Contribution from the Department of Chemistry, University of Modena, Via Campi, 183, 41100 Modena, Italy, and Ministero dell'Universitá e Ricerca Scientifica e Tecnologica (40%) of Italy

N-(Arylsulfonyl)glycines as Cyclometalating Ligands. Crystal and Molecular Structures of Disodium Bis(μ-chloro)bis[μ-*N*-(phenylsulfonyl)glycinato-*O*,*N*,*C*]-bis[μ-*N*-(phenylsulfonyl)glycinato-*O*,*O'*]tetrapalladate(II) Hexahydrate and Disodium Bis(μ-chloro)bis(μ-*N*-tosylglycinato-*O*,*N*,*C*)bis(μ-*N*-tosylglycinato-*O*,*O'*)-tetrapalladate(II)–4.5-Water–2-*N*-Tosylglycine

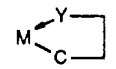
Ledi Menabue* and Monica Saladini

Received November 13, 1990

The interaction of *N*-(phenylsulfonyl)- and *N*-(4-tolylsulfonyl)- (*N*-tosyl hereafter) glycine (Bsgly and Tsgly, respectively) with Pd(II) ion at pH $\cong$ 3.5 gives rise to "cyclometalation" reactions leading to complexes of the formulas $Na_2[Pd_4Cl_2(\text{Bsgly-}O,N,C)_2(\text{Bsgly-}O,O')_2]\cdot 6H_2O$ (I) and $Na_2[Pd_4Cl_2(\text{Tsgly-}O,N,C)(\text{Tsgly-}O,O')]_2\cdot 4.5H_2O\cdot 2\text{TsglyH}$ (II) (Bsgly-*O*,*N*,*C* and Tsgly-*O*,*N*,*C* = *O*,*N*,*C*-bonded ligand; Bsgly-*O*,*O'* and Tsgly-*O*,*O'* = carboxylate bridging ligand; TsglyH = neutral *N*-tosylglycine). The complexes crystallize in the triclinic $P\bar{1}$ space group with a = 13.469 (4) Å, b = 13.636 (4) Å, c = 15.005 (5) Å, α = 70.94 (2)°, β = 66.32 (2)°, γ = 88.59 (2)°, and Z = 2 for I and a = 17.058 (1) Å, 18.897 (2) Å, c = 13.194 (1) Å, α = 94.61 (1)°, β = 107.98 (1)°, γ = 74.32 (1)°, and Z = 2 for II. Both structures consist of two tetrameric units, symmetry generated from two independent $[Pd_2Cl(\text{L-}O,N,C)(\text{L-}O,O')]$ (L = Bsgly or Tsgly) monoanions. In each tetramer one Pd(II) atom is coordinated with the deprotonated sulfonamide nitrogen and the carbon atom of the aromatic ring in the ortho position to the sulfonyl group of a ligand molecule, the bridging chlorine atom, and one oxygen atom of a bridging carboxyl from a second ligand molecule. The other crystallographically independent Pd(II) atom is coordinated with the other oxygen of the bridging carboxyl, the chlorine atom, the deprotonated sulfonamide nitrogen, and the oxygen atom of a monodentate carboxylate group forming a N,O-chelate glycine-like ring. Both of the Pd(II) atoms show a slightly distorted square-planar coordination geometry. Infrared and NMR results are also reported.

Introduction

"Cyclometalation" reactions giving rise to the



ring system (M = metal ion; Y = N, P, As, O, S) are, in general, important because the formed complexes may be used in the synthesis of many unusual heterocyclic molecules.[1]

Among the cyclometalated complexes reported in literature, a very large number contain Pd(II) and Pt(II) ions and phenyl-substituted nitrogen-containing ligands, such as benzylamines, azobenzenes, benzoylamines, phenyldiimides, etc.,[1-3] that satisfy the major requirements for performing cyclometalation:[2] (a) the cyclometalated ring will contain five atoms; (b) the nitrogen atom is sterically hindered; (c) the carbon atom must be substituted by electrophilic attack. In these ligands, which contain nitrogen as the Y donor atom, it is suggested that the first step of reaction involves the formation of a M–N bond, which is followed by substitution of the metal on the carbon.[2] In the case of aromatic N-substituted α-amino acids, which can in principle lead to cyclopalladation, normally the formation of the more stable glycine-like N,O-chelate ring involving the ionized carboxyl group is preferred with respect to cyclometalation,[4] and this reaction takes place only with *N*,*N*-dimethyl-*C*-phenylglycine ethyl ester, where the carboxylate group is prevented from coordinating with the metal.[4] A similar type of behavior should reasonably be expected also for *N*-(arylsulfonyl)-α-amino acids such as *N*-(4-tolylsulfonyl)- and *N*-(phenylsulfonyl)glycine, which above pH = 4 form very stable, N,O-chelate complex species[5] of the formulas $[Pd(\text{L-}N,O)]$ and $[Pd(\text{L-}N,O)_2]^{2-}$ and at pH $\geq$ 5.7 separated the solid structurally known square-planar $Na_2[Pd(\text{L-}N,O)_2]\cdot xH_2O$ (x = 0, L = Tsgly; x = 1, L = Bsgly), where the ligand molecules act as a bidentate chelate through one carboxylate oxygen and the deprotonated sulfonamide nitrogen.[6,7] Nevertheless, at more acidic pH ($\cong$3.5), when almost half of the ligand should be still in its neutral form ($pK_{\text{carboxyl}} \cong 3.45$), two very unusual cyclopalladated complexes are obtained, whose structural and spectroscopic characterizations are here reported.

