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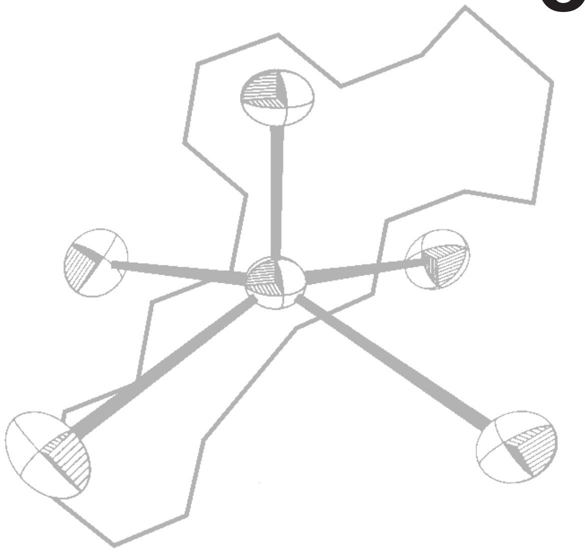

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Crystallographic Study on Metal(II) Complexes with *N*-(2-Nitrophenylsulfonyl)glycine

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The interaction of M^{II} ions ($M^{II} = Mn^{II}$, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II}, Pb^{II}) with *N*-(2-nitrophenylsulfonyl)glycine ($NO_2psglyH_2$) leads to the formation at acidic pH of the complex carboxylate-type M(NO_2psgly-*O*)$_2$.xH$_2$O species. At higher pH the deprotonation reaction of the sulfonamide nitrogen takes place, leading to the formation of the M(NO_2psgly-*N*,*O*).xH$_2$O species where the ligand acts as a chelating agent toward the metal ion through the carboxylic oxygen and the deprotonated sulfonamide nitrogen.

In ternary systems the addition of 2,2′-bipyridine (bpy) allows the deprotonation of the sulfonamide nitrogen also in presence of metal ions such as Zn^{II}, Co^{II} and Ni^{II}, which were inactive in the binary system, and the solid compounds isolated are in the M/bpy/L molar ratio 1 : 1 : 1 ($M^{II} = Cu^{II}$, Zn^{II}) or 1 : 2 : 1 ($M^{II} = Co^{II}$, Ni^{II}, Cd^{II}). Here we describe the crystal and molecular structures of $NO_2psglyH_2$ (1), [Pb(NO_2psgly-*N*,*O*)]$_n$ (2), [Cd(bpy)$_2$(NO_2psgly-*N*,*O*)].H$_2$O (3) and [Cu(bpy)(NO_2psgly-*N*,*O*)(H$_2$O)] (4).

Introduction

The coordination behaviour of *N*-sulfonyl amino acids is closely dependent on the metal-ion type; with copper(II), cadmium(II),[1] palladium(II)[2] and lead(II)[3] the binding mode switches from carboxylate-type coordination, at low pH, to an *N*,*O*-bidentate coordination (through a carboxylate oxygen and the deprotonated sulfonamide nitrogen) at higher pH. The deprotonation reaction of the sulfonamide nitrogen takes place in the order of increasing pH:

$$Pd^{II} < Pb^{II} < Cu^{II} < Cd^{II}$$

with a pK_{NH} somewhat less with respect to the free ligand.

The addition in the *N*-arylsulfonyl amino acid molecule of a third donor site leads to a potentially tridentate ligand. The presence of an amide group on the side chain, such as in *N*-*p*-tolylsulfonyl-asparagine (tsasn) and -glutamine, allows the formation of complexes involving the amide oxygen in the coordination as found in [Cu(bpy)(tsasn-*N*,*O*,*O*′)].H$_2$O[4] or the deprotonated amide nitrogen as found in solution in the Pd^{II} system with *N*-*p*-tolylsulfonylasparagine.[5]

Also the coordination behaviour of substituted hippuric acids is strongly dependent on the nature of the additional donor site. 4-Aminohippuric acid, despite the low basicity of the amino nitrogen, acts as a bidentate bridging ligand through the carboxylic and the amine groups giving rise to stable polymers.[6] On the other hand, 4-nitrohippuric acid still acts as a carboxylate ligand toward copper(II) ion,[7] while 2-hydroxyhippuric acid in presence of copper(II) undergoes deprotonation of the phenolic oxygen with the formation of a five-membered *O*,*O*-chelate ring.[8]

We now decided to investigate the effect of the NO_2 group on the coordination ability of *N*-(2-nitrophenylsulfonyl)glycine ($NO_2psglyH_2$). Therefore, we have synthesized a series of compounds of M^{II} ions ($M^{II} = Mn^{II}$, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}, Cd^{II}, Pb^{II}) with $NO_2psglyH_2$. In addition, ternary 2,2′-bipyridine adducts have been isolated and characterized.

In this paper we describe the crystal and molecular structures of $NO_2psglyH_2$ (1), [Pb(NO_2psgly-*N*,*O*)]$_n$ (2), [Cd(bpy)$_2$(NO_2psgly-*N*,*O*)].H$_2$O (3) and [Cu(bpy)(NO_2psgly-*N*,*O*)(H$_2$O)] (4).

Results and Discussion

Description of Structures

$NO_2psglyH_2$ (1)

Bond distances and angles are reported in Table 1 with the atom numbering as in Fig. 1. The two C–O bond lengths are markedly different from one another as a consequence of the un-ionized carboxylic acid group. The sulfonamide nitrogen atom presents an sp^2 hybridization, and the S–N distance is comparable with that found in neutral *N*-*p*-tolylsulfonylglycine[9]

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* Abbreviations: $NO_2psglyH_2$, *N*-(2-nitrophenylsulfonyl)glycine; NO_2psgly-*O*, *N*-(2-nitrophenylsulfonyl)glycine monoanion; NO_2psgly-*N*,*O*, *N*-(2-nitrophenylsulfonyl)glycine dianion.

