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An Atropisomeric Chiral 2,2'-bipyridyl-3,3'-dicarboxylic Acid and Corresponding Platinum(II) Complex

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2,2'-Bipyridyl-3,3'-dicarboxylic acid (H₂BDC) spontaneously resolves on crystallization from water, giving monohydrated crystals of the space group *P*2₁2₁2₁. In any individual crystal, all the atropisomeric-skewed molecules are of one hand; however, on dissolution in water, optical activity is lost. Strong hydrogen bonding leads to a helical structure, via O–H ··· N links, and 3 further strong bonds between water and carboxylate groups produce a framework structure. The p*K*_a values measured for H₂BDC (3.18 ± 0.04 and 4.59 ± 0.02 at 20 ± 1 °C, in dilute aqueous solution) agree with the zwitterionic form. The reaction of H₂BDC with potassium tetrachloroplatinate(II) in water gives Pt(H₂BDC)Cl₂·H₂O. The complex was characterized by elemental analysis and spectroscopic techniques.

Key Words: Platinum complexes, 3,3'-dicarboxyl-2,2'-bipyridine ligand, Crystal structure, Spontaneous resolution, Hydrogen bonding.

Introduction

2,2'-Bipyridine and its derivatives have been receiving considerable attention, largely because of their intrinsic properties and also because of their ability to form coordination compounds with metal ions¹. The recent focus on this type of compound is derived from the fact that dicarboxy derivatives form rigid rod aromatic polymers. These compounds have found applications as high performance thermoplastics². The chiral atropisomeric quaternized 2,2'-bipyridyl-3,3'-dicarboxylic acid functions as an acceptor for light-induced electron transfer systems³. Crystal structure and antitumor activity studies of the complex *cis*-Pt(H₂BDC)Cl₂ · 2DMF have been previously reported⁴.

Spontaneous resolution of racemic compounds leads to conglomerates of crystals of pure enantiomers. A list of some 200 organic conglomerates is available⁵. None involve a case of a classical atropisomeric bi-aryl, enantiomeric resolution due to restricted rotation about the single bond between 2 aromatic rings. We report the first such case, for bi-nicotinic acid.

In metal complexes of bi-nicotinic acid, coordination occurs either in a bidentate fashion through pyridine nitrogen atoms⁶ or in a tridentate fashion through pyridine nitrogen atoms and an oxygen atom of

carboxylate⁷. As part of our study of the metal complexes of skewed bipyridyls^{8,9} we report the coordinating properties of 2,2'-bipyridyl-3,3'-dicarboxylic acid with platinum(II).

Experimental

Materials and methods

All chemicals were reagent grade and were used as purchased without further purification. Non-aqueous solvents were dried before use. 1,10-Phenanthroline, potassium permanganate, potassium tetrachloroplatinate, standard sodium hydroxide solution, and sodium hydroxide pellets were purchased from Aldrich. Air and moisture sensitive D₂O, NaOD and DCl were purchased from Aldrich and kept in a reaction flask under dry nitrogen gas.

UV-visible spectra were obtained using a Kontron Instruments Uvikon 930 spectrophotometer for the ligand and a Perkin-Elmer UV/VIS spectrometer Lambda 20 for the complex. IR spectra (given as cm⁻¹) were recorded on a Nicolet 510 FT-IR spectrometer (4000-400) using fluorolube mulls between KBr disks for the ligand and on a Perkin-Elmer 783 infrared spectrophotometer (4000-250) using a Nujol mull between CsI disks for the complex. Proton NMR spectra were recorded on a Bruker WM360 spectrometer for the ligand and on a Bruker DPX400 spectrometer for the complex. Thermogravimetric results were obtained using a Stanton Redcroft TG-750 temperature programmed thermogravimetric balance with sample weights between 5 and 10 mg. The samples were heated in air at a rate of 15° min⁻¹. Melting points were measured using a Reichert hot stage microscope.

All temperatures are in °C.

