Deprotonated Amide Nitrogen Co-ordination to the Cadmium(II) Ion in Ternary 2,2′-Bipyridine Complexes with *N*-Sulfonyl Amino Acids[†]

Anna Bonamartini Corradi,[*,a] **Ledi Menabue, Monica Saladini,**[a] **Marco Sola**[a] **and Luigi P. Battaglia**[b]

[a] *Dipartimento di Chimica, University of Modena, Via Campi, 183, 41100 Modena, Italy*

[b] *Istituto di Chimica Generale e Inorganica, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., University of Parma, Viale delle Scienze, 43100 Parma, Italy*

A solid-state investigation of cadmium(II) and zinc(II) ternary 2,2′-bipyridine (bipy), complexes of *N*-(benzenesulfonyl)glycine (bsgly) and *N*-(toluene-*p*-sulfonyl)glycine (tsgly) is presented. The crystal structure of $[\{Cd(bipy)(tsglyO)_2\}_2]$ **1**, separated from preparations at pH 7, and of $[\{Cd(bipy)(bsglyNO)\}_4]\cdot 8H_2O$ **2** separated at pH 11 are described. Complex **1** crystallizes in the triclinic space group $P\bar{1}$, $Z = 2$, $a = 10.474(10)$, $b = 15.902(3)$, $c = 18.202(9)$ Å, $\alpha = 98.49(2)$, $\beta = 91.17(5)$ and $\gamma = 98.31(3)°$. The structure consists of dimeric units in which the cadmium atoms are bridged by two carboxylic oxygens. Metal co-ordination is *via* the two nitrogens of a bipy molecule and four carboxylate oxygens from the amino acid monoanion. A long Cd$\cdots$O contact completes seven co-ordination. The final *R* index was 0.0509. Complex **2** crystallizes in the monoclinic space group $P2_1/c$, $Z = 4$, $a = 12.525(5)$, $b = 15.251(4)$, $c = 21.717(3)$ Å and $\beta = 92.36(3)°$. The structure is built up of tetrameric units in which the cadmium atoms are joined by monoatomic bridging carboxylic oxygens. Each cadmium is six-co-ordinated through bipy nitrogens and sulfonamide nitrogen and carboxylate oxygen of the amino acid molecules. The final *R* index was 0.0398. Infrared data for the homologous zinc(II) complexes, very similar to those of the above derivatives, indicate that zinc is also able to promote sulfonamide nitrogen deprotonation in these amino acid ligands in the solid state.

N-sulfonyl amino acids display a characteristic pH-dependent metal binding mode toward a number of dipositive metals, including Pd^{2+}, Cu^{2+} and Cd^{2+}, switching from a carboxylate-type co-ordination at low pH to an N,O-bidentate co-ordination (*via* a carboxylate oxygen and a deprotonated sulfonamide nitrogen) at higher pH.[1] In ternary systems M–bipy–L, where M = Zn^{2+} or Cd^{2+}, bipy = 2,2′-bipyridine and L = *N*-(benzenesulfonyl)glycine (bsgly) or *N*-(toluene-*p*-sulfonyl)glycine (*N*-tosylglycine, tsgly) the additional ligand 2,2′-bipyridine was found to lower the pK_a of cadmium(II)-promoted sulfonamide-nitrogen deprotonation of the amino acid ligand (from 8 in the binary systems to 7.6) and to enable the zinc(II) ion, ineffective as a promoter of amide deprotonation in the corresponding binary systems, to substitute for the sulfonamide nitrogen-bound hydrogen with a pK_a of about 7.5.[1] Knowledge of the most favourable conditions in terms of pH range and ligand-to-metal molar ratio for the formation of carboxylate and nitrogen-deprotonated ternary complexes allowed us to separate the corresponding complexes in the solid state. Herein we describe the crystal and molecular structures of $[\{Cd(bipy)(tsglyO)_2\}_2]$ **1** and $[Cd(bipy)(bsglyNO)\}_4]\cdot 8H_2O$ **2**, and compare solution and solid-state data.

Experimental

Preparation of the Complexes.—Complexes of empirical formula $M(bipy)(LO)_2$ (M = Cd^{2+} or Zn^{2+}, LO = monoanion of tsgly or bsgly) were prepared by adding a methanolic solution (6 cm^3) of 2,2′-bipyridine (0.01 mol dm^{-3}) to an aqueous solution (60 cm^3) of the corresponding binary complexes (0.001 mol dm^{-3}) obtained as described in refs. 2 and 3. Colourless crystals separated after a few days. By adding NaOH up to pH 11, compounds of formula $M(bipy)(LNO)\cdot xH_2O$ separated (x = 1 for M = Zn^{2+}, L = bsgly or M = Cd^{2+}, L = tsgly; x = 2 for M = Cd^{2+}, L = bsgly and x = 3 for M = Zn^{2+}, L = tsgly; LNO = dianion of amino acid).