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and in neutral N-(phenylsulfonyl)-DL-alanine.[10] The phenyl ring is planar (maximum deviation from the plane 0·007 Å) and forms an angle of 31·4(2)° with the NO_2 group. The crystal packing is due to inter- and intra-molecular hydrogen bonds involving the sulfonamide nitrogen and the oxygen atoms of the NO_2 group. In addition, short intramolecular $C–H\cdots O$ contacts with an angle $C–H\cdots O > 90°$ are present which may be considered as hydrogen bonds.[11]

*[Pb(NO_2psgly-*N,O*)] (2)*

Interatomic distance and angles are reported in Table 2, and Fig. 2 shows an ORTEP of the [Pb(NO_2psgly-*N,O*)] moiety. The lead(II) ion is coordinated at short distances by O(1), N(1), $O(3)^{I}$ and $O(1)^{II}$ (in the range 2·402(3)–2·530(4) Å), and at longer distances by $O(4)^{III}$ (2·961 Å) and $O(5)^{IV}$ (2·894(5) Å). The Pb^{II} ion exhibits a hexacoordination which has previously been found in the [Pb(tsgly-*N,O*)(H_2O)] (tsgly = *N-p*-tolylsulfonylglycine) complex.[3] This kind of coordination is not common for the lead(II) ion, which prefers coordination numbers from 7 to 9.[12]

Each NO_2psgly-*N,O* dianion coordinates five lead(II) ions giving rise to a three-dimensional polymeric arrangement, with the shortest $Pb\cdots Pb$ separation being 4·188(1) Å. The Pb–N(1) bond, within the glycine-like chelate ring (2·450(4) Å), is longer than the 2·38(1) Å value observed in [Pb(tsgly-*N,O*)(H_2O)] [3] but is slightly shorter than Pb–N bonds involving amino, pyridyl and imino nitrogens (2·470–2·668 Å).[13–16]

The O(1) atom forms a fairly symmetric monoatomic bridge between two Pb^{II} ions (2·402(3), 2·530(4) Å) while in the [Pb(tsgly-*N,O*)(H_2O)] complex[3] the two Pb–O(1) distances were very different from one another (2·314(8), 2·827(9) Å); nevertheless in the present complex, these distances fall in the range observed for $Pb–O_{carbox}$ bonds (2·40–3·11 Å).[17,18] The O(2) atom does not participate in the coordination contrary to what occurs in the [Pb(tsgly-*N,O*)(H_2O)] complex.[3]

Another significant difference from the cited tsgly complex lies in the coordination mode of the sulfonyl group which acts as bidentate through both the O(3) and O(4) atoms in the present case and as monodentate in the tsgly complex.

The O(5) atom of the NO_2 group gives rise to an interaction at a rather long distance, with Pb–O(5) 2·895(5) Å, but this does not affect the distance within the NO_2 group with respect to the free ligand. The four short distances (<2·54 Å), in particular Pb–N 2·450(4) Å, together with the low coordination number (namely 6) for lead(II), suggest that the lone pair is sterically active in the opposite direction to the two carboxylic oxygen atoms which form *trans* angles furthest from 180° ($O(1)–Pb–O(4)^{III}$ 133·9(1)° and $O(1)^{II}–Pb–N(1)$ 128·37(12)°).[19]

The five atoms of the glycine-like ring are almost planar, with deviations from the mean plane from −0·02 to 0·06 Å. The carboxylate group and the nitro group are also planar with maximum deviation from the plane of −0·01 and −0·02 Å, respectively.

The presence of a short Pb–O(3) sulfonyl distance lengthens the S–O(3) bond distance; the lessening of the S–N distance, as a consequence of the deprotonation of sulfonamide nitrogen, was not surprising, but the value of 1·548(4) Å is by far the shortest ever found.[1,3]

The remaining bond distances and angles within the ligand are similar to those observed in $NO_2psglyH_2$.

*[Cd(bpy)$_2$(NO_2psgly-*N,O*)].H_2O (3)*

Bond distances and angles are reported in Table 3 with the atom numbering as in Fig. 3. In the complex molecule the cadmium(II) environment can be described as approximately octahedral with an N_5O donor set. Four nitrogen atoms are derived from the two bpy ligands, while the oxygen and the fifth nitrogen are from the NO_2psgly-*N,O* dianion, so three five-membered chelate rings are formed. N(1), N(2), N(3) and N(5) act as equatorial ligands with deviations from the mean plane <0·1 Å; N(4) and O(1) are the apical ligands with a *trans* angle of 147·6(2)°. This kind of geometry is similar to that observed in the other structurally known bisbipyridinecadmium(II) complexes: $[Cd(bpy)_2(NO_3)_2].0{\cdot}5H_2O$, $[Cd(bpy)_2(NCS)_2]$,[20] and [Cd(bpy)$_2$(tsgly-*N,O*)].[21]

The N–Cd–N angles within the chelate rings are less than 90·0°, ranging from 69·9(2) to 73·4(2)°, and are comparable with the values reported for the cited $(bpy)_2Cd^{II}$ complexes.

The Cd–N(5) sulfonamide distance (2·240(6) Å) is shorter than the average Cd–N in cadmium complexes of simple amino acids (2·306 Å) because of the greater ligand strength of the deprotonated sulfonamide nitrogen with respect to an amine nitrogen, whereas it is longer than the corresponding one in [Cd(bpy)(psgly-*N,O*)]$_4$.8H_2O (2·171(9), 2·191(8) Å)[22] and in [Cd(bpy)$_2$(tsgly-*N,O*)] (2·215(5) Å).[21] This lengthening is accompanied by a comparable shortening of the $Cd–O_{carbox}$ distance within the chelate ring, a distance which is 2·289(6) Å as against 2·361(1) and 2·332(8) Å for the respective previously cited complexes.

The Cd^{II}–bpy distances range (2·343–2·377 Å) falls within the range found in structurally known $[Cd(bpy)_2X_2]$ ($X = NCS^-$, NO_3^-).[20]

The glycine-like ring forms a dihedral angle of 100 and 102° with the chelate rings involving the bipyridine molecules; the angle between the chelate rings of the bipyridine is 73·6°.