Synthesis

3,3'-dicarboxy-2,2'-bipyridine [H₂BDC],(I; bi-nicotinic acid)

The modification¹⁰ of the original method of Inglet and Smith¹¹ has advantages in terms of simplicity and yield. 1,10-Phenanthroline monohydrate (16 g, 0.08 mol) and sodium hydroxide (6.4 g, 0.16 mol) were dissolved in water (700 cm³) under reflux. After cooling the homogeneous solution but before it started to solidify, solid potassium permanganate (38 g, 0.24 mol) was added very slowly with vigorous stirring. The mixture was set to reflux for 3 h. The precipitated manganese dioxide was removed by filtration, the filtrate evaporated to approximately 300 cm³ on a rotary evaporator, and its pH was adjusted to ~ 2 with concentrated hydrochloric acid. Decolorizing charcoal was added and the solution was boiled and filtered, the filtrate being concentrated to 200 cm³. The precipitated bi-nicotinic acid was collected, washed with ethanol and water and dried over P₂O₅ in a desiccator. Successive crystallizations from water gave white crystals that looked cubic (14 g, 70%), m.p. 262 (decomp.). Literature 258¹⁰, 260¹¹, 250-252¹². Found: C, 58.6; H, 3.3; N, 11.4. Calc. for C₁₂H₈N₂O₄ (anhydrous): C, 59.02; H, 3.30; N, 11.47%. ¹H-NMR (DMSO-d₆, d/ppm): 8.65 (2H, d, J_{6,5} = 4.75 Hz, H6, H6'); 8.24 (2H, d, J_{4,5} = 7.78 Hz, H4, H4'); 7.50 (2H, dd, J_{5,6} = 4.75 Hz, J_{4,5} = 7.78 Hz, H5, H5'); 12.92 (2H, s, 2COOH). IR spectrum (cm⁻¹): 3085 m, 3000-2500 br, 2572 w, 1714 s, 1588 s, 1570 w, 1440 s and 1400 m. The electronic spectrum showed absorption at 269 nm (ε = 8580 dm³mol⁻¹cm⁻¹) [Lit.¹³ 270 nm (ε = 8530 dm³mol⁻¹cm⁻¹)]. There was a shift to a shorter wavelength (265 nm) upon the addition of alkali.

[Pt(H₂BDC)Cl₂].H₂O (II)

A hot aqueous solution (100 cm³) of bi-nicotinic acid (1.3 g, 5 mmol) was added to a hot solution (15 cm³) of potassium tetrachloroplatinate (2 g, 4.8 mmol). The mixture was heated and stirred for 90 min. The orange precipitate was collected by filtration and washed with water, ethanol and diethyl ether. The crude product was recrystallized from aqueous methanol to yield 2.2 g of the 85% pure yellow-orange crystalline product dichloro-3,3'-dicarboxy-2,2'-bipyridylplatinum(II) monohydrate. Found: C, 27.2; H, 1.9; N, 5.8. Calc. for C₁₂H₁₀N₂O₅Cl₂Pt: C, 27.29; H, 1.91; N, 5.30%. ¹H-NMR (DMSO-d₆, d/ppm): 8.69 (2H, dd, J_{6,5} = 4.85 Hz, J_{6,4} = 1.54 Hz, H6, H6'); 8.27 (2H, dd, J_{4,5} = 7.89 Hz, J_{4,6} = 1.54 Hz, H4, H4'); 7.54 (2H, dd, J_{5,6} = 4.85 Hz, J_{5,4} = 7.89 Hz, H5, H5'). IR spectrum (cm⁻¹): 3530-3460 d, m, 3088 m, 1720 s, 1585 s, 1420 s, 1320 m, 1276 m, 1125-1107 d, m, 864 m, 822 m, 754 m, 516 m, br, 330 m. The last 2 values were obtained using a Nujol mull between CsI disks. The electronic spectrum (in water at 25) showed absorption at 255 nm ($\epsilon = 19800 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$), 324 nm ($\epsilon = 7900 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$), 335 nm ($\epsilon = 7800 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$), 388 nm ($\epsilon = 2800 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$). In DMSO absorption was found at 423, 331 and 271 nm.