Experimental Section

$Na_2[Pd_4Cl_2(\text{Bsgly-}O,N,C)_2(\text{Bsgly-}O,O')_2]\cdot 6H_2O$. To 2 mmol of Bsgly, dissolved at 25 °C with aqueous NaOH to pH $\cong$ 11.5, was added 0.5 mmol of $PdCl_2$ dissolved in the minimum amount of 1 M HCl. The yellow-red solution was filtered, the pH value corrected to 3.5 with NaOH, and the final volume adjusted to 30 mL. After a few days, red crystals separated out of solution. Anal. Found: C, 25.65; H, 2.52; N, 3.61; S, 8.80. Calcd for $C_{32}H_{28}Cl_2N_4Na_2O_{16}Pd_4S_4\cdot 6H_2O$: C, 25.55; H, 2.68; N, 3.73; S, 8.48.

$Na_2[Pd_4Cl_2(\text{Tsgly-}O,N,C)_2(\text{Tsgly-}O,O')]_2\cdot 4.5H_2O\cdot 2\text{TsglyH}$. This compound was obtained by the procedure similar to that of the above Bsgly complex, but the ligand to metal molar ratio was 2:1 and the ligand was dissolved in a methanol–water (1:5 v/v) solution. Anal. Found: C, 31.46; H, 3.29; Cl, 3.93; N, 3.90; Na, 2.24; Pd, 20.70; S, 9.63. Calcd for $C_{54}H_{58}Cl_2N_6Na_2O_{24}Pd_4S_6\cdot 4.5H_2O$: C, 32.68; H, 3.41; Cl, 3.58; N, 4.24; Na, 2.32; Pd, 21.46; S, 9.68.

Physical Measurements. Infrared spectra were recorded with a Bruker 113v FT-IR instrument as KBr pellets in the 4000–400-cm^{-1} spectral range and as polythene pellets in the 500–50-cm^{-1} spectral range. Proton NMR spectra were obtained on a Varian XL-200 spectrometer operating at 200.057 MHz. Typical parameters were as follows: spectral bandwidth, 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.

Crystal Data Collection. Crystal data and details of parameters associated with data collection are given in Table I. Cell dimensions were determined by diffractometry with an Enraf-Nonius CAD4 single-crystal diffractometer and refined by a least-squares fit using 25 automatically centered reflections from different regions of reciprocal space (Mo Kα radiation). Intensity data were collected with the ω–2θ scan technique up to $\theta \leq 25°$, scan width 0.80 + 0.35 tan θ and scan speed 2.06–5.48° min^{-1} for I and 1.18–5.48° min^{-1} for II. Three standard reflections, monitored every 4 h, showed no significant changes. The data were corrected for Lorentz and polarization effects and for II an empirical absorption correction based on a ψ scan[8] was applied (0.918 $\leq T$ factor $\leq$ 0.995). The structures were solved by conventional Patterson and

---

*To whom correspondence should be addressed at the University of Modena.

(1) Bruce, M. I. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 73.

(2) Dehand, J.; Pfeffer, M. *Coord. Chem. Rev.* **1976**, *18*, 327 and references therein.

(3) Omae, I. *Chem. Rev.* **1979**, *79*, 287 and references therein.

(4) Ryabov, A. D.; Polyakov, V. A.; Yatsimirsky, A. K. *Inorg. Chim. Acta* **1984**, *91*, 59.

(5) Battistuzzi Gavioli, G.; Borsari, M.; Menabue, L.; Pellacani, G. C.; Saladini, M.; Sola, M. *J. Chem. Soc., Dalton Trans.* **1990**, 1585.

(6) Menabue, L.; Saladini, M.; Sola, M. *Inorg. Chem.* **1990**, *29*, 1293.

(7) Menabue, L.; Saladini, M.; Sola, M. *Inorg. Chim. Acta* **1990**, *176*, 95–98.

(8) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect A* **1968**, *24*, 351.

0020-1669/91/1330-1651$02.50/0

Table I. Crystal Data

	$Na_2[Pd_4Cl_2(Bsgly)_4]\cdot6H_2O$ (I)	$Na_2[Pd_4Cl_2(Tsgly)_4]\cdot4.5H_2O\cdot2TsglyH$ (II)
mol formula	$C_{32}H_{28}Cl_2N_4Na_2O_{16}$-$Pd_4S_4\cdot6H_2O$	$C_{54}H_{58}Cl_2N_6Na_2O_{24}$-$Pd_4S_6\cdot4.5H_2O$
mol wt	1503.41	1983.11
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	13.469 (4)	17.058 (1)
b, Å	13.636 (4)	18.897 (2)
c, Å	15.005 (5)	13.194 (1)
α, deg	70.94 (2)	94.61 (1)
β, deg	66.32 (2)	107.98 (1)
γ, deg	88.59 (2)	74.32 (1)
V, Å^3	2367.33	3894.74
Z	2	2
d_{obsd}, g cm^{-3}	2.08	1.68
d_{calcd}, g cm^{-3}	2.11	1.69
cryst size, mm	0.20 × 0.25 × 0.22	0.18 × 0.20 × 0.25
radiation (λ, Å)	Mo Kα (λ = 0.71069)	Mo Kα (λ = 0.71069)
2θ limits, deg	2.5–22	2.0–25
temp, °C	20	20
μ(Mo Kα), cm^{-1}	18.60	19.87
F(000)	1480	1994
reflecns collected	6089	14770
unique data used ($I \geq 3\sigma(I)$)	4769	10761
R	0.0280	0.0441
R_w	0.0288	0.0441