Bond distances and angles within the ligand are similar to those observed in the free ligand (1) and in complex (2). The main difference is the dihedral angle formed by the benzene ring and the NO_2 group which is 63·0(1)° in this complex, 32·9(6)° in compound (2) and 31·5(1)° in the $NO_2psglyH_2$ molecule. This may be attributed to the presence of an intramolecular ring-stacking interaction between the NO_2psgly-*N,O*

Table 1. Selected bond lengths and angles for (1)

Distances (Å)		Angles (degrees)	
C(1)–O(2)	1·214(3)	O(2)–C(1)–O(1)	124·9(2)
C(1)–O(1)^{I}	1·310(3)	O(2)–C(1)–C(2)	124·3(2)
C(1)–C(2)	1·497(3)	O(1)–C(1)–C(2)	110·8(2)
C(2)–N(1)	1·444(3)	N(1)–C(2)–C(1)	115·4(2)
N(1)–S	1·597(2)	C(2)–N(1)–S	123·6(2)
S–O(4)	1·427(2)	O(4)–S–O(3)	119·14(11)
S–O(3)	1·428(2)	O(4)–S–N(1)	110·02(11)
S–C(3)	1·789(2)	O(3)–S–N(1)	105·77(11)
		O(4)–S–C(3)	106·17(10)
		O(3)–S–C(3)	107·37(11)
		N(1)–S–C(3)	107·92(10)

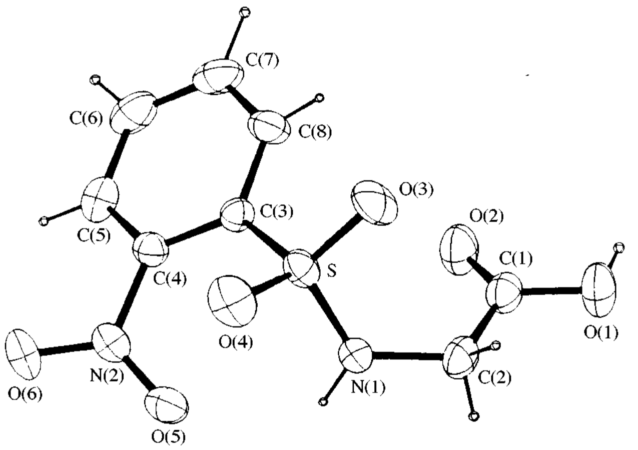

Fig. 1. ORTEP view (50% ellipsoids) of NO2psglyH2 molecule with atom numbering scheme.

Table 2. Selected bond lengths and angles for (2)

Symmetry transformations used to generate equivalent atoms: I $-x+1,-y,-z+1$; II $-x,-y,-z+1$; III $x-1,y,z$; IV $x-1/2,-y-1/2,z$; V $x+1/2,-y-1/2,z$; VI $x+1,y,z$

Distances (Å)				Angles (degrees)			
Pb–O(1)	2·402(3)	O(2)–C(1)	1·224(5)	O(1)–Pb–N(1)	65·66(12)	O(1)^{II}–Pb–O(4)^{IV}	101·46(11)
Pb–N(1)	2·450(4)	C(1)–C(2)	1·532(6)	O(1)–Pb–O(3)^{I}	82·37(12)	O(5)^{III}–Pb–O(4)^{IV}	60·08(12)
Pb–O(3)^{I}	2·461(3)	C(2)–N(1)	1·454(6)	N(1)–Pb–O(3)^{I}	84·89(12)	O(2)–C(1)–O(1)	124·6(5)
Pb–O(1)^{II}	2·530(3)	N(1)–S	1·548(4)	O(1)–Pb–O(1)^{II}	63·80(13)	O(2)–C(1)–C(2)	118·2(4)
Pb–O(5)^{III}	2·897(4)	S–O(4)	1·438(3)	N(1)–Pb–O(1)^{II}	128·37(12)	O(1)–C(1)–C(2)	117·2(4)
Pb–O(4)^{IV}	2·961(3)	S–O(3)	1·464(3)	O(3)^{I}–Pb–O(1)^{II}	78·85(11)	N(1)–C(2)–C(1)	109·7(4)
O(1)–C(1)	1·282(5)	S–C(3)	1·793(5)	O(1)–Pb–O(5)^{III}	73·87(13)	C(2)–N(1)–S	119·2(3)
O(1)–Pb^{II}	2·530(3)	O(3)–Pb^{I}	2·461(3)	N(1)–Pb–O(5)^{III}	100·26(13)	O(4)–S–O(3)	116·9(2)
		O(4)–Pb^{V}	2·961(3)	O(3)^{I}–Pb–O(5)^{III}	150·68(12)	O(4)–S–N(1)	107·7(2)
				O(1)^{II}–Pb–O(5)^{III}	75·39(12)	O(3)–S–N(1)	114·0(2)
				O(1)–Pb–O(4)^{IV}	133·95(12)	O(4)–S–C(3)	108·6(2)
				N(1)–Pb–O(4)^{IV}	121·04(12)	O(3)–S–C(3)	101·8(2)
				O(3)^{I}–Pb–O(4)^{IV}	140·32(11)	N(1)–S–C(3)	107·3(2)

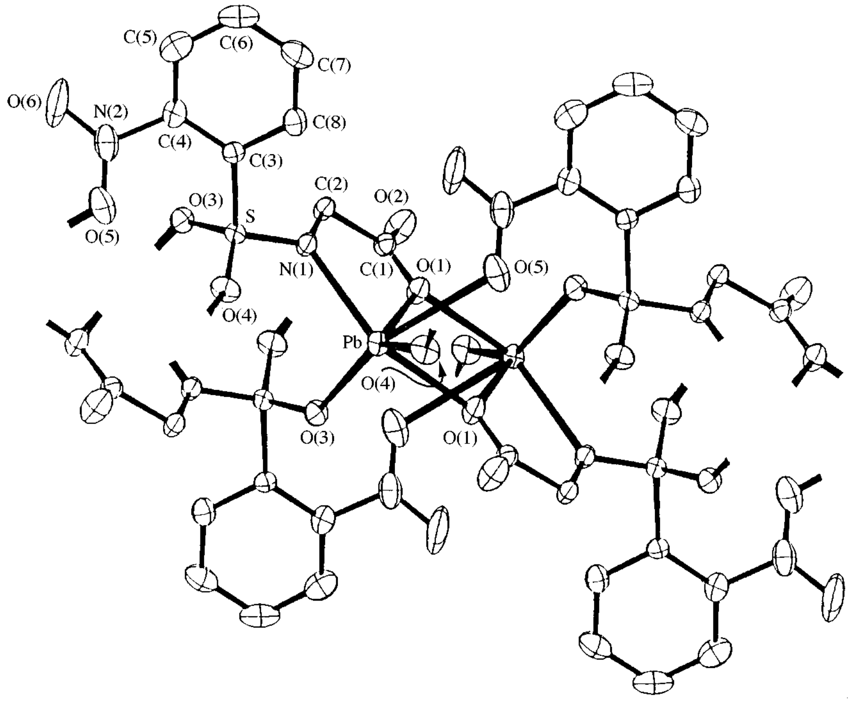

Fig. 2. ORTEP view (50% ellipsoids) of [Pb(NO2psgly-*N*,*O*)] moiety with atom numbering scheme.

dianion and bpy(2) (range 3·54–3·88 Å) with a dihedral angle between the involved aromatic moieties of 2·5(1)°. Crystal packing is completed by intermolecular ring-stacking interactions involving bpy(1) molecules.

