Inorganica Chimica Acta, *185* (1991) 201–210

Synthesis and characterization of square-planar platinum(II) and palladium(II) complexes with pyridine-2,6-dicarboxylic acid (H_2dipic). X-ray crystal structure of *trans*-$Na_2[Pt(dipic)_2]\cdot 6H_2O$ and $K[Pt(dipic)I]\cdot 1/2H_2O$

Gavino Chessa, Giampaolo Marangoni, Bruno Pitteri*

Dipartimento di Chimica, Facoltà di Scienze matematiche, fisiche e naturali, Università di Venezia, Calle Larga S. Marta 2137, 30 123 Venice (Italy)

Valerio Bertolasi, Gastone Gilli and Valeria Ferretti

Dipartimento di Chimica e Centro di Strutturistica Diffrattometrica, Università di Ferrara, via Borsari 46, 44 100 Ferrara (Italy)

(Received December 13, 1990; revised March 7, 1991)

Abstract

The tetra-coordinate complexes *trans*-$[Pt(Hdipic)_2]\cdot 2H_2O$ (**1**) and *trans*-$[Pd(Hdipic)_2]\cdot 2H_2O$ (**2**) as well as their potassium and sodium derivatives *trans*-$K_2[Pt(dipic)_2]$ (**3**), *trans*-$Na_2[Pt(dipic)_2]\cdot 6H_2O$ (**4**) and *trans*-$Na_2[Pd(dipic)_2]\cdot 2H_2O$ (**5**) have been obtained in high yield by reacting aqueous solutions of $K_2[PtCl_4]$ and $K_2[PdCl_4]$ with pyridine-2,6-dicarboxylic acid (H_2dipic) or its potassium or sodium salts, respectively, in 1:2 molar ratio. **1** and **2** are also formed on reacting equimolar amounts of reagents in water (pH 1.4) leaving in solution unreacted $K_2[PtCl_4]$ and $K_2[PdCl_4]$. The resulting mixtures brought to pH 5 with KOH undergo a redistribution reaction with formation of the monoanionic species $K[Pt(dipic)Cl]\cdot H_2O$ (**6**) and $K[Pd(dipic)Cl]\cdot H_2O$ (**7**), respectively. The iodo derivative $K[Pt(dipic)I]\cdot 1/2H_2O$ (**8**) was obtained from the chloro species by replacement of the coordinated chloride with iodide in aqueous solution. All the complexes have been characterized by a number of physico-chemical measurements including the X-ray analysis of *trans*-$Na_2[Pt(dipic)_2]\cdot 6H_2O$ (**4**) and $K[Pt(dipic)I]\cdot 1/2H_2O$ (**8**). Crystals of **4** are monoclinic, space group $P2_1/c$, $Z=2$, with unit-cell dimensions $a=11.912(1)$, $b=6.544(1)$, $c=12.699(1)$ Å, $\beta=91.56(1)°$. Crystals of **8** are triclinic, space group $P\bar{1}$, $Z=4$, with unit-cell dimensions $a=11.018(1)$, $b=11.585(2)$, $c=9.946(1)$ Å, $\alpha=97.99(1)$, $\beta=115.07(1)$, $\gamma=73.14(1)°$. The structures were solved from three dimensional counter data by Patterson and Fourier methods and refined by full-matrix least-squares to $R=0.019$ and 0.030 for 1556 and 4118 observed reflections, respectively. The crystal of **4** is built up by centrosymmetric $Pt(dipic)_2^{2-}$ anions and Na^+ cations hexa-coordinated by four water molecules and two carboxylate oxygens belonging to the ligands. Each dipicolinate ion behaves as a bidentate ligand, and the resulting coordination around the platinum is square planar. The asymmetric unit of compound **8** contains two independent square planar $Pt(dipic)I^-$ anions, in each of them the dipicolinate ion acts as a tridentate ligand and the fourth position is occupied by an iodine atom. The planar complex anions $Pt(dipic)I^-$ are stacked but not parallel and Pt atoms form infinite zigzag chains.

Introduction

Pyridine-2,6-dicarboxylic acid (H_2dipic) is a versatile ligand which is known to bind, as a neutral, monobasic, or dibasic chelating agent, to a large number of bivalent and trivalent transition metal ions as well as lanthanides(III) and actinides in different oxidation states [1].

As a part of our interest in square planar tetra-coordinate complexes of d^8 transition metal ions, we have recently synthesized a series of anionic platinum(II) complexes of the type $[Pt(dipic)X]^-$ ($X=Cl$, Br, I, NO_2, SCN) in which the dipicolinate anion behaves as a tridentate ligand, and have determined the rate constants for the displacement of the coordinated chloride from the substrate $[Pt(dipic)Cl]^-$ by H_2O, Br^-, I^-, SCN^-, $SeCN^-$, CN^- and SO_3^{2-} in water [2].

---

*Author to whom correspondence should be adressed.

0020-1693/91/$3.50

At approximately the same time a paper appeared dealing with the unusual behaviour of $[Pt(dipic)Cl]^-$ in aqueous solution [3] which has shown that at higher temperatures or lower concentrations the complex is yellow and monomeric, whereas at lower temperatures or higher concentrations it is red and probably polymeric. A spectroscopic and crystallographic study of the discrete monomer and evidence for a stacked polymer are also reported as well as the preparation of the bis(bidentate) complex $K_2[Pt(dipic)_2]$ to which a *trans* configuration has been assigned on the basis of stereochemical considerations.

We have now systematically re-examined the interaction of H_2dipic with $PtCl_4^{2-}$ in aqueous solution by varying the ligand to metal molar ratio, pH and temperature. The new chelated species $[Pt(Hdipic)_2]\cdot 2H_2O$ and its sodium form *trans*-$Na_2[Pt(dipic)_2]\cdot 6H_2O$ have been obtained as well as the previously known $[Pt(dipic)Cl]^-$ in a very pure form and high yield.

The same preparative route allowed us to isolate the analogous palladium(II) species for the first time. All the species were characterized by a number of analytical and physico-chemical measurements including the X-ray structure determination of *trans*-$Na_2[Pt(dipic)_2]\cdot 6H_2O$ and $K[Pt(dipic)I]\cdot 1/2H_2O$.

