Palladium(II) Complexes of *N*-Sulfonylamino Acids. Part 1. Solid-state Behaviour of Binary and Ternary 2,2′-Bipyridine-containing Systems†

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The crystal and molecular structure of the complexes $K_2[Pd(bs\text{-}\alpha\text{-}alaNO)_2]\cdot3.5H_2O$ **1**, [Pd(tsglyNO)(bipy)] **2** and [Pd(bs-β-alaNO)(bipy)]·H_2O **3** were determined by X-ray diffraction (bs-α-alaNO = phenylsulfonyl-DL-α-alaninate dianion; tsglyNO = *N*-*p*-tolylsulfonylglycinate dianion; bipy = 2,2′-bipyridine; bs-β-alaNO = *N*-phenylsulfonyl-β-alaninate dianion). Compound **1** crystallizes in the triclinic space group $P\bar{1}$ with a = 13.457(3), b = 9.855(2), c = 10.739(2) Å, α = 104.0(1), β = 100.8(1), γ = 78.0(1)°, Z = 2. The Pd atom has a square-planar-environment, being *trans* co-ordinated by two centrosymmetrically related ts-α-alaNO dianions acting in a bidentate manner through one carboxylic oxygen and the deprotonated sulfonamide nitrogen. Compound **2** crystallizes in the monoclinic space group $P2_1/c$ with a = 12.210(1), b = 6.897(3), c = 21.449(2) Å, β = 95.55(1)°, Z = 4. Compound **3** crystallizes in the monoclinic space group Pc, with a = 8.320(5), b = 14.403(3), c = 8.477(4) Å, β = 101.81(4), Z = 2. Both complexes contain a Pd^{2+} ion co-ordinated to the N atoms of the bipy molecule and to the deprotonated sulfonamide nitrogen and one carboxylic oxygen of the amino acid molecule in a square-planar geometry. The amino acid dianion forms a five-membered glycine-like chelate ring in **1** and **2**, and a six-membered ring in **3**. Infrared data are also discussed and compared with those of the free ligands and the corresponding binary complexes.

The metal binding properties of peptides and amides in general mainly rely on substitution of the metal for the amide nitrogen-bound hydrogen occurring at pH values much lower than the pK_{NH} of the free ligand. The effectiveness of Pd^{2+} in such a promotion of amide-nitrogen deprotonation is not matched by any other transition-metal ion of biological and pharmacological relevance. Values of pK_{NH} as low as 2 have been observed in binary palladium(II) –peptide systems.[1] We have previously investigated the interaction of Pd^{2+} with RSO_2 N-protected α-amino acids through d.c. polarography and X-ray diffractometry.[2–4] In the range pH 4–11.5 the amino acids invariably bind the metal as bidentate chelate ligands through one carboxylate oxygen and the deprotonated sulfonamide nitrogen generating the species [Pd(LNO)] and $[Pd(LNO)_2]^{2-}$. The stability constants of these complexes are much higher than those of the corresponding species formed by Cu^{2+} and Cd^{2+}, as observed for peptides.[1] Solid compounds of formula $Na_2[Pd(LNO)_2]\cdot xH_2O$ (x = 0, L = tsgly;[2] x = 1, L = bsgly[3])‡ separated from aqueous solutions at pH 6. These species show a *trans*-co-ordinated square-planar metal geometry with an N_2O_2 donor atom set. In both compounds intramolecular contacts with S,O and aromatic C atoms contribute to their remarkable stability.[4]

The Pd^{2+} ion was found to lower the pK value of the sulfonamide nitrogen from about 11.5 for the free ligand to values lower than 4.[4] We have now carried out a detailed study of the low-pH co-ordination behaviour of these systems, including N-protected-β-amino acids and the characterization of the ternary complexes with 2,2′-bipyridine. The possibility that Pd^{2+} induces amide deprotonation in RCON-amino acids has been also considered. The large amount of experimental data will be presented in three papers. The crystal structures of binary and ternary complexes are reported in Part 1, while the solution study of binary and ternary systems is described in Parts 2 and 3, respectively.

Experimental

Preparation of the Complexes.—Solid $Pd(NO_3)_2\cdot2H_2O$ (2.5 mmol) (Fluka) was slowly added to aqueous methanol (4 : 1 v/v, 100 cm^3) solution containing ts-α-ala (10^{-2} mol) at pH 11 with rapid stirring. The pH dropped to 3.5 and it was corrected to 6 with concentrated NaOH. After a few days at room temperature, yellow crystals of $Na_2[Pd(ts\text{-}\alpha\text{-}alaNO)_2]\cdot4H_2O$ separated. The same methodology, applied using concentrated KOH solution instead of NaOH, produced crystals of $K_2[Pd(bs\text{-}\alpha\text{-}alaNO)_2]\cdot3.5H_2O$ **1** suitable for X-ray analysis. Several attempts to separate solid complexes of N-protected β-alanine and of *N*-acetyl, *N*-benzoyl- and *N*-benzyloxycarbonyl-glycine were unsuccessful. The ternary complexes $[Pd(LNO)(bipy)]\cdot xH_2O$ (x = 0, L = tsgly **2** or ts-α-ala) were prepared by adding a methanolic solution (0.01 dm^3) of 2,2′-bipyridine (0.05 mol dm^{-3}) to an aqueous solution (0.02 dm^3) of the corresponding binary complexes (0.025 mmol dm^{-3}). The complexes (x = 1, L = ts- or bs-β-ala, $PhCH_2OCO$- or dns-gly; x = 2, L = PhCO-gly) were prepared by dropping a methanolic aqueous (1 : 1 v/v) solution (0.02 dm^3) of $Pd(NO_3)_2$ and bipy (0.05 mol dm^{-3}) into an alkaline (pH 11) aqueous solution (0.01 dm^3) of the amino acid (0.20 mol dm^{-3}). By evaporating the filtered solutions, yellow solid crystalline

