

C18 or C8 column. The adsorption amounts of benzoic acid (4), phthalic acid (6), isophthalic acid (5), and terephthalic acid (1) on alumina were determined by measurement of the UV absorption of the supernatant solution at 270.4 nm (ϵ 899.6), 276.4 (1292), 288.2 (846.3), and 283 (1840), respectively. For the other dicarboxylic acids, the adsorption amounts adsorbed were determined by acid-base titration of the supernatant solution.

Acknowledgment. We are grateful to Erika Waniguchi for her cooperation.

Registry No. 1, 100-21-0; 2, 1679-64-7; 3, 120-61-6; 4, 65-85-0; 5,

121-91-5; 5 (monomethyl ester), 1877-71-0; 6, 88-99-3; 7, 619-81-8; 7 (monomethyl ester), 1011-85-4; 8, 619-82-9; 8 (monomethyl ester), 15177-67-0; 6 (monomethyl ester), 4376-18-5; HO₂C(CH₂)₆CO₂H, 505-48-6; HO₂C(CH₂)₁₀CO₂H, 693-23-2; HO₂C(CH₂)₃CO₂H, 110-94-1; HO₂C(CH₂)₄CO₂H, 124-04-9; HO₂C(CH₂)₅CO₂H, 111-16-0; HO₂C(CH₂)₇CO₂H, 123-99-9; HO₂C(CH₂)₈CO₂H, 111-20-6; HO₂C(CH₂)₃COOCH₃, 1070-62-8; (CH₃O)₂SO₂, 77-78-1; HO₃C(CH₂)₄COOCH₃, 627-91-8; HO₂C(CH₂)₃COOCH₃, 20291-40-1; HO₂C(CH₂)₆COOCH₃, 3946-32-5; HO₂C(CH₂)₇COOCH₃, 2104-19-0; HO₂C(CH₂)₈COOCH₃, 818-88-2; HO₂C(CH₂)₁₀COOCH₃, 3903-40-0; *p*-CH₃C₆H₄N=NNHCH₃, 21124-13-0; (CH₃)₂NCH(OCH₃)₂, 4637-24-5; BF₃CH₃OH, 373-57-9; diazomethane, 334-88-3; alumina, 1344-28-1.

α - and β -Carboxylic Groups as Primary Ligating Groups in Promoting Amide Deprotonation. Solid-State Behavior of *N*-Tosylalaninate-Copper(II) Complexes: Crystal and Molecular Structures of Bis(*N*-tosyl- β -alaninato)bis(imidazole)copper(II), Polymeric (*N*-Tosyl- α -alaninato)diaquacopper(II) Monohydrate, and Dipiperidinium Bis(*N*-tosyl- α -alaninato)cuprate(II) Monohydrate Complexes

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Contribution from Ministero della Pubblica Istruzione of Italy, Istituto di Chimica Generale e Inorganica, University of Modena, 41100 Modena, Istituto di Chimica Generale e Inorganica, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., University of Parma, 43100 Parma, and Istituto di Chimica, Facoltà di Medicina-Veterinaria, University of Bari, 70126 Bari, Italy. Received March 28, 1984

Abstract: The interaction between *N*-tosyl- α - and *N*-tosyl- β -alanine and the copper(II) ion in aqueous solution at different pH gives rise to the formation of two types of compounds differing from each other by virtue of the presence on the amino acid of neutral (type 1) or deprotonated (type 2) NH group. Type 1 complexes are simple green complexes of formula Cu(Tsala)₂ (Tsala⁻ = *N*-tosylalaninate anion), which show physical properties indicating dimeric or polymeric structure like copper(II) acetates and their amine adducts of formula Cu(Tsala)₂B₂ (B = imidazole (ImH), *N*-methylimidazole (MeImH), piperidine (PipdH), and morpholine (MorfH), and Tsala⁻ = *N*-tosyl- β -alaninate anion; B = ImH and MeImH, and Tsala⁻ = *N*-tosyl- α -alaninate anion), which present physical properties similar to those of Cu(Ts- β -ala)₂(ImH)₂, the crystal structure of which has also been determined. The Cu(Ts- β -ala)₂(ImH)₂ complex crystallizes in monoclinic *P*2₁/*n* space group with *a* = 14.287 (2) Å, *b* = 7.169 (1) Å, *c* = 16.363 (2) Å, β = 110.6 (1)°, *Z* = 2. Coordination around the copper, lying on the center of symmetry, is square planar and involves two centrosymmetric carboxylic oxygens of two amino acids and two imidazole molecules. Type 2 complexes contain only compounds of *N*-tosyl- α -alanine which present a coordinative behavior, strictly dependent on the pH of the solution, separating at pH \geq 5 a blue compound of formula Cu(Ts- α -H₁ala)·3H₂O (Ts- α -H₁ala²⁻ = *N*-tosyl- α -alaninate dianion; the NH group is also deprotonated) and at pH > 7 compounds of formula A₂[Cu(Ts- α -H₁ala)₂] (A = K⁺, piperidinium (PipdH₂⁺), morpholinium (MorfH₂⁺) cations). The crystals of [Cu(Ts- α -H₁ala)(H₂O)₂]·H₂O are orthorhombic, space group *Pbca* with *a* = 27.198 (3) Å, *b* = 9.001 (1) Å, *c* = 11.908 (1) Å, and *Z* = 8. The structure consists of polymeric [Cu(Ts- α -H₁ala)(H₂O)₂]_n units, in which each copper atom is five-coordinated in a distorted square pyramid involving, at the base, the deprotonated amide nitrogen, one carboxylic oxygen, and two water molecules. The apex of the pyramid is occupied by a second carboxylate oxygen belonging to an adjacent amino acid molecule. The [PipdH₂]₂[Cu(Ts- α -H₁ala)₂]·H₂O complex crystallizes in monoclinic *C*2/*c* space group with *a* = 19.407 (2) Å, *b* = 9.950 (1) Å, *c* = 18.930 (2) Å, β = 99.35 (1)°, and *Z* = 4. The structure consists of piperidinium cations and [Cu(Ts- α -H₁ala)₂]²⁻ anions. Coordination around the copper involves two centrosymmetric amino acid molecules coordinating via deprotonated sulfonamide nitrogen and one carboxylate oxygen in a square-planar arrangement. Magnetic and spectroscopic (EPR, IR, and vis) properties of all the complexes are reported. The ability of α - and β -carboxylic groups to behave as primary ligating groups is discussed.