Experimental

Reagents

Crystalline $K_2[PtCl_4]$ and $K_2[PdCl_4]$ were prepared from high purity metals by standard methods. Pyridine-2,6-dicarboxylic acid and deuteriated solvents for ^1H NMR with a minimum isotopic purity of 99.9%, were Aldrich products.

Preparation of complexes

trans-$[Pt(Hdipic)_2]\cdot 2H_2O$ *(1)*

A solution of K_2PtCl_4 (0.415 g, 1 mmol) in water (10 cm^3) was added, with stirring, to a warm solution of pyridine-2,6-dicarboxylic acid (0.334 g, 2 mmol) in water (30 cm^3). The mixture was allowed to react at 80 °C for 3 h, during which time a pale yellow product gradually precipitated. The crude product was filtered off, dried under reduced pressure (0.40 g, 71%), and crystallized from a dilute boiling aqueous solution slowly cooled at room temperature.

trans-$[Pd(Hdipic)_2]\cdot 2H_2O$ *(2)*

A solution of K_2PdCl_4 (0.326 g, 1 mmol) in water (10 cm^3) was added, with stirring, to a solution of pyridine-2,6-dicarboxylic acid (0.334 g, 2 mmol) in water (30 cm^3). The mixture was allowed to react at 80 °C for 10 min, during which time a yellow–ochre product gradually precipitated. After addition of boiling water (50 cm^3) the product dissolved completely and the yellow–orange crystals slowly obtained on cooling the clear orange solution at room temperature were filtered off and dried under vacuum (0.360 g, 76%).

trans-$K_2[Pt(dipic)_2]$ *(3)*

A solution of K_2PtCl_4 (0.415 g, 1 mmol) in water (10 cm^3) was slowly added, with stirring, to a solution of pyridine-2,6-dicarboxylic acid (0.334 g, 2 mmol) in water (30 cm^3), brought to pH 6 with 1 N KOH. The mixture was allowed to react at 80 °C for 10 min, during which time the colour of the solution gradually changed from reddish to pale yellow and a cream coloured powder precipitated. Recrystallization of the powder from hot water gave a poor quality microcrystalline product unsuitable for X-ray analysis (0.51 g, 85%).

trans-$Na_2[Pt(dipic)_2]\cdot 6H_2O$ *(4)*

A solution of K_2PtCl_4 (0.415 g, 1 mmol) in water (10 cm^3) was slowly added, with stirring, to a solution of pyridine-2,6-dicarboxylic acid (0.334 g, 2 mmol) in water (30 cm^3), brought to pH 6 with 1 N NaOH. The mixture was allowed to react at 80 °C for 10 min, during which time the colour of the solution gradually changed from reddish to pale yellow. Cream-coloured crystals suitable for X-ray structure determination were obtained on slowly cooling the solution at room temperature and were filtered off and air dried under vacuum (0.370 g, 54%).

trans-$Na_2[Pd(dipic)_2]\cdot 2H_2O$ *(5)*

A solution of K_2PdCl_4 (0.326 g, 1 mmol) in water (10 cm^3) was added, with stirring, to a warm solution of pyridine-2,6-dicarboxylic acid (0.334 g, 2 mmol) in water (30 cm^3), brought to pH 6 with 1 N NaOH. The mixture was allowed to react at 80 °C for 10 min, and its colour gradually changed from brown to red–orange. Yellow crystals which were obtained on slowly cooling the solution at room temperature were filtered off and dried under vacuum (0.360 g, 69%).

$K[Pt(dipic)Cl]\cdot H_2O$ *(6) and* $K[Pt(dipic)I]\cdot \frac{1}{2}H_2O$ *(8)*

These complexes were prepared as reported in the literature [2]. Their purity was checked by elemental analysis and comparison of the IR and UV–Vis spectra with those reported. $K[Pt(dipic)Cl]\cdot H_2O$ was also prepared by an alternative method. A solution of K_2PtCl_4 (0.415 g, 1

TABLE 1. Analytical and physical data

Compound	Colour	Melting point (°C)	Λ_M (Ω^{-1} cm^2 mol^{-1})	Analysis (%)[a]			
				C	H	Cl	N
$Pt(Hdipic)_2 \cdot 2H_2O$ (**1**)	yellow	>220	5[b]	29.6	2.13		4.68
				(29.8)	(2.15)		(4.97)
$Pd(Hdipic)_2 \cdot 2H_2O$ (**2**)	yellow–orange	>220	3[b]	35.2	2.49		5.75
				(35.4)	(2.55)		(5.90)
$K_2[Pt(dipic)_2]$ (**3**)	cream	>220	182[c]	27.8	0.95		4.73
				(27.9)	(1.00)		(4.64)
$Na_2[Pt(dipic)_2] \cdot 6H_2O$[d] (**4**)	cream	>220	185[c]	25.3	2.71		4.32
				(24.7)	(2.67)		(4.12)
$Na_2[Pd(dipic)_2] \cdot 2H_2O$[d] (**5**)	yellow	>220	212[c]	32.3	1.12		5.33
				(32.4)	(1.94)		(5.40)
$K[Pt(dipic)Cl] \cdot H_2O$ (**6**)	red	>220	66[b]	18.7	0.8	7.88	2.99
				(18.6)	(1.11)	(7.83)	(3.09)
$K[Pd(dipic)Cl] \cdot H_2O$ (**7**)	yellow–ochre	>220	60[b]	23.1	1.01	9.70	3.71
				(23.1)	(1.38)	(9.74)	(3.85)
$K[Pt(dipic)I] \cdot 1/2H_2O$ (**8**)	orange	>220	54[b]	15.7	0.70		2.52
				(15.7)	(0.75)	(23.7)	(2.62)

[a] Calculated values in parentheses. [b] In dimethylformamide. [c] In water. [d] Potassium absent by atomic absorption spectrophotometry analysis.

mmol) in water (10 cm^3) was slowly added, with stirring, to a warm solution of pyridine-2,6-dicarboxylic acid (0.167 g, 1 mmol) in water (30 cm^3, pH1.4). The mixture was allowed to react at 80 °C for 3 h, during which time a pale yellow product (**1**) gradually separated from the solution which remained reddish due to the presence of unreacted K_2PtCl_4. The pH of the mixture was then slowly raised to 5 by addition of 1 M KOH under stirring and at the same temperature. Under these conditions the precipitate dissolved giving an yellow–orange solution from which, on cooling on a ice bath, the chloro species precipitated as a gel-like red product which was filtered off and dried under vacuum at room temperature (0.362 g, 80%).