Microanalytical data are given in Table 1.

Table 1 Chemical analyses (%)*

Compound	C	N	H
$[Zn(bsglyO)_2]\cdot 4H_2O$	33.50	5.05	4.35
	(33.95)	(4.95)	(4.30)
$[Cd(bsglyO)_2]\cdot 4H_2O$	31.50	4.80	4.10
	(31.35)	(4.55)	(3.95)
$[Cd(bsglyNO)]\cdot H_2O$	28.05	3.90	2.70
	(27.95)	(4.10)	(2.65)
$[Zn(bipy)(tsglyO)_2]$	49.50	8.15	4.25
	(49.55)	(8.25)	(4.15)
$[Zn(bipy)(bsglyO)_2]$	48.75	8.65	3.75
	(48.05)	(8.60)	(3.70)
$[\{Cd(bipy)(tsglyO)_2\}_2]$	46.50	7.75	3.85
	(46.35)	(7.75)	(3.90)
$[Cd(bipy)(bsglyO)_2]$	44.90	8.10	3.55
	(44.80)	(8.05)	(3.45)
$[Zn(bipy)(tsglyNO)]\cdot 3H_2O$	44.35	8.30	4.45
	(45.35)	(8.35)	(4.60)
$[Zn(bipy)(bsglyNO)]\cdot H_2O$	47.55	9.15	3.70
	(47.70)	(9.30)	(3.80)
$[Cd(bipy)(tsglyNO)]\cdot H_2O$	44.45	8.10	3.60
	(44.40)	(8.20)	(3.75)
$[\{Cd(bipy)(bsglyNO)\}_4]\cdot 8H_2O$	41.75	8.05	3.20
	(41.75)	(8.10)	(3.70)

* Required values are given in parentheses.

[†] *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 2 Experimental data for the crystallographic analyses

	[{Cd(bipy)(tsglyO)$_2$}$_2$] **1**	[{Cd(bipy)(bsglyNO)}$_4$]·8H$_2$O **2**
Formula	$C_{56}H_{56}Cd_2N_8O_{16}S_4$	$C_{72}H_{76}Cd_4N_{12}O_{24}S_4$
M	1450.14	2071.30
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a/Å	10.474(10)	12.525(5)
b/Å	15.902(3)	15.251(4)
c/Å	18.202(9)	21.717(3)
α/°	98.49(2)	90
β/°	91.17(5)	92.36(3)
γ/°	98.31(3)	90
U/Å^3	2964(2)	4126(2)
Z	2	2
D_c, D_m/g cm^{-3}	1.62, 1.60	1.67, 1.65
F(000)	1472	2080
h,k,l range	−11 to 11, −16 to 16, 0–19	−12 to 12, 0–15, 0–21
Crystal size/mm	0.05 × 0.15 × 0.20	0.23 × 0.23 × 0.28
μ/cm^{-1}	9.22	11.89
θ limits/°	2.5–22.0	3.0–21.0
No. of reflections measured	7546	2738
No. of reflections used in the refinement [$I > 2\sigma(I)$]	5606	2638
R	0.0509	0.0398
R′	0.0561	0.0429