It is known that the metal ion substitution of amide proton is a very difficult process as it suffers from competition from the metal ion hydrolysis reaction. Only the presence of a primary ligating site (or anchor) or the ligand molecule favoring a 5- or 6-membered chelate ring formation, permits pH regions to be

reached where substitution of a metal ion for an amide hydrogen may occur.²

In particular, the COO⁻ group is commonly believed to be ineffective as primary ligating group in promoting ionization of

(1) (a) University of Modena. (b) University of Parma. (c) University of Bari.

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Table I. Crystal Data

	[Cu(Ts- β -ala) ₂ (ImH) ₂] (I)	[Cu(Ts- α -H ₁ -ala)- (H ₂ O) ₂]-H ₂ O (II)	[pipdH ₂] ₂ - [Cu(Ts- α -H ₁ -ala) ₂]-H ₂ O (III)
mol formula	C ₂₆ H ₃₂ CuN ₆ O ₈ S ₂	C ₁₀ H ₁₇ CuNO ₇ S	C ₃₀ H ₄₈ CuN ₄ O ₉ S ₂
mol wt	684.2	358.8	736.4
a, Å	14.287 (2)	27.198 (3)	19.407 (2)
b, Å	7.169 (1)	9.001 (1)	9.950 (1)
c, Å	16.363 (2)	11.908 (1)	18.930 (2)
α , deg	90.0	90.0	90.0
β , deg	110.6 (1)	90.0	99.35 (1)
γ , deg	90.0	90.0	90.0
V, Å ³	1568.8 (1.1)	2915.2 (5)	3606.8 (6)
Z	2	8	4
d _{obsd} (by flotation), g·cm ⁻³	1.43	1.62	1.34
d _{calcd} , g·cm ⁻³	1.449	1.635	1.356
space group	P2 ₁ /n	Pbca	C2/c
crystal dims, mm	0.10 × 0.23 × 0.39	0.10 × 0.19 × 0.45	0.16 × 0.49 × 0.52
radiation (λ , Å)	Cu K α (λ = 1.541 78)	Cu K α (λ = 1.541 78)	Cu K α (λ = 1.541 78)
2 θ limits, deg	6–120	6–120	6–120
temp, °C	20	20	20
abs coeff, cm ⁻¹	26.57	36.87	23.45
F(000), electrons	710	1480	1556
reflections collected	2605	2866	3763
unique data used	1418	1816	2219
I < 2 σ (I)			
no. of variables	260	249	207
R	0.040	0.037	0.075
R _w	0.042	0.038	0.084

amide group;²⁻⁴ this is also demonstrated by the fact that the N-protected (by an acetyl or a benzoyl group) amino acids always coordinate the copper(II) ion (a metal which, by lowering the pK_a of the amide group, favors its deprotonation) only through the carboxylate group.³⁻⁵ This behavior is generally attributed to the weak coordinating ability of the carboxylate group.

On the contrary, we have previously demonstrated the ability of the carboxylate group to act as primary ligating group in promoting the amide deprotonation, depending on the amide hydrogen acidity.⁶ In fact the substitution of a tosyl group in place of an acetyl or a benzoyl group on the glycine, making the amide group more acidic than the peptide hydrogen, gives rise to the formation, with the copper(II) ion of solid state and solution complexes in which the ligand acts as bidentate through an oxygen atom of the carboxylate group and deprotonated nitrogen atom of the amide group.⁶ A similar bonding mode is also observed in some polypeptide complexes.²

To investigate how far this behavior really depends on the amide hydrogen acidity or on the type of substituent (the tosyl group in our case) on the amino acid, in this paper we report a study on the solid-state copper(II) complexes of two N-tosyl amino acids,

the N-tosyl- α - and N-tosyl- β -alanine, which only differ in the position of the primary ligating (carboxylic) group. The results of this work may be further utilized for an unambiguous interpretation of previous solution data reported for the Cu²⁺-N-tosyl- α -alaninate system.⁷

Experimental Section

Preparation of Green Bis(N-tosylalaninato)copper(II) Complexes: Cu(Ts- α -ala)₂ and Cu(Ts- β -ala)₂. A hot aqueous solution of copper acetate monohydrate (10 mmol) was added to a methanolic solution of the amino acid (20 mmol). By cooling and slow evaporation of the solution a green compound precipitated.

Preparation of Polymeric [Cu(Ts- α -H₁-ala)(H₂O)₂]-H₂O. Pale blue crystals were obtained after several weeks by recrystallization for slowly evaporation at room temperature (20 °C) of an aqueous solution of the green Cu(Ts- α -ala)₂ complex above described.

Preparation of Dication Bis(N-tosyl- α -alaninato)cuprate(II) Complexes: A₂[Cu(Ts- α -H₁-ala)₂] (A = Potassium, Morpholinium, and Piperidinium Cations). Violet crystals of the compounds were obtained by slow evaporation of aqueous methanolic solutions containing the Cu(Ts- α -ala)₂ complex, above described, and the appropriate base, in a complex to base molar ratio of 1:2.

Preparation of Bis(amine)bis(N-tosyl-alaninato)copper(II) Complexes: Cu(Tsala)₂B₂ (B = ImH, MelmH, PipdH, and MorfH for Ts- β -ala⁻; B = ImH and MelmH for Ts- α -ala⁻). All the amine adducts were prepared by evaporation of methanolic solution containing the Cu(Tsala)₂ complex (3 mmol) and the appropriate amine (6 mmol).

Analyses. Sulfur, nitrogen, carbon, and hydrogen were analyzed with a C. Erba Elemental Analyzer Instrument Model 1106 by G. Goldoni and water thermogravimetrically with a Mettler TA3000 Instrument. The results (reported in supplementary material) are closely consistent with the proposed formulae.

Physical Measurements were made as reported in ref 6a and 12.