K[Pd(dipic)Cl]·H$_2$O (7)

A solution of K_2PdCl_4 (0.326 g, 1 mmol) in water (10 cm^3) was added, with stirring, to a solution of pyridine-2,6-dicarboxylic acid (0.167 g, 1 mmol) in water (30 cm^3), brought to pH 6 with 1 N KOH at room temperature. The addition of the Pd(II) salt was accompanied by rapid formation of an immobile, yellow–ochre, gel-like product which was filtered off and dried under reduced pressure (0.327 g, 90%).

Analytical results and some physical data for the complexes are reported in Table 1, while spectroscopic ^{1}H NMR, IR and UV–Vis data are summarized in Table 2.

Physical measurements

IR spectra were recorded on Perkin-Elmer 683 (4000–250 cm^{-1}, KBr pellets) and Perkin-Elmer 180 (300–150 cm^{-1}, polyethylene pellets) spectrophotometers; UV–Vis spectra (500–200 nm) were measured on Varian-Cary 219 and Perkin-Elmer Lambda 5 spectrophotometers with 1 cm quartz cell at 25 °C; ^{1}H NMR spectra were obtained on a Varian FT 80 spectrometer at 34 °C; conductometric measurements were carried out with a CDM 83 Radiometer Copenhagen Conductivity Meter and CDC 334 immersion electrode at 25 °C; atomic absorption spectrophotometry was performed with a Perkin-Elmer 2380 instrument.

Crystal structure determinations

Intensity data were collected on an Enraf-Nonius CAD4 diffractometer with monochromated Mo Kα radiation and $\omega/2\theta$ scan technique. Cell parameters were obtained from least-squares refinement of the setting angles of 25 centered reflections in the range $8 < \theta < 13°$. Crystal data are reported in Table 3. Intensities were corrected for Lorentz, polarization and absorption (minimum transmission factors: 59% and 69% for **4** and **8**, respectively). Scattering factors and anomalous dispersion parameters were taken from ref. 4; solution by Patterson and Fourier methods. The structure of compound **4** was refined by full-matrix least-squares using anisotropic thermal parameters for all non-hydrogen atoms and isotropic ones for hydrogens. The structure of compound **8** was refined by full matrix least-squares using anisotropic thermal parameters for all non-hydrogen atoms and H atoms in calculated fixed positions. Weights for the last cycle were applied according

TABLE 2. ^{1}H NMR, UV–Vis band maxima, and selected IR absorptions data for the complexes

Compound	Spin system (pyridine protons)	^{1}H NMR$^{a, b, c}$	UV–Vis (nm)	IR (cm^{-1})
Pt(Hdipic)$_2$·2H$_2$O (**1**)	ABC	$\delta_A=8.53$, $\delta_B=8.08$, $\delta_C=8.08$ (J (AB)$=7.92$, J (AC)$=8.00$, J (BC)$=1.53$)	324(sh) 272 244(sh)	3460m, 3170mb, 3080m, 1715s, 1665sb, 1603m, 1481w, 1430m, 1345s, 1308s, 1260s, 1204m, 1195m, 1171s, 1090m, 1035w, 918s, 842m, 811m, 782m, 768s, 726m, 709m, 675w, 600w, 588w, 486m, 400w, 355w, 311w
Pd(Hdipic)$_2$·2H$_2$O (**2**)			268	3470m, 3080m, 1725s, 1670s, 1610s, 1445w, 1381m, 1330s, 1308s, 1265sb, 1170m, 1132w, 1090w, 1075w, 1000w, 910m, 845m, 813w, 762m, 750s, 690s, 670m, 648m, 595w, 545m, 490w, 455w, 430w, 402w
K$_2$[Pt(dipic)$_2$] (**3**)		ref. 3	324(sh) 281(sh) 272 248(sh)	3440sb, 3090w, 3052m, 1670s, 1640sb, 1470m, 1410s, 1385s, 1335s, 1260s, 1211m, 1180m, 1154m, 1098m, 1035m, 922m, 840m, 800m, 765s, 736s, 689m, 600w, 578w, 490ms, 462vw, 370w, 351m, 322m
Na$_2$[Pt(dipic)$_2$]·6H$_2$O (**4**)	ABC	$\delta_A=8.16$, $\delta_B=7.74$, $\delta_C=7.55$ (J (AB)$=7.83$ J (AC)$=7.91$, J (BC)$=1.54$)	324(sh) 281(sh) 272 248(sh)	3440sb, 3090w, 3052m, 1670s, 1640sb, 1470m, 1410s, 1390s, 1342s, 1265s, 1211m, 1180m, 1154m, 1098m, 1032m, 926m, 840m, 798m, 765s, 735s, 687m, 600w, 580w, 490ms, 470vw, 370w, 351m, 318m
Na$_2$[Pd(dipic)$_2$]·2H$_2$O (**5**)	ABC	$\delta_A=8.10$, $\delta_B=7.64$, $\delta_C=7.63$ (J (AB)$=7.42$, J (AC)$=8.22$, J (BC)$=8.10$)	274(sh) 268 260(sh)	3440sb, 3080w, 3040w, 3018vw, 1670sb, 1640sb, 1469w, 1412s, 1385s, 1335s, 1260s, 1205s, 1174s, 1160m, 1093s, 1028s, 992w, 916s, 840m, 796m, 765s, 750w, 730s, 682s, 600m, 570w, 480s, 450w, 400m, 370m, 351w, 316
K[Pt(dipic)Cl]·H$_2$O (**6**)	AB$_2$	$\delta_A=8.48$, $\delta_B=7.82$ (J (AB)$=7.9$)	334 286(sh) 246 230(sh)	3500mb, 3085mmult, 1670sb, 1324smult, 1151m, 1138m, 1111m, 1106m, 916m, 832m, 770m, 753ms, 675m, 601w, 465m, 334wsh, 324m, 303w
K[Pd(dipic)Cl]·H$_2$O (**7**)	AB$_2$	$\delta_A=8.42$, $\delta_B=7.85$ (J (AB)$=7.9$)	384 272(sh) 213	3520mb, 3058wmult, 3040w, 1670s, 1660ms, 1322s, 1148m, 1143m, 1095, 910m, 845w, 818w, 765s, 743m, 698w, 670s, 592w, 453m, 308m, 301w
K[Pt(dipic)I]·1/2H$_2$O (**8**)	AB$_2$	$\delta_A=8.56$, $\delta_B=7.88$ (J (AB)$=7.9$)	348 262(sh)	1324s, 1157m, 1147m, 1139m, 1097m, 996w, 911m, 830wb, 760m, 751m, 700w, 668m, 595w, 458w, 362w, 172mb

[a] Chemical shifts (δ) in ppm from SiMe$_4$ as internal standard, coupling constants in Hz, measurements at ambient temperature. [b] Measured in D$_2$O (compounds **4** and **5**), (CD$_3$)$_2$SO (**1**), (CD$_3$)$_2$NCOD (**6**, **7**, **8**). [c] Chemical shift (δ) for the proton of the uncoordinated–COOH in compound **1** $\delta=8.20$.

