Side-chain Effect on the Co-ordination Behaviour of Glycine Derivatives toward Copper(II). Crystal Structure of Bis(μ-*N*-tritylglycinato-*O*)-bis[(2,2'-bipyridine)(*N*-tritylglycinato-*O*)copper(II)] *

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N-Triphenylmethylglycine (tgly) reacts with Cu^{II} producing a violet compound of formula [Cu(tglyO)$_2$]·3H$_2$O whose electronic spectrum is characteristic of an essentially square-planar CuN$_2$O$_2$ chromophore. This compound readily reacts with 2,2'-bipyridine (bipy), and a blue complex of empirical formula Cu(tglyO)$_2$(bipy) was crystallized and its crystal structure determined. The crystals are triclinic, space group $P\bar{1}$, with cell parameters a = 10.098(1), b = 12.573(11), c = 16.979(3) Å, α = 93.11(3), β = 102.70(1), γ = 99.99(2)°, Z = 1, and R = 0.053. The structure consists of discrete dimeric [{Cu(tglyO)$_2$(bipy)}$_2$] units with CuN$_2$O$_3$ chromophores. The metal atoms are bridged through two unidentate carboxyl groups. The tglyO anions act as simple carboxylate ligands with no nitrogen bonding. The co-ordination behaviour in the mixed complex may be explained by the discriminatory effect of bipy toward the second ligand, favouring oxygen- over nitrogen-donor ligands, and by the steric hindrance of the three phenyl rings which prevent direct metal co-ordination of the nitrogen atom.

As compared with simple amino acids, the binary and ternary metal(II) complexes of *N*-alkyl- and *N*-aryl-amino acids have been rather neglected, although the presence of non-polar substituents can in principle influence the metal environment and favour the formation of less extensively hydrated or anhydrous complexes. In particular the aquabis(*N*,*N*-dimethylglycinato)copper(II) dihydrate complex[1] shows a square-pyramidal geometry due to the repulsion between the methyl groups and the aqua-ligand, the methyl groups being below the basal plane and blocking access to the sixth co-ordination site. In bis(*N*,*N*-diethylalaninato)copper(II)[2] the metal environment is truly square planar as a consequence of the steric hindrance caused by the ethyl and methyl groups. For many years, we have been interested in the co-ordination behaviour of *N*-substituted amino acids, focusing our attention on electron-withdrawing and size effects of various substituents.[3,4] We are now investigating the effect of both steric and hydrophobic effects of *N*-substituted amino acids and report here a study on the binding properties of *N*-triphenylmethylglycine (hereafter abbreviated as tritylglycine, tgly). We have focused interest on this ligand because of its biological importance as an intermediate in the synthesis of oxytocin and calcitonin analogues.[5] The study was carried out in the solid state and the crystal and molecular structure of the adduct bis(μ-*N*-tritylglycinato-*O*)-bis[(2,2'-bipyridine)(*N*-tritylglycinato-*O*) copper(II)] is also reported.

Experimental

Preparation of [Cu(tglyO)$_2$]·3H$_2$O.—By mixing a methanolic solution (0.05 dm^3) of tritylglycine (0.02 mol dm^{-3}) with an aqueous solution (0.05 dm^3) of copper(II) acetate monohydrate (0.01 mol dm^{-3}) a violet compound precipitated instantly (Found: C, 68.00; H, 5.65; N, 3.75. Calc. for $C_{42}H_{42}CuN_2O_7$: C, 67.20; H, 5.65; N, 3.75%).

Preparation of [{Cu(tglyO)$_2$(bipy)}$_2$].—By dissolving the above binary violet compound in methanol (1 mmol) (0.05 dm^3) and adding 2,2'-bipyridine (bipy) (1 mmol) a crystalline blue compound separated (Found: C, 72.60; H, 5.25; N, 6.50. Calc. for $C_{104}H_{88}Cu_2N_8O_8$: C, 73.25; H, 5.20; N, 6.60%).

Physical Measurements.—Electronic spectra were obtained with a Varian Cary 2300 u.v.–visible spectrophotometer and i.r. spectra as KBr pellets with a Bruker FT-IR IFS113v spectrophotometer.

X-*Ray Data Collection and Structure Determination.*—$C_{104}H_{88}Cu_2N_8O_8$, M = 1 703.84, triclinic, a = 10.098(1), b = 12.573(11), c = 16.979(3) Å, α = 93.11(3), β = 102.70(1), γ = 99.99(2)°, U = 2 061.38 Å^3, space group $P\bar{1}$, Z = 1, D_m = 1.39 g cm^{-3}, $F(000)$ = 890, μ(Mo-K_α) = 5.36 cm^{-1}, crystal size 0.20 × 0.25 × 0.30 mm.