[Cu(bpy)(NO$_2$psgly-N,O)(H$_2$O)] (4)

An ORTEP view with the labelling scheme is given in Fig. 4; bond distances and angles are reported in Table 4. The copper(II) ion exhibits a tetrahedrally distorted square-pyramidal N_3O_2 coordination. The four basal ligands are the nitrogen atoms of the bpy molecule, the deprotonated sulfonamide nitrogen and one carboxylate oxygen of the NO$_2$psgly-*N*,*O* dianion; the apical position is occupied by the oxygen atom of the water molecule. The Cu–O(1) distance (1·906(13) Å) is significantly shorter than the value observed in analogous ternary species formed by R-sulfonylamino acidate-*N*,*O* dianions, e.g. tosylglycinate,[23] phenylsulfonylglycinate,[24] 5-dimethylaminonaphthalen-1-ylsulfonylglycinate,[25] and tosyl-DL-asparaginate[4] (mean value 1·95 Å); consequently a lengthening in the Cu–N(3) distance is observed (2·03(2) versus mean value of 1·96 Å)[4,23–25] in view of the constraint imposed by the O–Cu–N angle within the glycine-like ring. The Cu–N$_{\rm bpy}$ and the Cu–O$_{\rm w}$ distances are quite similar to those observed in the above-cited complexes. The four equatorial donor atoms are almost planar with deviations from their mean least-squares plane in the range from −0·07 to +0·08 Å. Nevertheless some extent of tetrahedral distortion is indicated by the dihedral angle of 23·8(3)° between the mean planes of the two five-membered chelate rings; the same value was found in the [Cu(bpy)(psgly-*N*,*O*)(H$_2$O)] complex.[24] The angle between the Cu–O$_{ax}$ vector and the normal to the mean equatorial plane is 5·5° and is the smallest ever found in such kinds of adducts. Bond distances and angles within the ligand are similar to those observed in compounds (2) and (3); the NO$_2$ group is planar and forms a dihedral angle with the phenyl ring of 24·1(4)°; likewise, the structural parameters of the bpy molecule are normal, the two pyridine rings being planar within ±0·003 Å and twisted by 3·3(6)° about the 2,2′ bond.

Electronic Spectra

Copper(II) *Complexes*

The d–d band maxima of the electronic spectra are reported in Table 5. The Cu(NO$_2$psgly-*O*)$_2$.4H$_2$O complex shows a very large d–d band maximum at 14280 cm^{-1} which is consistent with the presence of a tetragonal copper(II)–oxygen system.

In the K$_2$Cu(NO$_2$psgly-*N*,*O*)$_2$.H$_2$O complex a maximum band shift occurs at higher energy (15870 cm^{-1}) and a new band appears at 19230 cm^{-1}, this behaviour being consistent with the stronger ligand field owing to *N*-deprotonated coordination. A similar electronic spectrum was found in the structurally known [pipdH$_2$]$_2$[Cu(ts-α-ala-*N*,*O*)$_2$].H$_2$O[26] (pipdH = piperidinium cation, ts-α-ala = *N*-*p*-tolylsulfonyl-α-alanine) where the [Cu(ts-α-ala-*N*,*O*)$_2$]$^{2-}$ dianion shows a strictly square planar geometry. The electronic spectrum of [Cu(bpy)(NO$_2$psgly-*O*)$_2$].H$_2$O shows a maximum at 15900 cm^{-1} with a shoulder at 16950 cm^{-1}; this indicates an essentially square planar CuN$_2$O$_2$ chromophore as is often found in the 2,2′-bipyridine adducts of copper(II)–*N*-protected amino acidates.[1]

In the [Cu(bpy)(NO$_2$psgly-*N*,*O*)(H$_2$O)] complex the d–d band maximum is centred at 14850 cm^{-1} in line with the short Cu–O$_{\rm w}$ apical distance.

Cobalt(II) *and Nickel*(II) *Complexes*

The electronic spectrum of Co(NO$_2$psgly-*O*)$_2$.4H$_2$O shows the typical pattern of a high-spin octahedral complex; the observed bands are assigned as follows: 7810 ν_1, $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$; 19120, 21200 (shoulder) cm^{-1}, ν_3, $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$; Dq = 900 cm^{-1} and B = 973 cm^{-1} calculated from ν_1 and ν_3.[27]

For the Ni(NO$_2$psgly-*O*)$_2$.4H$_2$O complex the O_h symmetry leads to the following assignments: 8730 ν_1, $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$; 13590 $^3A_{2g}(F) \rightarrow {}^1E_g(D)$; 14860 ν_2, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$; 28225 cm^{-1} ν_3, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$; Dq = 873 cm^{-1} and B = 1128 cm^{-1} calculated by using ν_1, ν_2 and ν_3,[28] or Dq = 881 cm^{-1} and B = 1112 cm^{-1} calculated from ν_2 and ν_3.[29]

The spectral data of the M(bpy)$_2$(NO$_2$psgly-*N*,*O*)$_2$.2H$_2$O adducts (M = Ni$^{\rm II}$ or Co$^{\rm II}$) are also interpreted in terms of O_h symmetry, being not far from the values reported for [M(en)$_3$]$^{2+}$ ions,[30], and the calculated Dq are 1102, 1109 cm^{-1} while B are 905 and 870 cm^{-1} for Co$^{\rm II}$ and Ni$^{\rm II}$ respectively. A similar behaviour was also found in the corresponding [M(bpy)$_2$(tsgly-*N*,*O*)$_2$].2H$_2$O compounds[31] where the crystal structure revealed a distorted octahedral geometry.

