Stabilizing effects in Pd(II)–N–$ArSO_2$–amino acidate complexes: crystal and molecular structure of disodium bis(*N*-benzenesulfonylglycinato-*NO*)palladate(II) monohydrate

Ledi Menabue*, Monica Saladini and Marco Sola
Department of Chemistry, University of Modena, via Campi 183, 41 100 Modena (Italy)

(Received March 12, 1990; revised May 7, 1990)

Abstract

The crystal structure and ^1H NMR study of $Na_2[Pd(BsglyNO)_2]\cdot H_2O$ (BsglyNO = *N*-benzenesulfonylglycinate dianion) are reported. The crystals are monoclinic, space group $P2_1/c$ with cell parameters: $a = 8.868(2)$, $b = 22.716(5)$, $c = 10.046(4)$ Å, $\beta = 98.07(3)°$, $Z = 4$. The structure consists of monomeric $[Pd(BsglyNO)_2]^{2-}$ anions, sodium ions and lattice water molecules. The Pd atom shows a slightly distorted *trans*-coordination given by two independent BsglyNO dianions acting as bidentate ligands through one carboxylate oxygen and the deprotonated sulfonamide nitrogen. Intramolecular contacts of Pd with S, O and aromatic C atoms, and intramolecular stacking interactions involving phenyl rings are present. Some ^1H NMR data in aqueous solution are also reported.

Introduction

Hydrogen bonding, hydrophobic contacts and stacking interactions between aromatic rings influence the stability of a variety of metal complexes [1]. In addition, ring carbons of aromatic ligands may interact with the metal ion and play a stabilizing effect, as found for Pd^{2+} complexes in aqueous solution [2]. The presence of such an interaction has been confirmed by the crystal structure of the Pd(II)–bis(tyrosine) complex in which the distances between the metal and two carbon atoms of the tyrosine ring were found lower than the sum of the van der Waals radii [3]. We have recently carried out an investigation of the solution behavior of some Pd(II)–N–Ar–SO_2–amino acid systems: the stability constants of the species given by *N*-benzenesulfonylglycine, were found greater than those of the corresponding species formed by *N*-tosylglycine, despite the close structural similarity of the two ligands [4]. The crystal and molecular structure of $Na_2[Pd(TsglyNO)_2]$ (TsglyNO = *N*-tosylglycinate dianion, BsglyNO = *N*-benzenesulfonylglycinate dianion), besides the bidentate N,O-coordination of the ligand through the carboxylate oxygen and the deprotonated sulfonamide nitrogen, showed some additional interactions of the sulfonyl group and a carbon atom of the toluene ring with the metal ion [5]. We here report the X-ray structure of the homologous complex given by *N*-benzenesulfonylglycine and some ^1H NMR data on both complexes in aqueous solution with the aim to relate their different solution stability to definite structural factors.

*Author to whom correspondence should be addressed.

Experimental

The $Na_2[Pd(BsglyNO)_2]\cdot H_2O$ complex was prepared as described in ref. 5. Proton NMR spectra were obtained on a Varian XL-200 spectrometer operating at 200.057 MHz. Typical parameters were as follows: spectral band width, 2.4 KHz; pulse width, 9 μs (50° pulse); pulse delay, 2 s; collected number of scans, 15–50. Spectra were run in D_2O and the residual water signal was suppressed by a presaturation pulse from the decoupler.

X-ray data collection and structure determination

Crystal data: $C_{16}H_{16}N_2Na_2O_9PdS_2$, $M = 596.65$; monoclinic, $a = 8.868(2)$, $b = 22.716(5)$, $c = 10.046(4)$ Å, $\beta = 98.07(3)°$, $V = 2003.53$ Å^3, space group $P2_1/c$ (C_{2h}^5 No. 14), $D_m = 1.97$ g cm^{-3} (by flotation), $Z = 4$, $D_c = 1.98$ g cm^{-3}, $F(000)$ 1192, μ(Mo Kα) = 11.09 cm^{-1}. A crystal of approximate dimensions $0.18 \times 0.32 \times 0.22$ mm was mounted on an Enraf-Nonius CAD4 single crystal diffractometer. Cell dimensions were determined from least-squares refinement on diffractometer angles for 25 automatically