Table II. Selected Bond Distances (Å) for $Na_2[Pd_4Cl_2(Bsgly)_4]\cdot6H_2O$[a]

complex molecule I		complex molecule II	
Pd(1)–Cl(1)	2.292 (2)	Pd(3)–Cl(2)	2.301 (2)
Pd(1)–O(1)	1.963 (4)	Pd(3)–O(9)″	1.979 (5)
Pd(1)–N(1)	2.027 (6)	Pd(3)–N(3)″	2.041 (4)
Pd(1)–O(6)	2.005 (4)	Pd(3)–O(13)	2.003 (4)
Pd(1)···Pd(1)′	4.513 (2)	Pd(3)···Pd(3)″	4.472 (2)
Pd(1)···Pd(2)′	3.127 (1)	Pd(3)···Pd(4)″	3.131 (1)
C(2)–N(1)	1.491 (8)	C(18)–N(3)	1.504 (8)
N(1)–S(1)	1.676 (5)	N(3)–S(3)	1.670 (7)
S(1)–C(3)	1.735 (8)	S(3)–C(19)	1.732 (7)
Pd(2)–Cl(1)	2.355 (2)	Pd(4)–Cl(2)	2.336 (2)
Pd(2)–O(5)	2.141 (4)	Pd(4)–O(14)	2.131 (5)
Pd(2)–N(1)′	2.070 (6)	Pd(4)–N(3)	2.064 (6)
Pd(2)–C(4)′	1.960 (6)	Pd(4)–C(20)	1.961 (7)
Pd(2)···Pd(2)′	4.151 (1)	Pd(4)···Pd(4)″	4.264 (1)
Pd(2)···Pd(1)	3.003 (1)	Pd(4)···Pd(3)	3.048 (1)
C(10)–N(2)	1.452 (9)	C(26)–N(4)	1.445 (9)
N(2)–S(2)	1.605 (5)	N(4)–S(4)	1.602 (6)
S(2)–C(11)	1.755 (8)	S(4)–C(27)	1.758 (6)

[a] Symmetry transformations: for single-primed atoms, $-x, -y + 1, z$; for double-primed atoms, $-x, -y, -z + 1$.

Table III. Selected Bond Angles (deg) for $Na_2[Pd_4Cl_2(Bsgly)_4]\cdot6H_2O$[a]

complex molecule I		complex molecule II	
O(1)–Pd(1)–N(1)	84.2 (2)	O(9)″–Pd(3)–N(3)″	84.3 (2)
O(1)–Pd(1)–O(6)	176.9 (2)	O(9)″–Pd(3)–O(13)	176.7 (2)
O(1)–Pd(1)–Cl(1)	90.2 (2)	O(9)″–Pd(3)–Cl(2)	91.7 (2)
N(1)–Pd(1)–O(6)	95.4 (2)	N(3)″–Pd(3)–O(13)	94.1 (2)
N(1)–Pd(1)–Cl(1)	172.7 (2)	N(3)″–Pd(3)–Cl(2)	174.5 (2)
O(6)–Pd(1)–Cl(1)	90.4 (2)	O(13)–Pd(3)–Cl(2)	86.4 (2)
Pd(1)–O(1)–C(1)	115.2 (5)	Pd(3)″–O(9)–C(17)	115.8 (5)
Pd(1)–Cl(1)–Pd(2)	80.5 (1)	Pd(3)–Cl(2)–Pd(4)	82.2 (1)
Pd(1)–O(6)–C(9)	124.4 (5)	Pd(3)–O(13)–C(25)	124.7 (4)
C(2)–N(1)–Pd(1)	108.2 (4)	C(18)–N(3)–Pd(3)″	107.2 (4)
C(2)–N(1)–S(1)	109.5 (5)	C(18)–N(3)–S(3)	109.9 (4)
C(2)–N(1)–Pd(2)′	112.5 (4)	C(18)–N(3)–Pd(4)	112.7 (4)
S(1)–N(1)–Pd(1)	116.0 (3)	S(3)–N(3)–Pd(3)″	115.4 (3)
S(1)–N(1)–Pd(2)′	110.8 (3)	S(3)–N(3)–Pd(4)	111.8 (3)
Pd(2)′–N(1)–Pd(1)	99.5 (3)	Pd(4)–N(3)–Pd(3)″	99.4 (2)
C(3)–C(4)–Pd(2)′	117.6 (5)	C(19)–C(20)–Pd(4)	117.8 (5)
Pd(2)′–C(4)–C(5)	126.1 (5)	Pd(4)–C(20)–C(21)	125.6 (5)
O(5)–Pd(2)–Cl(1)	88.7 (1)	O(14)–Pd(4)–Cl(2)	88.3 (1)
O(5)–Pd(2)–N(1)′	90.0 (2)	O(14)–Pd(4)–N(3)	91.1 (2)
O(5)–Pd(2)–C(4)′	175.9 (2)	O(14)–Pd(4)–C(20)	176.3 (2)
Cl(1)–Pd(2)–N(1)′	176.2 (2)	Cl(2)–Pd(4)–N(3)	177.8 (2)
Cl(1)–Pd(2)–C(4)′	95.2 (2)	Cl(2)–Pd(4)–C(20)	95.1 (2)
N(1)′–Pd(2)–C(4)′	86.2 (3)	N(3)–Pd(4)–C(20)	86.4 (2)
Pd(2)–O(5)–C(9)	127.7 (5)	Pd(4)–O(14)–C(25)	129.4 (5)
C(10)–N(2)–S(2)	119.0 (5)	C(26)–N(4)–S(4)	119.0 (5)

[a] Symmetry transformations: for single-primed atoms, $-x, -y + 1, -z$; for double-primed atoms, $-x, -y, -z + 1$.

