

# Synthesis and Spectroscopic Studies of Platinum(II) Complexes of *N,N'*-Dicyclohexylethylenediamine

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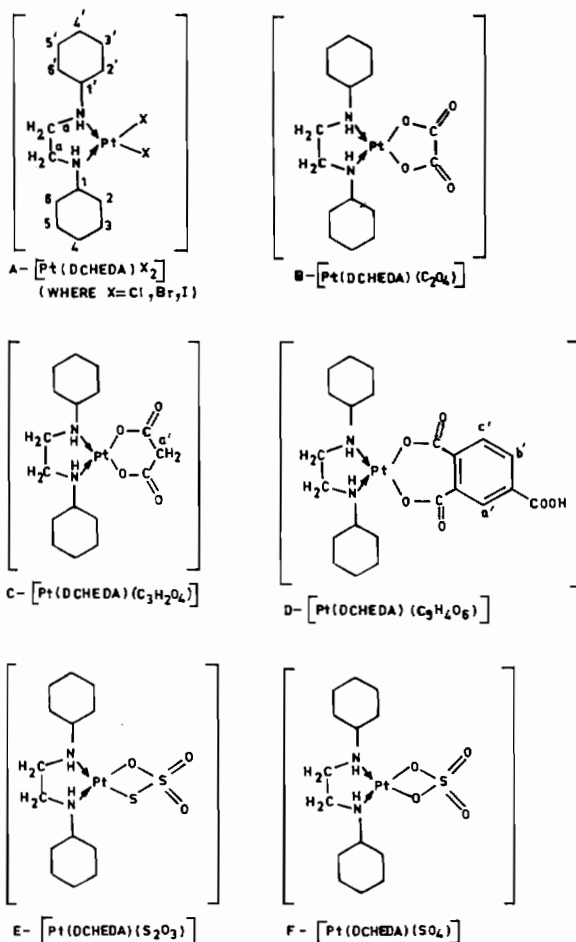
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## Abstract

The platinum(II) complexes of the formula  $[\text{Pt}(\text{DCHEDA})\text{X}_2]$ , where DCHEDA is *N,N'*-dicyclohexylethylenediamine and  $\text{X}^-$  is  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $0.5\text{C}_2\text{O}_4^{2-}$  (oxalate),  $0.5\text{C}_3\text{H}_2\text{O}_4^{2-}$  (malonate),  $0.5\text{C}_9\text{H}_4\text{O}_6^{2-}$  (4-carboxyphthalate),  $0.5\text{S}_2\text{O}_3^{2-}$  or  $0.5\text{SO}_4^{2-}$ , have been synthesized and characterized by UV-Vis, IR, and  $^1\text{H}$  NMR spectral techniques. All the above complexes are non-electrolytes in DMF/ $\text{H}_2\text{O}$ , except the sulphate complex which becomes a 1:1 electrolyte after incubation for 24 h at 28 °C. The halide complexes were also studied by X-ray photoelectron spectroscopy and these data suggest that there is  $\pi$ -bonding from platinum to halide in these complexes. The oxalate, malonate and sulphate bind in their complexes as bidentate ligands to platinum through two oxygen atoms whereas the thiosulphate in its complex binds as a bidentate ligand to platinum through one oxygen atom and one sulphur atom.

## Introduction

Many platinum complexes of substituted diamine-alkane ligands have been shown to have higher therapeutic indices than diamminedichloroplatinum(II) and that they are potential second generation anticancer drugs [1, 2]. Some of the most promising platinum compounds are derivatives of 1,2-diaminocyclohexane with various anions such as malonate, sulphate, 4-carboxyphthalate, etc. [3]. Therefore, in the present investigation a structural variation in the ethylenediamine molecule has been made by symmetrically substituting hydrogen on nitrogen atoms of ethylenediamine by cyclohexyl groups. Thus the ligand, *N,N'*-dicyclohexylethylenediamine, and its several 1:1 platinum complexes with anions such as  $2\text{Cl}^-$ ,  $2\text{Br}^-$ ,  $2\text{I}^-$ ,  $\text{C}_2\text{O}_4^{2-}$ ,  $\text{C}_3\text{H}_2\text{O}_4^{2-}$ ,  $\text{C}_9\text{H}_4\text{O}_6^{2-}$ ,  $\text{S}_2\text{O}_3^{2-}$  and  $\text{SO}_4^{2-}$  are reported here.