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

‡ Abbreviations: bs = phenylsulfonyl; ts = *p*-tolylsulfonyl (tosyl); dns = 5-dimethylaminonaphthalene-1-sulfonyl(dansyl); gly = glycine; α- or β-ala = DL-α- or β-alanine; LNO = N-protected amino acidate dianion; bipy = 2,2′-bipyridine, R = aliphatic or aromatic residue.

Table 1 Chemical analyses *

Complex	Analysis (%) C	H	N
$Na_2[Pd(ts\text{-}\alpha\text{-}alaNO)_2]\cdot 4H_2O$	33.00 (33.95)	4.40 (4.25)	3.70 (3.95)
$K_2[Pd(bs\text{-}\alpha\text{-}alaNO)_2]\cdot 3.5H_2O$	30.80 (30.75)	3.40 (3.60)	3.75 (4.00)
[Pd(tsglyNO)(bipy)]	46.50 (46.55)	3.45 (3.50)	8.30 (8.60)
$[Pd(bsglyNO)(bipy)]\cdot H_2O$	43.25 (43.75)	3.25 (3.45)	8.40 (8.50)
[Pd(ts-α-alaNO)(bipy)]	47.60 (47.65)	3.85 (3.80)	8.35 (8.35)
$[(Pd(bs\text{-}\alpha\text{-}alaNO)(bipy)]\cdot H_2O$	44.45 (44.90)	3.50 (3.75)	8.05 (8.30)
$[Pd(ts\text{-}\beta\text{-}alaNO)(bipy)]\cdot H_2O$	46.25 (46.00)	3.95 (4.05)	8.35 (8.05)
$[Pd(bs\text{-}\beta\text{-}alaNO)(bipy)]\cdot H_2O$	44.65 (44.90)	3.70 (3.75)	8.20 (8.30)
$[Pd(dnsglyNO)(bipy)]\cdot H_2O$	49.95 (49.00)	4.25 (4.15)	9.55 (9.55)
$[Pd(PhCO\text{-}glyNO)\text{-}(bipy)]\cdot 2H_2O$	48.15 (47.95)	3.75 (4.05)	8.55 (8.85)
$[Pd(PhCH_2OCO\text{-}glyNO)\text{-}(bipy)]\cdot H_2O$	49.35 (49.20)	3.55 (3.95)	8.70 (8.60)

* Calculated values in parentheses.

compounds separated after 1 d at room temperature. Microanalytical data for C, N, H, are given in Table 1.

X-Ray Data Collection and Structure Refinement.—A crystal of complex **1** was mounted in a random orientation on a Philips PW 1100 diffractometer, while crystals of **2** and **3** were mounted on an Enraf-Nonius CAD4 diffractometer. Lattice constants were determined by least-squares refinement of angular setting of 20 reflections for **1** and 25 for **2** and **3**; crystal data are summarized in Table 2.

Intensity data were collected by using Mo-Kα radiation (λ = 0.710 69 Å), with the ω–2θ scan technique. All data were corrected for Lorentz and polarization effects and an empirical absorption correction for complex **1** was applied following Walker and Stuart[8] [absorption correction minimum (maximum) 0.927 (1.069)]. A correction based on ψ scans[9] was applied for the other two crystals [absorption correction minimum (maximum) 0.95 (1.0) for **2** and 0.94 (1.0) for **3**]. The structures were solved by conventional Patterson and Fourier techniques and refined through full-matrix least-squares calculations minimizing $\Sigma w(|F_o| - |F_c|)^2$. Anisotropic refinements were carried out for Pd, K, S, O, C and N atoms; the oxygen atoms of the water molecules in **1** were refined isotropically. The hydrogen atoms in **1** were introduced in the final structure-factor calculation in the calculated positions; in **2** and **3**, hydrogen atoms were located in the ΔF map then treated as fixed contributors. The final refinement for **1** gave an R 0.049 and R' 0.055 using the weighting scheme $w = 0.9555/(\sigma^2 F_o + 0.0019 F_c^2)$; for **2** the final R was 0.026 and $R' = 0.027$ using $w = 0.313/(\sigma^2 F_o + 0.0005\ F_c^2)$; for **3** the final R was 0.039 and $R' = 0.041$ using $w = 1.4692/(\sigma^2 F_o + 0.0002 F_c^2)$. Complex neutral atom scattering factors[10] were used throughout. All calculations for **1** were carried out on a GOULD 32/77 computer of the Centro di Studio per la Strutturistica Diffrattometrica del CNR of Parma, for **2** and **3** on a VAX 6310 computer of the Centro Interdipartimentale di Calcolo of the University of Modena, using SHELX 76,[11] PARST[12] and ORTEP[13] programs. The final fractional coordinates of **1**–**3** are listed in Tables 3–5 respectively.