X-ray Data Collection and Structure Determination. Crystal data and details of parameters associated with data collection are given in Table I. Cell dimensions were determined by diffractometry with an "on-line"

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Table II. Fractional Atomic Coordinates ($\times 10^4$) for Cu, S, O, N, and C Atoms with Esd's in Parentheses for $\text{Cu}(\text{Ts-}\beta\text{-ala})_2(\text{ImH})_2$

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Cu	0	0	0
S	481 (2)	-4024 (2)	3246 (2)
O(1)	415 (3)	-241 (7)	1265 (3)
O(2)	1707 (3)	1456 (7)	1227 (3)
O(3)	749 (5)	-5883 (7)	3096 (4)
O(4)	-540 (4)	-3398 (9)	2835 (4)
N(1)	1189 (5)	-2650 (6)	2921 (4)
N(2)	-713 (4)	2330 (9)	57 (4)
N(3)	-1340 (5)	5150 (11)	-264 (4)
C(1)	1257 (5)	577 (10)	1635 (4)
C(2)	1723 (6)	432 (13)	2624 (4)
C(3)	1122 (6)	-634 (11)	3068 (5)
C(4)	828 (7)	-3639 (14)	4387 (6)
C(5)	1756 (6)	-4285 (13)	4948 (5)
C(6)	2064 (7)	-3868 (14)	5823 (5)
C(7)	1462 (7)	-2847 (12)	6166 (5)
C(8)	1808 (10)	-2383 (19)	7125 (6)
C(9)	539 (8)	-2258 (12)	5600 (6)
C(10)	221 (7)	-2639 (12)	4714 (6)
C(11)	-935 (7)	3055 (15)	753 (6)
C(12)	-1304 (7)	4779 (15)	565 (6)
C(13)	-987 (6)	3667 (11)	-555 (6)

single-crystal Siemens AED diffractometer and refined by least squares using 2θ values of 20 high-angle reflections ($80^\circ \leq 2\theta \leq 120^\circ$) accurately measured. The intensities were collected on the same diffractometer using Cu $K\alpha$, Ni-filtered, radiation and the θ - 2θ scan method, with individual profile analysis.⁸ One reflection was measured every 50 reflections as a check of the alignment of the crystal and instrument stability. The standard deviations are evaluated by a statistical countings and 1418 for I, 1816 for II, and 2219 for III reflections, having $I > 2\sigma(I)$ were considered as "observed" and used in the structural analyses. The structure amplitudes were obtained after the usual Lorentz and polarization reduction and put on absolute scale by least squares. No correction for absorption was applied. For I and II the μr values were very low (0.22 and 0.26, respectively) and the absorption coefficients practically invariant over the range of θ values 3 - 60° ($A^* = 1.45$ - 1.43 for I and 1.52 - 1.50 for II, assuming cylindrical shape for the crystals). For complex III ($\mu r = 0.38$, $A^* = 1.89$ - 1.80 in the same θ range) the correction for absorption did not give an appreciable improvement of the R index. The structures were solved by the heavy-atom technique and refined by least squares. The function minimized in the refinement was $\sum w(|F_o| - |F_c|)^2$, using the weighting scheme $w^{-1} = \sigma^2 F_o + g F_o^2$. Residual R and weighting residual R_w indices were defined as $R = \sum |\Delta F| / \sum |F_o|$, $R_w = [\sum (w|\Delta F|^2) / \sum w|F_o|^2]^{1/2}$.

For I, after anisotropic refinement of Cu, S, O, N, and C atoms ($R = 6.1\%$), the hydrogen atoms were localized from a ΔF map. A successive refinement, including the hydrogen atoms with isotropic thermal parameters, gives an R index of 4.0% ($R_w = 4.2\%$ using the weighting scheme $w^{-1} = \sigma^2 F_o + 0.003075 F_o^2$). Two reflections (-101 and -312), affected by extinction or counting error, were excluded from the final refinement.

For II the anisotropic refinement of Cu, S, O, N, and C atoms gave an R index of 6.2%. The final structure factors calculation, including the hydrogen atoms located from a ΔF map with isotropic thermal parameters, improved the R index to 0.037 ($R_w = 0.038$ using the weighting scheme $w^{-1} = \sigma^2 F_o + 0.003776 F_o^2$). Four reflections, 200, 210, 020, 302, were excluded from the final refinement. For III the R index, after refinement including the non-hydrogen atoms, with anisotropic thermal parameters, was of 8.4%. The water molecule, placed on the twofold axis, is affected by a very high thermal motion and refined isotropically. The final R index, with the contribution of the hydrogen atoms, located from a ΔF map and introduced in the structure factors calculation with isotropic thermal parameter, was 0.075 ($R_w = 0.084$, $w^{-1} = \sigma^2 F_o + 0.002479 F_o^2$). Only the hydrogen atoms of the water molecule are not located.

The atomic scattering factors used, corrected for anomalous dispersion, were taken from International Tables.⁹ All the calculations were performed by using the CYBER 76 of the Centro di Calcolo Interuniversitario dell'Italia Nord-Orientale, Bologna, with SHELX system of programs.¹⁰

The final atomic parameters of non-hydrogen atoms, with their estimated standard deviations are listed in Tables II-IV.

Results and Discussion

The coordinative behavior toward the copper(II) ion of *N*-tosylalanines (only that of the α -derivative is dependent on the pH

Table III. Fractional Atomic Coordinates ($\times 10^4$) for Cu, S, O, N and C Atoms with Esd's in Parentheses for $[\text{Cu}(\text{Ts-}\alpha\text{-H-ala})(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Cu	2076 (1)	1315 (1)	1561 (1)
S	1457 (1)	960 (1)	3717 (1)
O(1)	2385 (1)	3229 (3)	1772 (2)
O(2)	2333 (1)	5342 (3)	2690 (2)
O(3)	1736 (1)	1148 (3)	4741 (2)
O(4)	1436 (1)	-561 (3)	3282 (3)
O(5)	2468 (1)	910 (3)	220 (2)
O(6)	1625 (1)	-283 (3)	1052 (3)
O(7)	3057 (1)	2048 (3)	4311 (3)
N	1619 (1)	1991 (3)	2722 (3)
C(1)	2172 (1)	4086 (4)	2453 (3)
C(2)	1689 (1)	3578 (4)	2991 (3)
C(3)	1268 (2)	4526 (5)	2544 (4)
C(4)	846 (1)	1457 (5)	4062 (4)
C(5)	752 (2)	2395 (6)	4940 (5)
C(6)	267 (2)	2789 (7)	5169 (5)
C(7)	-113 (2)	2270 (6)	4548 (6)
C(8)	-650 (2)	2670 (10)	4802 (9)
C(9)	-12 (2)	1334 (7)	3672 (6)
C(10)	466 (2)	906 (7)	3427 (5)

Table IV. Fractional Atomic Coordinates ($\times 10^4$) for Cu, S, O, N, and C Atoms with Esd's in Parentheses for $[\text{PipdH}_2]_2[\text{Cu}(\text{Ts-}\alpha\text{-H-ala})_2]\cdot\text{H}_2\text{O}$