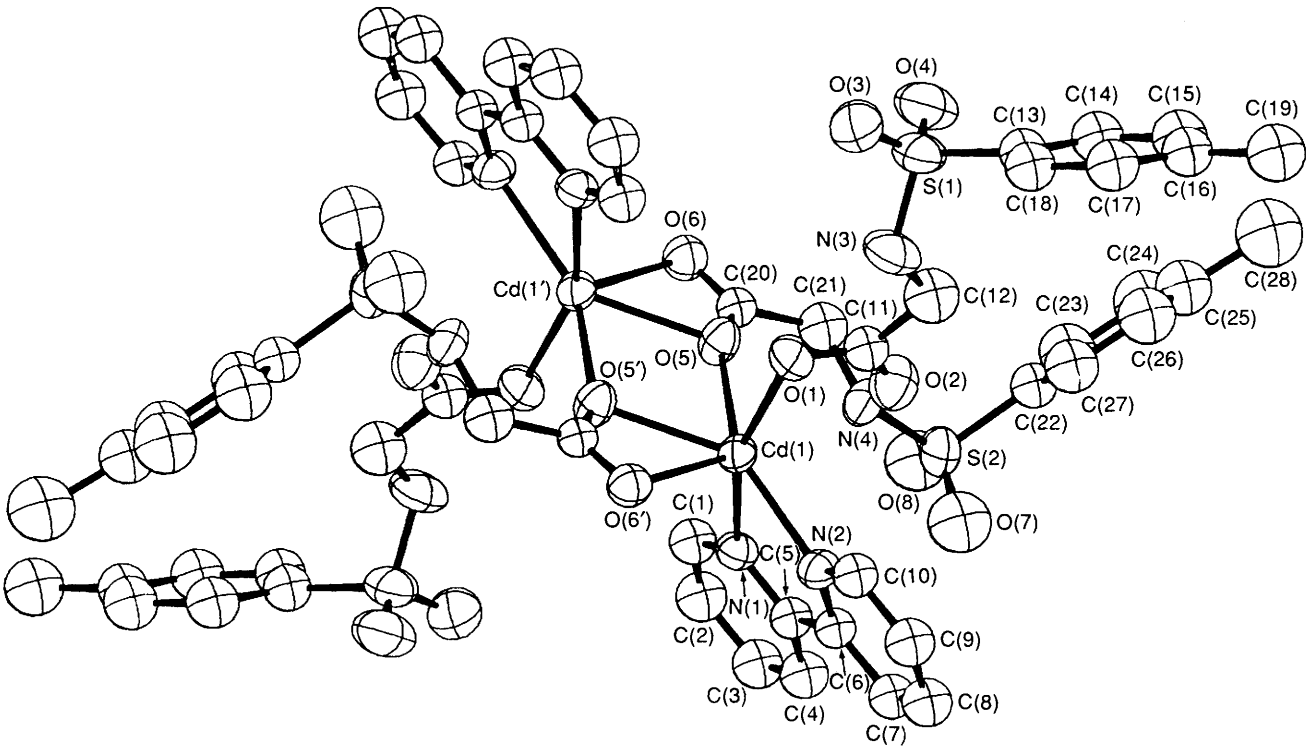

Fig. 1 An ORTEP view of [{Cd(bipy)(tsglyO)$_2$}$_2$][Cd(1) dimer] showing the atom numbering and the thermal motion ellipsoids (40%); hydrogen atoms are omitted for clarity

X-Ray Data Collection and Structure Refinement.—Single crystals of **1** suitable for X-ray analysis, proved very difficult to grow, mainly because of their small thickness.

For both compounds the structure was determined on an Enraf–Nonius CAD4 single-crystal diffractometer. Lattice constants were determined by least-squares refinement of the angular setting of 25 and 20 reflections for **1** and **2**, respectively. Crystal data details 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 in the θ range 2.5–22° with scan speeds of 1.64–5.41° min^{-1} for **1**, and θ range 3.0–21° with scan speeds 0.82–2.75° min^{-1} for **2**. All data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied based on ψ scans[4] [absorption correction min. (max.) 0.928 (0.999)] for **1** and following Walker and Stuart[5] [absorption correction min. (max.) 0.988 (1.040)] for **2**. The space group $P\bar{1}$ for **1** was assumed and confirmed by structure analysis.

The structures were 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. For **1** anisotropic refinement was carried out for Cd, S, O and N

Table 3 Fractional atomic coordinates (× 10⁵ for Cd, × 10⁴ for other atoms) for complex **1**