Table IV. Selected Bond Distances (Å) for $Na_2[Pd_4Cl_2(Tsgly)_4]\cdot4.5H_2O\cdot2TsglyH$[a]

complex molecule I		complex molecule II	
Pd(1)–Cl(1)	2.328 (2)	Pd(3)–Cl(2)	2.318 (2)
Pd(1)–O(1)′	1.986 (4)	Pd(3)–O(13)″	1.990 (7)
Pd(1)–N(1)′	2.042 (6)	Pd(3)–N(4)″	2.052 (6)
Pd(1)–O(6)	1.999 (4)	Pd(3)–O(17)	2.010 (7)
Pd(1)···Pd(1)′	4.310 (1)	Pd(3)···Pd(3)″	4.464 (1)
Pd(1)···Pd(2)′	3.101 (1)	Pd(3)···Pd(4)″	3.144 (1)
C(2)–N(1)	1.508 (9)	C(29)–N(4)	1.498 (13)
N(1)–S(1)	1.687 (6)	N(4)–S(4)	1.689 (6)
S(1)–C(3)	1.729 (9)	S(4)–C(30)	1.741 (11)
Pd(2)–Cl(1)	2.341 (2)	Pd(4)–Cl(2)	2.340 (2)
Pd(2)–O(5)	2.151 (4)	Pd(4)–O(18)	2.157 (6)
Pd(2)–N(1)	2.071 (7)	Pd(4)–N(4)	2.057 (6)
Pd(2)–C(4)	1.965 (7)	Pd(4)–C(31)	1.963 (9)
Pd(2)···Pd(2)′	4.344 (1)	Pd(4)···Pd(4)″	4.268 (1)
Pd(2)···Pd(1)	3.104 (1)	Pd(4)···Pd(3)	3.031 (1)
C(11)–N(2)	1.448 (10)	C(38)–N(5)	1.437 (12)
N(2)–S(2)	1.625 (8)	N(5)–S(5)	1.618 (7)
S(2)–C(12)	1.749 (8)	S(5)–C(39)	1.746 (10)
Neutral *N*-Tosylglycine			
C(19)–O(9)	1.19 (1)	C(46)–O(21)	1.31 (1)
C(19)–O(10)	1.31 (1)	C(46)–O(22)	1.21 (1)
C(19)–C(20)	1.51 (1)	C(46)–C(47)	1.48 (1)
C(20)–N(3)	1.44 (1)	C(47)–N(6)	1.46 (1)
N(3)–S(3)	1.61 (1)	N(6)–S(6)	1.60 (1)
S(3)–O(11)	1.42 (1)	S(6)–O(23)	1.43 (1)
S(3)–O(12)	1.42 (1)	S(6)–O(24)	1.43 (1)
S(3)–C(21)	1.79 (1)	S(6)–C(48)	1.75 (1)

[a] Symmetry transformations: for single-primed atoms, $-x, -y + 1, z$; for double-primed atoms, $-x + 1, -y, -z$.

Fourier techniques[9] and refined through full-matrix least-squares calculations; because of the large number of variable parameters, the atoms were subdivided into two groups, which were refined one at a time, in alternate cycles. For both complexes all non-hydrogen atoms were refined anisotropically, except phenyl carbons and for II also water oxygens, which were refined isotropically. All the hydrogen atoms of I were located on a ΔF map, while for II only 32 hydrogens were located, among which are those bonded to uncoordinated N atoms and that bonded to the carboxylate O(10) of one neutral Tsgly molecule, and then they were treated as fixed contributors with isotropic thermal parameters 1.0 Å^2 higher than those of bonded atoms. Further refinement of this model gives for I an *R* index of 0.0280 (R_w = 0.0288) with use of the weighting scheme $w = 1.545/(\sigma^2 F_o + 0.0002F_o^2)$. For complex II, least-squares refinement yielded very large thermal motion parameters for Na(3) and for the water oxygen Ow(5), suggesting partial site occupancy (0.50 according to stoichiometric requirements and elemental analysis). Zero weight was assigned to ten strong low-order reflections, which may be affected by secondary extinction. The final *R* index was 0.044. Complex neutral scattering factors (except for Na$^+$)[10] were used throughout; all calculations were carried out on a Wax 6310 computer of the CICAIA of the University of Modena by using SHELX76,[11] PARST,[12] and ORTEP[13] programs.

---

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

(10) *International Tables for X-ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 99–101, 149–150.

(11) Sheldrick, G. M. *SHELX-76 Program for crystal structure determination*; University Chemical Laboratory: Cambridge, England, 1976.

(12) Nardelli, M. *Comput. Chem.* **1983**, *7*, 95.

(13) Johnson, C. K. *ORTEP*; Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.

