocation centers were stabilized by conjugation with aromatic rings. The first aliphatic carbodications were reported by Olah et al.,[5] who showed that these ions can be formed only if the carbocation centers are separated by at least two carbon atoms. Since then a limited number of carbodications such as Hückeloid cyclic dications,[6] including cyclobutadiene and cyclooctatetraene dications, Hogeveen's pyramidal dication,[7] rigid bridgehead bicyclo[2.2.2]octyl[8] and bicyclo[3.3.3]undecyl[9] dications, and alkyl/aryl substituted acyclic dications,[10] have been studied. In our continuing studies on carbodications we now report the preparation and ^{13}C NMR spectroscopic study of the parent and a series of substituted 2,5-diphenyl-2,5-norbornyl dications (**1**-R).



1 2 3

R = C_6H_5, 4-$C_6H_4(CH_3)$, 4-$C_6H_4(OCH_3)$, 4-$C_6H_4(CF_3)$, 3,5-$C_6H_4(CF_3)_2$, C_6F_5, OH

Introduction of two electron-deficient centers into the norbornyl skeleton and the effect of substituted phenyl rings on the system are of particular interest in view of the extensive studies[11] on the

(1) Stable Carbocations 230. For part 229, see: Olah, G. A.; Prakash, G. K. S.; Nakajima, T., *Angew. Chem.*, in press.

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Table I. ^{13}C NMR Chemical Shifts[a] of Observed Carbodications in FSO_3H–SbF_5–SO_2ClF or SbF_5–SO_2ClF Solution at −70 °C[a]

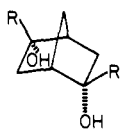
dictation	C-1	C-2	C-3	C-4	C-5	C-6	C-7	others
1-4-$C_6H_4(OCH_3)$	49.3	213.6	42.5	49.3	213.6	42.5	42.1	OCH_3 60.7, C_p 184.6, C_o 149.0, 146.3, C_m 124.5, 117.2, C_i 129.9
1-4-$C_6H_4(CH_3)$	52.2	234.3	45.3	52.2	234.3	45.3	42.8	CH_3 26.20, C_p 180.5, C_o 145.0, C_m 135.0, C_i 134.1
1-C_6H_5	54.3	245.1	46.9	54.3	245.1	46.9	44.0	C_p 161.1, C_o 146.3, C_i 136.5, C_m 134.3
1-4-$C_6H_4(CF_3)$	56.9	254.4	49.1	56.9	254.4	49.1	44.2	C_p 156.6 (J_{C-C-F} = 37.5 Hz), C_o 147.7, C_i 138.3, C_m 131.3, CF_3 122.5 (J_{C-F} = 276.0 Hz)
1-3,5-$C_6H_3(CF_3)_2$	58.0	258.2	50.0	58.0	258.2	50.0	45.10	C_p 152.2, C_o 145.3, C_m 138.0 (J_{C-C-F} = 35.5 Hz), C_i 136.8, CF_3 122.1 (J_{C-F} = 272.7 Hz)
1-C_6F_5	58.2	241.1	52.1	58.2	241.1	52.1	47.1	C_p 165.1 (J_{C-F} = 303.7 Hz), C_o 155.2 (J_{C-F} = 301.0 Hz), C_m 140.9 (J_{C-F} = 268.9 Hz), C_i 118.2
1-OH	51.0	242.3	41.2	51.0	242.3	41.2	40.9	
6-C_6H_5	247.9	37.2	37.2	247.9	37.2	37.2		C_p 160.1, C_o 142.8, C_m 134.1, C_i 139.1
6-4-$C_6H_4(CH_3)$	237.4	35.7	35.7	237.4	35.7	35.7		C_p 178.9, C_m 134.9, C_o 142.1, C_i 137.1
9	39.8	32.8	32.8	32.8	32.8	39.8		C^+ 333.2, CH_2 69.7, CH_3 46.7

[a] Chemical shifts are in parts per million from external capillary tetramethylsilane.

mode of charge delocalization in the parent 2-norbornyl cation. The application of the "tool of increasing electron demand" has been carried out previously on 2-phenyl-2-norbornyl cations **3**-R,[12,13] and the study gave unambiguous evidence for the onset of nonclassical σ delocalization in cations **3**-R with strongly electron-withdrawing substituents.