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Cd(1)	17 158(5)	5 249(4)	53 318(3)	Cd(2)	35 961(5)	5 953(4)	3 226(3)
N(1)	2 677(6)	324(4)	4 204(3)	N(5)	2 422(6)	315(4)	−771(3)
N(2)	3 904(6)	972(4)	5 523(4)	N(6)	1 684(6)	1 133(4)	515(4)
C(1)	2 052(8)	−32(6)	3 568(5)	C(29)	2 833(8)	−75(6)	−1 406(5)
C(2)	2 618(9)	−54(6)	2 894(5)	C(30)	2 200(9)	−139(6)	−2 075(6)
C(3)	3 882(9)	308(6)	2 875(5)	C(31)	1 061(10)	200(7)	−2 094(6)
C(4)	4 548(9)	682(6)	3 526(5)	C(32)	616(9)	585(6)	−1 452(5)
C(5)	3 926(7)	664(5)	4 200(4)	C(33)	1 297(7)	648(5)	−789(4)
C(6)	4 597(7)	1 012(5)	4 920(4)	C(34)	886(7)	1 070(5)	−80(4)
C(7)	5 921(8)	1 365(6)	4 997(5)	C(35)	−292(9)	1 376(6)	−7(5)
C(8)	6 469(9)	1 638(6)	5 686(5)	C(36)	−622(10)	1 744(6)	695(6)
C(9)	5 754(9)	1 596(6)	6 301(5)	C(37)	209(10)	1 831(6)	1 282(6)
C(10)	4 461(8)	1 259(5)	6 206(5)	C(38)	1 371(9)	1 506(6)	1 181(5)
O(1)	1 067(5)	1 236(4)	6 397(3)	O(9)	4 652(6)	1 315(4)	1 362(3)
O(2)	1 709(6)	2 206(4)	5 687(4)	O(10)	4 660(7)	2 296(5)	617(3)
C(11)	1 312(8)	1 992(6)	6 280(5)	C(39)	4 964(9)	2 053(6)	1 223(6)
C(12)	1 163(10)	2 722(7)	6 891(6)	C(40)	5 768(10)	2 731(7)	1 777(6)
N(3)	602(7)	2 414(5)	7 563(4)	N(7)	5 954(8)	2 393(5)	2 467(5)
S(1)	−455(2)	2 914(2)	7 997(2)	S(3)	7 048(3)	2 995(2)	3 046(2)
O(3)	−1 291(6)	3 147(5)	7 462(4)	O(11)	8 187(7)	3 159(5)	2 656(5)
O(4)	−974(7)	2 347(4)	8 514(4)	O(12)	7 082(8)	2 594(5)	3 682(4)
C(13)	297(8)	3 873(6)	8 533(5)	C(41)	6 486(8)	3 978(5)	3 281(5)
C(14)	389(9)	4 643(6)	8 271(6)	C(42)	6 831(10)	4 644(7)	2 887(6)
C(15)	992(10)	5 399(7)	8 690(6)	C(43)	6 310(11)	5 414(7)	3 066(6)
C(16)	1 516(9)	5 383(6)	9 389(5)	C(44)	5 479(10)	5 507(7)	3 623(6)
C(17)	1 404(9)	4 614(6)	9 652(5)	C(45)	5 103(10)	4 817(8)	3 981(7)
C(18)	812(9)	3 851(6)	9 225(5)	C(46)	5 593(10)	4 061(7)	3 832(6)
C(19)	2 197(11)	6 203(7)	9 851(6)	C(47)	4 963(13)	6 355(9)	3 842(8)
O(5)	−232(8)	703(3)	4 674(3)	O(13)	5 506(5)	676(4)	−352(3)
O(6)	−1 878(5)	652(3)	3 919(3)	O(14)	7 120(5)	552(4)	−1 072(3)
C(20)	−808(8)	995(5)	4 177(4)	C(48)	6 227(7)	923(5)	−850(4)
C(21)	−166(9)	1 800(6)	3 894(5)	C(49)	5 992(9)	1 713(6)	−1 173(5)
N(4)	1 199(6)	1 972(4)	4 108(4)	N(8)	4 824(6)	2 037(4)	−921(4)
S(2)	2 151(3)	2 601(2)	3 680(2)	S(4)	4 061(2)	2 551(2)	−1 435(1)
O(7)	3 394(8)	2 565(5)	3 977(5)	O(15)	4 039(7)	2 127(5)	−2 182(4)
O(8)	1 850(8)	2 399(5)	2 905(5)	O(16)	2 881(6)	2 655(4)	−1 078(5)
C(22)	1 830(8)	3 657(5)	3 963(5)	C(50)	4 941(8)	3 586(5)	−1 427(5)
C(23)	1 349(10)	4 107(7)	3 470(6)	C(51)	6 010(9)	3 665(6)	−1 859(5)
C(24)	1 154(12)	4 971(8)	3 719(7)	C(52)	6 723(10)	4 496(7)	−1 856(6)
C(25)	1 443(10)	5 326(7)	4 425(6)	C(53)	6 347(9)	5 207(6)	−1 425(5)
C(26)	1 833(10)	4 863(7)	4 918(6)	C(54)	5 274(9)	5 101(6)	−1 009(5)
C(27)	2 048(10)	4 021(7)	4 690(6)	C(55)	4 589(9)	4 307(6)	−1 008(5)
C(28)	1 251(13)	6 278(9)	4 669(8)	C(56)	7 148(12)	6 087(8)	−1 441(7)

atoms, while C atoms, O(7), O(8) and N(7) were refined isotropically. For **2**, Cd, S, O and N atoms were refined anisotropically, while carbon atoms and water oxygen were refined isotropically. In particular, two water oxygens O(W4) and O(W5), were introduced with a population of 0.5. For **1** a subsequent ΔF map provides the position of 32 hydrogen atoms which were treated as fixed contributors along with the remaining hydrogen atoms fixed in their calculated positions. For **2**, hydrogen atoms, except those of the water molecules, were located in a ΔF map and introduced in the final structure factor calculation. The final refinement of **1** gives an *R* index of 0.0509 and an *R′* value of 0.0561 using the weighting scheme $w = 3.323/(\sigma^2F_o + 0.0007F_c)$. An attempt to refine the model in the non-centric space group *P*1, provided no significant improvement, and hence the modest agreement factor was interpreted as due to the poor quality of the crystal. For **2** the final *R* index was 0.0398 and $R' = 0.0429$ using the weighting scheme $w = 0.2869/(\sigma^2F_o + 0.0002F_c^2)$. Complex neutral-atom scattering factors[6] were used throughout; all calculations were carried out on a Vax 6310 computer of the Centro Interdipartimentale di Calcolo of the University of Modena and on a GOULD 32/77 of the Centro di Studio per la Strutturistica Diffrattometrica del CNR, University of Parma, using SHELX 76,[7] PARST[8] and ORTEP[9] programs.