Determination of pK_a Values

A gently stirred aqueous solution (50 mL, 0.01 M) of bi-nicotinic acid was titrated with aqueous sodium hydroxide (0.1 M) at 20 ± 1; very slowly using 0.1 mL increments. pH was measured 30 s after each addition using a Mettler-Toledo AG analytical pH meter. The pK_a values obtained using the “overlapping method”¹⁴ were 3.18 and 4.59. The diagram as shown in Figure 1 describes the nature of the stoichiometric species present in the aqueous solution of bi-nicotinic acid. It was obtained using the species program¹⁵.

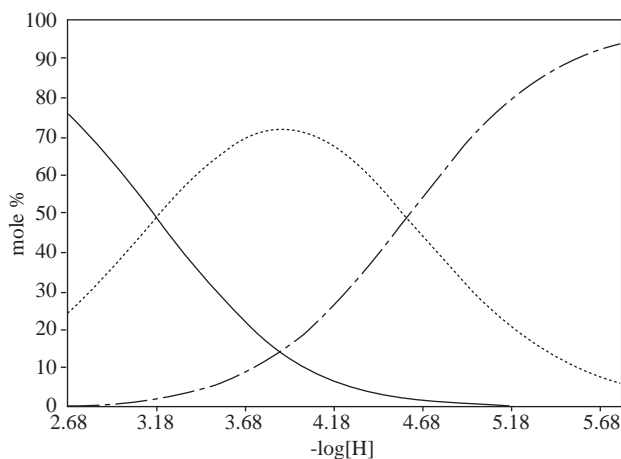


Figure 1. The nature of the stoichiometric species present in aqueous solution of bi-nicotinic acid.

Solubility of H₂BDC

Bi-nicotinic acid (1.25 g) was stirred with water (100 mL) at 25 ± 0.5 and the pH recorded every 30 min until no further change was observed. After 21 h, this pH was found to be 2.70. The saturated aqueous solution was filtered: the dried undissolved solid weighed and found to be 0.9 g. This meant 0.35 g had dissolved, with a solubility of 0.013 mol.dm⁻³. The solute concentrations calculated from the final pH and from the absorption of the final filtered solution agree, giving a value of 0.012 mol.dm⁻³.

X-ray structure determination

X-ray data were collected at -153 °C on a Delft Instruments FAST TV area detector. X-rays were produced by a rotating anode generator using Mo-K α radiation ($\lambda = 0.71069 \text{ \AA}$) and controlled by a Micro Vax 3200 workstation driven by MADNES¹⁶ software. Data collection was performed using the ABSMAD¹⁷ program. The unit cell dimensions were determined from 5304 reflections with setting angles of between 2.49° and 25.40° θ . The crystal system was determined to be orthorhombic and the space group was uniquely determined to be $P2_12_12_1$. Relevant data collection parameters are given in Table 1. The structure was solved by direct methods (SHELXS97¹⁸) and refined on F^2 (anisotropic for all non-H atoms) using SHELXL-93¹⁹, with all 1866 unique items of data. H atoms were refined freely with C–H and O–H distances in the range 0.90(3)–1.00(3) \AA and U_{iso} values in the range 0.005(5)–0.053(9) \AA^2 . Final R [$F^2 > \sigma(F^2)$] = 0.0361, Rw (all data) = 0.083.

Table 1. Crystallographic data and details of the structure refinement.