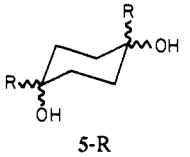
Results

Precursor alcohols **4**-R were prepared by the addition of corresponding organomagnesium or -lithium reagents to the diketone **2**.[14] The parent diol **4**-H was obtained by the reported[14] hydroboration–oxidation procedure. To prepare a series of substituted cyclohexyl dications **6** for comparison, we also synthesized the precursor cyclohexyl derivatives by literature procedures.[15] The aryl-substituted dications **1**-R and **6**-R were prepared by



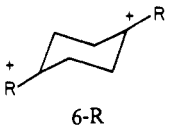
4-R

R = CH_3, H, C_6H_5, 4-$C_6H_4(CH_3)$, 4-$C_6H_4(OCH_3)$, 4-$C_6H_4(CF_3)$, 3,5-$C_6H_4(CF_3)_2$, C_6F_5



5-R

R = C_6H_5, H, *n*-C_4H_9, CH_3, 4-$C_6H_4(CH_3)$



6-R

R = C_6H_5, 4-C_6H_4-(CH_3)

ionizing the corresponding diols **4**-R and **5**-R in FSO_3H–SbF_5 or SbF_5/SO_2ClF solution at −78 °C. The diketone **2** was diprotonated in FSO_3H–SO_2ClF media. The parent or alkyl-substituted dications **1**-R and **6**-R (R = H or alkyl) were either not stable or found to rearrange even at −140 °C.

The ^{13}C NMR spectroscopic data of observed dications are summarized in Table I. The chemical-shift assignments were made by off-resonance decoupling experiments. Figure 1 shows a plot of the C-1 vs. C-3 carbon chemical shifts of dications **1**-R. Figure 2 exhibits the plot of the carbocation center shift of dications **1**-R against those of substituted 1-phenyl-1-cyclopentyl cations.[13] In both plots excellent linear fit was observed.

Discussion

Attempts to prepare the parent disecondary dication **1**-H or the ditertiary dimethyl substituted analogue **1**-CH_3 by ionizing the corresponding diols **4**-H and **4**-CH_3 under a variety of superacidic conditions at −78 or −140 °C were unsuccessful and gave

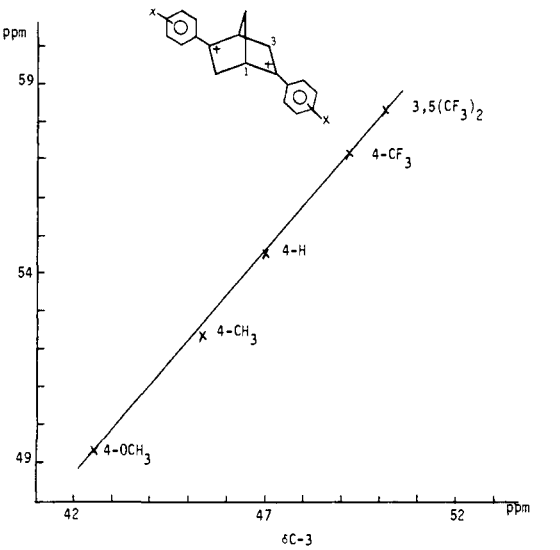
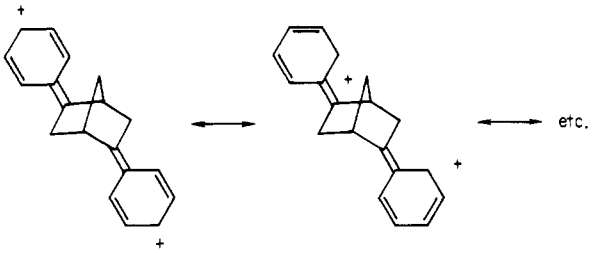


Figure 1. A plot of ^{13}C NMR chemical shifts of C-1 vs. C-3 in 2,5-diphenyl-2,5-norbornyl dications.

only unidentifiable polymeric species. The diketone **2**, however, underwent facile protonation to the corresponding dioxonium ion in FSO_3H–SO_2ClF. In the ^{13}C NMR spectrum the carbonyl carbon absorbs at $\delta^{13}C$ 242.3, which is about 28 ppm deshielded over that in the neutral precursor **2**.[16a] Similar deshielding effects are also observed in the case of protonated 2-norbornanone.[16b] This demonstrates that there is very little contribution of 2,5-dihydroxy-2,5-norbornyl dication structure **1**-OH to the overall protonated diketone structure.