Infrared Spectra

The complexes may be divided in two groups: type A complexes in which the amino acid NO$_2$psglyH$_2$ is in the monoanionic form and acts as a carboxylate ligand, and type B complexes in which the amino acid is in the dianionic form and coordinates the metal ion through carboxylate oxygens and deprotonated sulfonamide nitrogen. A common feature for all complexes is the position of ν(OCO)$_{\rm asym}$ (*c.* 1600 cm^{-1}) as a consequence of the dissociation and coordination to the metal ion of the carboxylic group.

In the type B complexes the disappearance of ν(NH), which is present in type A complexes, is in line with the presence of a deprotonated and metal-coordinated nitrogen atom.

As a general behaviour, the deprotonation and metal coordination of the sulfonamide nitrogen increases the bond order of S–N and slightly decreases the S–O bond order[26]. This fact leads ν(S–N) to higher frequency,

Table 3. Selected bond lengths and angles for (3)

Distances (Å)				Angles (degrees)			
Cd–N(5)	2·240(6)	Cd–N(4)	2·377(7)	N(5)–Cd–O(1)	73·4(2)	N(3)–Cd–N(4)	70·0(2)
Cd–O(1)	2·289(6)	N(5)–S	1·548(6)	N(5)–Cd–N(2)	99·7(2)	N(1)–Cd–N(4)	95·7(2)
Cd–N(2)	2·343(6)	S–O(4)	1·423(6)	O(1)–Cd–N(2)	91·6(2)	O(1)–C(21)–O(2)	123·3(8)
Cd–N(3)	2·368(7)	S–O(3)	1·439(6)	N(5)–Cd–N(3)	100·5(2)	O(1)–C(21)–C(22)	120·6(7)
Cd–N(1)	2·371(6)	S–C(23)	1·790(8)	O(1)–Cd–N(3)	84·4(2)	O(2)–C(21)–C(22)	116·0(8)
				N(2)–Cd–N(3)	157·3(2)	N(5)–C(22)–C(21)	112·2(7)
				N(5)–Cd–N(1)	169·3(2)	C(22)–N(5)–S	119·7(5)
				O(1)–Cd–N(1)	103·7(2)	O(4)–S–O(3)	117·2(4)
				N(2)–Cd–N(1)	69·9(2)	O(4)–S–N(5)	112·3(4)
				N(3)–Cd–N(1)	89·3(2)	O(3)–S–N(5)	109·1(3)
				N(5)–Cd–N(4)	91·6(2)	O(4)–S–C(23)	106·3(4)
				O(1)–Cd–N(4)	147·6(2)	O(3)–S–C(23)	103·1(3)
				N(2)–Cd–N(4)	119·7(2)	N(5)–S–C(23)	108·0(4)

Table 4. Selected bond lengths and angles for (4)

Distances (Å)				Angles (degrees)			
Cu–O(1)	1·906(13)	Cu–O$_W$	2·338(14)	O(1)–Cu–N(1)	159·0(5)	O(2)–C(11)–O(1)	133(2)
Cu–N(1)	1·988(13)	N(3)–S	1·585(14)	O(1)–Cu–N(3)	85·1(6)	O(2)–C(11)–C(12)	115(2)
Cu–N(3)	2·03(2)	S–O(4)	1·40(2)	N(1)–Cu–N(3)	102·8(6)	O(1)–C(11)–C(12)	112(2)
Cu–N(2)	2·016(12)	S–O(3)	1·394(12)	O(1)–Cu–N(2)	90·4(5)	N(3)–C(12)–C(11)	114(2)
		S–C(13)	1·77(2)	N(1)–Cu–N(2)	78·8(5)	C(12)–N(3)–S	111·9(11)
				N(3)–Cu–N(2)	171·0(6)	O(4)–S–O(3)	118·6(8)
				O(1)–Cu–O$_W$	101·4(5)	O(4)–S–N(3)	107·7(8)
				N(1)–Cu–O$_W$	96·6(5)	O(3)–S–N(3)	114·1(8)
				N(3)–Cu–O$_W$	99·2(5)	O(4)–S–C(13)	109·0(9)
				N(2)–Cu–O$_W$	89·4(5)	O(3)–S–C(13)	105·5(8)
				N(3)–S–C(13)			100·2(9)

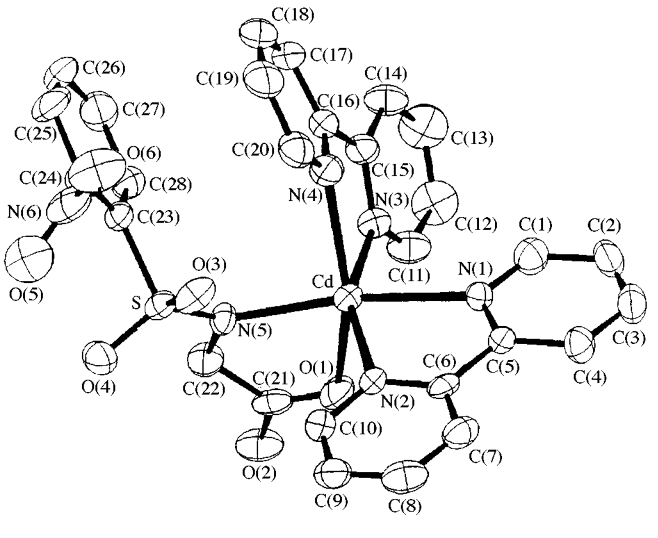

Fig. 3. ORTEP view (50% ellipsoids) of [Cd(bpy)$_2$(NO$_2$psgly-*N*,*O*)] moiety with atom numbering scheme.