TABLE 3. Crystal data[a]

Compound	4	8
M	679.37	535.21
Crystal size (mm)	0.17×0.24×0.36	0.26×0.24×0.50
Space group	$P2_1/c$	$P\bar{1}$
Unit cell parameters		
a (Å)	11.912(1)	11.018(1)
b (Å)	6.544(1)	11.585(2)
c (Å)	12.699(1)	9.946(1)
α (°)	90	97.99(1)
β (°)	91.56(1)	115.07(1)
γ (°)	90	73.14(1)
U (Å^3)	989.6(2)	1100.3(3)
F(000)	656	959
Z	2	4
D_c (g cm^{-3})	2.28	3.23
μ (Mo Kα) (cm^{-1})	72.6	160.3
Independent reflections	2156	4796
Reflections with $I > 3\sigma(I)$	1556	4118
Variables (last cycle)	191	281
Final R, R'[b]	0.019, 0.024	0.030, 0.046
Final shift/error max.	0.2	0.05
Largest peak (e Å^{-3}) in the final Fourier difference map	0.35	0.82
Weighting scheme (w)[c]	$p=0.03$	$p=0.02$
S = error in an observation of unit weight	1.20	1.69

[a]Data common to both determinations: graphite-monochromated Mo Kα radiation, $\lambda=0.71069$ Å, $T=22$ °C; $\theta_{min}-\theta_{max}=2-27°$. [b]$R=\Sigma|\Delta F_o|/\Sigma|F_o|$; $R'=(\Sigma w|\Delta F_o|^2/\Sigma w|F_o|^2)^{1/2}$. [c]$w=4F_o^2/[\sigma^2(F_o^2)+(pF_o^2)^2]$.

to the scheme given in Table 3. All calculations were performed by the SDP [5] and PARST [6] system of programs. Final positional parameters are given in Tables 4 and 5. See also 'Supplementary material'.

TABLE 4. Positional parameters ($\times 10^4$) of complex **4** with e.s.d.s. in parentheses

Atom	x	y	z
Pt	0	0	0
O(1)	−1526(2)	762(5)	−601(2)
O(2)	−2477(2)	953(6)	−2132(2)
O(3)	2244(2)	2891(5)	−525(2)
O(4)	3347(3)	608(5)	−1291(3)
N	420(3)	702(6)	−1484(2)
C(1)	−485(3)	682(7)	−2158(3)
C(2)	−379(3)	698(7)	−3228(3)
C(3)	694(4)	723(7)	−3641(3)
C(4)	1605(3)	848(7)	−2962(3)
C(5)	1454(3)	916(6)	−1873(3)
C(6)	−1601(3)	773(7)	−1623(3)
C(7)	2438(3)	1487(7)	−1144(3)
Na	4175(1)	−2635(3)	−1738(1)
O(1w)	5006(3)	−1274(5)	−3323(2)
O(2w)	3407(3)	−3621(5)	−69(3)
O(3w)	5836(3)	−1466(7)	−988(3)

Results and discussion

Treatment of stoichiometric (2:1) amounts of H_2dipic and $K_2[PtCl_4]$ in water gives in good yield complex **1** which is virtually insoluble at room temperature and analyzes as a compound with a molar ratio Pt:ligand of 1:2. The presence in the IR spectrum of two strong stretching vibrations centred at 1665 and 1715 cm^{-1} indicates the presence of both coordinated carboxylate groups and free carboxylic acid groups, respectively. Accordingly the spectra of the potassium and sodium derivatives **3** and **4** do not display the higher frequency vibration but a band at 1640 cm^{-1}, typical of the asymmetric stretching of free carboxylate anion, is present. The X-ray structure confirmed the expected bis(bidentate) square planar *trans* configuration of **4**, which can be reasonably proposed also for compounds **1** and **3** as well as for the parent palladium(II) species **2** and **5**, which have been obtained under the same experimental conditions and show IR spectra very similar to those of compounds **1** and **4**. The ^{1}H NMR spectra of these compounds (Table 2) are consistent with the proposed structures.

The bis(bidentate) complex **1** is also formed on reacting equimolar amounts of $K_2[PtCl_4]$ and H_2dipic in water (pH 1.4), in which it is very insoluble, leaving in solution unreacted $K_2[PtCl_4]$. This mixture,

TABLE 5. Positional parameters ($\times 10^4$) of complex **8** with e.s.d.s. in parentheses

Atom	*x*	*y*	*z*
Pt(A)	3964.1(3)	6766.6(3)	4473.2(3)
I(A)	4319.3(6)	8355.4(6)	6609.1(6)
O(1A)	1926(5)	6867(5)	3895(5)
O(2A)	207(5)	6145(6)	2149(6)
O(3A)	5933(5)	6270(5)	4545(6)
O(4A)	7145(5)	5074(6)	3336(7)
N(A)	3683(6)	5650(5)	2811(6)
C(1A)	2411(7)	5511(6)	2039(8)
C(2A)	2158(8)	4788(9)	768(9)
C(3A)	3236(8)	4277(8)	338(9)
C(4A)	4569(7)	4438(7)	1197(9)
C(5A)	4758(7)	5146(7)	2454(8)
C(6A)	1401(7)	6182(7)	2683(8)
C(7A)	6042(8)	5509(7)	3502(8)
Pt(B)	−1948.1(3)	11398.8(2)	8906.9(3)
I(B)	−4412.7(5)	11691.8(5)	8767.1(6)
O(1B)	−2093(5)	10302(5)	7078(6)
O(2B)	−802(6)	9377(6)	5822(6)
O(3B)	−1199(6)	12363(6)	10841(6)
O(4B)	782(7)	12815(6)	12371(6)
N(B)	−145(6)	11239(6)	898(6)
C(1B)	180(7)	10645(7)	7897(8)
C(2B)	1429(7)	10536(8)	7850(9)
C(3B)	2356(8)	11082(9)	9040(10)
C(4B)	2012(9)	11673(9)	10150(10)
C(5B)	734(7)	11756(7)	10111(8)
C(6B)	−961(7)	10072(7)	6804(8)
C(7B)	104(8)	12377(8)	11194(9)
K(1)	1149(2)	7188(2)	6282(2)
K(2)	−3042(2)	8336(2)	5140(2)
O(w)	−1249(6)	6756(6)	4012(7)