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Cu	2500	2500	0
S	1524 (1)	1644 (1)	1052 (1)
O(1)	2448 (2)	4429 (4)	73 (2)
O(2)	1728 (3)	6095 (4)	197 (3)
O(3)	1507 (2)	242 (4)	853 (2)
O(4)	950 (2)	2134 (5)	1369 (2)
O(5)	0	3722 (7)	2500
N(1)	1633 (2)	2528 (4)	375 (3)
N(2)	3509 (2)	-3541 (5)	450 (3)
C(1)	1865 (3)	4879 (6)	181 (3)
C(2)	1321 (3)	3868 (6)	320 (4)
C(3)	713 (4)	3931 (9)	-312 (6)
C(4)	2278 (3)	1815 (6)	1712 (3)
C(5)	2309 (4)	2777 (7)	2237 (4)
C(6)	2902 (4)	2907 (8)	2746 (4)
C(7)	3470 (4)	2104 (8)	2736 (4)
C(8)	4121 (5)	2232 (9)	3303 (4)
C(9)	3444 (4)	1147 (8)	2188 (4)
C(10)	2846 (4)	998 (7)	1683 (4)
C(11)	3333 (4)	-3386 (8)	1166 (4)
C(12)	3556 (5)	-4633 (9)	1617 (4)
C(13)	4334 (5)	-4937 (8)	1626 (5)
C(14)	4502 (4)	-5009 (8)	876 (5)
C(15)	4266 (3)	-3748 (7)	481 (4)

of the solution) gives rise to the formation of two types of complexes, differing from one another by the presence on the amino acid of neutral (type 1 complexes) or deprotonated (type 2 complexes) NH group.

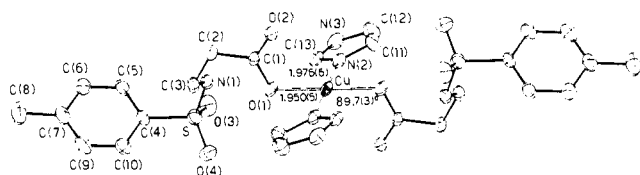
Type 1 Complexes. Colors, magnetisms and EPR spectra, and infrared and electronic spectra of the complexes are such that they are further divided into two classes a and b.

Class a. This class contains the green microcrystalline bis(*N*-tosylalaninato)copper(II) complexes, $\text{Cu}(\text{Tsala})_2$ ($\text{Tsala}^- = \text{N-tosylalaninato monoanion}$), obtained by interaction of copper(II) acetate monohydrate and *N*-tosylalanines in aqueous-methanolic solution, which show magnetic (in the 150-320 K temperature range) and spectroscopic properties (Table V), measured on powdered samples, very similar to one another and suggestive of binuclear species with strong antiferromagnetic exchange. In particular the $[2J]$ values, calculated with the usual Bleaney-Bowers equation for exchange coupled dimers,¹¹ by using for the Landé splitting factor (g) values determined by EPR and for Van Vleck temperature independent constant, $N\alpha$, a value of 60×10^{-6} emu/mol, are very similar to those of the copper(II) dimers of other *N*-protected amino acids (273 - 351 cm^{-1})¹² and carboxylic

Table V. Magnetic and Room-Temperature Spectroscopic Results for the Solid Type 1 (Class a) Compounds

	Cu(Ts- α -ala) ₂	Cu(Ts- β -ala) ₂
μ_{eff} (293 K)	1.33	1.44
g_{\parallel}	2.367	2.337
g_{\perp}	2.095	2.063
g	2.19	2.16
D , cm ⁻¹	0.35	0.33
E , cm ⁻¹		<0.0002
$ 2J $, cm ⁻¹	358 \pm 3	277 \pm 10
d-d band max, cm ⁻¹	14970	15000
CT band, cm ⁻¹	27000 sh	27000 sh
$\nu(\text{NH})$, cm ⁻¹	3320 s	3270 ms
	3240 s	
$\nu(\text{OCO})_{\text{as}}$, cm ⁻¹	1640 vs	1590 vs
$\nu(\text{OCO})_{\text{s}}$, cm ⁻¹	1420 vs	1440 s
		1410 ms
$\nu(\text{SO}_2)_{\text{as}}$, cm ⁻¹	1330 vs	1320 vs
	1290 vs	
$\nu(\text{SO}_2)_{\text{s}}$, cm ⁻¹	1165 vs	1160 vs
	1155 vs	
$\nu(\text{SN})$, cm ⁻¹	975 ms	945 ms

^aEPR parameters for monomer: $g_1 = 2.354$; $g_2 = 2.074$; $g_3 = 2.039$; $A \times 10^4 \text{ cm}^{-1} = 220$ for Cu(Ts- α -ala)₂ at 123 K; $g_{\parallel} = 2.271$ and $g_{\perp} = 2.111$ for Cu(Ts- β -ala)₂ at 123 K.

**Figure 1.** ORTEP view of Cu(Ts- β -ala)₂(ImH)₂.

acids (275–340 cm⁻¹)^{13,14} and may account for an interaction via a superexchange mechanism and for structures similar to copper acetates.

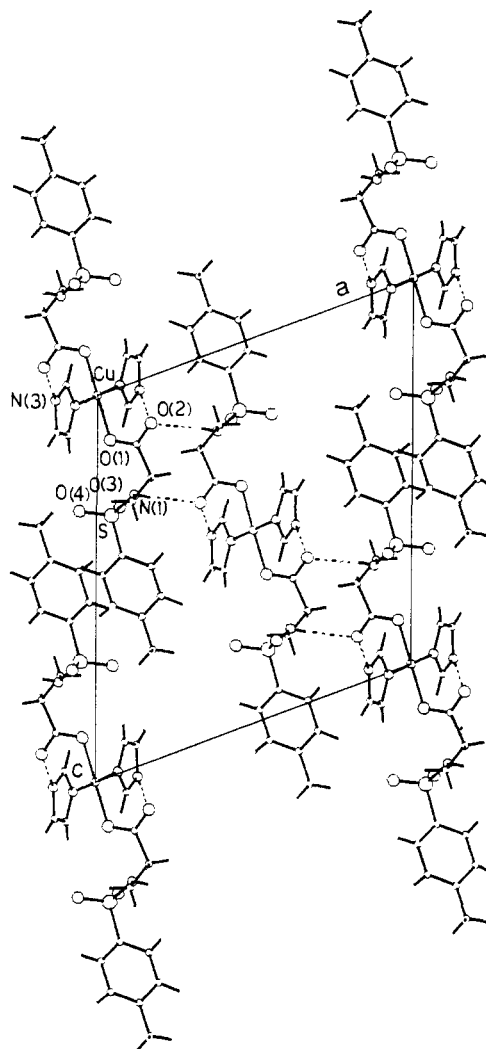
The electronic and infrared data (Table V) strictly resembling those found for the structurally known tetrakis[μ -(*N*-acetyl-glycinato)]diaquadicopper(II),^{4c,15} tetrakis[μ -(*N*-acetyl- β -alaninato)]diaquadicopper(II) dihydrate,^{3d} and the strongly coupled polymeric *N*-tosylglycinato copper(II) complex¹⁶ confirm the presence of dimeric structures in which syn-syn coordinated carboxylate groups are present. The splitting of all the IR bands (Table V) of the sulfonamide group (NH, SO₂, SN) in the Cu(Ts- α -ala)₂ complex indicates the presence of 50% of SO₂ groups axially bonded to the copper atoms of neighboring units, as found in the polymeric *N*-tosylglycinato copper(II) complex.¹⁶