The final fractional coordinates for non-hydrogen atoms of **1** and **2** are listed in Tables 3 and 4, 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-instrument as KBr pellets in the spectral range of 4000–400 cm^{-1}.

Results

Two types of complexes, $[\mathrm{M(bipy)(LO)_2}]$ (type A) and $[\mathrm{M(bipy)(LNO)}]\cdot x\mathrm{H_2O}$ (type B), where M = $\mathrm{Cd^{2+}}$ or $\mathrm{Zn^{2+}}$, were separated in the solid state from the preparations at pH's of *ca.* 7 and 11, respectively.

Only the crystals of the cadmium complexes $[\{\mathrm{Cd(bipy)(tsglyO)_2}\}_2]$ **1** and $[\{\mathrm{Cd(bipy)(bsglyNO)}\}_4]\cdot 8\mathrm{H_2O}$ **2** were found to be suitable for X-ray structure determination.

Type A Complexes.—Description of the structure of $[\{\mathrm{Cd(bipy)(tsglyO)_2}\}_2]$. Selected interatomic distances are reported in Table 5 with atom numbering as in Fig. 1. The structure consists of two crystallographically independent but structurally similar dimeric symmetry-generated $[\{\mathrm{Cd(bipy)(tsglyO)_2}\}_2]$ units. Each dimer contains cadmium atoms bridged by two oxygens from two symmetry-related carboxylate groups [O(5), O(5′) for Cd(1); O(13), O(13′) for Cd(2)] with Cd(1) ··· Cd(1′) 3.829(1) and Cd(2) ··· Cd(2″) 3.835(1) Å (′ $-x$, $-y$, $-z + 1$;

Table 4 Fractional atomic coordinates (× 10^5 for Cd, × 10^4 for other atoms) for complex **2**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cd(1)	−5 718(6)	18 191(6)	43 988(4)
Cd(2)	13 515(6)	11 374(6)	62 969(4)
S(1)	−1 568(2)	3 776(2)	4 585(1)
S(2)	3 994(2)	1 329(2)	6 179(2)
O(1)	420(6)	1 816(5)	5 352(3)
O(2)	1 046(6)	2 631(5)	6 126(4)
O(3)	−1 234(6)	4 680(5)	4 522(4)
O(4)	−2 083(6)	3 408(6)	4 039(4)
O(5)	1 193(6)	−183(6)	5 756(4)
O(6)	2 104(6)	−1 208(5)	5 300(4)
O(7)	4 922(6)	773(6)	6 309(4)
O(8)	3 735(7)	1 955(6)	6 651(4)
N(1)	−651(7)	3 133(6)	4 782(4)
N(2)	972(7)	1 527(6)	3 918(4)
N(3)	−967(7)	1 733(6)	3 351(4)
N(4)	2 964(6)	794(6)	6 024(5)
N(5)	−378(7)	934(6)	6 614(4)
N(6)	1 374(7)	1 118(6)	7 358(4)
C(1)	5 374(9)	2 540(8)	5 612(6)
C(2)	398(9)	3 376(8)	5 326(6)
C(3)	−2 529(9)	3 783(8)	5 163(5)
C(4)	−2 608(8)	3 072(8)	5 567(5)
C(5)	−3 390(10)	3 087(9)	6 005(6)
C(6)	−4 082(11)	3 805(10)	6 033(6)
C(7)	−3 996(12)	4 508(10)	5 631(7)
C(8)	−3 212(11)	4 524(9)	5 184(6)
C(9)	−1 973(10)	1 737(9)	3 118(6)
C(10)	−2 218(11)	1 508(10)	2 486(7)
C(11)	−1 385(11)	1 311(10)	2 125(7)
C(12)	−323(11)	1 319(10)	2 360(6)
C(13)	−153(9)	1 535(8)	2 992(6)
C(14)	906(9)	1 483(8)	3 296(7)
C(15)	1 831(11)	1 411(10)	2 954(7)
C(16)	2 817(13)	1 357(11)	3 268(8)
C(17)	2 884(12)	1 359(11)	3 899(8)
C(18)	1 901(10)	1 463(9)	4 220(6)
C(19)	2 034(9)	−471(8)	5 554(5)
C(20)	3 086(9)	60(8)	5 602(6)
C(21)	4 289(9)	1 925(8)	5 515(5)
C(22)	5 149(9)	1 699(8)	5 167(6)
C(23)	5 364(10)	2 207(9)	4 642(6)
C(24)	4 720(12)	2 935(10)	4 487(7)
C(25)	3 823(11)	3 140(10)	4 836(7)
C(26)	3 622(10)	2 650(9)	5 358(6)
C(27)	2 290(12)	1 121(10)	7 707(7)
C(28)	2 297(13)	1 065(11)	8 364(8)
C(29)	1 306(13)	1 015(10)	8 640(8)
C(30)	3 617(11)	9 973(9)	8 270(7)
C(31)	4 286(9)	1 052(8)	7 625(6)
C(32)	−5 402(9)	1 010(8)	7 225(6)
C(33)	−1 571(11)	1 035(9)	7 457(6)
C(34)	−2 431(12)	1 000(10)	7 032(7)
C(35)	−2 263(11)	903(9)	6 406(6)
C(36)	−1 216(10)	863(8)	6 214(6)
O(W1)	1 991(9)	764(8)	1 445(5)
O(W2)	5 225(11)	2 444(11)	2 601(7)
O(W3)	5 293(12)	665(11)	2 811(7)
O(W4)*	5 968(15)	3 754(14)	3 307(9)
O(W5)*	4 019(17)	4 688(14)	6 893(10)

* Population 0.5.