The phenyl-substituted dication **1**-C_6H_5 was found to be re-



1-C_6H_5

markably stable, permitting a detailed study. The stability of **1**-C_6H_5 can be explained by its ability to accommodate the di-

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(16) (a) The ^{13}C NMR chemical shifts of diketone **2** in $CDCl_3$ solution are $\delta^{13}C$ 214, 50.7, 41.0, and 38.4 for (C_2, C_5), (C_1, C_4), (C_3, C_6), and C_7 respectively. (b) Olah, G. A.; Liang. G.; Mateescu, G. D. *J. Org. Chem.* **1974**, *39*, 3750–3754.

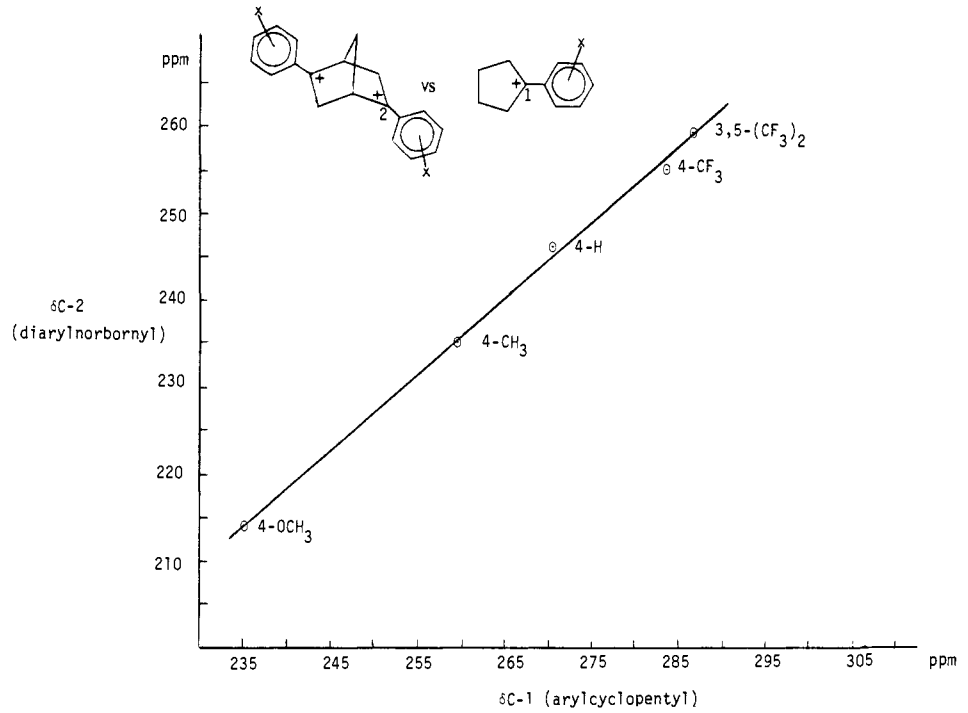
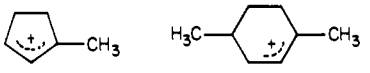


Figure 2. A plot of the ^{13}C NMR chemical shifts of cationic centers in 2,5-diphenyl-2,5-norbornyl dications against those in 1-phenyl-1-cyclopentyl cations.

positive charge via delocalization into phenyl rings (involving the ortho and para resonance forms), thus minimizing charge–charge replusion effects. No such stabilization is possible for either **1**-H or **1**-CH_3.

For comparison, the 1,4-diphenyl-1,4-cyclohexyl dications **6**-C_6H_5 and **6**-4-$C_6H_4(CH_3)$ were also prepared. Again, their stability reflects the delocalizing ability of phenyl groups, which decrease charge–charge repulsions. The chemical-shift data in Table I show that carbocation centers in dications **1**-C_6H_5, **6**-C_6H_5, and **6**-4-$C_6H_4(CH_3)$ are observed at $\delta^{13}C$ 245.1, 247.9, and 237.4, respectively. The carbocation centers are thus shielded by almost 15 ppm as compared to those in the analogous monocations.[12,17] The positive charge is increasingly delocalized into the phenyl rings in both dications resulting in increased deshielding of the ortho and para carbon chemical shifts ($\simeq$4 and $\simeq$6 ppm, respectively) relative to those in analogous monopositive systems.