Class b. This class contains the violet Cu(Ts- α -ala)₂B₂ (B = imidazole (ImH), *N*-methylimidazole (MeImH)) and Cu(Ts- β -ala)₂B₂ (B = ImH, MeImH, piperidine (PipdH), morpholine (MorfH)) adducts, obtained by mixing the class a complexes with the appropriate amine in methanol.

For one of these ternary complexes, the bis(*N*-tosyl- β -alaninato)bis(imidazole)copper(II), the crystal and molecular structure was also determined.

Description of the Structure of Cu(Ts- β -ala)₂(ImH)₂. A drawing of the structure showing the atom numbering and selected bond distances and angles is given in Figure 1. The structure consists of copper atoms coordinated to two centrosymmetric carboxylic oxygens of two amino acids and two imidazole molecules in a square-planar arrangement.

The Cu-N(2) (imidazole) bond distance of 1.976 (6) Å lower than those found in [Cu(ImH)₃SO₄]¹⁷ complex, 2.000 (5)–2.021 (5) Å, is consistent with the presence of strong π back-bonding

**Figure 2.** Projection of the structure of Cu(Ts- β -ala)₂(ImH)₂ along the [010] axis.

from Cu²⁺ to heteroaromatic N-bases, which are considered very important in stabilizing mixed-ligand complexes containing oxygen donors.¹⁸ The distance of the Cu(II) from the mean plane of the imidazole ring is 0.22 (1) Å.

Two weak centrosymmetric interactions with copper(II) ions involve the second carboxylic oxygen atom (Cu...O(2)) = 2.761 (5) Å of two amino acids with an angle between the Cu...O(2) vector and the normal to the coordination plane of 36.8 (3)°.

The magnetic and spectroscopic properties of this complex (Table VI), very similar to those of essentially square-planar complexes with CuN₂O₂ chromophore,¹⁹ indicate that the Cu...O(2) distance of 2.761 (5) Å, although significant axial bonding to the copper(II) ion are reported up to 3.3 Å,²⁰ must be considered a nonbonding interaction. This may be justified by the presence of a distortion angle of 36.8° which prevents effective overlap of the metal-ligand orbitals. A correlation among (Cu...O) axial distance, bipyramidal distortion angle, and d-d band maximum for some truly square-planar complexes is reported in Table VII.

The similarity of magnetic and spectroscopic properties of all the adducts of Table VI suggests the same metal ion environment.

The bond distances and angles within the ligands are normal and reported in the supplementary material.

The C ^{α} -COO⁻ group is planar with C ^{β} -0.024 Å and N(1) 1.302 Å out of this plane and forms dihedral angles of 85.1 (4)°,

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Table VI. Room-Temperature Magnetic (μ_B) and Spectroscopic (cm^{-1}) Results for the Solid Type 1 (Class b) Compounds

	$\text{Cu}(\text{Ts-}\alpha\text{-ala})_2\text{-}(\text{ImH})_2$	$\text{Cu}(\text{Ts-}\alpha\text{-ala})_2\text{-}(\text{MeImH})_2$	$\text{Cu}(\text{Ts-}\beta\text{-ala})_2\text{-}(\text{ImH})_2$	$\text{Cu}(\text{Ts-}\beta\text{-ala})_2\text{-}(\text{MeImH})_2$	$\text{Cu}(\text{Ts-}\beta\text{-ala})_2\text{-}(\text{PipdH})_2$	$\text{Cu}(\text{Ts-}\beta\text{-ala})_2\text{-}(\text{MorfH})_2$
μ_{eff} (293 K)	1.85	1.92	1.90	1.85	1.86	1.84
g_{\parallel}	2.197	2.242 ^a	2.183	2.212	2.154	2.140
g_{\perp}	2.053	2.047	2.054	2.054	2.054	2.113
d-d band max	15630 sh 18180	15380 sh 17800	15270 sh 18180	14700 sh 17540	15630 sh 18350	15270 sh 18250
$\nu(\text{NH})$	3130 ms	3300 w 3130 ms	3160 m 3130 ms	3160 ms 3140 ms	3240 ms	3270 ms
$\nu(\text{OCO})_{\text{as}}$	1600 vs	1610 vs	1555 vs	1590 vs	1580 vs	1575 vs
$\nu(\text{OCO})_{\text{s}}$	1405 vs	1400 vs	1430 s 1408 m	1409 vs	1410 vs	1405 vs
$\nu(\text{SO}_2)_{\text{as}}$	1325 vs	1320 vs	1325 vs	1340 s 1325 vs	1340 vs 1320 vs	1324 vs 1318 vs
$\nu(\text{SO}_2)_{\text{s}}$	1160 vs	1155 vs 1140 vs	1160 vs	1160 vs	1160 vs	1155 vs
$\nu(\text{SN})$	950 ms 940 s	970 vs 955 s	940 s	955 s	940 m	945 s

^a $A_1 \times 10^4 \text{ cm}^{-1} = 188$.**Table VII.** Correlation among (Cu...O) Axial Distance (Å), Bipyramidal Distortion Angle (deg), and d-d Band Maximum (cm^{-1}) for Some Truly Planar (CuN₂O₂ Chromophore) Complexes