Table 5 Selected bond distances (Å) for complexes **1** and **2***

Complex **1**			
Cd(1)–N(1)	2.305(6)	Cd(2)–N(5)	2.270(6)
Cd(1)–N(2)	2.303(6)	Cd(2)–N(6)	2.302(7)
Cd(1)–O(1)	2.265(6)	Cd(2)–O(9)	2.241(6)
Cd(1) • • • O(2)	2.657(6)	Cd(2) • • • O(10)	2.742(7)
Cd(1)–O(5)	2.417(5)	Cd(2)–O(13)	2.366(6)
Cd(1)–O(5′)	2.312(5)	Cd(2)–O(13″)	2.357(6)
Cd(1)–O(6′)	2.494(6)	Cd(2)–O(14″)	2.478(6)
Complex **2**			
Cd(1)–O(1)	2.361(7)	Cd(2)–O(1)	2.532(7)
Cd(1)–N(1)	2.172(9)	Cd(2)–O(2)	2.337(8)
Cd(1)–N(2)	2.277(9)	Cd(2)–O(5)	2.332(8)
Cd(1)–N(3)	2.302(9)	Cd(2)–N(4)	2.191(8)
Cd(1)–O(5′)	2.632(7)	Cd(2)–N(5)	2.319(9)
Cd(1)–O(6′)	2.254(8)	Cd(2)–N(6)	2.294(10)

* Symmetry operations: for **1**, (′) $-x, -y, -z + 1$, (″) $-x + 1, -y, -z$; for **2**, (′) $-x, -y, 1 - z$.

″ $-x + 1$, $-y$, $-z$) separations, generating planar Cd_2O_2 rings. The metal environment is formed by the two nitrogens of the bipy molecule, and four carboxylate oxygens from the tosylglycine monoanions, with Cd–O bond lengths in the range 2.265(6)–2.494(6) Å for the Cd(1) dimer and 2.241(6)–2.478(6) Å for the Cd(2) dimer, and a fifth carboxylate oxygen at a significantly longer distance [Cd(1) • • • O(2) 2.657(6) and Cd(2) • • • O(10) 2.742(7) Å]. The Cd–N distances (2.270–2.305 Å), are notably markedly shorter than those of previously structurally characterized cadmium–bipy complexes (Cd–N 2.33–2.43 Å).[10,11]

One of the co-ordinated tosylglycine molecules acts as a bidentate chelate and bridging ligand and the other as a strongly asymmetric bidentate chelate ligand. A similar carboxylate binding mode leading to discrete dimers with cadmium(II) co-ordinated by seven oxygens is observed also for tetraaqua bis(μ-*o*-hydroxybenzoato)bis(*o*-hydroxybenzoato)dicadmium(II) but the range of Cd–O distances is 2.243–2.535 Å.[12]

In the present complex the cadmium atom may be considered as seven-co-ordinated since the long contacts, Cd • • • O, are much shorter than the sum of the van der Waals radii (3.10 Å); nevertheless the geometry around the metal ion cannot be described by a polyhedron typical for seven-co-ordination.

Strong intradimeric hydrogen bonds occur between sulfonamide nitrogens and weakly co-ordinated carboxylate oxygens, O(2) and O(10): [N(4) • • • O(2) 2.87(1) Å, N(4)–H(21) • • • O(2) 170(1)°; N(8) • • • O(10) 2.78(1) Å, N(8)–H(49) • • • O(10) 161(1)°].

Crystal packing is mainly determined by aromatic ring stacking interactions between bipy molecules that give rise to two separated infinite chains of Cd(1) dimers (ring–ring separation range 3.40–3.87 Å) and Cd(2) dimers (ring–ring separation range 3.56–3.99 Å). Bond distances and angles in the amino acid skeleton fall in the range previously observed for cobalt(II) and copper(II) complexes with *N*-tosylglycinate monoanions.[2,13] Finally, the pyridine rings are nearly planar and the internal rotation angles about the 2,2′ bond are 0.9 and 3.7° for the Cd(1)- and Cd(2)-dimer respectively.