0020-1693/90/$3.50

centered reflections from different regions of reciprocal space (Mo Kα radiation). Intensity data were collected at room temperature using graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) with ω–2θ scan technique, 2θ limits 2.5–25°, scan width $1.2 + 0.35 \tan\theta$ and scan speed 2.06–5.48° min^{-1}. Three standard reflections monitored at 3 h intervals, showed no significant changes. The data were corrected for Lorentz and polarization effects and an empirical absorption correction, based on ψ scan [6] was applied ($0.64 \leqslant T \leqslant 0.99$). A total of 3166 independent non-zero reflections ($\pm h$, $+k$, $+l$) was measured, of which 3125 with $I \geqslant 3\sigma(I)$ were used in the structural determination. The structure was solved by conventional Patterson and Fourier techniques, and refined through full-matrix least-squares calculations. Unit weights were used at all stages. All non-hydrogen atoms were refined anisotropically; hydrogen atoms were treated as fixed contributors at their located position ($B_H = B_C + 1.0$ Å^2). Final R and R_w values were 0.034*. A final difference map was featureless with no peaks heigher than 0.25 e Å^{-3}. There was no evidence of secondary extinction. Complex neutral atom scattering factors [7] were used throughout; major calculations were carried out on a Vax-6310 computer using SHELX-76 system of programs [8] and ORTEP plotting program [9]. Final fractional coordinates for non-hydrogen atoms are given in Table 1.

*The quantity minimized during refinement was $\Sigma w(|F_o| - |F_c|)^2$ were w is the weighting factor. The unweighted and weighted residuals were defined as follows: $R = \Sigma(|F_o| - |F_c|)/\Sigma F_o|$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2}$.

Results and discussion

A drawing of the structure showing the labelling scheme is given in Fig. 1. Selected bond distances and angles are reported in Tables 2 and 3.

The structure consists of monomeric units of $[Pd(BsglyNO)_2]^{2-}$ anions, sodium ions and lattice water molecules. The Pd atom shows a slightly distorted square-planar *trans*-coordination given by two independent BsglyNO dianions acting as a bidentate ligand through one carboxylate oxygen and the deprotonated sulfonamide nitrogen. The distortion of the coordination polyhedron can be described with the distances of each atom from the mean least-squares coordination plane N1–O1–N2–O5: N1 = 0.0842, N2 = 0.0838, O1 = −0.0835, O5 = −0.0845 Å; the Pd atom is 0.0883 Å out of the plane. The four atoms of the chelate rings show deviations from their mean plane ranging from −0.0798 to 0.0710 for O1–C1–C2–N1 and from −0.1121 to 0.1007 Å for O5–C9–C10–N2. The dihedral angles of these planes with the coordination plane are 9.12 and 6.94°, respectively. In the corresponding $[Pd(TsglyNO)_2]^{2-}$ complex the PdN_2O_2 plane (exactly planar for symmetry requirements) forms with the chelating group a dihedral angle of 10.39° [5].

In the complex, the Pd–N and Pd–O bond distances are slightly different for the two ligand molecules and the Pd–O bonds are longer as compared to the homologous *N*-tosylglycinate species (2.001(4) and 1.995(4) versus 1.979(2) [5]). It is worth noting a shortening of the C–C and C–N bonds within the two chelating rings as compared to the mean values found for other *N*-tosyl- and *N*-benzenesulfonylaminoacidate-*N*,*O*–metal complexes [10, 11], (1.519(7)