Empirical formula	H ₈ N ₂ O ₄ ·H ₂ O
Formula weight	262.22
Temperature	120(2) K
Wavelength	0.71069 \AA
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions	$a = 8.2730(10) \text{ \AA}$, $b = 8.4420(10) \text{ \AA}$, $c = 16.769(4) \text{ \AA}$ $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$
V	1171.2(3) \AA^3
Z	4
Density (calculated)	1.487 Mg/m ³
Absorption coefficient	0.118 mm ⁻¹
$F(000)$	544
Crystal	Clear; block
Crystal size (mm)	0.28 x 0.14 x 0.14
θ range for data collection	2.43 – 25.03°
Index ranges	$-7 \leq h \leq 9$, $-8 \leq k \leq 9$, $-18 \leq l \leq 18$
Reflections collected	5204
Independent reflections	1866 [$R_{int} = 0.0639$]
Completeness to $\theta = 25.03^\circ$	93.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.952 and 0.742
Refinement method	Full-matrix least-squares on F_2
Data / restraints / parameters	1866 / 0 / 212
Goodness-of-fit on F^2	1.012
Final R indices [$F^2 > 2\sigma(F^2)$]	$R1 = 0.0361$, $wR2 = 0.0821$
R indices (all data)	$R1 = 0.0393$, $wR2 = 0.0830$
Largest diff. peak and hole	0.233 and -0.233 e \AA^{-3}

Results and Discussion

X-ray structure

An ORTEP²⁰ drawing of the I·H₂O is shown in Figure 2 and the unit cell diagram is shown in Figure 3. The crystal parameters and details of data collection are summarized in Table 1. The atomic coordinates

and equivalent isotropic thermal parameters are listed in Table 2. Bond lengths and angles are provided in Table 3. Strong hydrogen bonded interactions are shown in Table 4.

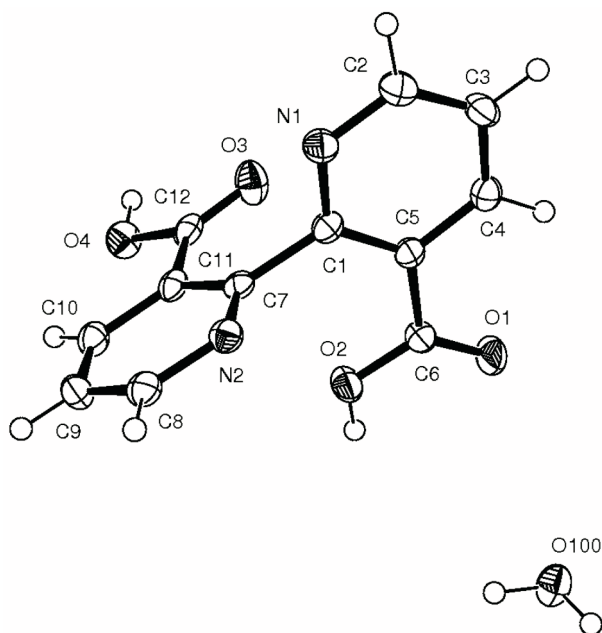


Figure 2. An ORTEP drawing of the title compound with H atom numbering scheme. The thermal ellipsoids are drawn at the 50% probability level.