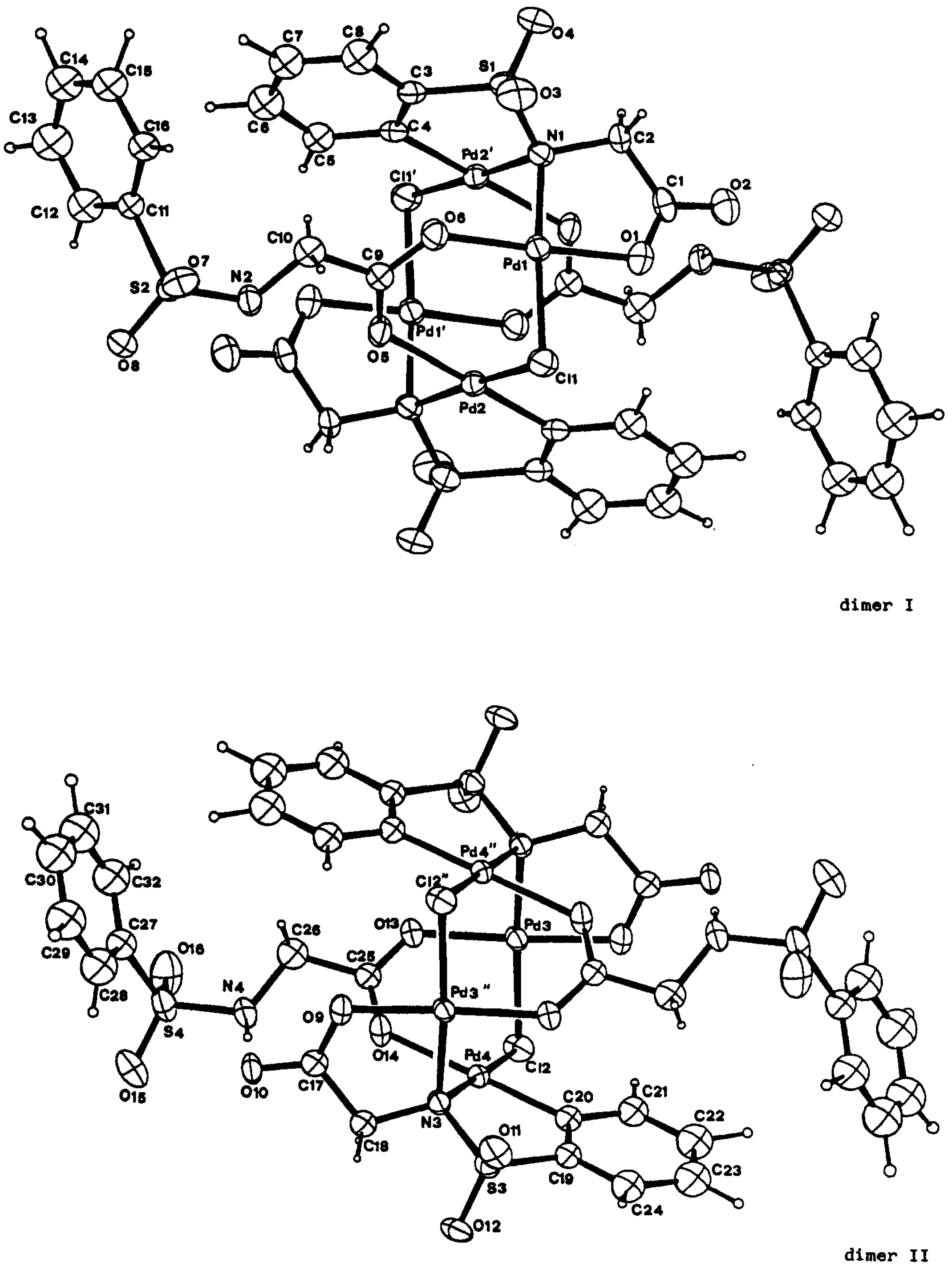


Figure 1. ORTEP view of the two crystallographically independent tetramers of $[Pd_4Cl_2(Bsgly\text{-}O,N,C)_2(Bsgly\text{-}O,O')_2]^{2-}$ with numbering scheme and thermal motion ellipsoids (35%) for non-hydrogen atoms. The hydrogen atoms are represented as spheres of arbitrary radius.

Analyses. Carbon, hydrogen, nitrogen, and sulfur were analyzed with a C. Erba Model 1106 instrument by Mr. G. Goldoni; palladium, chlorine, and sodium were determined by Mikroanalytischer Labor Pascher (Remagen, Germany).

Results and Discussion

A drawing of the structures for the Bsgly complexes showing the labeling scheme is given in Figure 1. Bond distances and angles are reported in Tables II and III for Bsgly-Pd(II) complexes and in Tables IV and V for Tsgly-Pd(II) ones.

The crystals of both Bsgly- and Tsgly-Pd complexes contain two crystallographically independent but structurally similar $[Pd_2Cl(L\text{-}O,N,C)(L\text{-}O,O')]$ monoanions. Each of them upon symmetry transformation generates one tetrameric dianion; sodium ions, lattice water molecules and, in Tsgly complex, two neutral crystallographically independent tosylglycine molecules (Figure 2) are also present.

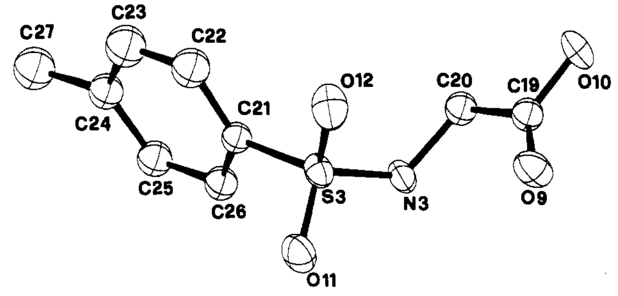


Figure 2. ORTEP view of neutral *N*-tosylglycine.

In each tetramer one Pd(II) atom is coordinated with the deprotonated sulfonamide nitrogen and with the carbon atom of the aromatic ring in the position ortho to the sulfonyl group of

Table V. Selected Bond Angles (deg) for $Na_2[Pd_4Cl_2(Tsgly)_4]\cdot4.5H_2O\cdot2TsglyH^a$