Attempted generation of the parent 1,4-cyclohexyl dication **6**-H and the 1,4-dimethyl-1,4-cyclohexyl dication **6**-CH_3 starting from the corresponding alcohol precursors resulted only in rearranged allylic cations **7** and **8**, respectively. Their formation can be rationalized by an ionization–elimination mechanism.[18]



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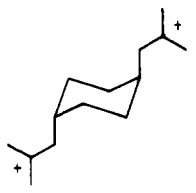
Ionization of 1,4-di-*n*-butyl-1,4-cyclohexanediol (**5**-C_4H_9) in SbF_5–SO_2ClF either at −78 or −140 °C gave only the rearranged dication **9** (single isomer), in which the carbocation centers are separated by six carbon atoms. The rearrangement occurs through a series of H and CH_3 shifts to the more stable dication **9**, resulting in minimized charge–charge repulsion. The ^{13}C NMR chemical shift of the carbocation centers in dication **9** is observed at $\delta^{13}C$ 333.2, which is comparable to that of the monopositive *tert*-butyl cation[19] found at $\delta^{13}C$ 335.2.



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Tool of Increasing Electron Demand. In order to further explore the effect of dipositive charge on the norbornyl skeleton, we prepared a series of 2,5-diphenyl-2,5-norbornyl dications **1**-R with both electron-releasing and electron-withdrawing substituents on the phenyl rings. The ^{13}C NMR chemical shifts of the carbocation centers range from $\delta^{13}C$ 213.6 for the 4-OCH_3 substituent to $\delta^{13}C$ 258.2 for the 3,5-bis(trifluoromethyl) groups (a range of $\simeq$45 ppm). A comparison with the related 2-phenyl-2-norbornyl cations **3**-R[12] reveals a range of 238.3–264.5 ppm (a much narrower spread of $\simeq$27 ppm). Figure 1 shows the plot of the C-1 vs. C-3 carbon chemical shifts of dications **1**-R. An excellent linear relationship is observed (correlation coefficient = 0.999). Such a linear fit demonstrates similar neighboring group deshielding effects experienced by the C-1 and C-3 carbons as the substituents on the phenyl ring are changed from electron-releasing to electron-withdrawing groups. A similar plot in the case of substituted 2-phenyl-2-norbornyl cations **3**-R,[12] however, shows significant deviation for electron-withdrawing substituents, indicating the onset of nonclassical σ delocalization due to decreased charge-delocalizing ability of the deactivated phenyl ring. No such C_1–C_6 or C_2–C_5 bond interaction with the electron-deficient centers at C_2 and C_5 positions is occurring in the case of dications **1**-R. The lack of any onset of σ-bond delocalization in **1**-R can be understood based on electronic effects. The charge–charge repulsion is rather significant, and this renders the whole norbornyl skeleton electron deficient. However, this effect is partly relieved by the dispersal of charge into the aryl groups. The charge delocalization into the aryl ring even in the case of electron-withdrawing substituents such as 4-CF_3, 3,5-$(CF_3)_2$, and pentafluoro groups is evidenced by the significant deshielding of ortho and para carbon chemical shifts and shielding of carbocationic centers (Table I) as compared to those in the monopositive analogues. The regular phenyl-carbenium ion nature of 2,5-diphenyl-2-5-norbornyl dications **1**-R is also evident from the plot of carbocation center shifts with those of substituted 1-phenyl-1-cyclopentyl cations[13] (Figure 2). A linear

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(18) Farcasiu, D. *J. Am. Chem. Soc.* **1978**, *100*, 1015–1016.
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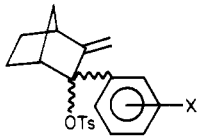
fit (r = 0.999) similar to the plot in Figure 1 is also observed.

Brown and his co-workers in a recent paper[20] questioned the previous ^{13}C NMR spectroscopic conclusions[12,13] on the onset of nonclassical σ delocalization in 2-phenyl-2-norbornyl cations **3**-R with electron-withdrawing substituents. They argued that they have observed high exo/endo rate ratios in most tertiary derivatives including systems such as **10** and **11**[21] with a wide variety of



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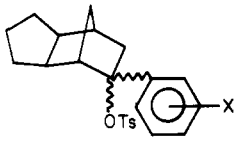

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substituents on the aryl ring. We reiterate our view that the "tool of increasing electron demand" as applied to solvolytic studies is too coarse to fully detect changes in the electron demand of a system unless the magnitude of such a demand is indeed large. Even negatively substituted phenyl rings are 6π systems capable of significant charge delocalization; thus, the residual σ-bond delocalization effect should be small in 2-phenyl-2-norbornyl cations. Moreover, the observation of high exo/endo rate ratios in tertiary norbornyl systems does not provide any diagnostic test for the presence or absence of nonclassical σ delocalization. As pointed out by Brown in many of his works,[11b,21] such an effect may be of steric origin. Our present ^{13}C NMR spectroscopic study demonstrates the regular phenylcarbenium ion nature of 2,5-diphenyl-2,5-norbornyl dications **1**-R, even with strong electron-withdrawing substituents, in contrast to 2-phenyl-2-norbornyl cations **3**-R, where the onset of σ delocalization is observed with electron-withdrawing substituents. This study is in accord with the structure and stability of the parent 2-norbornyl cation based on a variety of spectroscopic[11,22] and calorimetric studies[23] in the condensed phase.