	(Cu...O) axial distance	distortion angle	d-d band max $\times 10^3$	ref
$[\text{Cu}(\text{Ts-}\beta\text{-ala})_2(\text{ImH})_2]$	2.761 (5)	36.8	18.2	this work
$[\text{Cu}(\text{Ac-}\alpha\text{-ala})_2(\text{MeImH})_2 \cdot \text{H}_2\text{O}]$	2.907 (4)	41.1	18.2	3g
$[\text{Cu}(\text{Hippu})_2(\text{ImH})_2]$	2.736 (4)	37.2	17.5	3f
$[\text{Cu}(\text{Tsgly})_2(\text{MeImH})_2]$	2.758 (4)	37.8	17.9	31
CuN ₄ chromophore			20.4	20

114.7 (2)°, and 96.0 (3)° with sulfonate group and phenyl and imidazole ring, respectively. Conformation of β -alaninate can be described by using the torsion angles around the C'-C α (179.2 (7)° and C α -C β (74.9 (9)°) bonds; the corresponding torsion angles in β -alanine are 9.6° and 83.7°. ²¹

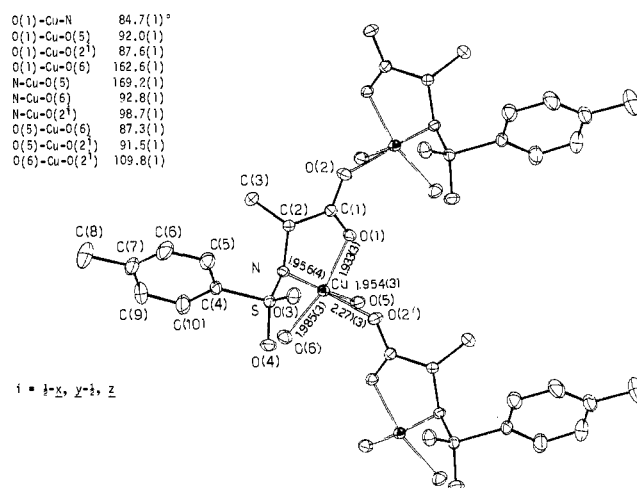
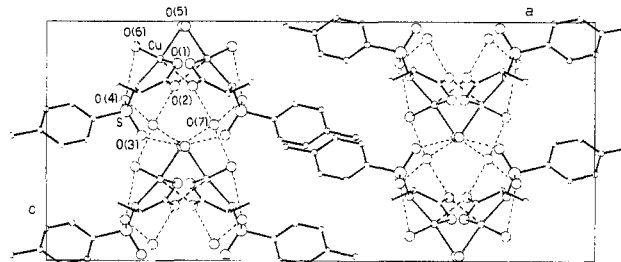
Packing (Figure 2) is determined by hydrogen bonds involving the uncoordinated carboxylic oxygen and the amide nitrogen (N(1)) and imidazole nitrogen (N(3)) and by C α -H...O interaction (C α ...O(3)ⁱ = 3.20 (1) Å) ($i = x, 1 + y, z$) with the H...O distance (2.40 (4) Å) lower than the sum of the van der Waals radii. The shorter aromatic-aromatic contact is C(4)...C(9) ($-x, -y - 1, 1 - z$) = 3.54 (1) Å.

Type 2 Complexes. Only compounds of *N*-tosyl- α -alanine, unlike *N*-tosyl- β -alanine, are members of this type; they present a coordinative behavior strictly dependent on the pH of the solution. The compounds are separated at pH ≥ 5 and are characterized by the presence of deprotonated amide nitrogen atom of the amino acid coordinated to the copper(II) ion.

By recrystallization from aqueous solution of the green Cu(Ts- α -ala)₂ compound at pH 4-5, a compound of formula [Cu(Ts- α -H₁ala)(H₂O)₂] \cdot H₂O precipitated. The deprotonation of the NH group in presence of copper(II) ion at pH value ≥ 5 , greatly anticipating its pK_A value,⁷ is consistent with the behavior of *N*-tosylglycine⁶ and of some glycine peptide ligands.²² Thermogravimetric analysis of the compound, similarly to that of the stoichiometrically analogous *N*-tosylglycinato derivative, [Cu(Ts-H₁gly)(H₂O)₃],⁶ shows the loss of two water molecules in the 90-140 °C temperature range, while the loss of the third water molecule, starting at 155 °C, is accompanied by decomposition of the compound.

At pH > 8 the *N*-tosyl- α -alanine separates compounds of formula A₂[Cu(Ts- α -H₁ala)₂] (A = K⁺, Morf H₂⁺, and Pipd H₂⁺ cations).

Description of the Structures. In blue [Cu(Ts- α -H₁ala)(H₂O)₂] \cdot H₂O complex, the most significant feature is

**Figure 3.** ORTEP view of [Cu(Ts- α -H₁ala)(H₂O)₂]_n.**Figure 4.** Projection of the structure of [Cu(Ts- α -H₁ala)(H₂O)₂] \cdot H₂O along [010] axis.

represented by the behavior of the carboxylate group, which acts as bidentate joining two adjacent copper atoms, so that the structure is built up of polymeric [Cu(Ts- α -H₁ala)(H₂O)₂]_n chains running along the [010] axis. As shown in Figures 3 and 4 each copper atom is five-coordinated, forming a distorted [4 + 1] square-based pyramid. In the coordination polyhedron, the base is occupied by the deprotonated amide nitrogen, one carboxylic oxygen and two water molecules; at the apex is situated a second carboxylate oxygen belonging to an adjacent amino acid molecule. This type of coordination in which a carboxylate group bridges two copper atoms in a syn-anti type configuration

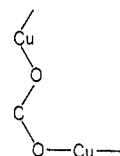
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Table VIII. Magnetic (μ_B) and Spectroscopic (cm^{-1}) Properties of the Solid *N*-Tosyl- α -alaninate Complexes Containing a Deprotonated NH Group

	[Cu(Ts- α -H ₁ ala)-(H ₂ O) ₂]-H ₂ O	[PipdH ₂] ₂ -[Cu(Ts- α -H ₁ ala) ₂]-H ₂ O	[MorH ₂] ₂ -[Cu(Ts- α -H ₁ ala) ₂]	K ₂ [Cu(Ts- α -H ₁ ala) ₂]
chromophore	CuNO ₄	CuN ₂ O ₂	CuN ₂ O ₂	CuN ₂ O ₂
μ_{eff} (293 K)	1.80	1.75	1.80	1.84
g_{\parallel}	2.258	2.234	2.212	2.221
g_{\perp}	2.153	2.047	2.060	2.053
A_{\parallel} (cm^{-1}) $\times 10^4$		180		
d-d band max	13650	14490 17860 19050 sh	15270 19100	14290 16670 19230 sh
CT band	28170	26700	26800	
$\nu(\text{OCO})_{\text{as}}$	1570 vs	1635 vs	1660 vs	1630 vs
$\nu(\text{OCO})_{\text{s}}$	1420 s	1370 vs	1330 s	1385 vs
$\nu(\text{SO}_2)_{\text{as}}$	1230 vs	1260 vs	1250 vs	1250 vs
$\nu(\text{SO}_2)_{\text{s}}$	1120 vs	1133 vs 1120 s	1130 vs	1130 vs
$\nu(\text{SN})$	1000 vs	990 s	988 s	1000 vs