## Experimental

### Starting Materials

The reagent grade chemicals were normally used without further purifications. However, the cyclohexylamine was used after distillation and the solvents used were purified by the standard methods [4].

### Synthetic Procedures

*N,N'*-Dicyclohexylethylenediamine (abbreviated as DCHEDA) was prepared by refluxing one mole of 1,2-dichloroethane, five moles of cyclohexylamine and three moles of distilled water for 15 h. The excess cyclohexylamine was removed by distillation under reduced pressure. The white solid thus obtained was dissolved in water (100 ml) and an excess sodium hydroxide solution was then added in small portions with vigorous shaking. The DCHEDA separated out from the aqueous layer. The compound was filtered, washed several times with cold water and finally recrystallized by acetone. The yield was 90%.

#### [Pt(DCHEDA)I<sub>2</sub>]

K<sub>2</sub>PtCl<sub>4</sub> (1 mmol) was dissolved in 20 ml of distilled water and 4 g (24 mmol) of KI was added to this solution. DCEDA·H<sub>2</sub>O (1 mmol) in methanol was added to the above solution with continuous stirring and the precipitate of the diiodo compound was obtained. This precipitate was filtered, washed with water, water-ethanol mixture, ethanol and diethylether. The compound was dried in a vacuum desiccator over anhydrous CaCl<sub>2</sub>. The yield was 90%.

#### [Pt(DCEDA)Cl<sub>2</sub>]

[Pt(DCEDA)I<sub>2</sub>] (1 mmol) was suspended in 20 ml of water and a solution of AgNO<sub>3</sub> (1.90 mmol) in distilled water was added to it. The suspension was stirred for 24 h in the dark at room temperature. The solution was centrifuged and the precipitate of AgI was removed by filtration. NaCl in twenty-fold excess in water was added and the precipitate of dichloro was obtained. The precipitate was filtered, washed with water, water-ethanol mixture, ethanol and diethylether. The solid was dried in a vacuum desiccator over anhydrous CaCl<sub>2</sub>. The yield was 70%.

#### [Pt(DCEDA)Br<sub>2</sub>], [Pt(DCEDA)(C<sub>2</sub>O<sub>4</sub>)], [Pt(DCEDA)(C<sub>3</sub>H<sub>2</sub>O<sub>4</sub>)], [Pt(DCEDA)(C<sub>9</sub>H<sub>4</sub>O<sub>6</sub>)] and [Pt(DCEDA)(S<sub>2</sub>O<sub>3</sub>)]

The above compounds were prepared by following the preparative method of [Pt(DCEDA)Cl<sub>2</sub>] except that KBr (25 mmol), Na<sub>2</sub>C<sub>2</sub>O<sub>4</sub> (1 mmol), Na<sub>2</sub>C<sub>3</sub>H<sub>2</sub>O<sub>4</sub> (1 mmol), Na<sub>2</sub>C<sub>9</sub>H<sub>4</sub>O<sub>6</sub> (1 mmol) and Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (1 mmol) respectively per mmol of [Pt(DCEDA)I<sub>2</sub>] were used in place of NaCl. The yields of the above compounds were in the range of 55 to 70%.

#### [Pt(DCEDA)(SO<sub>4</sub>)]

[Pt(DCEDA)I<sub>2</sub>] (1 mmol) was suspended in 20 ml of distilled water and Ag<sub>2</sub>SO<sub>4</sub> (0.9 mmol) in water was added to it. The suspension was stirred for 24 h in the dark. The precipitate of AgI was removed by filtration. The clear filtrate was con-

centrated to dryness on a water bath and a white solid was obtained. This solid was dried in a vacuum desiccator over anhydrous CaCl<sub>2</sub>. The yield was 60%.

Chemical analyses of the above compounds were performed at the Microanalytical laboratory, IIT Bombay.

### Physical Measurements

The <sup>1</sup>H NMR spectra of the above compounds were obtained in (CD<sub>3</sub>)<sub>2</sub>SO on a Varian XL-100 NMR Spectrometer using TMS as an internal reference. The Pye Unicem SP-2000 Infrared Spectrophotometer was used for recording infrared spectra of the compounds (KBr or Nujol) in the range of 4000 to 200 cm<sup>-1</sup>. The electronic absorption spectra of the compounds in dimethylformamide (DMF) were recorded on a Varian Superscan 3 UV-Vis Spectrophotometer. The conductivity measurements of the compounds in DMF or conductivity water were carried out on a Systronics Conductivity Bridge 305 using conductivity cell of cell constant of 0.0784.