complex molecule I		complex molecule II	
O(1)′–Pd(1)–N(1)′	84.3 (2)	O(13)″–Pd(3)–N(4)″	83.9 (3)
O(1)′–Pd(1)–O(6)	176.1 (2)	O(13)–Pd(3)–N(17)	177.7 (3)
O(1)′–Pd(1)–Cl(1)	92.3 (2)	O(13)″–Pd(3)–Cl(2)	91.2 (2)
N(1)′–Pd(1)–O(6)	92.2 (2)	N(4)″–Pd(3)–O(17)	94.2 (2)
N(1)′–Pd(1)–Cl(1)	176.1 (2)	N(4)″–Pd(3)–Cl(2)	173.9 (2)
O(6)–Pd(1)–Cl(1)	91.1 (2)	O(17)–Pd(3)–Cl(2)	90.6 (2)
Pd(1)′–O(1)–C(1)	114.9 (5)	Pd(3)″–O(13)–C(28)	114.7 (5)
C(2)–N(1)–Pd(1)′	107.7 (4)	C(29)–N(4)–Pd(3)″	107.0 (5)
C(2)–N(1)–S(1)	109.9 (5)	C(29)–N(4)–S(4)	108.4 (5)
C(2)–N(1)–Pd(2)	112.3 (5)	C(29)–N(4)–Pd(4)	108.4 (5)
S(1)–N(1)–Pd(1)′	115.5 (3)	S(4)–N(4)–Pd(3)″	116.4 (3)
S(1)–N(1)–Pd(2)	113.1 (3)	S(4)–N(4)–Pd(4)	111.9 (3)
Pd(2)–N(1)–Pd(1)′	97.8 (3)	Pd(4)–N(4)–Pd(3)″	99.8 (3)
C(3)–C(4)–Pd(2)	117.7 (5)	C(30)–C(31)–Pd(4)	117.6 (6)
Pd(2)–C(4)–C(5)	125.6 (5)	Pd(4)–C(31)–C(32)	127.0 (6)
O(5)–Pd(2)–Cl(1)	88.8 (2)	O(18)–Pd(4)–Cl(2)	88.6 (2)
O(5)–Pd(2)–N(1)	89.1 (2)	O(18)–Pd(4)–N(4)	89.3 (2)
O(5)–Pd(2)–C(4)	175.8 (3)	O(18)–Pd(4)–C(31)	175.9 (3)
Cl(1)–Pd(2)–N(1)	177.8 (2)	Cl(2)–Pd(4)–N(4)	177.0 (2)
Cl(1)–Pd(2)–C(4)	95.4 (2)	Cl(2)–Pd(4)–C(31)	95.4 (3)
N(1)–Pd(2)–C(4)	86.7 (3)	N(4)–Pd(4)–C(31)	86.6 (3)
Pd(1)–Cl(2)–Pd(2)	83.3 (1)	Pd(3)–Cl(2)–Pd(4)	81.2 (1)
Pd(2)–O(5)–C(10)	130.1 (5)	Pd(4)–O(18)–C(37)	129.4 (6)
Pd(1)–O(6)–C(10)	124.7 (4)	Pd(3)–O(17)–C(37)	123.3 (5)
C(11)–N(2)–S(2)	118.5 (6)	C(38)–N(5)–S(5)	120.8 (6)
	Neutral *N*-Tosylglycine		
O(9)–C(19)–O(10)	124.5 (10)	O(21)–C(46)–O(22)	122.8 (10)
O(9)–C(19)–C(20)	125.4 (9)	O(21)–C(46)–C(47)	112.4 (10)
O(10)–C(19)–C(20)	110.1 (8)	O(22)–C(46)–C(47)	124.7 (10)
C(19)–C(20)–N(3)	112.8 (8)	C(46)–C(47)–N(6)	110.7 (9)
C(20)–N(3)–S(3)	122.8 (7)	C(47)–N(6)–S(6)	121.0 (7)
N(3)–S(3)–O(11)	106.2 (5)	N(6)–S(6)–O(23)	107.5 (5)
N(3)–S(3)–O(12)	107.9 (5)	N(6)–S(6)–O(24)	104.8 (4)
N(3)–S(3)–C(21)	107.9 (4)	N(6)–S(6)–C(48)	108.6 (5)
O(11)–S(3)–O(12)	120.8 (5)	O(23)–S(6)–O(24)	119.4 (5)
O(11)–S(3)–C(21)	105.9 (5)	O(23)–S(6)–C(48)	108.4 (5)
O(12)–S(3)–C(21)	107.5 (5)	O(24)–S(6)–C(48)	107.7 (5)
S(3)–C(21)–C(22)	119.1 (8)	S(6)–C(48)–C(49)	118.7 (8)
S(3)–C(21)–C(26)	118.6 (8)	S(6)–C(48)–C(53)	120.1 (8)

[a] Symmetry transformations: for single-primed atoms, $-x, -y + 1, -z$; for double-primed atoms, $-x + 1, -y, -z$.

a ligand molecule, with the bridging chlorine atom and with one oxygen atom of a bridging carboxyl from a second ligand molecule. The other crystallographically independent Pd(II) atom is coordinated to the other oxygen of the bridging carboxyl, the chlorine atom, the deprotonated sulfonamide nitrogen, and the oxygen atom of a monodentate carboxylate group, forming a N,O-chelate glycine-like ring. Both of the Pd(II) atoms show a slightly distorted square-planar coordination geometry.

In the tetramer two symmetrically related ligand molecules are monoanions with only the carboxylate group in the ionized form, which acts as syn–syn bridge, while the other ligands present three active binding sites and bridge two Pd(II) atoms through the deprotonated sulfonamide nitrogen, which gives rise to two five-membered chelate rings.

Some features of these structures are worth emphasizing as they demonstrate the coordinative versatility of *N*-(arylsulfonyl)glycines: (i) two differently ionized forms of the coordinated ligands are present; (ii) the deprotonated sulfonamide nitrogen atom surprisingly acts as a bridging group (only one previous report exists on a similar behavior for a peptide nitrogen[14]; (iii) the formation of the N,O-glycine like ring, as normally observed for *N*-(arylsulfonyl)amino acids–metal(II) complexes (metal(II) = Pd(II) and Cu(II)[5,6,15]) at high pH, in our case does not prevent the cyclometalation reaction, unlike what is reported for simple amino acid complexes.[4]

In the complex molecules, bond distances and angles at Pd(1) are similar to those corresponding at Pd(3) (NO_2Cl chromophore), and the same holds true for Pd(2) with respect to Pd(4) (NOCCl chromophore). In the N,O-chelate rings, Pd–O and Pd–N distances are close to those found for $Na_2[Pd(L\text{-}N,O)_2]\cdot xH_2O$[5,6] complexes, and in the N,C-chelate rings, the Pd–C and Pd–N distances (av 1.963 (2) and 2.065 (5) Å, respectively) are shorter than the corresponding mean values of 2.00 (2) and 2.12 (5) Å in previously reported complexes.[3,16–19] The bridging syn–syn carboxylate group forms two markedly different Pd–O bonds and the great trans influence[20] of the σ-bonded aromatic carbon may be considered responsible for the lengthening of Pd–O bond trans to it.