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

Physical Measurements.—Infrared spectra were recorded with a Bruker 113v-FT-IR instrument as KBr pellets in the range 4000–400 cm^{-1}.

Results and Discussion

The reaction of the Pd^{2+} ion with RSO_2-α-alanines at pH ⩾ 6 yielded two crystalline complexes of formula $M_2[Pd(RSO_2\text{-}\alpha\text{-}$

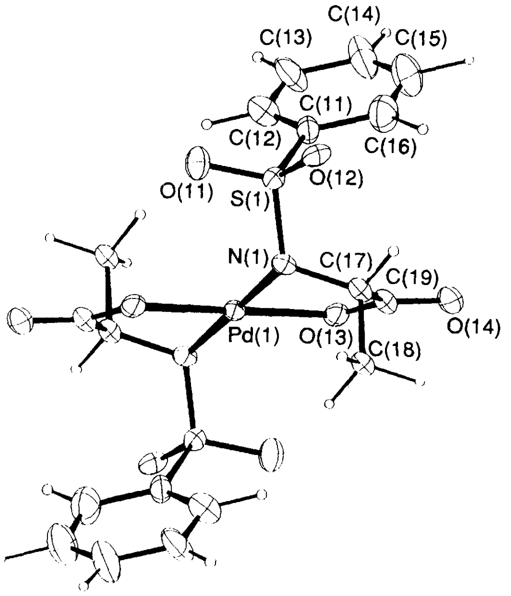

Fig. 1 An ORTEP view of the $[Pd(bs\text{-}\alpha\text{-}alaNO)_2]^{2-}$ anion showing the atom numbering and the thermal ellipsoids (40%) for non-hydrogen atoms

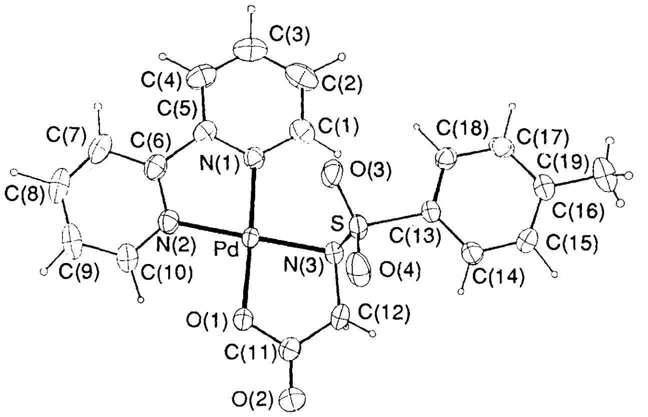

Fig. 2 An ORTEP view of the [Pd(tsglyNO)(bipy)] moiety showing the atom numbering and the thermal ellipsoids (40%) for the non-hydrogen atoms

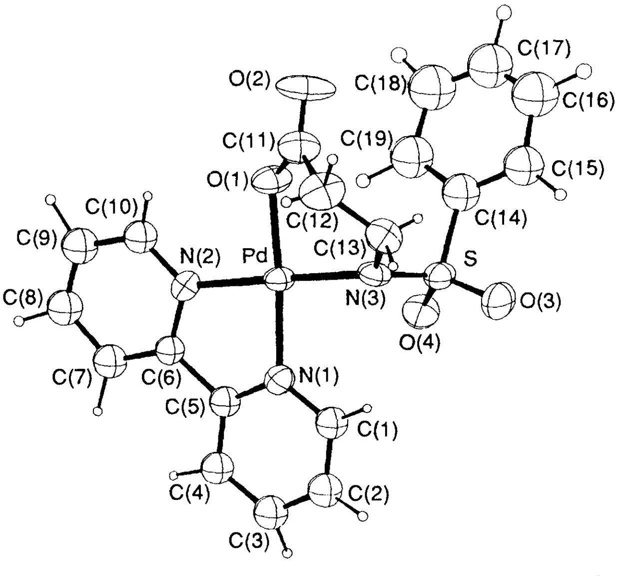

Fig. 3 An ORTEP view of the [Pd(bs-β-alaNO)(bipy)] moiety showing the atom numbering and the thermal ellipsoids (40%) for the non-hydrogen atoms