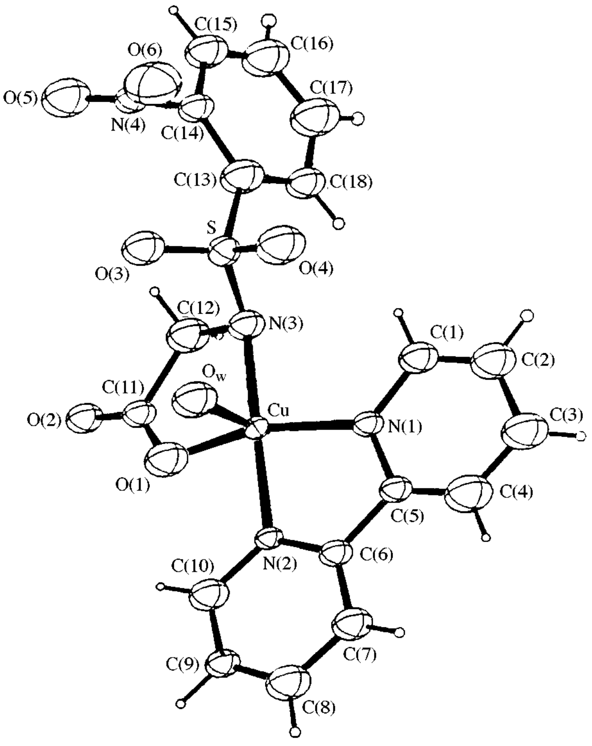

Fig. 4. ORTEP view (50% ellipsoids) of [Cu(bpy)(NO$_2$psgly-*N*,*O*)(H$_2$O)] complex with atom numbering scheme.

whereas asymmetric and symmetric $\nu(SO_2)$ are shifted to lower frequencies;[26] this fact is better evidenced in the $[Pb(NO_2psgly\text{-}N,O)]_n$ complex where the SO_2 group is involved in metal coordination.

Table 5. d–d band maxima

Complex	Colour	d–d maxima (cm^{-1})
$Cu(NO_2psgly\text{-}O)_2.4H_2O$	light blue	14280
$K_2Cu(NO_2psgly\text{-}N,O)_2.H_2O$	violet	15870, 19230
$Cu(bpy)(NO_2psgly\text{-}O)_2.H_2O$	blue	15900, 16950sh
$[Cu(bpy)(NO_2psgly\text{-}N,O)(H_2O)]$	electric blue	14850
$Co(NO_2psgly\text{-}O)_2.4H_2O$	pink	7810, 19120, 21200sh
$Ni(NO_2psgly\text{-}O)_2.4H_2O$	green	8730, 14860, 28225
$Co(bpy)_2(NO_2psgly\text{-}N,O).2H_2O$	orange	9740, 19000, 22030
$Ni(bpy)_2(NO_2psgly\text{-}N,O).2H_2O$	grey-blue	11090, 17330, 2800sh

Experimental

Preparation of Solid Compounds

$NO_2psglyH_2$

A solution of glycine (C. Erba) (3 g, 0·04 mol) in ethanol (80 ml) containing NaOH (0·08 g, 2 mmol) was added to a solution of 2-nitrobenzenesulfonyl chloride (Fluka) (8 g, 0·04 mmol) in ethanol (120 ml). The solution was kept under continuous stirring for 3–4 h and after the water phase was separated from the ethereal phase. The water phase was acidified with 1 M HCl and at pH 3 the precipitation of solid species started, helped by means of an ice bath for 15 min. The solid was collected by vacuum filtration and washed with acetone, and the precipitate was recrystallized in the minimum amount of water.

Type A Complexes

*$M(NO_2psgly\text{-}O)_2.xH_2O$.** A solution of $NO_2psglyH_2$ (1 g, 4 mmol) in ethanol (100 ml) was added to a solution of metal(II) acetate hydrate (2 mmol) in water (20 ml). Upon slow evaporation of the solution, solid compounds were obtained.

$Cu(bpy)(NO_2psgly\text{-}O)_2.H_2O$. A solution $Cu(NO_2psgly\text{-}O)_2.4H_2O$ (0·33 g, 0·5 mmol) in hot water (20 ml) was added to a solution of 2,2′-bipyridine (78 mg, 0·5 mmol) in ethanol (10 ml). Upon evaporation at room temperature blue microcrystals were separated.

Type B Complexes

$[Pb(NO_2psgly\text{-}N,O)]_n$ and $K_2Cu(NO_2psgly\text{-}N,O).H_2O$. A solution of $NO_2psglyH_2$ (1 g, 4 mmol) in ethanol (100 ml) was added to a solution of metal(II) acetate hydrate (2 mmol) in water (20 ml). Concentrated aqueous KOH was added to maintain the pH at 8·0. Upon slow evaporation of the solution, solid compounds separated. From the lead(II)-containing solution crystals suitable for X-ray structural analysis were obtained.

$M(bpy)(NO_2psgly\text{-}N,O).xH_2O$.† A solution of the corresponding $M(NO_2psgly)_2.xH_2O$ complex (0·5 mmol) in hot water (20 ml) was added to a solution of 2,2′-bipyridine (78 mg, 0·5 mmol) in ethanol (10 ml). Aqueous concentrated NaOH solution was added to maintain the pH at 8·0. Upon slow evaporation solid compounds separated. For the copper(II)-containing solution crystals suitable for X-ray structural analysis were obtained.

$[M(bpy)_2(NO_2bsgly\text{-}N,O)].xH_2O$.‡ A solution of 2,2′-bipyridine (0·31 g, 2 mmol) in ethanol (10 ml) was added to a solution of metal(II) acetate hydrate (1 mmol) in water (50 ml) containing $NO_2psglyH_2$ (0·52 g, 2 mmol). Aqueous concentrated NaOH was added to maintain the pH at 8·0. Upon slow evaporation solid compounds separated. For the cadmium(II)-containing solution crystals suitable for X-ray structural analysis were obtained.

Microanalytical Data

Data for C, H, N, S are reported as part of the Supplementary Material (see below).

Infrared Spectroscopy

The infrared spectra of the solid compounds in KBr pellets were obtained by means of a Bruker 113 V FT-IR instrument. The range investigated was 4000–400 cm^{-1}. The assignment of the more relevant bands is reported as part of the Supplementary Material (see below).

Electronic Spectra

The diffuse reflectance electronic spectra of the solid compounds were recorded at room temperature with a Perkin–Elmer Lambda 19 spectrophotometer equipped with a DM60 integration sphere.