X-ray photoelectron spectra of the compounds were recorded using a VG-ESCA-2 Mark-3 Photoelectron Spectrometer equipped with a polyphenylether oil pump. Both Al Kα (1486.6 eV) and Mg Kα (1253.6 eV) radiation sources were used in conjunction with a 7.9 cm mode shield. Samples were mounted by silver epoxy on a copper sample holder which was fitted to the rod entering the observation chamber. Enough time was given for degassing the sample so that the observations were carried out at a vacuum better than 5 × 10<sup>-10</sup> torr. Standardization was achieved using a characteristic component of the C(1s) spectrum with the binding energy of 284.5 eV. Visual examination of the compounds after measurement revealed no evidence of radiation damage.

### Results and Discussion

Eight platinum(II) complexes of formula [Pt(DCHEDA)X<sub>2</sub>] (where DCHEDA is *N,N'*-dicyclohexylethylenediamine and X<sup>-</sup> is Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, 0.5C<sub>2</sub>O<sub>4</sub><sup>2-</sup>, 0.5C<sub>3</sub>H<sub>2</sub>O<sub>4</sub><sup>2-</sup>, 0.5C<sub>9</sub>H<sub>4</sub>O<sub>6</sub><sup>2-</sup>, 0.5S<sub>2</sub>O<sub>3</sub><sup>2-</sup> or 0.5SO<sub>4</sub><sup>2-</sup>) were prepared. The chemical analyses of these complexes along with their colour and conductivity data are given in Table I. The conductivity data of these complexes suggest them to be non-electrolyte in DMF [5]. However, the sulphate complex shows a molar conductance of a non-electrolyte (19.4 cm<sup>2</sup> ohm<sup>-1</sup> mol<sup>-1</sup>) for the freshly dissolved complex in conductivity water (10<sup>-3</sup> M), but its molar conductance increases with time at 28 °C (room temperature) till it reaches a constant value of 256.4 cm<sup>2</sup> ohm<sup>-1</sup> mol<sup>-1</sup>. The latter value

TABLE I. Chemical Analyses, Colour and Conductivity Data of [Pt(DCHEDA) $X_2$ ] Complexes

Compound	Colour	Calculated (%)			Found (%)			Molar conductance of complex in DMF/H <sub>2</sub> O (cm <sup>2</sup> ohm <sup>-1</sup> mol <sup>-1</sup> )
		C	H	N	C	H	N	
DCHEDA·H <sub>2</sub> O	white	69.37	11.64		69.16	11.78		
[Pt(DCHEDA)Cl <sub>2</sub> ]·H <sub>2</sub> O	yellow	33.07	5.90	5.51	33.00	5.98	5.59	1.6 <sup>a</sup>
[Pt(DCHEDA)Br <sub>2</sub> ]·H <sub>2</sub> O	yellow	28.15	4.72	4.68	28.16	4.93	4.49	3.9 <sup>a</sup>
[Pt(DCHEDA)I <sub>2</sub> ]·H <sub>2</sub> O	greenish-yellow	24.32	4.08	4.07	24.08	4.23	4.12	14.9 <sup>a</sup>
[Pt(DCHEDA)(C <sub>2</sub> O <sub>4</sub> )]·H <sub>2</sub> O	white	36.57	5.37	5.33	36.45	5.25	5.30	20.5 <sup>b</sup>
[Pt(DCHEDA)(C <sub>3</sub> H <sub>2</sub> O <sub>4</sub> )]·H <sub>2</sub> O	white	37.84	5.60	5.19	37.88	5.73	5.09	20.7 <sup>a</sup>
[Pt(DCHEDA)(C <sub>9</sub> H <sub>4</sub> O <sub>6</sub> )]	yellow	44.02	5.13	4.46	43.91	5.01	4.39	14.4 <sup>a</sup>
[Pt(DCHEDA)(S <sub>2</sub> O <sub>3</sub> )]	yellow	31.62	5.30	5.27	31.32	5.28	5.47	26.4 <sup>a</sup>
[Pt(DCHEDA)(SO <sub>4</sub> )]	white	32.64	5.47	5.43	32.28	5.25	5.21	19.4 <sup>b</sup> (256.4) <sup>c</sup>

<sup>a</sup>10<sup>3</sup> M solution in DMF. <sup>b</sup>10<sup>3</sup> M solution in conductivity water. <sup>c</sup>After incubating for 24 h at room temperature.