Cell dimensions were determined from least-squares refinement on the angular settings of 25 automatically centred reflections from different regions of reciprocal space (Mo-K_α radiation). Intensity data were collected on an Enraf-Nonius CAD4 diffractometer, at room temperature, by using graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å) with the ω—2θ scan technique, θ ranging from 2.0 to 24.0°, scan width = 0.65 + 0.35 tanθ, and scan speed 1.03—2.74° min^{-1}. Three standard reflections, monitored at 4-h intervals, showed no significant changes. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction[6] was applied (1.00 $\leqslant$ T factor $\leqslant$ 0.986). A total of 4 663 independent non-zero reflections ($\pm h, \pm k, +l$) having $I \geqslant 2\sigma(I)$ was measured and used in the structure determination.

The structure was solved by conventional Patterson and Fourier techniques, and refined through full-matrix least-squares calculations with $\Sigma w(|F_o| - |F_c|)^2$ being minimized: Cu, O, and N atoms were refined anisotropically, C atoms isotropically. Hydrogen atoms were located on a Fourier difference map; two belonging to C(39) and C(49) were calculated, then all were treated as fixed contributors with isotropic thermal parameters 1.0 Å^2 higher than those of the

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

Table 1. Final positional parameters for [{Cu(tglyO)$_2$(bipy)}$_2$]

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu	0.163 51(6)	0.490 43(5)	0.054 75(4)
N(1)	0.277 4(4)	0.383 6(3)	0.106 8(2)
N(2)	0.241 3(4)	0.444 7(3)	−0.039 6(2)
C(1)	0.279 2(6)	0.348 6(4)	0.180 0(3)
C(2)	0.360 9(6)	0.275 0(5)	0.210 6(4)
C(3)	0.443 1(7)	0.239 3(5)	0.164 3(4)
C(4)	0.443 0(6)	0.275 1(5)	0.089 6(4)
C(5)	0.357 2(5)	0.347 3(4)	0.061 0(3)
C(6)	0.343 2(5)	0.386 9(4)	−0.019 1(3)
C(7)	0.426 4(6)	0.366 5(4)	−0.072 0(3)
C(8)	0.399 5(6)	0.404 9(5)	−0.147 5(4)
C(9)	0.291 4(6)	0.459 5(5)	−0.169 1(4)
C(10)	0.215 0(5)	0.478 1(4)	−0.113 2(3)
O(1)	0.073 3(3)	0.602 2(3)	−0.000 7(2)
O(2)	0.279 7(3)	0.696 2(3)	−0.004 1(2)
C(11)	0.153 5(5)	0.683 1(4)	−0.019 1(3)
C(12)	0.079 5(5)	0.764 7(4)	−0.064 8(3)
N(3)	0.178 9(4)	0.850 1(3)	−0.085 5(3)
C(13)	0.140 1(5)	0.899 7(4)	−0.162 4(3)
C(14)	0.066 8(5)	0.813 7(4)	−0.233 4(3)
C(15)	0.115 6(6)	0.716 8(4)	−0.239 4(3)
C(16)	0.053 3(6)	0.636 8(5)	−0.301 8(4)
C(17)	−0.058 6(7)	0.649 7(5)	−0.360 1(4)
C(18)	−0.105 7(7)	0.745 4(6)	−0.356 8(4)
C(19)	−0.044 3(6)	0.827 2(5)	−0.294 3(4)
C(20)	0.048 3(5)	0.982 9(4)	−0.150 1(3)
C(21)	0.087 9(6)	1.092 5(5)	−0.155 3(3)
C(22)	0.001 4(6)	1.165 5(5)	−0.144 0(4)
C(23)	−0.124 5(6)	1.130 0(5)	−0.127 8(4)
C(24)	−0.166 1(7)	1.021 0(5)	−0.122 0(4)
C(25)	−0.080 3(6)	0.948 3(5)	−0.133 6(4)
C(26)	0.275 7(5)	0.960 3(4)	−0.179 2(3)
C(27)	0.379 4(6)	1.017 7(5)	−0.116 1(4)
C(28)	0.494 6(7)	1.083 9(5)	−0.131 5(4)
C(29)	0.508 0(7)	1.092 6(6)	−0.209 2(4)
C(30)	0.408 7(7)	1.033 7(5)	−0.272 0(4)
C(31)	0.292 2(6)	0.967 2(5)	−0.257 3(4)
O(3)	0.113 6(3)	0.528 6(3)	0.154 0(2)
O(4)	0.311 3(4)	0.644 5(4)	0.198 9(3)
C(32)	0.197 0(5)	0.602 6(4)	0.204 8(3)
C(33)	0.139 8(6)	0.632 2(4)	0.277 8(3)
N(4)	0.202 1(4)	0.739 9(3)	0.317 9(2)
C(34)	0.175 2(5)	0.762 1(4)	0.398 6(3)
C(35)	0.219 0(5)	0.884 3(4)	0.424 1(3)
C(36)	0.325 7(7)	0.944 0(5)	0.398 7(4)
C(37)	0.374 7(8)	1.054 7(6)	0.430 7(5)
C(38)	0.316 9(7)	1.099 8(6)	0.485 1(4)
C(39)	0.211 7(7)	1.041 0(5)	0.510 3(4)
C(40)	0.160 4(6)	0.933 5(5)	0.479 5(4)
C(41)	0.271 0(5)	0.710 1(4)	0.462 6(3)
C(42)	0.261 6(6)	0.714 9(5)	0.543 3(3)
C(43)	0.355 3(6)	0.677 5(5)	0.602 2(4)
C(44)	0.461 9(7)	0.634 0(5)	0.582 1(4)
C(45)	0.472 9(7)	0.629 3(5)	0.503 4(4)
C(46)	0.379 5(6)	0.666 7(5)	0.444 4(4)
C(47)	0.019 7(5)	0.723 4(4)	0.394 2(3)
C(48)	−0.073 4(6)	0.778 5(5)	0.348 8(3)
C(49)	−0.214 8(6)	0.742 5(5)	0.336 2(4)
C(50)	−0.264 1(7)	0.652 4(5)	0.370 2(4)
C(51)	−0.174 9(6)	0.596 8(5)	0.415 7(4)
C(52)	−0.032 2(6)	0.632 6(5)	0.427 6(3)