Table 2 Crystallographic data

Compound	$K_2[Pd(bs\text{-}\alpha\text{-}alaNO)_2]\cdot 3.5H_2O$ **1**	[Pd(tsglyNO)(bipy)] **2**	$[Pd(bs\text{-}\beta\text{-}alaNO)(bipy)]\cdot H_2O$ **3**
Formula	$C_{18}H_{18}K_2N_2O_8PdS_2\cdot 3.5H_2O$	$C_{19}H_{17}N_3O_4PdS$	$C_{19}H_{19}N_3O_5PdS$
M	702.12	489.82	507.84
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	Pc
a/Å	13.457(3)	12.210(1)	8.320(5)
b/Å	9.855(2)	6.897(3)	14.403(3)
c/Å	10.739(2)	21.449(2)	8.477(4)
α/°	104.0(1)		
β/°	100.8(1)	95.55(1)	101.81(4)
γ/°	78.0(1)		
U/Å^3	1337.5(9)	1797.8(8)	994.3(8)
Z	2	4	2
D_c, D_m/g cm^{-3}	1.74, 1.72	1.81, 1.78	1.70, 1.70
$F(000)$	710	984	512
h,k,l range	−14 to 14, −11 to 11, 0–12	−14 to 14, 0–7, 0–24	−9 to 9, 0–17, 0–10
Crystal size/mm	0.32 × 0.32 × 0.42	0.25 × 0.20 × 0.30	0.20 × 0.30 × 0.35
μ(Mo-Kα)/cm^{-1}	12.02	11.61	10.56
θ limits/°	2.5–22	2.5–24	2.5–25
Scan speed/° min^{-1}	3–12	1.7–9.2	1.6–8.2
No. of reflections measured	4244	3171	1973
No. of reflections used in the refinement [$I > 2\sigma(I)$]	3278	2138	1619

Table 3 Final fractional coordinates for $K_2[Pd(bs\text{-}\alpha\text{-}alaNO)_2]\cdot 3.5H_2O$

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Pd(1)	0.5	0.5	0.5	S(2)	0.1338(2)	0.7328(2)	0.0939(2)
K(1)	0.1841(1)	0.0441(2)	0.3595(2)	O(21)	0.1371(5)	0.8810(6)	0.1158(5)
S(1)	0.3963(1)	0.2377(2)	0.3660(2)	O(22)	0.1810(5)	0.6627(7)	0.1987(5)
O(11)	0.3781(4)	0.1031(5)	0.3803(7)	O(23)	−0.0355(3)	0.5497(4)	−0.1747(4)
O(12)	0.3068(4)	0.3366(6)	0.3293(7)	O(24)	−0.0731(4)	0.7301(5)	−0.2737(5)
O(13)	0.6394(3)	0.3796(4)	0.4987(4)	N(2)	0.0175(4)	0.7076(5)	0.0587(5)
O(14)	0.7246(4)	0.1681(5)	0.5183(5)	C(21)	0.1984(5)	0.6520(8)	−0.0387(7)
N(1)	0.4578(4)	0.3128(5)	0.4970(5)	C(22)	0.1949(6)	0.7207(9)	−0.1377(8)
C(11)	0.4704(6)	0.1995(8)	0.2391(7)	C(23)	0.2431(7)	0.6525(11)	−0.2430(9)
C(12)	0.5439(7)	0.0719(9)	0.2242(9)	C(24)	0.2927(8)	0.5146(13)	−0.2545(10)
C(13)	0.6014(8)	0.0484(13)	0.1199(12)	C(25)	0.2984(7)	0.4456(11)	−0.1548(12)
C(14)	0.5906(12)	0.1401(19)	0.0457(12)	C(26)	0.2516(6)	0.5125(10)	−0.0475(9)
C(15)	0.5219(12)	0.2633(16)	0.0615(10)	C(27)	−0.0454(5)	0.7823(6)	−0.0413(6)
C(16)	0.4620(8)	0.2937(10)	0.1589(10)	C(28)	−0.1560(7)	0.8320(8)	−0.0068(8)
C(17)	0.5491(5)	0.2216(7)	0.5524(6)	C(29)	−0.0513(5)	0.6817(7)	−0.1727(7)
C(18)	0.5547(6)	0.2565(8)	0.7026(8)	O(w1)	0.2606(18)	0.1329(22)	0.6201(19)
C(19)	0.6458(5)	0.2557(7)	0.5196(6)	O(w2)	−0.0351(18)	0.2085(26)	0.4519(17)
Pd(2)	0.0	0.5	0.0	O(w3)	0.0	0.5	0.5
K(2)	0.8346(1)	0.4438(2)	0.6032(2)	O(w4)	−0.0668(13)	−0.2468(19)	0.3135(13)

alaNO)$_2$]·xH$_2$O (M = Na$^+$, R = tolyl, x = 4; M = K$^+$, R = phenyl, x = 3.5). For the latter compound the crystal and molecular structure was determined.