when brought to pH 5 with KOH solution, undergoes the following redistribution reaction

$$K_2[Pt(dipic)_2] + K_2[PtCl_4] \longrightarrow 2K[Pt(dipic)Cl] + 2KCl$$

with formation in high yield of the previously reported [2, 3] red monoanionic complex, K[Pt(dipic)Cl] (**6**), in which the dipicolinate anion acts as a tridentate ligand. The IR spectrum of solid **6** displays only one asymmetric stretching vibration for the coordinated carboxylate groups at 1670 cm^{-1}. The band at 324 cm^{-1} with a shoulder at 334 cm^{-1}, previously assigned to the stretching ν(Pt–O) [3], is very likely to be due to the ν(Pt–Cl) stretching. This band is not present in the bromo and iodo derived complexes and is replaced by the Pt–Br and Pt–I vibrations at 246 and 172 cm^{-1}, respectively [2].

A redistribution reaction analogous to that reported above leads under comparable experimental conditions to the formation of K[Pd(dipic)Cl] (**7**).

It is already known [2] that K[Pt(dipic)Cl] dissolves in water giving rise to an aquation equilibrium of the type

$$[Pt(dipic)Cl]^- + H_2O \underset{k_{-1}}{\overset{k_1}{\longrightarrow}} [Pt(dipic)(H_2O)] + Cl^-$$

($k_1 = 4.4 \times 10^{-3}$ s^{-1}; $k_{-1} = 6.6 \pm 0.2$ s^{-1} mol^{-1} dm^3)

The electronic spectrum of the solvolysed mixture is that reported in the literature [3], whereas the spectrum of the pure chloro species, obtained in the presence of $[Cl^-] > 5 \times 10^{-3}$ mol dm^{-3}, is quite different and shows two absorption bands at 334 and 246 nm accompanied by two shoulders at 286 and 230 nm.

The iodo species K[Pt(dipic)I] (**8**), the X-ray structure of which is reported below, was readily obtained from the chloro species **6** by replacement of the coordinated chloride with iodide in aqueous solution, on taking into account our previous kinetic study on this reaction [2] which showed that the substitution proceeds in a single stage, even in the presence of a tenfold excess of iodide, with a second order rate constant k_2 of 1.74×10^{-3} s^{-1} mol^{-1} dm^3, at 25 °C and ionic strength $I = 0.5$ mol dm^{-3}.

Structure of $PtC_{14}H_6N_2O_8^{2-} \cdot 2Na^+ \cdot 6H_2O$ *(4)*

Figure 1 reports the structure of compound **4** together with the coordination around the Na$^+$ cation. Bond distances and angles are reported in Table 6. The crystal is built up by the centrosymmetric

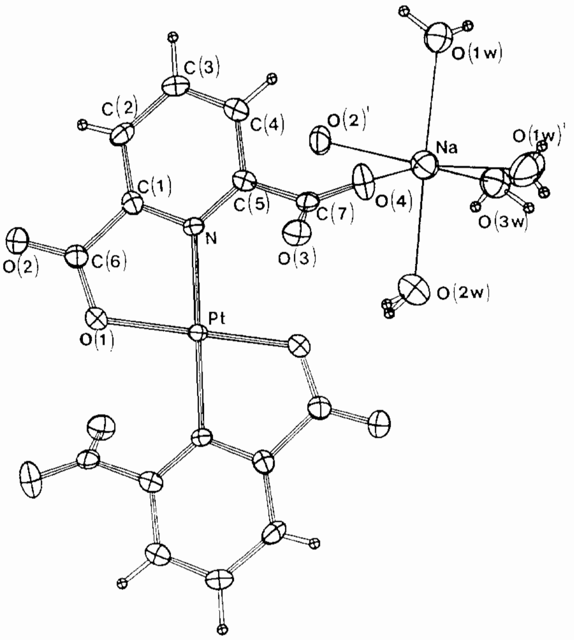

Fig. 1. ORTEP [7] view of the centrosymmetric complex Pt(dipic)$^{2-}$ anion together with the coordination around Na$^+$ cation (see Table 7). Thermal elipsoids are drawn at the 40% probability level.

TABLE 6. Bond distances (Å) and angles (°) for compound **4** with e.s.d.s. in parentheses

Pt–O(1)	2.015(2)	N–C(5)	1.347(5)
Pt–N	2.016(5)	C(1)–C(2)	1.368(5)
O(1)–C(6)	1.298(5)	C(1)–C(6)	1.510(5)
O(2)–C(6)	1.218(4)	C(2)–C(3)	1.395(6)
O(3)–C(7)	1.235(5)	C(3)–C(4)	1.370(6)
O(4)–C(7)	1.245(5)	C(4)–C(5)	1.400(5)
N–C(1)	1.358(5)	C(5)–C(7)	1.520(5)
Average C–H	0.91(6)		
O(1)–Pt–N	80.4(1)	C(3)–C(4)–C(5)	120.2(3)
Pt–O(1)–C(6)	114.6(2)	N–C(5)–C(4)	120.2(3)
Pt–N–C(1)	112.0(2)	N–C(5)–C(7)	120.0(3)
Pt–N–C(5)	128.3(2)	C(4)–C(5)–C(7)	119.4(3)
C(1)–N–C(5)	119.2(3)	O(1)–C(6)–O(2)	124.4(3)
N–C(1)–C(2)	122.2(3)	O(1)–C(6)–C(1)	114.3(3)
N–C(1)–C(6)	114.2(3)	O(2)–C(6)–C(1)	121.1(3)
C(2)–C(1)–C(6)	123.5(3)	O(3)–C(7)–O(4)	128.2(4)
C(1)–C(2)–C(3)	118.9(4)	O(3)–C(7)–C(5)	114.6(3)
C(2)–C(3)–C(4)	118.8(4)	O(4)–C(7)–C(5)	117.0(4)