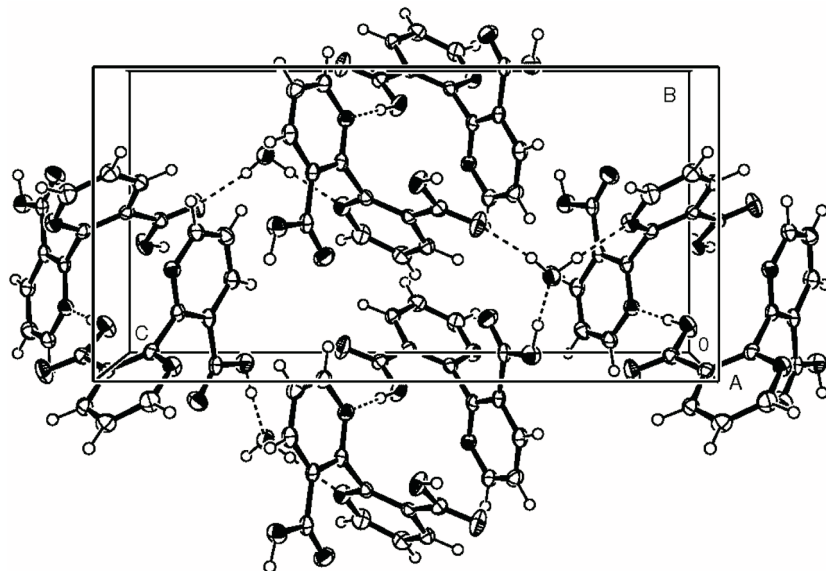


Figure 3. The packing diagram. The intra- and intermolecular hydrogen bonds are shown by dashed lines.

As shown in Figure 2, the individual molecules are skewed, with a dihedral angle, ϕ , of $78.5(1)^\circ$. This is a common feature for many bi-aryls, particularly those substituted at the positions next to the link between rings. For example, ϕ is $42.9(1)^\circ$, $23.6(1)^\circ$ and $53.2(2)^\circ$ respectively for **I** with $X = \text{NO}_2$ ²¹, CN ²² and CO_2CH_3 ²³. However, these three 2,2'-bipyridyls are not enantiomeric: their space groups are

$P2_1/c$, $P\bar{1}$ and $Pbcn$ respectively. In the present case, the space group is $P2_12_12_1$: therefore, in a given single crystal, all the molecules of bi-nicotinic acid have the same optical hand.

Table 2. Atomic coordinates [$\times 10^4$] and equivalent isotropic displacement parameters [$\text{\AA}^2 \times 10^3$]. U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Atom	x	y	z	U_{eq}
O2	1313(2)	8771(2)	5186(1)	31(1)
O1	367(2)	10215(2)	6187(1)	37(1)
O3	865(2)	11271(2)	3602(1)	34(1)
O4	2829(2)	10175(2)	2872(1)	29(1)
N1	-2848(2)	9727(2)	3843(1)	26(1)
N2	-1099(2)	6680(2)	3934(1)	22(1)
C1	-1516(2)	9377(2)	4265(1)	20(1)
C2	-3903(3)	10753(3)	4156(1)	31(1)
C3	-3697(3)	11470(3)	4879(1)	27(1)
C4	-2342(2)	11095(3)	5318(1)	23(1)
C5	-1223(2)	10025(2)	5016(1)	20(1)
C6	231(2)	9680(3)	5525(1)	22(1)
C7	-491(2)	8152(2)	3865(1)	20(1)
C8	-355(3)	5479(3)	3567(1)	25(1)
C9	1031(3)	5681(3)	3128(1)	27(1)
C10	1660(3)	7183(3)	3046(1)	25(1)
C11	895(3)	8457(3)	3411(1)	20(1)
C12	1510(2)	10119(3)	3318(1)	23(1)
O100	992(29)	7027(2)	7543(1)	32(1)

The crystal structure (see Table 4) data show intermolecular hydrogen bonding between the basic nitrogen and carboxylic proton of molecules in the *bipy* complex. Additionally, there is strong intermolecular hydrogen bonding between the water molecules and the carboxylic and nitrogen atoms of the acid. The strong hydrogen bond with the water molecule is O(4)-H(40) \cdots O(100). The shortest distance between a ring nitrogen atom N(2) and carboxylic proton H(20) of an adjacent pyridine ring is 1.725 (3) Å with an angle of 179.24 (3)°. This shows that there is strong linear hydrogen bonding within this system, as can be seen in the packing diagram in Figure 3. The other important structure forming short contacts are shown in Table 4. All indications are that the hydrogen bonds stabilize the molecule as a chiral structure in the solid state.