TABLE 1. Final positional parameters

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
Pd	0.24440(5)	0.32350(2)	0.03233(4)	O6	−0.1060(4)	0.2791(2)	0.2204(4)
O1	0.4582(4)	0.3228(2)	−0.0101(4)	C9	0.0158(6)	0.2972(2)	0.1906(5)
O2	0.5910(4)	0.3092(2)	−0.1776(4)	C10	0.1511(6)	0.3085(3)	0.2940(5)
C1	0.4698(6)	0.3224(3)	−0.1370(5)	N2	0.2916(5)	0.3091(2)	0.2343(4)
C2	0.3338(6)	0.3392(3)	−0.2335(5)	S2	0.4300(2)	0.33858(6)	0.3251(1)
N1	0.1958(5)	0.3374(2)	−0.1689(4)	O7	0.4284(5)	0.3225(2)	0.4640(4)
S1	0.0623(2)	0.37737(6)	−0.2421(1)	O8	0.5673(4)	0.3256(2)	0.2696(4)
O3	0.0476(5)	0.3685(2)	−0.3858(4)	C11	0.4080(6)	0.4161(3)	0.3160(6)
O4	−0.0717(5)	0.3674(2)	−0.1816(4)	C12	0.4637(8)	0.4462(3)	0.2134(7)
C3	0.1080(6)	0.4530(3)	−0.2165(6)	C13	0.4473(9)	0.5064(3)	0.2041(8)
C4	0.0978(9)	0.4898(3)	−0.3257(8)	C14	0.3745(9)	0.5363(4)	0.295(1)
C5	0.124(1)	0.5500(3)	−0.3035(9)	C15	0.318(1)	0.5063(4)	0.396(1)
C6	0.1608(9)	0.5713(3)	−0.1775(9)	C16	0.3357(8)	0.4454(3)	0.4080(8)
C7	0.171(1)	0.5339(3)	−0.0686(9)	Na1	−0.1572(3)	0.2175(1)	0.3977(2)
C8	0.1451(8)	0.4742(3)	−0.0868(7)	Na2	0.6028(3)	0.2454(1)	0.1187(2)
O5	0.0318(4)	0.3094(2)	0.0684(4)	Ow	−0.2205(5)	0.3053(2)	0.5038(4)

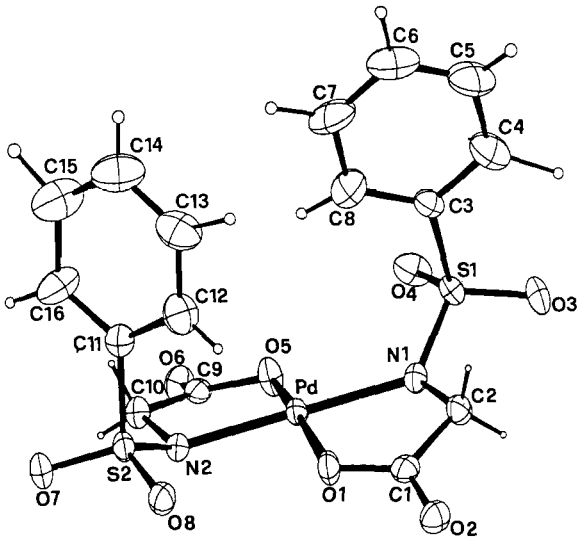

Fig. 1. ORTEP view of $[Pd(BsglyNO)_2]^{2-}$.

TABLE 2. Selected bond distances (Å)[a]

Pd–O1	2.001(4)	Pd–O5	1.995(4)
Pd–N1	2.032(4)	Pd–N2	2.040(4)
O1–C1	1.293(6)	O5–C9	1.286(6)
O2–C1	1.239(6)	O6–C9	1.231(6)
C1–C2	1.487(7)	C9–C10	1.495(7)
C2–N1	1.464(7)	C10–N2	1.456(7)
N1–S1	1.587(5)	N2–S2	1.573(4)
S1–O3	1.446(4)	S2–O7	1.445(4)
S1–O4	1.426(4)	S2–O8	1.440(4)
S1–C3	1.775(6)	S2–C11	1.772(6)
Short contacts			
Na1···O4′	2.257(5)	Na2···Ow‴	2.379(5)
Na1···O5′	2.307(5)	Na2···O2′	2.408(5)
Na1···O2″	2.335(5)	Na2···O8	2.420(5)
Na1···O6	2.360(5)	Na2···O1	2.439(5)
Na1···Ow	2.366(5)	Na2···O7⁗	2.548(6)
		Na2···O6⁗	2.750(6)
Intramolecular contacts involving Pd(II) atom, less than 4 Å			
Pd···S2	3.18	Pd···C11	3.67
Pd···S1	3.23	Pd···C8	3.68
Pd···O4	3.43	Pd···C12	3.71
Pd···O8	3.46	Pd···C3	3.94
Pd···O7	3.80		