TABLE II. Electronic Absorption Spectra of [Pt(DCHEDA) $X_2$ ] Complexes in DMF

Compound	Band 1	$\lambda_{\max}$ (kK) <sup>a</sup>		Band 4	Band 5
		Band 2	Band 3		
[Pt(DCHEDA)Cl <sub>2</sub> ]·H <sub>2</sub> O		35.46 (0.22) <sup>b</sup>		31.64 (0.02)	
[Pt(DCHEDA)Br <sub>2</sub> ]·H <sub>2</sub> O		37.31 (0.27)		30.03 (0.13)	24.87 (0.03)
[Pt(DCHEDA)I <sub>2</sub> ]·H <sub>2</sub> O		35.46 (0.42)		31.94 (0.16)	26.10 (0.11)
[Pt(DCHEDA)(C <sub>2</sub> O <sub>4</sub> )]·H <sub>2</sub> O <sup>c</sup>	45.45 (0.34)	38.46 (0.02)		33.11 (0.01)	
[Pt(DCHEDA)(C <sub>3</sub> H <sub>2</sub> O <sub>4</sub> )]·H <sub>2</sub> O		35.71 (0.26)		33.11 (0.15)	
[Pt(DCHEDA)(C <sub>9</sub> H <sub>4</sub> O <sub>6</sub> )]		36.76 (0.33)	34.24 (0.21)	33.33 (0.15)	27.02 (0.01)
[Pt(DCHEDA)(S <sub>2</sub> O <sub>3</sub> )]		37.03 (0.21)		32.25 (0.08)	
[Pt(DCHEDA)(SO <sub>4</sub> )]	47.61 (0.10)	39.21 (0.02)		34.48 (0.01)	29.41 (0.004)

<sup>a</sup>kK is 10<sup>3</sup> cm<sup>-1</sup>. <sup>b</sup>Extinction coefficients in litre mol<sup>-1</sup> cm<sup>-1</sup> × 10<sup>-4</sup> are given in parentheses. <sup>c</sup>10<sup>-3</sup> M solution in distilled water.

suggests that the sulphate complex dissociates into [Pt(DCHEDA)(H<sub>2</sub>O)<sub>2</sub>]<sup>2+</sup> and free sulphate ion [6].

The electronic absorption maxima ( $\lambda_{\max}$ ) of the platinum(II) complexes with their extinction coefficients ( $\epsilon_{\max}$ ) in DMF are given in Table II. The spectra of these complexes show several bands which can be tentatively assigned by following the band assignments of the platinum(II) complexes of *N,N'*-disubstituted ethylenediamine [7]. The band 1 may be assigned to an internal diamine transition. The band 2 is assigned to a singlet → singlet transition ( $d_{z^2} \rightarrow d_{x^2-y^2}$ ). The band 3 is assigned to a  $\pi \rightarrow \pi^*$  transition of 4-carboxyphthalate moiety. The band 4 is assigned to a singlet → singlet transition ( $d_{xz}, d_{yz} \rightarrow d_{z^2}$ ). The band 5 is assigned to a

$d-d$  transition of the lowest energy  $d_{xy} \rightarrow d_{x^2-y^2}$ .

The <sup>1</sup>H nuclear magnetic resonance (NMR) spectral data of the free ligand, DCHEDA, and its platinum(II) complexes in (CD<sub>3</sub>)<sub>2</sub>SO are given in Table III. The <sup>195</sup>Pt-proton coupling constants (<sup>3</sup>*J*(Pt-H)) have also been observed in some complexes and are also given in Table III. Wherever the <sup>3</sup>*J*(Pt-H) is located it suggests that the nitrogen atoms of DCHEDA are coordinated to platinum [8]. The coordination of platinum invariably produces downfield shifts for H<sub>ax</sub> and H<sub>eq</sub> protons of DCHEDA.