Structure of $K_2[Pd(bs\text{-}\alpha\text{-}alaNO)_2]\cdot 3.5H_2O$ **1**.—The structure consists of monomeric units of $[Pd(bs\text{-}\alpha\text{-}alaNO)_2]^{2-}$ anions, potassium ions and lattice water molecules. The unit cell contains two crystallographically independent but structurally equivalent complex molecules. The structure of one of them, with the labelling scheme, is shown in Fig. 1. Selected bond distances and angles are reported in Table 6. In each molecule the Pd atom shows the usual square-planar *trans* co-ordination given by two centrosymmetrically related bs-α-alaNO dianions acting as bidentate ligands through one carboxylate oxygen and the deprotonated sulfonamide nitrogen. Bond distances and angles in the two non-equivalent molecules are strictly similar and close to the values reported for $Na_2[Pd(tsglyNO)_2]$ [2] and $Na_2[Pd(bsglyNO)_2]\cdot H_2O$.[3] Likewise, the four atoms of the chelate rings show comparable deviations from their mean plane in the two molecules, ranging from −0.125 to 0.141 Å for Pd(1) and from −0.104 to 0.120 Å for Pd(2), with Pd(1) and Pd(2) −0.507 and −0.521 Å out of the plane, respectively.

Also in the present complex the Pd atom interacts with the skeleton of the ligand with distances to the sulfonic group and the aromatic ring in the range 3.07–3.55 Å for Pd(1) and 3.11–3.58 Å for Pd(2). The K(1) atom is co-ordinated to five oxygens (2.67–2.79 Å), while K(2) is co-ordinated to six oxygens in a distorted-octahedral geometry (2.62–2.94 Å). Both potassium ions are involved in longer contacts with oxygen atoms up to 3.40 Å, so it appears that the complex molecules are connected within the unit cell by the potassium ions. The crystal packing is completed by other strong contacts formed by water oxygens (2.61–3.15 Å) and by carbon atoms of the phenyl rings belonging to molecule 2 (3.26–3.46 Å).

Crystals of ternary complexes suitable for X-ray analysis were obtained for tsgly and bs-β-ala which form a five- and a six-membered chelate ring, respectively. This allows one to compare the structural features of the two types of metal ligation.

Structures of [Pd(tsglyNO)(bipy)] **2** *and* $[Pd(bs\text{-}\beta\text{-}alaNO)(bipy)]\cdot H_2O$ **3**.—Selected interatomic distances and angles are reported in Table 7 with atom numbering as in Figs 2 and 3. Both structures consist of discrete [Pd(LNO)(bipy)] units with essentially square-planar geometry arising from the N_3O donor atom set. In the bs-β-ala complex the crystal lattice water

Table 4 Final fractional atomic coordinates for [Pd(tsglyNO)(bipy)]

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pd	0.199 94(2)	0.203 20(5)	0.532 59(1)
N(1)	0.275 2(2)	0.200 9(5)	0.453 6(1)
N(2)	0.067 8(3)	0.237 6(5)	0.469 4(2)
C(1)	0.382 8(3)	0.168 0(6)	0.450 9(2)
C(2)	0.429 4(4)	0.163 9(6)	0.394 5(2)
C(3)	0.362 1(4)	0.198 4(7)	0.340 6(2)
C(4)	0.250 8(4)	0.237 1(6)	0.342 7(2)
C(5)	0.209 0(3)	0.233 8(6)	0.400 2(2)
C(6)	0.091 6(3)	0.261 0(6)	0.409 4(2)
C(7)	0.009 8(4)	0.310 5(7)	0.362 6(2)
C(8)	−0.095 4(4)	0.335 7(7)	0.377 9(2)
C(9)	−0.119 8(3)	0.307 9(7)	0.438 6(2)
C(10)	−0.036 2(3)	0.258 7(6)	0.483 2(2)
O(1)	0.117 2(2)	0.194 5(5)	0.608 2(1)
O(2)	0.137 3(3)	0.113 1(7)	0.708 6(1)
C(11)	0.174 6(3)	0.134 6(7)	0.658 8(2)
C(12)	0.294 3(3)	0.083 1(7)	0.650 7(2)
N(3)	0.333 1(3)	0.183 1(5)	0.595 9(2)
S	0.390 13(7)	0.390 8(2)	0.612 14(4)
O(3)	0.384 3(2)	0.501 7(4)	0.555 1(1)
O(4)	0.349 8(2)	0.480 8(5)	0.666 4(1)
C(13)	0.530 7(3)	0.337 9(5)	0.633 4(2)
C(14)	0.568 8(3)	0.302 5(7)	0.695 5(2)
C(15)	0.678 2(3)	0.262 3(7)	0.711 4(2)
C(16)	0.753 2(3)	0.258 2(6)	0.666 8(2)
C(17)	0.713 5(3)	0.292 5(7)	0.604 6(2)
C(18)	0.603 3(3)	0.333 4(6)	0.587 7(2)
C(19)	0.872 6(4)	0.219 6(8)	0.685 3(3)