[a]Symmetry transformations: ′ = x, $-y+\frac{1}{2}$, $z+\frac{1}{2}$; ″ = $x-1$, $-y+\frac{1}{2}$, $z+\frac{1}{2}$; ‴ = $x+1$, $-y+\frac{1}{2}$, $z-\frac{1}{2}$; ⁗ = x, $-y+\frac{1}{2}$, $z-\frac{1}{2}$; ⁗′ = $x+1$, y, z.

and 1.474(11) Å, respectively), while the C–O bond distance is slightly longer than the corresponding mean value (1.276(13) Å); in the $[Pd(TsglyNO)_2]^{2-}$ complex the corresponding bond distances nearly coincide with the above mean values.

The Pd atom is involved in intramolecular contacts with S,O and aromatic C atoms (Table 2). Phenyl

TABLE 3. Selected bond angles (°)

O1–Pd–N1	82.2(2)	N1–Pd–O5	97.6(2)
O1–Pd–O5	170.2(2)	N1–Pd–N2	179.5(2)
O1–Pd–N2	98.2(2)	O5–Pd–N2	82.0(2)
Pd–O1–C1	114.7(3)	Pd–O5–C9	116.2(3)
O1–C1–O2	121.2(5)	O5–C9–C10	116.2(5)
O1–C1–C2	118.2(5)	O5–C9–O6	121.5(5)
O2–C1–C2	120.6(5)	O6–C9–C10	122.3(5)
C1–C2–N1	110.9(4)	C9–C10–N2	111.4(4)
C2–N1–Pd	111.8(3)	C10–N2–Pd	110.1(3)
Pd–N1–S1	126.1(3)	Pd–N2–S2	122.9(3)
C2–N1–S1	113.3(4)	C10–N2–S2	114.1(4)
N1–S1–O3	109.8(2)	N2–S2–O7	109.9(2)
N1–S1–O4	108.9(2)	N2–S2–O8	108.7(2)
N1–S1–C3	110.2(3)	N2–S2–C11	108.8(3)
O3–S1–O4	116.1(3)	O7–S2–O8	116.5(2)
O3–S1–C3	105.5(3)	O7–S2–C11	106.6(3)
O4–S1–C3	106.2(3)	O8–S2–C11	106.1(3)

rings are involved in intramolecular stacking interactions (C7···C13 = 3.45, C7···C14 = 3.83, C8···C13 = 3.73, C8···C12 = 3.87 Å) and their mean planes form a dihedral angle of 136.89°. The intramolecular stackings, not observed in the corresponding *N*-tosylglycinate complex, and the increased number and strength of Pd–ligand skeletal contacts may account for the greater stability constant value of the present complex (log $\beta = 24.4$ and 23.4 for $[Pd(BsglyNO)_2]^{2-}$ and $[Pd(TsglyNO)_2]^{2-}$, respectively [4]), otherwise unjustified because of the close structural similarity between *N*-tosyl- and *N*-benzensulfonylglycine. Such an increased stability may be also somewhat related to the decrease of the C–C and C–N bond distances that can be indicative of a different and more favorable charge distribution in the chelating plane as compared to the corresponding species formed by *N*-tosylglycine.

The sodium ions have two different environments formed by bonded oxygen atoms: the first Na^+ is pentacoordinated and the second has a distorted octahedral coordination.

The crystal packing is determined by hydrogen bonds involving the water molecule and the sulfonyl oxygens, and by intermolecular hydrophobic interactions between phenyl rings (from 3.42 to 3.97 Å).