Although the bond angles for $\mathbf{I} \cdot \text{H}_2\text{O}$ are very close to those for the protonated bipyridine²⁴ it is not a zwitterion in solid state, since the hydrogen bonds between the oxygen and the nitrogen atoms are not equidistant. The O-H distance, in this case, is about 0.9 Å and the N \cdots H is about 1.7 Å. This clearly indicates that 2,2'-bipyridyl-3,3'-dicarboxylic acid in the crystal state is an uncharged molecule. The selected bond lengths and angles are given in Table 3.

Spontaneous resolution and the Kuhn effect

Upon dissolution of the single crystals in water, the optical activity is lost. As found for other spontaneous resolutions, where the chiral equilibrium in solution is kinetically labile (e.g., the preparation solution of $(\text{NH}_4)_2[\text{PtS}_{17}] \cdot 2\text{H}_2\text{O}$)²⁵ or for the related cases where the symmetric solution yields handed crystals (e.g., NaClO_3)²⁶, our batches of a few dozen relatively large crystals usually have a preponderance of one

enantiomorph. The most direct analogy to the present observations lies in the remarkable early observations by Kuhn and Albrecht on 4,4'-dinitrodiphenic acid²⁷. Kuhn and Albrecht found that when solutions of 4,4'-dinitrodiphenic acid (with, of course, no rotation) and levorotatory solutions of (-) quinine were mixed, the rotation became strongly positive and a single diastereoisomeric salt could be crystallized in high yield (ca. 80%). They took this to stem from an asymmetric induction in solution, stabilizing one hand of the diacid.

Table 3. Selected bond lengths [Å] and angles [°].

O2-C6	1.309(3)
O2-H20	0.90(3)
O1-C6	1.203(3)
O3-C12	1.207(3)
O4-C12	1.324(3)
O4-H40	0.92(4)
N1-C2	1.336(3)
N1-C1	1.343(3)
N2-C8	1.336(3)
N2-C7	1.345(3)
C1-C7	1.497(3)
C6-O2-H20	113.0(19)
C12-O4-H40	108.3(18)
C2-N1-C1	118.13(19)
C8-N2-C7	119.28(18)
N1-C1-C5	122.19(19)
N1-C1-C7	112.36(18)
C5-C1-C7	125.30(18)
C1-C5-C6	125.19(18)
O1-C6-O2	123.84(19)
O1-C6-C5	121.73(18)
O2-C6-C5	114.42(19)
N2-C7-C11	121.54(19)
N2-C7-C1	112.82(17)
C11-C7-C1	125.48(19)
O3-C12-O4	124.0(2)
O3-C12-C11	124.18(19)
O4-C12-C11	111.8(2)
H102-O100-H101	107(39)

Table 4. The hydrogen bonds.

Donor-H...A	D-H (Å)	H...A (Å)	D...A (Å)	D-H...A (°)
O2-H20...N2 ⁱ	0.903(3)	1.725(3)	2.628(2)	179(3)
O4-H40...O100 ⁱⁱ	0.920(3)	1.718(3)	2.614(3)	164(3)
O100-H101...O1 ⁱⁱⁱ	0.901(3)	1.962(3)	2.853(2)	169(3)
O100-H102...N1 ⁱ	0.914(3)	2.017(3)	2.917(3)	168(2)

The symmetry code: (i) x+1/2, 3/2-y, -z+1, (ii) -x+1/2, -y+2, z-1/2, (iii) -x, y-1/2, -z+3/2

The skewed conformation of $\mathbf{I}\cdot\mathbf{H}_2\mathbf{O}$ in aqueous solution (albeit with equal concentrations of right and left enantiomers), is not unexpected, although the preferential assemblage of homochiral molecules into an enantiomorphous unit cell is.

We measured the values of pK_a for bi-nicotinic acid as 3.18 and 4.59, and so dilute solutions contain chiefly the anion **I**, where $X = \text{COO}^-$. Even when a handed single crystal is dissolved directly in alkali (NaOH) so that presumably the di-anion is formed as it dissolves, no optical rotation is measurable. The repulsion between the nitrogen lone pairs and the negatively charged carboxylate is, therefore, not enough to prevent racemization.