Table 5 Final fractional atomic coordinates for [Pd(bs-β-alaNO)(bipy)]·H_2O

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pd	0.0	0.188 67(4)	0.0
N(1)	0.003(1)	0.049 3(5)	0.033(1)
N(2)	−0.207(1)	0.156 7(7)	−0.154(1)
C(1)	0.119(1)	0.002 5(8)	0.138(1)
C(2)	0.111(1)	−0.094 4(8)	0.143(2)
C(3)	−0.006(2)	−0.142 6(7)	0.039(1)
C(4)	−0.125(1)	−0.093 3(7)	−0.070(1)
C(5)	−0.113(1)	0.003 3(8)	−0.069(1)
C(6)	−0.238(1)	0.061 9(7)	−0.174(1)
C(7)	−0.366(1)	0.029 5(7)	−0.287(1)
C(8)	−0.466(1)	0.092 3(8)	−0.384(1)
C(9)	−0.438(1)	0.186 0(8)	−0.361(2)
C(10)	−0.309(1)	0.216 1(8)	−0.245(1)
O(1)	−0.021(1)	0.322 4(5)	−0.056 2(9)
O(2)	0.038(2)	0.467 2(5)	0.014(2)
C(11)	0.025(2)	0.387 0(8)	0.050(1)
C(12)	0.058(2)	0.356 6(8)	0.228(2)
C(13)	0.211(1)	0.294 5(8)	0.274(1)
N(3)	0.210(1)	0.218 1(6)	0.161(1)
S	0.382 2(3)	0.199 1(2)	0.110 2(3)
O(3)	0.506(1)	0.184 4(5)	0.255(1)
O(4)	0.360(1)	0.125 2(5)	−0.007(1)
C(14)	0.442(1)	0.300 8(8)	0.020(2)
C(15)	0.581(2)	0.348(1)	0.099(2)
C(16)	0.614(2)	0.435(2)	0.013(3)
C(17)	0.521(3)	0.456(1)	−0.116(3)
C(18)	0.393(3)	0.413(2)	−0.200(3)
C(19)	0.342(2)	0.327(1)	−0.135(2)
O(w)	−0.055(1)	0.361 1(8)	−0.393(1)

Table 6 Selected bond distances (Å) and angles (°) for K_2[Pd(bs-α-alaNO)$_2$]·3.5H_2O

Pd(1)–N(1)	2.031(6)	Pd(2)–N(2)	2.039(5)
Pd(1)–O(13)	2.001(4)	Pd(2)–O(23)	2.000(5)
O(13)–C(19)	1.277(8)	O(23)–C(29)	1.269(8)
O(14)–C(19)	1.220(8)	O(24)–C(29)	1.250(10)
C(17)–C(19)	1.530(11)	C(27)–C(29)	1.515(9)
N(1)–S(1)	1.589(5)	N(2)–S(2)	1.596(6)
S(1)–O(11)	1.446(6)	S(2)–O(21)	1.431(6)
S(1)–O(12)	1.441(6)	S(2)–O(22)	1.440(7)
S(1)–C(11)	1.760(9)	S(2)–C(21)	1.745(8)
O(13)–Pd(1)–N(1)	82.4(4)	O(23)–Pd(2)–N(2)	82.7(2)
O(13)–Pd(1)–N(1′)	97.6(4)	O(23)–Pd(2)–N(2′)	97.3(4)
O(13)–C(19)–O(14)	123.3(9)	O(23)–C(29)–O(24)	122.6(7)
Pd(1)–N(1)–C(17)	107.5(6)	Pd(2)–N(2)–C(27)	106.8(4)
Pd(1)–O(13)–C(19)	115.3(6)	Pd(2)–O(23)–C(29)	114.7(4)
Pd(1)–N(1)–S(1)	117.6(4)	Pd(2)–N(2)–S(2)	114.8(4)
S(1)–N(1)–C(17)	115.3(5)	S(2)–N(2)–C(27)	114.5(6)
N(1)–C(17)–C(19)	109.1(6)	N(2)–C(27)–C(29)	110.0(6)
O(13)–C(19)–C(17)	116.5(8)	O(23)–C(29)–C(27)	117.5(7)
O(14)–C(19)–C(17)	120.1(8)	O(24)–C(29)–C(27)	119.8(7)

Primed atoms are related by the symmetry operation $-x, -y, -z$.

Table 7 Selected bond distances (Å) and angles (°) for: [Pd(tsglyNO)(bipy)] **2** and [Pd(bs-β-alaNO)]·H_2O **3**