Type B Complexes.—Description of the structure of [{Cd(bipy)(bsglyNO)}$_4$]·8H_2O. Selected interatomic distances are reported in Table 5 with atom numbering as in Fig. 2. The structure contains two crystallographically independent cadmium atoms, *N*-(benzenesulfonyl)glycine and bipy molecules. The amino acid molecule exists as a dianion: the sulfonamide nitrogen and the carboxylate group participating in co-ordination, with the latter bridging two cadmium atoms. Two bipyridine nitrogens complete the co-ordination polyhedron. The main interest of this structure lies in the N,O-chelate binding of the *N*-(benzenesulfonyl)glycinate dianion to the Cd^{2+} ion. Previous solution studies showed the ability of Cd^{2+}

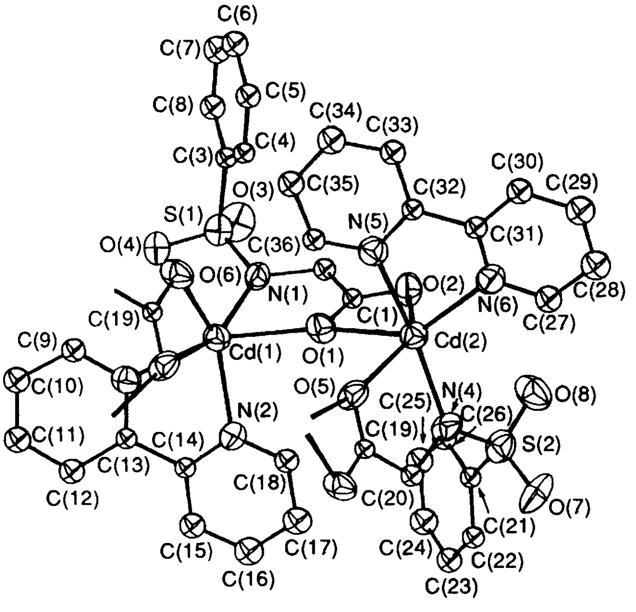

Fig. 2 An ORTEP view of a [{Cd(bipy)(bsglyNO)}$_2$] moiety in the tetramer [{Cd(bipy)bsglyNO)}$_4$]·8H$_2$O showing the atom numbering and the thermal motion ellipsoids (40%); hydrogen atoms are omitted for clarity

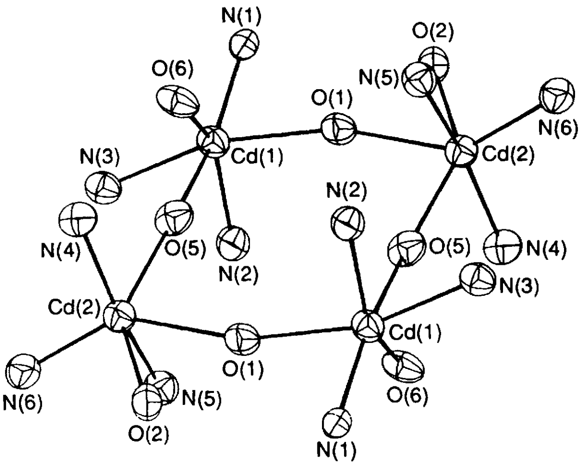

Fig. 3 An ORTEP drawing of the details of the cadmium atom environment in [{Cd(bipy)(bsglyNO)}$_4$]·8H$_2$O

in substituting the amide-nitrogen bound hydrogen of aryl-SO$_2$-*N*-amino acids,[1] but no solid complexes were obtained. The presence in the structure of two symmetry-related [Cd$_2$(bipy)$_2$(bsglyNO)$_2$] moieties originates tetrameric units [{Cd(bipy)(bsglyNO)}$_4$] in which each cadmium atom is five-co-ordinated *via* bipy nitrogens, sulfonamide nitrogen and carboxylate oxygen of the amino acid molecule in a trigonal-bipyramidal arrangement. At a greater distance [Cd(1)–O(5′) 2.632(7) (′ $-x, -y, 1-z$) and Cd(2)–O(1) 2.532(7) Å] a sixth co-ordination position in the equatorial planes of the bipyramids can be considered, with two trigonal oxygen atoms bridging two cadmiums as found in a cadmium maleate dihydrate complex.[14] Around Cd(1) one carboxylic oxygen O(1) and a bipy nitrogen N(3) occupy the axial positions of the bipyramid, while for Cd(2) these positions are occupied by amide nitrogen N(4) and the bipy nitrogen N(5).

The metal–metal separations Cd(1)···Cd(2) 4.786(2) and Cd(1)···Cd(2′) 4.840(2) Å exclude direct cadmium–cadmium bond interactions in the structure.