Table 2. Selected i.r. bands (cm^{-1}) of solid compounds

Compound	$\nu(NH_2^+)$	$\nu_{asym.}(CO_2)$	$\nu_{sym.}(CO_2)$
tgly	2 580w (br) 2 310mw (br)	1 580s	1 388s
[Cu(tglyO)$_2$]·3H$_2$O*	3 228m (br) 3 196s	1 653s	1 367s
[{Cu(tglyO)$_2$(bipy)}$_2$]	3 335s	1 641vs 1 607vs	1 374vs 1 279vs

* Stretching band of water molecules ν(OH) at 3 404ms (br) cm^{-1}.

atoms to which they are bonded. Final R and R' values 0.053. Unit weights were used at all stages, and no trend in $\Sigma w(|F_o| - |F_c|)^2$ *vs.* $|F_o|$, sinθ, or Miller indices was observed. A final difference map was featureless, with no peaks higher than 0.4 e Å^{-3}. There was no evidence of secondary extinction.

Complex neutral atom scattering factors were taken from ref. 7. Major calculations were carried out on a Vax 11/750 computer by using the SHELX 76 system of programs[8] and ORTEP[9] for the molecular plot. Final fractional co-ordinates for the non-hydrogen atoms are given in Table 1.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

Analyses.—Carbon, hydrogen, and nitrogen were analyzed with a C. Erba model 1106 instrument by Mr. G. Goldoni.

Results and Discussion

N-*Tritylglycine and* [Cu(tglyO)$_2$]·3H$_2$O.—The i.r. spectrum of the free ligand exhibits a pattern typical of a zwitterionic species (Table 2) with two broad bands in the region 2 600—2 300 cm^{-1} associated with this structure and with NH_2^+ stretching vibrations and a strong band at 1 580 cm^{-1} assigned to an ionic carboxylate group.[10] For the binary complex the appearance of intense absorption bands around 3 200 and 1 650 cm^{-1} is compatible with metal chelation through the amino nitrogen and carboxylate oxygen atoms as normally found for α-amino acids. This type of co-ordination is also confirmed by