The ^1H NMR spectral features of both ligands are modified upon metal complexation. For ligand-to-metal molar ratios higher than 2:1 two sets of signals are observed arising from the complex and the free ligand in slow exchange. In both complexes the pattern of the aromatic protons and the CH_2 signal are shifted to higher frequencies as compared to the free ligands (Fig. 2). The increased separation of the two subsets of aromatic signals may indicate that the interaction between the aromatic ring and the metal ion revealed by the X-ray structure, is

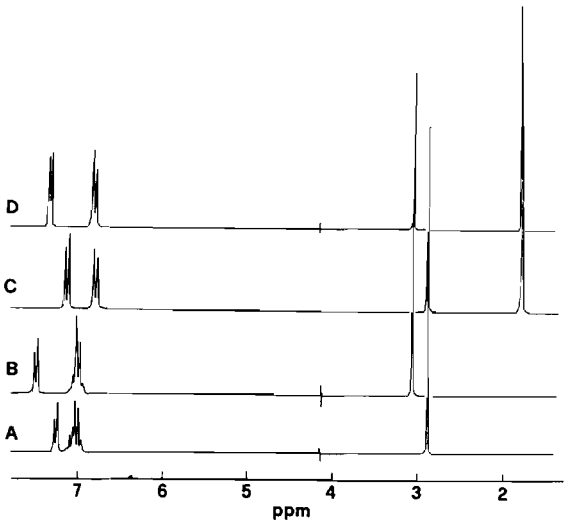

Fig. 2. 200 MHz ^{1}H NMR spectra of: (A) *N*-benzenesulfonylglycine; (B) $[Pd(BsglyNO_2)]^{2-}$; (C) *N*-Toluenesulfonylglycine; (D) $[Pd(TsglyNO)_2]^{2-}$. All spectra are recorded in D_2O at pH 7 (pH-meter reading uncorrected for isotopic effect).

maintained in the solution state. Accordingly, in the presence of the Zn(II) ion the aromatic proton signals of the same ligands, that, in this case, interact with the metal only through the carboxylate group [12], are unchanged as compared to those of the free ligand. *N*-benzenesulfonylglycine undergoes greater ^{1}H NMR spectral changes upon metal complexation than *N*-tosylglycine, and this indicates that it interacts more strongly with the Pd^{2+} ion, in line with the polarographic [4] and the above X-ray structural data.

Supplementary material

Listing of atomic temperature factors, hydrogen atoms parameters, angles and distances associated with phenyl rings, interatomic stacking interactions, hydrogen bonds and selected least-square planes (6 pages); tables of calculated and observed structure factors (9 pages). Ordering information is available from the authors on request.

Acknowledgements

We are grateful to the Centro Interdipartimentale Grandi Strumenti (C.I.G.S.) of the University of Modena which supplied the diffractometer and the NMR spectrometer, the Centro Interdipartimentale di Calcolo Elettronico of the University of Modena for computing support and the Ministero dell' Università e della Ricerca Scientifica of Italy for financial support.

References

1 B. E. Fischer and H. Sigel, *J. Am. Chem. Soc., 102* (1980) 2998, and refs. therein.
2 R. B. Martin and S. H. Kim, *J. Am. Chem. Soc., 106* (1985) 1707.
3 M. Sabat, M. Jezowska and H. Kozlowski, *Inorg. Chim. Acta, 37* (1979) L511.
4 G. Battistuzzi Gavioli, M. Borsari, L. Menabue, G. C. Pellacani, M. Saladini and M. Sola, *J. Chem. Soc., Dalton Trans.*, (1990) 1585.
5 L. Menabue, M. Saladini and M. Sola, *Inorg. Chem., 29* (1990) 1293.
6 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A, 24* (1968) 351.
7 *International Tables for X-ray Crystallography*, Vol. IV, Kynoch Press, Birmingham, U.K., 1974, pp. 99–101, 149–150.
8 G. M. Sheldrick, *SHELX-76*, program for crystal structure determination, University Chemical Laboratory, Cambridge, U.K., 1976.
9 C. K. Johnson, *ORTEP, Rep. ORNL-3794*, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.
10 L. Antolini, L. Menabue, M. Saladini and M. Sola, *Inorg. Chim. Acta, 152* (1988) 17, and refs. therein.
11 S. Chauduri, *J. Chem. Soc., Dalton Trans.*, (1984) 779.
12 L. P. Battaglia, A. Bonamartini Corradi, L. Menabue, M. Saladini, M. Sola and G. Battistuzzi Gavioli, *Inorg. Chim. Acta, 107* (1985) 73.