(20) Brown, H. C.; Rao, C. G. *J. Org. Chem.* **1979**, *44*, 133-136.
(21) Brown, H. C.; Rao, C. G. *J. Org. Chem.* **1979**, *44*, 3536-2540.

Experimental Section

The exo,exo diols **4**-R were prepared by the addition of organomagnesium or organolithium reagents to the diketone **2**.[14] exo,exo-2,5-Norbornanediol (**4**-H) was prepared by the reported "hydroboration-oxidation" of norbornadiene.[14] The diols **5**-R (mixture of cis and trans) were prepared from the commercially available cyclohexane-1,4-dione.[15] All the new diols showed satisfactory spectroscopic and analytical data.

Preparation of Dications. Freshly distilled SbF_5 and FSO_3H were used. To the appropriate superacid dissolved in about a twofold amount of SO_2ClF at dry ice-acetone (ca. -78 °C) or petroleum ether-liquid nitrogen slush temperature (-140 °C) was slowly added, with vigorous stirring, a cooled slurry or solution of the corresponding diol precursor in SO_2ClF, resulting in an approximately 10-15% solution of the ion.

^{13}C NMR Spectra were obtained by using a Varian Associates Model FT-80 spectrometer, equipped with a multinuclei broad band variable temperature probe. The chemical shifts were referenced from external capillary tetramethylsilane.

Acknowledgments. Support of our work by the National Science Foundation is gratefully acknowledged.

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Crystal Structure and Spectroscopic Properties of Violet Glutathione-Copper(II) Complex with Axial Sulfur Coordination and Two Copper Sites via a Disulfide Bridge

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Abstract: The violet glutathione-Cu(II) complex, $[Cu^{II}GSSGCu^{II}]Na_4 \cdot 6H_2O$, was firstly isolated as a single crystal. The X-ray crystallographic analysis of the binuclear complex showed that each Cu(II) atom is in a distorted square-pyramidal configuration and the Cu(II)-Cu(II) distance is 5.21 Å. The coordination of Cu(1) involved the two deprotonated peptide nitrogens, N(1) and N(2), the glutamic amine nitrogen, N(3), and the glycinyl terminal carboxylate oxygen, O(1), in an approximate planar coordination while the cysteinyl sulfur, S(1), is bonded apically to form a square pyramid. The Cu(51) ion is similarly coordinated to N(51), N(52), N(53), O(51), and S(51). The apical Cu(II)-S mean distance is 3.22 Å and a direction of this bond is bent by 22° from the perpendicular C_{4v} axis of the square-planar basal plane. Of special interest is the Cu(II) coordination by the sulfur atoms of the disulfide bridge. The Cu(II) complex was also characterized by magnetic susceptibility and electron spin resonance (ESR), electronic, circular dichroism, and X-ray photoelectron spectra (X-ray PES). The magnetic susceptibility and ESR spectra showed that the internuclear Cu(II)-Cu(II) interaction is negligibly small. The ESR parameters and X-ray PES binding energies determined were as follows: g_{zz} = 2.251, g_{xx} = 2.047, g_{yy} = 2.038, A_{zz} = 177.2, A_{xx} = 43.8, and A_{yy} = 36.0 G (ESR); Cu $2p_{3/2}$ = 933.1 and 943.9, S 2p = 163.4 and 167.5, N 1s = 399.4, O 1s = 531.2, and Na 1s = 1071.1 eV (X-ray PES). The present results provide valuable information for biologically significant glutathione-Cu(II) complexes.

Introduction

Glutathione-Cu(II) complexes are of biological and chemical interest. Marzullo and Friedhoff[2a] identified an inhibitor of opiate receptor binding as a glutathione-Cu(II) complex from human red blood cells and from rabbit brain. It has been reported that the Cu(II) complex is involved in rheumatoid arthritis and that the inhibitory activity is due to a complex of oxidized glutathione

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