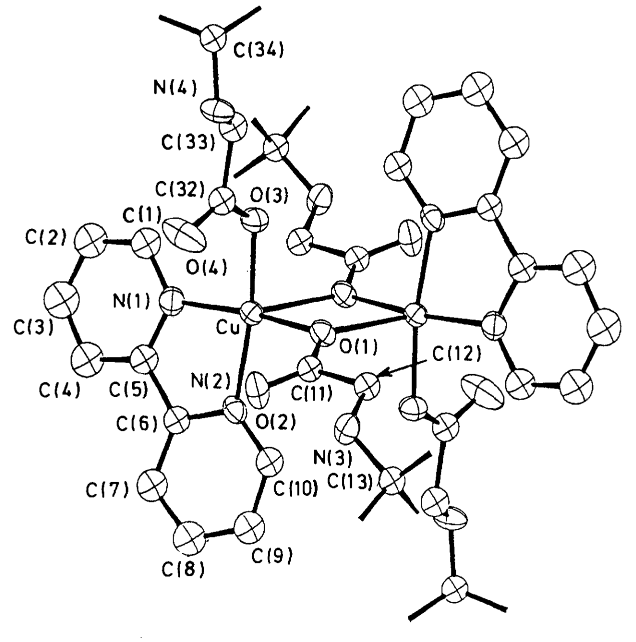

Figure. ORTEP view of [{Cu(tglyO)$_2$(bipy)}$_2$]; phenyl rings are omitted for clarity

Table 3. Selected bond distances (Å) and angles (°)

Cu–N(1)	2.031(4)	C(13)–C(14)	1.536(7)
Cu–N(2)	2.031(4)	C(13)–C(20)	1.548(7)
Cu–O(1)	1.975(3)	C(13)–C(26)	1.540(7)
Cu–O(3)	1.922(3)	O(3)–C(32)	1.281(6)
Cu–O(1′)	2.423(3)	O(4)–C(32)	1.211(6)
Cu ··· Cu′	3.470(1)	C(32)–C(33)	1.532(7)
O(1)–C(11)	1.284(5)	C(33)–N(4)	1.452(6)
O(2)–C(11)	1.224(6)	N(4)–C(34)	1.476(6)
C(11)–C(12)	1.520(6)	C(34)–C(35)	1.534(7)
C(12)–N(3)	1.451(6)	C(34)–C(41)	1.543(7)
N(3)–C(13)	1.482(6)	C(34)–C(47)	1.545(7)
Cu–O(1)–Cu′	103.7(1)		
N(1)–Cu–N(2)	79.9(2)	N(3)–C(13)–C(20)	108.7(4)
N(1)–Cu–O(1)	172.8(1)	N(3)–C(13)–C(26)	106.5(4)
N(1)–Cu–O(3)	92.6(2)	C(14)–C(13)–C(20)	111.4(4)
N(1)–Cu–O(1′)	109.4(2)	C(14)–C(13)–C(26)	109.4(4)
N(2)–Cu–O(1)	95.2(1)	C(20)–C(13)–C(26)	108.9(4)
N(2)–Cu–O(3)	171.6(2)	O(3)–C(32)–O(4)	125.2(5)
N(2)–Cu–O(1′)	97.4(1)	O(3)–C(32)–C(33)	113.0(4)
O(1)–Cu–O(3)	91.9(1)	O(4)–C(32)–C(33)	121.8(5)
O(1)–Cu–O(1′)	76.3(1)	C(32)–C(33)–N(4)	113.6(4)
O(3)–Cu–O(1′)	88.6(2)	C(33)–N(4)–C(34)	115.2(4)
O(1)–C(11)–O(2)	125.1(4)	N(4)–C(34)–C(35)	108.7(4)
O(1)–C(11)–C(12)	114.7(4)	N(4)–C(34)–C(41)	109.8(4)
O(2)–C(11)–C(12)	120.1(4)	N(4)–C(34)–C(47)	109.2(4)
C(11)–C(12)–N(3)	110.2(4)	C(35)–C(34)–C(41)	104.3(4)
C(12)–N(3)–C(13)	119.1(4)	C(35)–C(34)–C(47)	110.9(4)
N(3)–C(13)–C(14)	111.7(4)	C(41)–C(34)–C(47)	113.8(4)

Primed atoms are at $-x, 1 - y, -z$.