TABLE 7. Bond distances (Å) with e.s.d.s. in parentheses and bond valences involving the Na^+ cation in compound **4**

	Symmetry	Translation vector	Distance	*s*
Na–O(4)	I[a]	0, 0, 0	2.414(4)	0.180
Na–O(1w)	I	0, 0, 0	2.436(3)	0.171
Na–O(2w)	I	0, 0, 0	2.419(4)	0.178
Na–O(3w)	I	0, 0, 0	2.303(4)	0.234
Na–O(2)′	II	0, −1, −1	2.616(3)	0.115
Na–O(1w)′	II	1, −1, −1	2.574(4)	0.126
				$\Sigma s = 1.004$

[a] $I = x, y, z$; $II = -x, \frac{1}{2}+y, \frac{1}{2}-z$.

$Pt(dipic)_2{}^{2-}$ anions and Na^+ cations hexa-coordinated by four water molecules and two carboxylate oxygens belonging to the ligands. Each dipicolinate ion behaves as a bidentate ligand, and the resulting coordination around the platinum is square planar with Pt–N and Pt–O(1) bond distances of 2.016(3) and 2.015(3) Å, respectively, in agreement with other Pt(II)–N and Pt(II)–O bond distances found in similar complexes (2.032(7), 1.994(7) Å in *trans*-(O, S)[Pt(pyca)(Me_2SO)Cl] (pyca = pyridine-2-carboxylato) [8]; 1.990(2), 2.014(3) Å in [Pt(qnl)$_2$(TCNQ)] (qnl = bis(8-hydroxyquino-linato), TCNQ = 7,7,8,8-tetracyanoquinodimethane) [9]). The two carboxylate groups present different conformations and significant differences in the C–O bond distances. The carboxylate group coordinated to the platinum is situated on the coordination plane and the values of the carbon oxygen bond distances (C(6)–O(1) = 1.298(5), C(6)–O(2) = 1.218(4) Å) show that the negative charge is practically localized on the O(1) atom linked to the Pt. Conversely the latter carboxylate group, not coordinated to platinum, is rotated with respect to the pyridine ring by some 43°. Bond distances C(7)–O(4) = 1.245(5) and C(7)–O(3) = 1.235(5) Å are indicative of an almost full delocalization of the negative charge on the two oxygens. No short contacts between Pt(II) atoms exist, the minimum distance Pt–Pt being 6.544(1) Å, and then this complex does not form linear metal chains through stacking of molecules or ions as observed in similar compounds [10–12]. The arrangement of the oxygens around the Na^+ ion is approximately octahedral as shown in Fig. 1. The cation coordination can be rationalized in terms of the concept of bond valence [13, 14] which assumes that the total charge of the cations has to be saturated by the summation of the separated bond valence s_i of each coordinated atom or ion. Quantities s can be calculated by the expression $s = \exp[(r_0 - r)/B]$, where r is the actual Na^+–O distance, and r_0, B are parameters empirically determined ($r_0 = 1.803$ and $B = 0.37$) [15]. Table 7 reports Na–O bond distances and quantities s calculated for each interaction. The value of 1.004 for Σs_i obtained for the sodium cation in the present structure is in good agreement with the expected charge value of 1. This complex crystallizes with three molecules of water per ligand. The analysis of the packing shows that all the water

TABLE 8. Hydrogen bond parameters for compound **4**; distances in Angstrom and angles in degrees

	Symmetry	Translation vector	O...O	O–H	H...O	O–H...O
O(1w)–H(1w1)...O(4)	II[a]	(1, −1, −1)	2.882(5)	0.76(6)	2.13(6)	170(6)
O(1w)–H(2w1)...O(2w)	IV	(0, −1, −1)	2.884(5)	0.87(4)	2.02(4)	170(4)
O(2w)–H(2w1)...O(3)	I	(0, −1, 0)	2.724(5)	1.07(4)	1.74(4)	151(4)
O(2w)–H(2w2)...O(1)	III	(0, 0, 0)	3.058(4)	0.68(4)	2.39(4)	168(4)
O(3w)–H(1w3)...O(2)	I	(1, 0, 0)	2.969(5)	0.61(6)	2.36(6)	170(8)
O(3w)–H(2w3)...O(4)	III	(1, 0, 0)	3.080(5)	0.62(8)	2.46(8)	179(9)

[a] $I = x, y, z$; $II = -x, \frac{1}{2}+y, \frac{1}{2}-z$; $III = -x, -y, -z$; $IV = x, \frac{1}{2}-y, \frac{1}{2}+z$.

molecules are involved in hydrogen bonds whose parameters are listed in Table 8.

Structure of $PtIC_7H_3NO_4^- \cdot K^+ \cdot 1/2H_2O$ *(8)*

The asymmetric unit of compound **8** contains two Pt(dipic)I$^-$ anions, two K$^+$ cations and one water molecule. Figure 2 reports the structure together with the complete coordination around the potassium cations. In the two complexes constituting the asymmetric unit, the dipicolinate ion acts as a tridentate ligand and the resulting geometry in both cases is square planar where the fourth ligand is an I atom. Bond distances and angles are reported in Table 9.