^a $\nu(\text{OH}) = 3450$ vsb. ^b $\nu(\text{OH}) = 3520$ ms, $\nu(\text{OH})_{\text{s}} = 3480$ ms.

unusual for *N*-protected amino acids, strongly resembles that observed in some (aspartato)- and (glutamato)copper(II) complexes.^{23,24}

The planarity analysis quoted in supplementary material, shows that the four equatorial atoms N, O(1), O(5), and O(6) are roughly coplanar, with copper 0.240 Å out of the mean plane, toward the apex of pyramid, O(2)ⁱ ($i = 1/2 - x, y - 1/2, z$). The distortion of the coordination polyhedron can be measured using the angle between the Cu-O(2)ⁱ vector and the normal to the coordination plane (11.9 (1)°). This kind of geometry and Cu-O and Cu-N bond lengths (Figure 3) are very similar to those found in [Cu(Ts-H₁gly)(H₂O)₃],⁶ where the apex of the pyramid are occupied by a third water molecule (Cu-O(H₂O) = 2.259 (4) Å.^{6a} In the present complex, the third water molecule, which completes the crystallographic units, located 4.27 Å from the copper, is not directly coordinated, but participates in the network of hydrogen bonds. The C^α-COO⁻ group is planar, with the sulfonamide nitrogen 0.225 Å out of plane and forms dihedral angles of 42.7 (1)° and 87.2 (1)° with phenyl and sulfonate groups, respectively.

In the lilac [PipdH₂]₂[Cu(Ts- α -H₁ala)₂]-H₂O complex the structure consists of piperidinium cations and [Cu(Ts- α -H₁ala)₂]²⁻ anions (Figures 5 and 6). The copper atom, lying on the symmetry center, shows a square-planar coordination through the deprotonated sulfonamide nitrogen and one carboxylate oxygen, forming a five-membered chelate ring, as found in the [Cu(Ts- α -H₁ala)(H₂O)₂]-H₂O complex. In the copper(II) environment, perfectly planar for symmetry requirement, the Cu-O (1.928 (4) Å) and Cu-N (1.937 (4) Å) are shorter than those found in other *N*-tosyl-substituted amino acids, containing deprotonated amide nitrogen.⁶ The second carboxylic oxygen and water molecules are not involved in the coordination. The sulfonamide nitrogen is 0.179 Å out of the mean plane through the carboxylate, which forms dihedral angles of 58.3 (2)° and 18.2 (2)° with sulfonamide and phenyl groups.

Conformation of α -alaninate moieties in the two compounds is very similar, as shown by the torsion angles around the C-N and C-C bonds, C(1)-C(2)-N-S 134.4 (2)°, O(1)-C(1)-C(2)-N 10.1 (4)° for [Cu(Ts- α -H₁ala)(H₂O)₂]-H₂O and C(1)-C(2)-N(1)-S 130.4 (5)°, O(1)-C(1)-C(2)-N(1) 6.2 (7)° for [PipdH₂]₂[Cu(Ts- α -H₁ala)₂]-H₂O. In this last complex the piperidinium cation exhibits a "chair" conformation, as indicated by the puckering parameters: $q_2 = 0.037$ Å, $q_3 = 0.574$ Å, $\Phi_2 = -33.28^\circ$, and $Q = 0.57$ Å. The water molecule, lying on the twofold axis, is uncoordinated and participates only in the van der Waals contacts.

In both compounds, packing is mainly determined by hydrogen bonds, the network of contacts depending on the ability of the

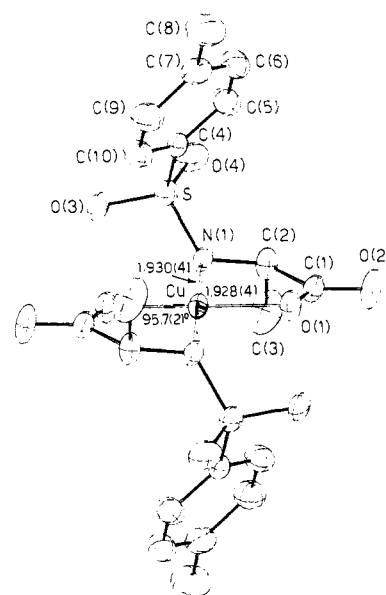


Figure 5. ORTEP view of [Cu(Ts- α -H₁ala)₂]²⁻ anion.

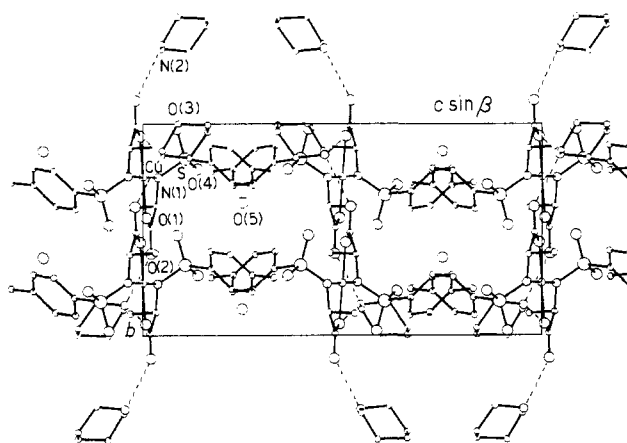


Figure 6. Projection of the structure of [PipdH₂]₂[Cu(Ts- α -H₁ala)₂]-H₂O along the [010] axis.

complex to form hydrogen bonds. In [Cu(Ts- α -H₁ala)(H₂O)₂]-H₂O (Figure 4), coordinated water molecules act as donors with respect to the sulfonate oxygen atoms and uncoordinated water molecule, which join adjacent units of the complex via carboxylic and sulfonate oxygens, so as to form layers parallel to (100) plane. In this way the structure consists of alternate layers of polar and nonpolar regions of the ligand. In particular the