Crystallography

Data collection and processing. Intensity data were collected at room temperature (293 K) by using Mo Kα radiation (λ = 0·71069 Å) on a Siemens P4RA diffractometer for $NO_2psglyH_2$ (1) using the θ–2θ scan technique, and on an Enraf Nonius CAD4 diffractometer for $[Pb(NO_2psgly\text{-}N,O)]_n$ (2), $[Cd(bpy)_2(NO_2psgly\text{-}N,O)].H_2O$ (3) and $[Cu(bpy)(NO_2psgly\text{-}N,O)(H_2O)]$ (4) using the ω–2θ scan technique. Crystal data and details of the data collection are listed in Table 6. The data were corrected for Lorentz and polarization effects, and an empirical absorption correction based on a ψ scan[28] was applied. Structure determinations were solved by conventional Patterson and Fourier techniques. All structures were refined with full-matrix least-squares calculations based on F^2. All non-hydrogen atoms in (1)–(3) were refined anisotropically, whereas in (4) only the copper and sulfur atoms were refined anisotropically in view of the poor quality of the data. The hydrogen atoms in (2)–(4) were calculated and rode the atoms to which they were bonded, while for (1) hydrogen atoms were found in a difference-Fourier map and treated as fixed contributors. All calculations were carried out on an IBM personal computer with SHELX76,[32] SHELXL93[33] and ORTEP[34] programs. Final fractional coordinates for (1)–(4) are reported in Tables 7–10 respectively.

Supplementary Material

More important analytical data, infrared data, observed and calculated structure factors, anisotropic thermal parameters for non-hydrogen atoms, hydrogen atom parameters, mean least-squares planes, and bond lengths and angles form an Accessory Publication. Copies are available, until 31 December 2004, from the Australian Journal of Chemistry, P.O. Box 1139, Collingwood, Vic. 3066.

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* x = 0, M = Mn^{II}; x = 1, M = Pb^{II}; x = 2, M = Cd^{II}; x = 4, M = Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}.

† x = 0, M = Zn^{II}; x = 1, M = Cu^{II}.

‡ x = 1, M = Cd^{II}; x = 2, M = Ni^{II}, Co^{II}.

Table 6. Crystal data and structure refinement for (1)–(4)

	(1)	(2)	(3)	(4)
Empirical formula	$C_8H_8N_2O_6S$	$C_8H_8N_2O_6PbS$	$C_{28}H_{24}CdN_6O_7S$	$C_{18}H_{14}CuN_4O_7S$
Molecular weight	260·22	465·40	700·99	493·93
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0·71069	0·71069	0·71069	0·71069
Crystal system	monoclinic	monoclinic	triclinic	triclinic
Space group	$P\,2_1/c$	$P\,2_1/a$	$P\,\bar{1}$	$P\bar{1}$
a (Å)	7·922(1)	7·884(6)	9·505(3)	7·639(3)
b (Å)	6·752(1)	12·504(3)	11·967(4)	9·478(3)
c (Å)	19·148(2)	11·077(4)	13·221(3)	14·430(4)
α (degrees)	90	90	83·65(3)	97·82(2)
β (degrees)	92·53(1)	108·5(4)	76·89(3)	95·66(2)
γ (degrees)	90	90	77·20(3)	106·55(2)
V (Å^3)	1023·2(2)	1038·2(9)	1425·4(8)	981·7(8)
Z	4	4	2	2
D_{calc} (g cm^{-3})	1·689	2·977	1·633	1·671
μ (cm^{-1})	3·37	164·7	8·97	12·70
$F(000)$	536	856	708	502
Crystal size (mm^3)	0·2×0·2×0·3	0·2×0·15×0·3	0·3×0·3×0·4	0·2×0·3×0·2
Scan speed (° min^{-1})	2÷30	1·2÷8·2	1·3÷8·2	1·4÷8·2
Scan width (degrees)	$K\alpha_1-0·5\div K\alpha_2+0·5$	$0·7+0·35\tan\theta$	$0·9+0·35\tan\theta$	$0·75+0·35\tan\theta$
θ range (degrees)	2·6–25·0	2·5–30·0	2·5–25·0	2·8–25·0
h, k, l range	−9 to 1	−11 to 10	−10 to 11	−9 to 9
	−8 to 1	0 to 17	−14 to 14	−11 to 11
	−22 to 22	0 to 15	0 to 15	0 to 17
Reflections collected	2918	3310	5264	3626
Reflections used in refinement	1781 (R_{int} = 0·016)	2409 (R_{int} = 0·021)	4966 (R_{int} = 0·048)	3270 (R_{int} = 0·150)
Transmission coefficients $T_{\min}$–$T_{\max}$	0·91–0·95	0·55–0·99	0·95–1·00	0·82–1·00
R [$I > 2\sigma(I)$]	0·040	0·023	0·056	0·089
R_w on F^2	0·1354	0·077	0·153	0·194

Table 7. Atomic coordinates for (1)

In Tables 7–10, the coordinates have been multiplied by 10^4, and the displacement parameters by 10^3

Atom	X/a	Y/b	Z/c	B_{eq}
C(1)	7865(3)	−3773(4)	9745(1)	36(1)
O(1)	7893(2)	−4726(3)	341(1)	51(1)
O(2)	9033(2)	−3697(3)	9355(1)	48(1)
C(2)	6191(3)	−2788(4)	9604(1)	45(1)
N(1)	6115(2)	−1417(3)	9025(1)	42(1)
S	7052(1)	677(1)	9035(1)	33(1)
O(3)	7843(2)	857(3)	9717(1)	50(1)
O(4)	5916(2)	2187(3)	8788(1)	51(1)
C(3)	8695(3)	571(3)	8424(1)	28(1)
C(4)	8463(3)	637(3)	7697(1)	29(1)
C(5)	9805(3)	716(3)	7266(1)	38(1)
C(6)	11431(3)	721(3)	7558(2)	44(1)
C(7)	11702(3)	681(4)	8271(2)	47(1)
C(8)	10342(3)	599(3)	8705(1)	38(1)
N(2)	6776(2)	577(3)	7347(1)	33(1)
O(5)	5651(2)	−347(3)	7615(1)	49(1)
O(6)	6592(2)	1426(3)	6784(1)	53(1)

Table 8. Atomic coordinates for (2)