The shortest carbon–oxygen bond distance C(6A)–O(2A) = 1.204(9) Å is observed on the carbonyl interacting by means of its O(2A) oxygen with only one water molecule (O(2A)---O(w) = 2.83(1) Å) while the carboxyl groups displaying medium distances C(6B)–O(2B) = 1.215(10) and C(7B)–O(4B) = 1.224(9) Å are involved in two interactions with potassium cations (O(2B)---K(1) = 2.756(6), O(2B)---K(2) = 2.844(8), O(4B)---K(1) = 2.957(9), O(4B)---K(2) = 2.806(5) Å); finally the largest exocyclic C=O bond distance C(7A)---O(4A) = 1.245(11) Å is observed in association with the shortest O(4A)---K(1) = 2.713(6) Å interaction combined with a water molecule contact O(4A)---O(w) = 2.83(1) Å. Another interesting feature of structure **8** is the Pt–N bond distance which is exceptionally short (1.925(6), 1.912(7) Å in the two complex anions) with respect to the Pt–N bond distance in compound **4**. This shortening, observed also in other dipicolinate Pt(II) [3] and terpyridine Pt(II) [16] complexes, has been interpreted [3] in terms of a partial multiplicity of the Pt–N bond. Anyway, the shortening of Pt–N distances is certainly caused by the chelating geometry of the *o,o'*-dicarboxylate group, which exerts a net attraction of Pt(II) towards the pyridine nitrogen. By comparison with structure **4** the Pt–O distance should be some 2.015 Å in the absence of steric hindrance, but a distance not shorter than 2.039 Å is achieved in **8** owing to

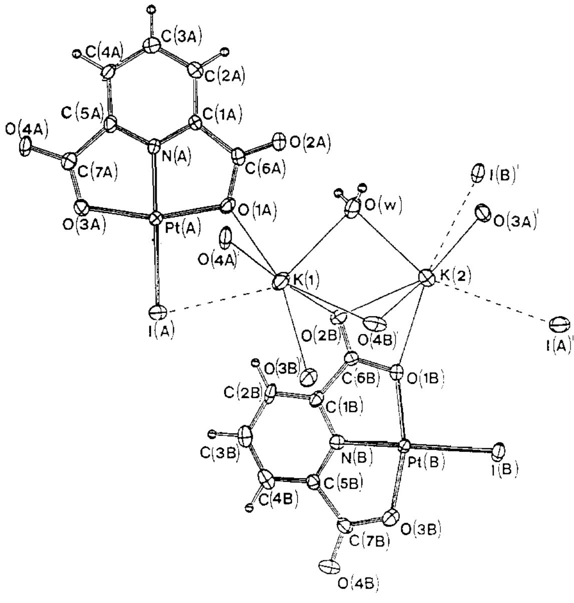

Fig. 2. ORTEP [7] view of the asymmetric unit of compound **8** together with the coordination around K$^+$ cations (see Table 10). Thermal ellipsoids are drawn at the 40% probability level.

TABLE 9. Bond distances (Å) and angles (°) for compound **8** with e.s.d.s. in parentheses

	A	B
Pt-I	2.5846(8)	2.5820(7)
Pt-O(1)	2.040(6)	2.044(6)
Pt-O(3)	2.049(6)	2.055(6)
Pt-N	1.925(5)	1.912(7)
O(1)-C(6)	1.352(9)	1.333(1)
O(2)-C(6)	1.204(9)	1.206(10)
O(3)-C(7)	1.288(10)	1.330(11)
O(4)-C(7)	1.245(11)	1.225(10)
N-C(1)	1.328(9)	1.319(10)
N-C(5)	1.330(11)	1.340(9)
C(1)-C(2)	1.386(11)	1.365(12)
C(1)-C(6)	1.489(12)	1.526(10)
C(2)-C(3)	1.377(14)	1.409(11)
C(3)-C(4)	1.405(11)	1.351(14)
C(4)-C(5)	1.368(11)	1.369(14)
C(5)-C(7)	1.496(10)	1.508(13)
I-Pt-O(1)	99.2(2)	98.7(2)
I-Pt-O(3)	98.4(2)	97.8(2)
I-Pt-N	176.9(2)	177.9(2)
O(1)-Pt-O(3)	162.3(2)	163.1(3)
O(1)-Pt-N	81.2(2)	81.7(3)
O(3)-Pt-N	81.2(2)	81.7(3)
Pt-O(1)-C(6)	112.7(5)	111.9(5)
Pt-O(3)-C(7)	112.2(5)	111.4(5)
Pt-N-C(1)	117.8(5)	118.9(6)
Pt-N-C(5)	117.2(5)	118.7(6)
C(1)-N-C(5)	124.8(6)	122.3(7)
N-C(1)-C(2)	118.9(8)	122.0(7)
N-C(1)-C(6)	113.7(6)	111.8(7)
C(2)-C(1)-C(6)	127.4(8)	126.1(7)
C(1)-C(2)-C(3)	118.0(8)	115.9(8)
C(2)-C(3)-C(4)	121.1(8)	121.3(9)
C(3)-C(4)-C(5)	118.1(8)	119.6(8)
N-C(5)-C(4)	119.1(8)	118.9(7)
N-C(5)-C(7)	112.5(7)	111.5(7)
C(4)-C(5)-C(7)	128.4(8)	129.6(8)
O(1)-C(6)-O(2)	122.6(7)	122.2(8)
O(1)-C(6)-C(1)	114.4(7)	115.4(7)
O(2)-C(6)-C(1)	123.0(7)	122.1(8)
O(3)-C(7)-C(4)	123.4(7)	121.7(9)
O(3)-C(7)-C(5)	116.9(7)	116.6(7)
O(4)-C(7)-C(5)	119.7(7)	121.6(8)

repulsion of the nitrogen. The Pt–I bond lengths (2.585(1) and 2.582(1) Å) are in good agreement with those found in other square planar Pt(II) compounds where the iodine is *trans* to the N atom (on average: 2.587 in 1,2-benzoquinonedioxime PtI_2 [17]; 2.586 in *cis*-$(NH_3)_2PtI_2$ [18] and 2.592 Å in *cis*-bis(cyclopropylamine)PtI_2] [19]). The coordination geometries are essentially planar with a small distortion mainly due to strains caused by the nitrogen position within the dipicolinate ligand. The planar complex anions are stacked but not parallel: Pt atoms form infinite zigzag chains of the type · ·Pt(A)· ·Pt(A)· ·Pt(B)· ·Pt(B)· ·, the values of the distances Pt(A)· ·Pt(A) = 4.102, Pt(A)· ·Pt(B) = 3.698, Pt(B)· ·Pt(B) = 4.433 Å and of the angles Pt(A)· ·Pt(A)· ·Pt(B) = 137.8 and Pt(A)· ·Pt(B)· ·Pt(A) = 142.5° prevent any interactions between Pt atoms [10–12]. The crystal packing reveals that each K^+ cation is seven-coordinate in an irregular way. K(1) interacts with five carboxylate oxygens, one water molecule and one iodine atom. Table 10 reports K–O and K–I distances together with the contributions of the separated bond valences calculated using the parameters $r_0 = 2.132$ Å for K–O and $B = 0.37$. The same parameters have been used for the K–I interaction with re-scaling [15] of the K–I distances for the difference (0.86 Å) of the oxygen radius (1.20 Å) and the values of the radius of the I^- ion (2.06 Å) [20]. The values of Σs for K(1) and K(2) are 1.071 and 1.029, respectively, and they fit well the expected value of 1. To complete the packing analysis, it can be noted that the water molecule, in addition to the two interactions with the potassium cations, forms two hydrogen bonds with two carboxylate oxygens with the following parameters:

O(w)–H(1w) = 0.83, O(w)---O(2A)(x, y, z)
= 2.83(1), H(1w)---O(2A)
= 2.16 Å, O(w)–H(1w)---O(2A)
= 138°;

O(w)–H(2w) = 0.82, O(w)---O(4A)($x, -1, y, z$)
= 2.83(1), H(2w)---O(4A)
= 2.10 Å, O(w)–H(2w)---O(4A)
= 149°.

TABLE 10. Bond distances (Å) with e.s.d.s. in parentheses and bond valences involving the K^+ cation in compound **8**

	Symmetry	Translation vector	Distance	s
K(1)–I(A)	I[a]	0, 0, 0	3.974(3)	0.070
K(1)–O(1A)	I	0, 0, 0	2.793(6)	0.168
K(1)–O(1B)	I	0, 0, 0	2.755(6)	0.186
K(1)–O(w)	I	0, 0, 0	2.780(6)	0.174
K(1)–O(4A)′	II	1, 1, 1	2.713(6)	0.208
K(1)–O(3B)′	II	0, 2, 2	2.816(7)	0.157
K(1)–O(4B)′	II	0, 2, 2	2.957(9)	0.108
				$\Sigma s = 1.071$
K(2)–I(A)′	I	−1, 0, 0	3.760(3)	0.125
K(2)–I(B)′	II	−1, 2, 1	3.708(2)	0.144
K(2)–O(1B)	I	0, 0, 0	2.907(6)	0.123
K(2)–O(2B)	I	0, 0, 0	2.844(8)	0.146
K(2)–O(w)	I	0, 0, 0	2.779(7)	0.174
K(2)–O(3A)′	I	−1, 0, 0	2.822(7)	0.155
K(2)–O(4B)′	II	0, 2, 2	2.806(5)	0.162
				$\Sigma s = 1.029$

[a] I = x, y, z; II = $-x, -y, -z$.

Supplementary material

Additional material available from the Cambridge Crystallographic Centre comprises thermal parameters.

Acknowledgements

We thank the Italian Ministry of Education and CNR (Rome) for financial support, Dr S. Antoniutti for NMR measurements, and Miss Tatiana Bobbo for technical assistance.

References

1 U. Casellato and P. A. Vigato, *Coord. Chem. Rev., 26* (1978) 85; G. D'Ascenso, A. Marino, M. Sabbatini and T. Bica, *Thermochim. Acta, 25* (1978) 325; S. Ghosh, T. K. Banerjee and P. K. Ray, *J. Indian Chem. Soc., 55* (1978) 610; W. Furst, P. Gouzerh and Y. Jannin, *J. Coord. Chem., 8* (1978) 237; G. Marangoni, S. Degetto, R. Graziani, G. Bombieri and E. Forsellini, *J. Inorg. Nucl. Chem., 36* (1974) 1787; L. Baracco, G. Bombieri, S. Degetto, E. Forsellini, R. Graziani and G. Marangoni, *Inorg. Nucl. Chem. Lett., 10* (1974) 1045.
2 L. Cattalini, G. Chessa, G. Marangoni, B. Pitteri and E. Celon, *Inorg. Chem., 28* (1989) 1944.
3 X.-Y. Zhou and N. M. Kostic, *Inorg. Chem., 27* (1988) 4402.
4 D. T. Cromer and J. T. Waber, *International Tables for X-ray Crystallography,* Vol. 4, Kynoch Press, Birminghan, U.K., 1974, Table 2.2 A.
5 B. A. Frenz, *SDP Structure Determination Package,* College Station, TX, U.S.A. and Enraf-Nonius, Delft, The Netherlands.
6 M. Nardelli, *Comput. Chem., 7* (1983) 95.

7 C. K. Johnson, *ORTEP II: a Fortran thermal-ellipsoids plot program for crystal structure illustrations, Rep. ORLN-5138*, Oak National Laboratory, Oak Ridge, TN, U.S.A., 1976.

8 G. Annibale, L. Cattalini, L. Canovese, B. Pitteri, A. Tiripicchio, M. Tiripicchio Camellini and M. L. Tobe, *J. Chem. Soc., Dalton Trans.*, (1986) 1101.

9 P. Bergamini, V. Bertolasi, V. Ferretti and S. Sostero, *Inorg. Chem. Acta, 126* (1987) 151.

10 D. W. Phelps, W. F. Little and D. J. Hodgson, *Inorg. Chem., 15* (1976) 2263.

11 K. W. Nordquest, D. W. Phelps, W. F. Little and D. J. Hodgson, *J. Am. Chem. Soc., 98* (1976) 1104.

12 J. Simon and J.-J. André, *Molecular Semiconductor*, 1985, Springer, Berlin, Ch. V.

13 L. Pauling, *J. Am. Chem. Soc., 51* (1929) 1010.

14 I. D. Brown, *Chem. Soc. Rev., 7* (1978) 359.

15 I. D. Brown and D. Aldermatt, *Acta Crystallogr., Sect. B, 41* (1985) 244.

16 K. W. Jennette, J. T. Gill, J. A. Sadownick and S. J. Lippard, *J. Am. Chem. Soc., 98* (1986) 6159.

17 M. Mégnamisi-Bélombé and H. Endres, *Acta Crystallogr., Sect. C, 41* (1985) 513.

18 G. Raudaschl-Sieber, B. Lippert, J. F. Britten and A. L. Beauchamp, *Inorg. Chim. Acta, 124* (1986) 213.

19 A. Oksanen, R. Kivekas, P. Lumme, J. Valkonen and T. Laitalinen, *Acta Crystallogr., Sect. C, 45* (1989) 1493.

20 R. D. Shannon, *Acta Crystallogr., Sect. A, 32* (1976) 751.