2		**3**	
Pd–N(1)	2.004(3)	Pd–N(1)	2.026(7)
Pd–N(2)	2.018(3)	Pd–N(2)	1.992(8)
Pd–N(3)	2.020(3)	Pd–N(3)	2.030(8)
Pd–O(1)	1.993(3)	Pd–O(1)	1.984(7)
C(12)–N(3)	1.479(5)	C(13)–N(3)	1.46(1)
N(3)–S	1.616(4)	N(3)–S	1.60(1)
S–O(3)	1.439(3)	S–O(3)	1.447(9)
S–O(4)	1.446(3)	S–O(4)	1.443(8)
S–C(13)	1.771(3)	S–C(14)	1.77(1)
N(1)–Pd–O(1)	176.2(1)	N(1)–Pd–O(1)	173.3(3)
N(2)–Pd–N(3)	177.2(1)	N(2)–Pd–N(3)	178.4(4)
O(1)–Pd–N(3)	83.6(1)	O(1)–Pd–N(3)	88.9(3)
N(2)–Pd–O(1)	96.6(1)	N(2)–Pd–O(1)	92.5(4)
N(1)–Pd–N(3)	99.4(1)	N(1)–Pd–N(3)	97.5(4)
N(1)–Pd–N(2)	80.5(1)	N(1)–Pd–N(2)	81.1(4)
Pd–O(1)–C(11)	114.5(2)	Pd–O(1)–C(11)	121.9(7)
Pd–N(1)–C(1)	124.7(3)	Pd–N(1)–C(1)	124.8(7)
Pd–N(1)–C(5)	115.4(2)	Pd–N(1)–C(5)	114.6(7)
Pd–N(2)–C(10)	125.3(3)	Pd–N(2)–C(10)	126.4(8)
Pd–N(2)–C(6)	114.8(2)	Pd–N(2)–C(6)	114.7(7)
Pd–N(3)–C(12)	105.5(2)	Pd–N(3)–C(13)	119.0(7)
Pd–N(3)–S	112.7(2)	Pd–N(3)–S	118.7(5)
C(12)–N(3)–S	114.0(3)	C(13)–N(3)–S	115.0(8)
O(1)–C(11)–O(2)	123.8(4)	O(1)–C(11)–O(2)	123(1)
O(2)–C(11)–C(12)	121.2(4)	O(2)–C(11)–C(12)	121(1)
O(1)–C(11)–C(12)	114.9(3)	O(1)–C(11)–C(12)	116(1)

molecules complete the unit-cell content. In both complexes the Pd^{2+} ion is co-ordinated to the bipy molecule and the chelating amino acid dianion. The latter ligand forms the normal five-membered glycine-like chelate ring in the tsgly adduct, and a six-membered ring in the bs-β-ala species. Bond distances and angles are similar in both complexes and comparable with the mean literature values [mean distances in the present complexes Pd–N_{sulf} 2.025(8), Pd–O_{carbox} 1.988(7), Pd–N_{bipy} 2.010(8) Å; mean literature distances Pd-N_{sulf} 2.037(4), Pd-O_{carbox} 1.994(4),[2,3] Pd-N_{bipy} 2.02(1) Å[14–16]]. The two complexes show a weak tetrahedral distortion which can be described by the deviations of the atoms from their mean least-squares co-ordination plane (in **2** the deviations range from −0.05 to +0.05, and in **3** from −0.02 to +0.03 Å) with the metal ion lying nearly on the plane.

The main structural differences between complexes **2** and **3** are ascribed to their different chelate ring sizes. In the tsgly adduct the angle internal to the chelate amino acidic ring O(1)–Pd–N(3) falls in the range (80.6–84.6°), also observed in **1** and other complexes of this class of ligand,[2,3,5,17–21] because of the constraints due to the geometry of the amino acid skeleton. In the bs-β-ala adduct, this angle significantly increases according

Table 8 Selected IR bands (cm^{-1}) and tentative assignments

Compound	$\nu(OH)_w$	$\nu_{asym}(CO_2)$	$\nu_{sym}(CO_2)$	$\nu_{asym}(SO_2)$	$\nu_{sym}(SO_2)$	$\nu(SN)$
$Na_2[Pd(ts\text{-}\alpha\text{-}alaNO)_2]\cdot 4H_2O$	3520s(br) 3450s(br)	1620vs	1365vs	1275vs 1264vs	1143vs	990s
$K_2[Pd(bs\text{-}\alpha\text{-}alaNO)_2]\cdot 3.5H_2O$	3500s(br)	1626vs	1380s	1284vs	1150vs	1012s
[Pd(tsglyNO)(bipy)]		1660vs	1319vs 1310vs	1281vs	1137vs	902s
$[Pd(bsglyNO)(bipy)]\cdot H_2O$	3555ms 3350m	1643vs	1357vs	1266vs	1136vs 1115s	909vs
[Pd(ts-α-alaNO)(bipy)]		1659vs	1323s	1275vs	1136vs	969vs
$[Pd(bs\text{-}\alpha\text{-}alaNO)(bipy)]\cdot H_2O$	3350ms 3430ms	1655vs	1340s	1265vs	1140vs 1135vs	970s
$[Pd(ts\text{-}\beta\text{-}alaNO)(bipy)]\cdot H_2O$	3500(sh) 3427m(br)	1647s	1384vs 1375s	1272s 1262vs	1136vs	920m
$[Pd(bs\text{-}\beta\text{-}alaNO)(bipy)]\cdot H_2O$	3498s 3443ms	1669vs	1367vs	1272vs	1139vs	955s
$[Pd(dnsglyNO)(bipy)]\cdot H_2O$	3505(sh) 3450ms(br)	1666vs	1385vs	1287s 1265vs[a]	1122s 1117vs	866vs
$[Pd(PhCO\text{-}glyNO)(bipy)]\cdot 2H_2O$	3422ms 3369s	1643vs	1385vs	1538vs		
$[Pd(PhCH_2OCO\text{-}glyNO)(bipy)]\cdot H_2O$	3400m(br)	1638vs, 1665(sh)[b]	1395s, 1385s, 1300vs, 1287s[c]			

[a] $\nu(CO)_{amide}$. [b] $\nu_{asym}(CO_2)_{carbox} + \nu_{asym}(CO_2)_{ester}$. [c] $\nu_{sym}(CO_2)_{carbox} + \nu_{sym}(CO_2)_{ester}$.

to the greater flexibility of the six-membered ring, and is well within the range previously observed in complexes of β-amino acids [90(1)–92(1)°].[22] Another meaningful difference concerns the sum of the angles involving the N(3) atom: in **3** it coincides with the mean literature value[3,5,17,20,21] [352.7(8)° in our complex *vs.* 352.8(4)°], while in **2** it is much smaller [332.2(3)°], indicating a great degree of distortion from the sp^2 hybridization of the sulfonamide nitrogen.