The <sup>1</sup>H NMR spectrum of the free ligand, DCHEDA, shows two multiplets centred at 1.03 and 1.62 ppm, which correspond to ten axial and ten equatorial protons of the cyclohexyl rings,

TABLE III.  $^1\text{H}$  NMR Spectral Data of  $[\text{Pt}(\text{DCHEDA})\text{X}_2]$  Complexes in  $\text{DMSO}-d_6^a$ 

Compound	Cyclohexyl ring protons			$^3J(\text{Pt}-\text{H})$ of $^{195}\text{Pt}-\text{N}-\text{C}-\text{H}(1,1')$	$\delta(\text{H-a})$	$^3J(\text{Pt}-\text{H}(\text{a}))$	$\delta(\text{H-3})$	$\delta(\text{H-5})$	$\delta(\text{H-6})$
	$\delta_{\text{H}_{\text{ax}}}$	$\delta_{\text{H}_{\text{eq}}}$	$\delta_{\text{H-1,1}'}$						
$\text{DCHEDA}\cdot\text{H}_2\text{O}$	1.03	1.62	2.30		2.57				
$[\text{Pt}(\text{DCHEDA})\text{Cl}_2]\cdot\text{H}_2\text{O}$	1.24	1.68	2.10	18	2.50				
$[\text{Pt}(\text{DCHEDA})\text{Br}_2]\cdot\text{H}_2\text{O}$	1.25	1.68	2.24		2.86	26			
$[\text{Pt}(\text{DCHEDA})\text{I}_2]\cdot\text{H}_2\text{O}$	1.27	1.70	3.10	22	3.26				
$[\text{Pt}(\text{DCHEDA})(\text{C}_2\text{O}_4)]\cdot\text{H}_2\text{O}$	1.24	1.87	3.06	24	3.25				
$[\text{Pt}(\text{DCHEDA})(\text{C}_3\text{H}_2\text{O}_4)]\cdot\text{H}_2\text{O}$	1.22	1.78	2.90		3.04		3.24		
$[\text{Pt}(\text{DCHEDA})(\text{C}_9\text{H}_4\text{O}_6)]$	1.20	1.70			2.96		8.77	8.24	7.98
$[\text{Pt}(\text{DCHEDA})(\text{S}_2\text{O}_3)]$	1.30	1.70	2.35	24	3.36	26			
$[\text{Pt}(\text{DCHEDA})(\text{SO}_4)]$	1.18	1.69	2.30		2.84				

<sup>a</sup>Chemical shifts are given in  $\delta$ , ppm.

respectively. The two methine protons (H-1,1') are deshielded by the NH group and therefore appear downfield centred at 2.30 ppm.

The four H-a ethylene protons of DCHEDA absorb as a singlet at 2.57 ppm. The  $^1\text{H}$  NMR spectra of  $[\text{Pt}(\text{DCHEDA})\text{Cl}_2]$ ,  $[\text{Pt}(\text{DCHEDA})\text{Br}_2]$ ,  $[\text{Pt}(\text{DCHEDA})\text{I}_2]$  and  $[\text{Pt}(\text{DCHEDA})(\text{C}_2\text{O}_4)]$  show the downfield shifts of  $\text{H}_{\text{ax}}$  and  $\text{H}_{\text{eq}}$  protons, respectively, suggesting the binding of nitrogen atoms of DCHEDA to platinum. The chloro and bromo complexes in  $(\text{CD}_3)_2\text{SO}(\text{L})$  may also have species,  $[\text{Pt}(\text{DCHEDA})(\text{L})\text{X}]\text{X}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ). The infrared (IR) spectrum of DCHEDA shows a  $\nu(\text{N}-\text{H})$  vibration of the secondary  $-\text{NH}$  group at  $3300\text{ cm}^{-1}$ . The other bands at  $2960$  and  $2882\text{ cm}^{-1}$  may be assigned to the methylene asymmetrical stretchings of the free ligand skeleton and the cyclohexyl groups [9]. They shift to lower frequencies of 20 to  $50\text{ cm}^{-1}$  in its platinum(II) complexes. The  $\delta(\text{N}-\text{H})$  vibration of DCHEDA also shifts to a lower frequency by about  $10\text{ cm}^{-1}$  in its platinum(II) complexes. These shifts of IR data indicate the coordination of DCHEDA to platinum through N atoms in the solid state [10]. The IR spectrum of the  $[\text{Pt}(\text{DCHEDA})\text{Cl}_2]$  complex shows  $\nu(\text{Pt}-\text{Cl})$  vibrations at  $340$  and  $320\text{ cm}^{-1}$  (shoulder) [11]. The oxalate complex shows a  $\nu(\text{COO})$  vibration at  $1650\text{ cm}^{-1}$  indicating binding of both  $-\text{COO}^-$  groups to platinum [10]. A similar mode of binding of oxalate in  $[\text{Pt}(\text{NH}_3)_2(\text{C}_2\text{O}_4)]$  has been established by the X-ray structural method [12].