IR spectra

The infrared spectrum of crystalline **I** H_2O shows a broad very strong absorption between 3100 and 2500 cm^{-1} , arising from the very strong hydrogen bonding of all OH units. No absorption is apparent at frequencies higher than 3150 cm^{-1} . A sharp band at 3100 cm^{-1} is superimposed on the broad absorption, which presumably arises from aromatic CH stretching modes. In the deuterio-isotopomer, [*bipy*-($\text{CO}_2[{}^2\text{H}]$) $_2$ · $[{}^2\text{H}]_2\text{O}$], this is shifted to 2300-1850 cm^{-1} . The band at 1724 cm^{-1} is assigned to the C=O stretching of the protonated carboxylic acid. The infrared spectrum of **II** is identical to **I** H_2O with the exception of 2 bands at 516 and 330 cm^{-1} . The broad band at 516 cm^{-1} is probably due to lattice water. The strong band at 330 cm^{-1} is assigned to the Pt-Cl stretching vibration, and is thus similar to that of the red form of $[\text{Pt}(\textit{bipy})\text{Cl}_2]$ and *cis*- $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$, which also show only one band due to (Pt-Cl)²⁸.

¹H-NMR spectra

Two doublets at 8.6 and 8.2 ppm for the 6,6' and 4,4' protons and a doublet of doublets at 7.5 ppm for the 5,5' protons are consistent with the presence of 2-fold symmetry in solution. A very broad resonance at 12.92 ppm is assigned to the 2 exchanging protons. Coordination of bi-nicotinic acid to platinum(II) through its nitrogen atoms is revealed by ¹H-NMR, showing that the molecule has C_2 symmetry in solution, having 3 peaks in the downfield region, which is characteristic of bipyridyl ring resonance. Therefore the coordination around the Pt atom is essentially square-planar with the 4 coordination sites occupied by 2 Cl atoms and 2 N atoms of the chelating bipyridyl ligand.

UV-visible spectra

Bi-nicotinic acid exhibits only 1 band in the ultraviolet region, due to a large twist in the molecule, in contrast with bipyridine, which exhibits 2 bands. The shift in the ultraviolet spectrum upon the addition of alkali observed for bi-nicotinic acid can be assigned to the zwitterionic form¹⁴.

Accordingly, the higher melting point of bi-nicotinic acid compared to diphenic acid may be due to its occurrence as an internal salt or to hydrogen bonding as depicted in the unit cell diagram. Bi-nicotinic acid does not melt quickly but decomposes gradually, which is very common for all zwitterions such as amino acids. TGA shows that bi-nicotinic acid undergoes decarboxylation at 318 ± 20 with a mass loss of about 36%, which corresponds to 2 moles of carbon dioxide. This provides an advantage for the synthesis of regioselectively deuterated bipyridine isotopomer⁸.

The electronic absorption spectrum of **II** in water (it is not soluble in chloroform or dichloromethane) is compared with $[\text{Pt}(\textit{bipy})\text{Cl}_2]$ in chloroform. The bands between 350 and 400 nm are characteristic of square-planar coordination for the *bipy* and *phen* complexes of Pt(II); they are also present in the spectrum

of $[\text{Pt}(\text{bipy})\text{Cl}_2]$ ²⁹. Houlding and Miskowski³⁰ reported that the MLCT absorption of $[\text{Pt}(3,3'-(\text{CO}_2\text{CH}_3)_2\text{-bipy})\text{Cl}_2]$ in CH_2Cl_2 occurs at 444 nm ($\epsilon = 3030 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$), which is within the energy range of the band at 388 nm ($\epsilon = 2800 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$) for **II** in water. This band shifts (2100 cm^{-1}) to the lower energy in dimethylsulfoxide. The lowest energy band in the spectra of $[\text{Pt}(\text{L})\text{X}_2]$ ($\text{L} = \text{bipy}$, substituted *bipy*, where $\text{X} = \text{Cl}$, Br , or I) shifts ca. 4000 cm^{-1} to a lower energy upon going from aqueous to chloroform solution³¹ and ca. 3000 cm^{-1} due to electron-withdrawing groups on the bipyridine³⁰.