Table 4. Comparison of structural parameters in $[\{CuL_2(bipy)\}_2]$ complexes (L = amino acid anion)

L	Tosylglycinate	Tosylvalinate	tglyO
Chromophore	CuN_2O_3	CuN_2O_3	CuN_2O_3
Cu ··· Cu/Å	3.317	3.501	3.470
$Cu–O_{eq}$[a]/Å	1.933	1.899	1.922
$Cu–O_{eq}$[b]/Å	1.968	1.983	1.975
$\Delta(Cu–O_{eq})$/Å	0.035	0.084	0.053
$Cu–O_{ax}$/Å	2.350	2.452	2.423
Cu–N/Å	1.992	1.967	2.031
	2.002	2.044	2.031
O–Cu–O′/°	80.0	76.2	76.3
Ref.	14	3	This work

[a] Unidentate carboxylate oxygen. [b] Monoatomic bridging carboxylate oxygen.

inspection of the electronic spectrum which shows two well resolved bands at 18 500 and 14 700 cm^{-1} characteristic of an essentially square-planar CuN_2O_2 chromophore.[11] Therefore it seems well established that, in this case, the abnormally great steric hindrance of the trityl group does not affect the N,O co-ordination. Indeed the concomitant contribution of the extremely high hydrophobic character of the ligand enables the stabilization of four-co-ordinated complexes as found in other copper(II) complexes with amino-acids bearing functional side-chains.[2,11,12]

Description of the Structure of $[\{Cu(tglyO)_2(bipy)\}_2]$.—Selected interatomic distances and angles are reported in Table 3 with atoms labelled as in the Figure. The structure consists of discrete dimeric $[\{Cu(tglyO)_2(bipy)\}_2]$ units. The metal atoms of the binuclear molecule are bridged through two oxygen atoms related by an inversion centre (which requires the bridging Cu_2O_2 unit to be planar) in the middle of the dimer. Each copper ion shows distorted square-pyramidal geometry, the four basal ligands being two nitrogen atoms of the bipy ligand and two carboxyl oxygens from two unidentate tglyO anions, while the axial site is occupied by a carboxyl oxygen that is basal to the other copper centre in the dimer. The amino nitrogen is unco-ordinated, and the amino acid acts as a simple carboxylate ligand. This behaviour can be mainly explained by the discriminatory effect of 2,2′-bipyridine toward the second ligand, favouring oxygen-donor ligands as against nitrogen ones,[13] as well as by the steric hindrance of the trityl groups which prevents co-ordination of the amino nitrogen. This kind of co-ordination geometry was previously found in 2,2′-bipyridine adducts of *N*-tosylamino acids[3,14] and can be considered as favoured by the hydrophobic character of the ligands which excludes water co-ordination and forces one carboxylate group to form a monoatomic bridge in order to attain the usual square-pyramidal co-ordination geometry for Cu^{II}–bipy complexes.

The equatorial Cu–O(1) bond distance is slightly longer than Cu–O(3) [$\Delta(Cu–O_{eq})$ = 0.053 Å], suggesting the effect of the different carboxyl bonding modes is quite moderate. The equatorial plane shows a very weak tetrahedral distortion with atomic deviations from their mean plane ranging from −0.0122 to 0.012 6 Å, with the Cu atom 0.089 Å out of this plane in the direction of the apical O(1) atom; the angle between the apical bond and the normal to the equatorial plane is 17.0(1)°. The dimensions of the co-ordination polyhedron of the present complex are intermediate between those of structurally analogous *N*-tosyl-glycinate and -valinate(dimer I) derivatives (Table 4). In this series, a trend in structural parameters involving the Cu atom is observed. The lengthening of Cu ··· Cu separation parallels an increase in $\Delta(Cu–O_{eq})$ and a decrease in the O–Cu–O′ angle which may be associated with the increasing tendency of the amino acid side chains to keep one another away; at the same time the lengthening of $Cu–O_{ax}$ bond and the diminishing of O–Cu–O′ angle are suggestive of a lowering in the $Cu–O_{ax}$ bond order.

A comparison of bond distances and angles in tritylglycinate anions with the corresponding ones of tritylglycine methylamide[15] indicates only a significantly greater value of the C(13)–N(3)–C(12) angle [119.1 *vs.* 116.7° calculated from the co-ordinates in ref. 15], possibly due to the minimization of steric hindrance between the two trityl groups without giving rise to steric strain in the Cu_2O_2 ring.

In the bipy ligands the pyridine rings are planar and twisted about the 2,2′ bond by 9.4°; this value is in the range of those found in other bipy complexes.[16]

In the i.r. spectrum the increasing energy of the NH stretching vibration, with respect to the binary complex, is in agreement with the presence of unco-ordinated NH groups in the adduct, while the splitting of the absorption frequencies of the carboxylate group may be explained by their two different binding modes.

The fact that the *d–d* bands [16 800 (sh) and 15 000 cm^{-1}] are at higher energy with respect to the structurally analogous *N*-tosylglycinate complex[14] is in line with a decrease in $Cu–O_{ax}$ bond order in the present complex.

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