In the tetramers Pd(1) is connected to Pd(2) and Pd(3) to Pd(4) by a monoatomic bridge formed by the chlorine and by a triatomic bridge represented by the carboxyl; the geometric constraint on the last group forces the Pd–Cl–Pd angles to diminish strongly (av 82.0 (1)°) with respect to the value of 93.0 in $PdCl_2$ and the mean value of 91.7 (10)° in chloro-bridged Pd(II) complexes,[20] while the mean Pd–Cl of 2.32 (2) Å, comparable to that in $PdCl_2$ (2.31 Å),[21] is significantly shortened as compared to those of the above-cited complexes (av 2.40 (4) Å).[20]

In the coordinated ligand molecules, the bond lengths and angles involving the nitrogen atom (N–S and N–C) and the S–C distance are strongly influenced from the bonding mode of the ligand. In the O,N,C-bonded ligand, the nitrogen atom, which acts as a monoatomic bridge, is involved in four bonds, adopting an sp^3 hybridization (mean S–N–C = 110.0°), and consequently the N–S and N–C bond distances move in the direction of values calculated from covalent bond radii for a single bond (N–C = 1.51 Å, N–S - 1.78 Å[22,23]); at the same time this fact results in an increase in the double-bond character of S–C with a slight decrease in bond length. On the contrary, the different bonding modes of the ligand seem not to affect the planarity of the benzene rings.

In the tetramers, the four Pd(II) atoms lie on the same plane for symmetry requirements and the metal–metal distances between two Pd atoms connected by a Cl or N atom are shorter than the sum of the van der Waals radii,[22] suggesting that some amount of interaction should be present. The fundamental and symmetry-generated Pd, Cl, and N atoms form a nearly planar eight-membered ring, and only the N atoms move significantly out of the best plane.

The coordination geometry around Pd(II) ions is slightly tetrahedrally distorted from square planar, as indicated by trans bond angles involving the metal that fall in the range 172.7–178.8°, similar to what is found for $Na_2[Pd(Bsgly\text{-}N,O)_2]\cdot H_2O$.[7] The four atoms in the glycine-like chelate rings deviate from planarity, and the dihedral angles formed by their best planes with the corresponding coordination planes are in the range 7.03–9.24°; for $Na_2[Pd(L\text{-}N,O)_2]\cdot xH_2O$ complexes, these angles are in the range 6.94–10.39°.[6,7]

The four atoms belonging to the chelate rings containing the aromatic carbons are far from planar; nevertheless, they turn out to form relatively small dihedral angles with the coordination plane and with the fused phenyl ring (the values range from 8.97 to 16.14°).

Except Na(3), which is tetracoordinated, the sodium ions show distorted octahedral geometry deriving from interactions with oxygen atoms.

Neutral *N*-Tosylglycine. In both molecules the two C–O bond

---

(14) Freeman, H. C.; Schoone, J. C.; Sime, J. G. *Acta Crystallogr.* **1965**, *18*, 381.

(15) Antolini, L.; Menabue, L.; Saladini, M.; Sola, M. *Inorg. Chim. Acta* **1988**, *152*, 17 and references therein.

(16) Russell, D. R.; Tucker, P. A. *J. Chem. Soc., Dalton Trans.* **1975**, 1743.

(17) Braunstein, P.; Matt, D.; Dusasoy, Y.; Fischer, J.; Mitschler, A.; Ricard, L. *J. Am. Chem. Soc.* **1981**, *103*, 5115.

(18) Arlen, C.; Pfeffer, M.; Bars, O.; Grandjean, D. *J. Chem. Soc., Dalton Trans.* **1983**, 1535.

(19) Omae, I. *Organometallic Intermolecular Coordination Compounds*; Elsevier: Amsterdam, 1986; Chapter 2.

(20) Hartley, F. R. *The Chemistry of Platinum and Palladium*; Applied Science: London, 1973; Chapters 2 and 11.

(21) Wells, A. F. *Z Kristallogr.* **1939**, *100*, 189.

(22) Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, NY, 1960.

(23) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

Table VI. More Relevant Infrared Bands (cm^{-1})

	BsglyH	$Na_2[Pd_4Cl_2(Bsgly)_4]\cdot 6H_2O$	TsglyH	$Na_2[Pd_4Cl_2(Tsgly)_4]\cdot 4.5H_2O\cdot 2TsglyH$
ν(OH)		3445 m br		3564 ms br
ν(NH)	3315 s	3190 w br	3273 s	3225 m sh
$\nu(COO)_{as}$	1729 vs	1626 vs, 1591 vs	1719 vs	1725 ms, 1607, 1598 vs, 1584 vs
$\nu(COO)_s$	1248 vs	1400 ms, 1379 ms	1231	1420 s, 1389 vs, 1250 ms
$\nu(SO_2)_{as}$	1318 vs	1325 ms, 1309 s, 1292 s	1336 vs	1326 vs, 1307 vs, 1290 s
$\nu(SO_2)_s$	1159, 1131 vs	1159 vs, 1123 s	1157 vs	1160 vs, 1136 s
ν(SN)	868 s	825 ms	890 ms	870 ms, 854 s
$\delta(SO_2)$	582 vs	574 s	550 m	569 s
$\rho(SO_2)$	556	564 s	532 ms	551 s
ν(Pd–Cl)		297 s		295 s

lengths are markedly different from one another and indicate that the carboxyl group is in the protonated form and the corresponding bond distances and angles are similar for both molecules; the nitrogen atom presents an sp^2 hybridization, and the S–N distance is comparable with that found in the metal(II) complexes containing Tsgly in the monoanionic form[24] and in neutral *N*-(phenylsulfonyl)-DL-alanine.[25]