Binding properties of bi-nicotinic acid, $[\text{Pt}(\text{H}_2\text{BDC})\text{Cl}_2]\cdot\text{H}_2\text{O}$ (**II**)

In the absence of steric effects, chelated *bipy* molecules are essentially planar⁸. When methyl substituents are placed in the 3,3'-positions of *bipy*, the molecule can still act as a chelating ligand but with a concomitant increase in the dihedral angle between the pyridyl rings to 30-35°¹⁰. If the size of the 3,3'-substituents is increased, a point will be reached where the ring closure step will be unlikely and monodentate coordination will result. Inglet and Smith¹¹ attempted to prepare iron(II) complexes of bi-nicotinic acid but since there was no color change when solutions of these compounds were mixed, they concluded that complex formation with this molecule was not possible. Furthermore, Gillard¹³ reported the preparation of $[\text{Ru}(\text{I})_3]^{2+}$ with lower optical purity, (5% L-(+) hand), than $[\text{Ru}(\text{bipy})_3]^{2+}$ (60% L-(-) hand) or $[\text{Ru}(\text{phen})_3]^{2+}$, (35% L-(-) hand). This low optical purity was attributed to the non-coplanarity of bi-nicotinic acid resulting from geometry unfavourable for complexation. The structure of $[\text{Cu}(\text{I})\text{Cl}_2]\cdot\text{H}_2\text{O}$ published by Goddard⁶ shows that bi-nicotinic acid is coordinated to the copper through its nitrogen atoms. The planar pyridine rings are twisted by about 30° relative to one another around the 2,2'-bond. Coordination around the copper atom is approximately square-planar with 2 chloride atoms and the nitrogen atoms of the bi-nicotinic acid occupying the 4 coordination sites. The other published structure of a copper(II) complex with bi-nicotinic acid, by Zhong⁷, revealed polymeric chains of $[\text{Cu}(\text{I})(\text{H}_2\text{O})_2]$ units. Each copper(II) ion pair is bridged by a di-anion of bi-nicotinic acid in a tridentate fashion through its 2 pyridine nitrogen atoms and 1 carboxylate oxygen atom. The dihedral angle between the two pyridine ring planes is 28.7°. It is clear that bi-nicotinic acid acts as a non-planar chelating ligand in both complexes. In the present case, coordination of bi-nicotinic acid to platinum(II) through its nitrogen atoms is revealed by ¹H-NMR, showing that the molecule has C_2 symmetry. This is confirmed by means of the spectroscopic techniques mentioned above. All data are in good agreement with the reported values for the analogous complexes. The possible intermolecular hydrogen bonding between the two carboxyl OH groups of neighboring units could lead to the formation of a 1-dimensional polymer, as found for the $\text{Pt}(3,3'-(\text{HOH}_2\text{C})\text{-bipy})\text{Cl}_2$ ⁴.

Conclusions

In contrast to other skewed bipyridyls, particularly those substituted at the 3,3'-positions, the preferential assemblage of homochiral molecules into an enantiomorphic unit cell is observed for 2,2'-bipyridyl-3,3'-dicarboxylic acid. The single crystal X-ray structure shows very strong intermolecular hydrogen bondings between the basic nitrogen and carboxylic proton of molecules in the *bipy* and a very strong one with the water molecule involved.

The ligand exists as a zwitterion in dilute aqueous solution at $\text{pH} \sim 4$ but as an unprotonated ligand in the solid. Upon dissolution of single handed crystals in water, optical activity is lost.

The helicate coordinated to Pt atoms adopts a square-planar geometry. Many attempts to obtain (1:2) complex ions with platinum(II) met with failure, presumably due to a large twist of the planar pyridine rings.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 187887 for compound **I**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

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