Atom	X/a	Y/b	Z/c	U_{eq}
Pb	1703(1)	−1214(1)	4770(1)	19(1)
O(1)	444(5)	521(3)	4123(3)	26(1)
O(2)	681(6)	2169(3)	3448(4)	41(1)
C(1)	1121(7)	1226(3)	3569(5)	21(1)
C(2)	2540(6)	846(4)	2983(5)	21(1)
N(1)	3109(5)	−231(3)	3421(4)	21(1)
S	4914(1)	−651(1)	3330(1)	16(1)
O(3)	6273(4)	180(3)	3480(3)	22(1)
O(4)	5401(5)	−1571(3)	4142(3)	27(1)
C(3)	4556(6)	−1068(3)	1721(4)	18(1)
C(4)	4119(7)	−1231(3)	1146(5)	24(1)
C(5)	5508(9)	−1417(5)	−133(6)	35(1)
C(6)	3745(10)	−1487(4)	−896(5)	36(1)
C(7)	2403(9)	−1362(5)	−348(6)	35(1)
C(8)	2790(7)	−1132(4)	931(5)	25(1)
N(2)	7783(7)	−1236(3)	1905(6)	33(1)
O(5)	8199(5)	−1586(4)	2978(4)	42(1)
O(6)	8860(7)	−953(5)	1380(6)	63(2)

Table 9. Atomic coordinates for (3)

Atom	X/a	Y/b	Z/c	B_{eq}
Cd	1924(1)	2075(1)	1774(1)	37(1)
N(1)	2301(7)	713(5)	516(5)	36(2)
C(1)	1618(11)	−141(8)	629(7)	53(2)
C(2)	1891(12)	−945(8)	−102(9)	62(3)
C(3)	2923(11)	−832(8)	−999(8)	56(2)
C(4)	3646(10)	56(8)	−1134(7)	48(2)
C(5)	3311(8)	831(6)	−363(6)	34(2)
N(2)	3776(7)	2435(5)	347(5)	36(2)
C(6)	4111(8)	1784(6)	−472(6)	35(2)
C(7)	5144(9)	1975(8)	−1333(7)	49(2)
C(8)	5904(11)	2836(9)	−1364(8)	61(3)
C(9)	5593(9)	3476(7)	−515(7)	49(2)
C(10)	4524(10)	3230(7)	330(8)	49(2)
N(3)	390(7)	988(6)	2952(5)	41(2)
C(11)	868(10)	−2(9)	3398(7)	57(2)
C(12)	−4(13)	−734(9)	3962(8)	67(3)
C(13)	−1526(14)	−364(11)	4038(9)	77(3)
C(14)	−2063(10)	668(9)	3605(7)	57(2)
C(15)	−1090(9)	1340(8)	3045(6)	44(2)
N(4)	−592(8)	2841(6)	1724(5)	46(2)
C(16)	−1594(9)	2474(7)	2489(6)	42(2)
C(17)	−3021(10)	3079(9)	2766(8)	58(3)
C(18)	−3445(12)	4071(10)	2196(10)	68(3)
C(19)	−2444(13)	4440(9)	1380(10)	71(3)
C(20)	−990(11)	3826(8)	1171(8)	55(2)
O(1)	3630(6)	1287(5)	2764(5)	51(2)
O(2)	4311(7)	1416(6)	4235(5)	60(2)
C(21)	3596(8)	1824(7)	3526(7)	42(2)
C(22)	2618(10)	2990(7)	3684(7)	49(2)
N(5)	1966(7)	3439(5)	2793(5)	37(2)
S	1611(2)	4751(2)	2533(2)	37(1)
O(3)	1613(6)	4966(5)	1439(4)	50(2)
O(4)	2473(7)	5341(5)	2952(5)	54(2)
C(23)	−272(8)	5285(6)	3134(6)	37(2)
C(24)	−1097(9)	6322(7)	2780(7)	48(2)
C(25)	−2580(11)	6716(10)	3206(9)	67(3)
C(26)	−3254(11)	6069(11)	3990(10)	74(3)
C(27)	−2499(12)	5034(10)	4376(8)	68(3)
C(28)	−998(10)	4649(8)	3934(7)	49(2)
N(6)	−436(10)	7052(7)	1922(8)	67(2)
O(5)	515(11)	7475(7)	2070(8)	101(3)
O(6)	−952(11)	7219(9)	1145(8)	114(4)
$O_w(1)$	4755(8)	−1073(6)	3857(5)	66(2)

Table 10. Atomic coordinates and equivalent isotropic displacement parameters for (4)

Atom	X/a	Y/b	Z/c	U_{eq}
Cu	324(4)	2687(2)	1113(2)	29(1)
N(1)	−430(19)	878(13)	1710(9)	25(3)
C(1)	235(26)	774(18)	2618(11)	39(5)
C(2)	−294(28)	−526(18)	2954(14)	49(6)
C(3)	−1645(29)	−1794(20)	2418(13)	52(6)
C(4)	−2262(30)	−1606(21)	1522(13)	56(6)
C(5)	−1651(23)	−334(16)	1166(12)	27(4)
N(2)	−1494(18)	1236(13)	57(9)	22(4)
C(6)	−2310(23)	−79(16)	240(12)	27(4)
C(7)	−3693(26)	−1128(19)	−379(12)	40(5)
C(8)	−4125(29)	−768(19)	−1256(13)	48(6)
C(9)	−3256(25)	571(17)	−1421(12)	32(5)
C(10)	−2029(26)	1585(19)	−782(11)	37(5)
C(11)	2855(26)	4959(19)	469(12)	28(4)
O(1)	1323(18)	3918(13)	235(9)	47(4)
O(2)	3666(17)	5882(13)	85(8)	35(3)
C(12)	3745(29)	5008(20)	1511(14)	46(6)
N(3)	2469(22)	4076(15)	2063(10)	33(4)
S	2005(7)	5061(5)	2928(3)	33(1)
O(3)	1585(18)	6324(13)	2705(9)	46(4)
O(4)	785(20)	4096(14)	3391(10)	59(4)
C(13)	4194(27)	5740(18)	3637(13)	43(6)
C(14)	4797(24)	7176(17)	4201(11)	31(5)
C(15)	6580(25)	7766(21)	4685(14)	57(6)
C(17)	7049(27)	5437(20)	4211(14)	58(6)
C(18)	5319(23)	4803(18)	3631(12)	35(5)
N(4)	3592(21)	8170(16)	4226(10)	30(4)
O(5)	14061(21)	9274(16)	3906(10)	60(4)
O(6)	12371(23)	7874(16)	4672(11)	73(5)
O_w	−2017(19)	3672(14)	1543(9)	51(4)

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