Crystal Packing. Crystal packing is mainly determined by hydrogen bonds involving amino groups, carboxylate and sulfonyl oxygens, and water molecules with N···O and O···O separation in the 2.79–3.13-Å range. In the Tsgly crystal, the two tetramers are held together by strong intermolecular ring-stacking interactions between phenyl residues, with distances in the range 3.50–3.90 Å and the dihedral angle between phenyl planes in the 19.90–20.11° range. This gives rise to a polymeric arrangement of alternate tetramer types, while in the Bsgly crystal the inter-tetramer interactions are due to hydrophobic contacts between carbons of nearly orthogonal phenyl rings belonging to the same type of tetramers.

Spectroscopic Results. The more relevant IR bands due to functional groups of the ligands and their tentative assignment are reported in Table VI. The absorptions of carboxylate and sulfonic groups are split because of the presence of differently ionized ligand molecules. The bands at 1626, 1400 and 1607, 1420 cm^{-1} are assigned to bridging carboxylate groups[26] in the Tsgly and Bsgly complexes, respectively; furthermore, in the Tsgly crystal the presence of neutral tosylglycine is strongly evidenced by the appearance of two bands (1735 and 1250 cm^{-1}) assigned to asymmetric and symmetric carboxyl stretching vibrations. As a general behavior, the deprotonation and metal coordination of the sulfonamide nitrogen increases the bond order of S–N and slightly decreases the S–O bond order.[27] This fact moves ν(S–N) to higher frequency, whereas asymmetric and symmetric $\nu(SO_2)$ are shifted to lower frequencies.[27] In the present case, the four bonds formed by the deprotonated sulfonamide nitrogen cause a marked lengthening of the S–N bond as compared to that in the free ligand, leaving the S–O distance almost unchanged. It is thus expected the stretching frequencies associated with these groups will be close to those observed for the free ligand, making it hazardous to assign the bands to the differently ionized amino acids. The presence of strong bands at values below 1300 cm^{-1} may be reasonably explained by the involvement of sulfonic oxygens in sodium coordination at distances in the 2.296–2.796-Å range. Inspection of the 700–800-cm^{-1} spectral region shows no evidence of cyclometalation, owing to the lack of extra bands suggestive of a further substitution on the phenyl rings.

By comparison with the free ligands, only one strong band is observed in 500–50-cm^{-1} spectral region, which is consistent with bridging Pd–Cl stretching vibration.[20] The involvement of a ring carbon atom in metal binding is also confirmed in aqueous solution at pH ≅ 3.0. The ^{1}H NMR spectra show a composite signal pattern in the aromatic region, which may be interpreted as a superimposition of an A_2X_2 multiplet characteristic of the free ligand, with slightly upfield shifted resonances arising from a different proton system.

The first conclusion is that *N*-(arylsulfonyl)glycines may be classified into the cyclometalating ligands, and the complexes can be obtained under mild experimental conditions. This coordination mode may be related primarily with the strong donor ability of the deprotonated sulfonamide nitrogen substantiated by the formation of a monoatomic bridge leading to closure of two fused N,O- and N,C-chelate rings. Furthermore, the preferential square-planar geometry for the Pd(II) ion and the requirements imposed by the bridging Cl atom are responsible for the short Pd–N distances. Consequently, a peculiar stability is derived for the tetrameric species, and, in spite of their complexity, they are present also in solution.

If the pH is raised, nitrogen deprotonation takes place in the carboxylate bridging ligand, with subsequent metal coordination; the resulting displacement of chlorine and aryl carbon atoms breaks the tetrameric building with formation of $[Pd(L\text{-}N,O)_2]^{2-}$ dianions.[5]

Acknowledgments. We are grateful to the Centro Interdipartimentale Grandi Strumenti (CIGS) of the University of Modena, which supplied the diffractometer, the FT-IR spectrophotometer, and the NMR spectrometer, to the Centro Interdipartimentale di Calcolo Elettronico (CICAIA) of the University of Modena for computing support, and to Mr. L. Locusti for recording infrared spectra.

Supplementary Material Available: Listings of atomic positional parameters and temperature factors, bond distances and angles involving the ligand molecules, interatomic contacts involving sodium ions and hydrogen bonds, and least-squares planes (24 pages); tables of calculated and observed structure factors for $Na_2[Pd_4Cl_2(Bsgly)_4]\cdot 6H_2O$ and $Na_2[Pd_4Cl_2(Tsgly)_4]\cdot 4.5H_2O\cdot 2TsglyH$ (45 pages). Ordering information is given on any current masthead page.

---

(24) Antolini, L.; Menabue, L.; Saladini, M. *Inorg. Chem.* **1985**, *24*, 1219.

(25) Chaudhuri, S. *J. Chem. Soc., Dalton Trans.* **1984**, 779.

(26) Antolini, L.; Battaglia, L. P.; Battistuzzi Gavioli, G.; Bonamartini Corradi, A.; Grandi, G.; Marcotrigiano, G.; Menabue, L.; Pellacani G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1687.

(27) Antolini, L.; Battaglia, L. P.; Bonamartini Corradi, A.; Marcotrigiano, G.; Menabue, L.; Pellacani, G. C. *J. Am. Chem. Soc.* **1985**, *107*, 1369 and references therein.