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Table IX. d-d Band Maximum (cm⁻¹) for Some Truly Square-Pyramidal Copper(II) Complexes

	d-d band max	chromophore	ref
[Cu(en) ₂ (NH ₃) ₂] ²⁺	17 400	CuN ₅	29
[Cu(Asp)bpv·H ₂ O]·3H ₂ O ^a	16 390	CuN ₃ O ₂	23b
[Cu(Ts-H ₁ gly)bpv·EtOH] ^a	16 400	CuN ₃ O ₂	30
[Cu(Asp)ImH]·2H ₂ O ^a	15 400	CuN ₂ O ₃	23a
K ₂ [Cu(Ts-H ₁ gly) ₂]	15 150	CuN ₂ O ₃	6
[Cu(Ts-H ₁ gly)(H ₂ O) ₃]	13 990	CuNO ₄	6
[Cu(Ts-α-H ₁ ala)(H ₂ O) ₂]·H ₂ O	13 650	CuNO ₄	this work

^a Asp²⁻ = aspartate dianion; Ts-H₁gly²⁻ = *N*-tosylglycinate dianion; bpv = 2,2'-bipyridine.

O(6)-H...O(4) 2.716 (5) Å is an intramolecular hydrogen bond. In the [PipdH₂]₂[Cu(Ts-α-H₁ala)₂]·H₂O complex (Figure 6) the piperidinium cation forms hydrogen bonds with coordinated and uncoordinated carboxylic oxygens. Possible hydrogen bonding and angles and contacts less than 3.5 Å, which complete the packing for all compounds are quoted in the supplementary material. In both structures no contacts between aromatic rings less than 3.6 Å were found.

Magnetic and Spectroscopic Results. The type 2 complexes (Table VIII) present room-temperature solid magnetic moments "normal" and typical of "magnetically dilute" complexes²⁵ and polycrystalline EPR spectra of axial type, suggesting an essentially d_{x²-y²} ground state, with g_{||} values consistent with the reported chromophores.²⁶⁻²⁸

The square-pyramidal [Cu(Ts-α-H₁ala)(H₂O)₂]·H₂O complex shows a d-d band maximum which correlates well with other CuN_xO_y (x + y = 5) chromophores^{6,23,29,30} (Table IX), while the electronic spectra of the [Cu(Ts-α-H₁ala)₂]²⁻ complexes are typical of strictly square-planar compounds.⁶

In Table VIII are also reported the absorptions assigned to the most significant ligand functions of *N*-tosyl-α-alanine. By comparing these data with those of the type 1 complexes (Tables V

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and VII) the main differences are observed in the NH and sulphonyl group spectral regions, as a consequence of the presence in type 2 complexes of a deprotonated nitrogen atom coordinated to the copper(II) ions.

Conclusions

The main conclusions to be drawn from this work are as follows:

(1) The Cu²⁺-promoted amide deprotonation needs ligands containing a primary group. The carboxylic group of the *N*-protected amino acids, reported in ref 2-7, may act as primary ligating group only if the protecting group is a sulfonyl group in α position (*N*-tosyl-α-amino acids). For these ligands the amide hydrogen deprotonation in presence of Cu²⁺, occurs at pH ≥ 5, strongly anticipating their pK_A values (11-12)^{6,7}, with formation of a five-membered chelate ring involving in the metal ion coordination the carboxylate oxygen and the deprotonated sulfonamide nitrogen donor atoms.

(2) The similarity of the solid-state copper(II) complexes of *N*-tosylglycine⁶ and *N*-tosyl-α-alanine also suggests a parallelism in their solution behavior, supporting for the copper(II) ion-*N*-tosyl-α-alanine system in aqueous solution the statements of Sigel and Martin.²

(3) The shift of the carboxylic group in β-position, decreasing the acidity of the NH group (pK_A ~ 14), makes it ineffective in promoting amide deprotonation also in accordance with the lower stability of six-membered chelate ring compared to five-membered ones. This parallels the coordinative behavior of β-alaninamide with respect to that of glycineamide.²

Acknowledgment. We are grateful to the Centro Strumenti dell'Università di Modena for recording the infrared spectra.

Registry No. I, 93923-32-1; II, 88764-97-0; III, 88390-92-5; Cu(Ts-α-ala)₂, 93923-28-5; Cu(Ts-β-ala)₂, 93923-29-6; K₂[Cu(Ts-α-H₁ala)₂], 93923-30-9; (MorfH₂)₂[Cu(Ts-α-H₁ala)₂], 93923-31-0; Cu(Ts-β-ala)₂·(MeImH)₂, 93942-83-7; Cu(Ts-β-ala)₂(PipdH)₂, 93923-33-2; Cu(Ts-β-ala)₂(MorfH)₂, 93923-34-3; Cu(Ts-α-ala)₂(ImH)₂, 88360-11-6; Cu(Ts-α-ala)₂(MeImH)₂, 93942-84-8.

Supplementary Material Available: Listings of atomic coordinates and thermal parameters of hydrogen atoms, anisotropic thermal parameters, complete bond distances and angles, possible hydrogen bonding and angles, intermolecular contacts less than 3.5 Å, weighted least-squares planes, observed and calculated structure factors for the reflections used in the refinements, elemental analyses, and experimental and calculated corrected molar susceptibilities (54 pages). Ordering information is given on any current masthead page.

Capture of Electron-Deficient Species with Aryl Halides. New Syntheses of Hypervalent Iodonium Ylides

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Contribution from the Department of Chemistry, University of Illinois at Chicago, Chicago, Illinois 60680. Received January 6, 1984.

Revised Manuscript Received September 2, 1984

Abstract: We have demonstrated the aryl iodide capture of β-diketocarbene, generated from the diazo compound by using rhodium(II) acetate, under very mild conditions. This is a useful general preparative method for iodonium ylides under non-hydroxylic conditions. The thermal, catalytic, and photochemical decompositions of various azides in the presence of aryl iodides were carried out. With highly reactive nitrenes, intramolecular rearrangement takes precedence over capture. In the case of *p*-toluenesulfonyl azide, thermolysis in the presence of aryl iodides requires conditions under which the iminoiodane is itself decomposed. The capture of oxene by iodobenzene is discussed. The application of these capture processes is discussed as a synthetic route to hypervalent ylides as well as on the basis of mechanism.

Recently a number of examples have appeared in the literature in which an electron-deficient species X (nitrene,¹ carbene,² or

oxene³) is transferred from a hypervalent iodine precursor (ArI=NSO₂C₆H₄-*p*-CH₃, ArI=C(CO₂R)₂, and ArI=O) to an