Both complexes are characterized by short intramolecular contacts of the Pd^{2+} ion with S, O and C atoms (3.03–3.05 and 2.89–3.14 Å in **2** and **3** respectively) which can contribute to their remarkable stability (see Part 3), possibly contributing to a homogeneous charge distribution. In **3** the flexibility of the six-membered ring allows the formation of intramolecular contacts of atoms of bipy with those of the amino acid [N(1) ··· N(3) 3.05, N(2) ··· O(1) 2.87 Å], in so doing favouring conjugation of the π-orbital systems of the ligands.

Bond distances and angles within the ligands are similar and both complexes have a S–N distance close to the value found in the free amino acid and in carboxylate complexes.[18,20,23,24] Furthermore, the C–O bond lengths of the carboxylate group are similar to those of CO$_2$H.

In complex **2** the crystal packing is determined by stacking interactions involving nearly coplanar bipy and phenyl rings [dihedral angle = 2.7(1)°], alternating along the *b* axis with distances in the range 3.40–3.75 Å. In **3** the stacking interactions involve the bipy molecules of different units with distances in the range 3.45–3.85 Å; the packing is completed by the contact of a water oxygen with an unco-ordinated O(2) atom [O(w) ··· O(2) 2.75 Å].

The IR spectra (Table 8) of the ternary palladium(II) complexes are compared to those of the free ligands, their alkali metal salts and of the corresponding binary complexes. All the hydrated compounds show two intense bands in the region 3600–3350 cm^{-1}, assigned to asymmetric and symmetric O–H stretching of the water molecules. No bands are observed in the range 3345–3250 cm^{-1}, where the vibration of the N–H group in the free ligands is normally located, thus confirming deprotonation of the nitrogen atom in the bipy adducts of the RSO$_2$ and in RCO N-protected amino acids.

A distinct feature of the structurally known complex **2** is the shift of both ν(CO$_2$) toward the values typical of the neutral CO$_2$H group, in agreement with the significant difference between the C–O bond lengths. A similar behaviour is observed for the anhydrous complex [Pd(ts-α-alaNO)(bipy)]. In complex **3**, although the C–O distances are nearly coincident with those of **2**, the formation of a short contact with the water oxygen moves the stretching vibrations of the carboxyl group to the values normally found for its ionized form. Another interesting feature of the IR spectra of **2** and **3** is the position of ν(SN): while in general the deprotonation of sulfonamide nitrogen diminishes the S–N distance (from ≈1.62[18,23,24] to ≈1.58 Å[2,3,5,17–21]), and this process is accompanied by a marked shift of ν(SN) to higher energy (from 800–900 to 960–1010 cm^{-1}), in these complexes we observe a S–N distance close to that of the free ligands and this finding can justify the moderate shift of ν(SN). A similar behaviour is observed for all the other bipy adducts. The position of the vibrations of the sulfonyl group is typical of an RSO$_2$ amino acidate dianion.[17,18]

For the PhCO- and PhCH$_2$OCO-glycine adducts, the presence of the amino acid in the dianionic form co-ordinated through the peptide nitrogen is indicated by the lack of ν(NH). In the former adduct this is also confirmed by the appearance of a new intense band at 1538 cm^{-1}, attributed to the carbonyl group of the ligand (in complexes of Cu^{2+} with nitrogen-deprotonated peptides, the carbonyl stretching similarly shifts toward low energy, from 1660 cm^{-1} for the free peptide to 1600 cm^{-1}),[25] and in the latter by a shift of the ν(CO$_2$) of the ester group which overlaps those of the carboxyl group.

These results suggest the following conclusions: (*i*) In the binary systems only RSO$_2$-α-amino acids which form five-membered chelate rings yield solid compounds. (*ii*) In the ternary systems, in the presence of bipy as a primary ligating group, the adducts of α- and β-amino acids are all easily separated, no matter what the type of chelate ring formed. (*iii*) In all binary and ternary complexes the co-ordination geometry around the metal ion is essentially square planar and the metal ion forms intramolecular contacts with the amino acid ligand which can contribute to the remarkable stability of the complexes. (*iv*) The greater effectiveness of Pd^{2+} in promoting sulfonamide and amide nitrogen deprotonation with respect to Cu^{2+}, Cd^{2+} and Zn^{2+} is confirmed by its ability to deprotonate also RCO glycines, although only in ternary systems with 2,2′-bipyridine.

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