The Cd(1)–N(1) 2.172(9) and Cd(2)–N(4) 2.191(8) Å distances are remarkably shorter than the average Cd–N distance in cadmium complexes of simple amino acids (2.306 Å).[15–18] Similarly, the Cd–N(bipy) distances, comparable to those found in **1**, are shorter than those found in other cadmium–bipy complexes.[10,11]

Analysis of the planarity of the Cd(1)O(1)Cd(2)O(5)Cd(1′)-O(1′)Cd(2′)O(5′) ring (Fig. 3) indicate that the cadmium atoms and O(1) deviate only by 0.01 and 0.02 Å from the mean plane, while O(5) is 0.45 Å out of this plane. The bipy molecules are nearly planar (internal rotation angle around the 2,2′ bonds 8.2 and 7.8°) and roughly coplanar (dihedral angle 10.7°); moreover, they are quite orthogonal to the Cd$_4$O$_4$ ring. The phenyl rings of amino acids are coplanar (dihedral angle 10.3°) and orthogonal to the bipy and Cd$_4$O$_4$ rings.

Bond distances and angles within the ligands are normal and are in the range previously observed in similar complexes.[19]

Packing is determined by O···O contacts (2.41–2.92 Å) involving water molecules and carboxylic and sulfonamidic oxygens, which can be considered as hydrogen bonds. Aromatic ring-stacking interactions between phenyl rings are also present (ring–ring separation range 3.29–3.64 Å).

IR Spectra.—The presence of multiple bands in the spectral region characteristic of the asymmetric and symmetric stretching frequencies of the CO$_2{}^-$ group is a common feature of the infrared spectra of both zinc and cadmium type A complexes. On the basis of the structure of **1** this may be related to the presence of two different co-ordination modes (chelate and chelate-bridging) of the carboxylic group. The spectra of both type B complexes lack the NH stretching vibration and show the expected displacement of the vibration frequencies of SO$_2$ and SN groups as compared to type A complexes. Moreover, the $\nu(\text{OCO})_{\text{asym}}$ and $\nu(\text{OCO})_{\text{sym}}$ bands (1594–1600, 1407–1423 cm^{-1}, respectively) of the zinc(II) complexes are very similar to those of **2**. Hence, the same ligand co-ordination mode found in **2** can be suggested for the homologous zinc(II) species.

Discussion

The pH-dependent co-ordination mode of *N*-sulfonyl amino acids toward Cd^{2+} in ternary complexes with 2,2′-bipyridine, thoroughly characterized in aqueous solution,[1] is reflected in the isolated solid-state species. The amino acid : ligand molar ratio of 1 : 1 that invariably characterized the stoicheiometry of the prevailing species in solution through the pH range investigated is conserved in the solid state for species bearing a N,O-deprotonated ligand molecule (type B complexes). This ratio is forcedly increased to 2 : 1 in the carboxylate complexes (type A complexes) to achieve electrical neutrality. In both cases the bridging bidentate behaviour of the carboxylate groups determines the formation of polynuclear species. The presence of polymeric complexes in solution cannot be revealed by polarography, but, reasonably, they are unlikely to occur since metal hydration should greatly disfavour the above binding mode of the carboxylate group, especially in very dilute solutions ([M^{2+}] = 10^{-4} mol dm^{-3}) on which the electrochemical measurements were carried out.

The short Cd–N(amino acid) distance in **2** as compared to that observed in cadmium(II) complexes of simple amino acids is due to the greater binding strength of the deprotonated amide nitrogen of the N,O-chelate form of the ligands as compared to the amino nitrogen, and is also responsible for the greater stability of the binary complexes formed by the former ligands in solution.[3,20] The co-ordination of the deprotonated amide nitrogen to Cd^{2+} is a unique feature of type B complexes. To our knowledge this is the only structurally characterized example reported to date.

Cadmium(II) complexes of *N*-sulfonyl amino acids, acting either as carboxylate or N,O-bidentate ligands, show distinct features. The interest of the above structure in the context of co-ordination chemistry of Cd^{2+} parallels that of the previously reported [Cd(ts-β-alaO)$_2$(H$_2$O)$_4$] [ts-β-alaO = anion of *N*-(toluene-*p*-sulfonyl)-β-alanine] complex, a monomeric species in which the metal is six-co-ordinated *via* two unidentate carboxylate groups of the ligands and four water molecules.[20] Also these structural features were unprecedented, given the general tendency of cadmium(II)–carboxylate complexes to form polymeric species through chelate-bridging carboxylate groups, often with the metals seven-co-ordinated.

The shortening of the Cd–N(bipy) distances in both complexes **1** and **2** as compared to other cadmium(II)–bipy species can be reasonably attributed to a likely weak metal ligation of the carboxylate group that contemporarily acts as a chelate bidentate and bridging ligand.

Acknowledgements

We are grateful to the Ministero dell'Universita' e della Ricerca Scientifica of Italy (40%) for financial support, the Centro Interdipartimentale Grandi Strumenti (C.I.G.S.) of the University of Modena which supplied the diffractometer and the FT–IR spectrophotometer, and the Centro Interdipartimentale di Calcolo of the University of Modena (C.I.C.A.I.A.) for computing support.

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Received 25th *October* 1991; *Paper* 1/05448A