The  $^1\text{H}$  NMR spectrum of the malonate complex shows two H-a methylene protons of malonate as a singlet at 3.24 ppm (see Table III). These protons are shifted downfield as compared to the corresponding protons in free malonic acid. This suggests the strong binding of malonate to platinum through two oxygen atoms one from each  $-\text{COO}^-$  groups. The  $\nu(\text{COO})$  band observed at  $1650\text{ cm}^{-1}$  in the malonate complex in the solid state also indicates the binding of the carboxylate groups of bidentate

malonate to platinum. A similar mode of binding of the malonate in  $[\text{Pt}(\text{NH}_3)_2(\text{C}_3\text{H}_2\text{O}_4)]$  has been established by the X-ray structural method [12]. The  $^1\text{H}$  NMR spectrum of the 4-carboxyphthalate complex shows the H-3, H-5, and H-6 protons centred at 8.77, 8.24 and 7.98 ppm, respectively. The more downfield shift of H-3 and H-6 protons as compared to the corresponding protons of the free ligand suggests the binding of two *ortho*  $-\text{COO}^-$  groups to platinum through two oxygen atoms one from each of two  $-\text{COO}^-$  groups. The IR spectrum of the 4-carboxyphthalate complex shows a band at  $1640\text{ cm}^{-1}$  thus indicating the binding of carboxylate groups to platinum in the solid state. The complexes also have a very strong band at  $1720\text{ cm}^{-1}$ , which is assigned to the uncoordinated  $-\text{COOH}$  group of the 4-carboxyphthalate moiety [10]. A similar mode of binding of 4-carboxyphthalate in (4-carboxyphthalato)(1,2-diaminocyclohexane)platinum(II) has been suggested [2].

The  $^1\text{H}$  NMR spectrum of  $[\text{Pt}(\text{DCHEDA})(\text{S}_2\text{O}_3)]$  shows the downfield shift of all protons of DCHEDA (see Table III). This suggests the binding of N atoms of DCHEDA to platinum. The IR spectrum of the thiosulphate complex shows two strong bands at  $1195$  and  $1140\text{ cm}^{-1}$ , which are assigned to  $\nu_s(\text{SO})$  vibrations. The presence of these bands suggests the coordination of the thiosulphate group to platinum through oxygen and sulphur [13]. The band at  $455\text{ cm}^{-1}$  in the complex due to the  $\nu(\text{SS})$  vibration is shifted to  $5\text{ cm}^{-1}$  as compared to the corresponding frequency in anhydrous  $\text{Na}_2\text{S}_2\text{O}_3$  ( $460\text{ cm}^{-1}$ ), thus it supports the coordination of sulphur to platinum. The  $^1\text{H}$  NMR spectrum of  $[\text{Pt}(\text{DCHEDA})(\text{SO}_4)]$  shows the downfield shifts of  $\text{H}_{\text{ax}}$  and  $\text{H}_{\text{eq}}$  protons, respectively. This suggests the binding of DCHEDA to platinum through N atoms of DCHEDA. The actual species present in  $(\text{CD}_3)_2\text{SO}$  solution may be  $[\text{Pt}(\text{DCHEDA})(\text{CD}_3)_2\text{SO}]_2$ . The IR spectrum of the sulphate complex shows bands at  $1125$ ,  $1040$ ,  $630$  and  $610\text{ cm}^{-1}$ . The presence of these

TABLE IV. X-ray Photoelectron Spectral Data of [Pt(DCHEDA)X<sub>2</sub>] Complexes

Compound	Pt(4d)	N(1s)	Cl(2p)	Br(2p)	I(3d)
[Pt(DCHEDA)Cl <sub>2</sub> ]	314.5 <sup>a</sup>	398.8	197.5		
[Pt(DCHEDA)Br <sub>2</sub> ]	314.7	399.0		187.7, 181.0	
[Pt(DCHEDA)I <sub>2</sub> ]	315.0	399.6			619.0

<sup>a</sup>Binding energies are given in eV.

vibrations suggests that the sulphate ion binds as a bidentate ligand to platinum in the solid state [14]. The Pt–O stretching band is observed at 470 cm<sup>-1</sup> in the sulphate complex; this confirms the binding of the sulphate ion to platinum through O atoms [10]. A similar mode of binding of the sulphate ion in 1,2-diaminocyclohexanesulphatoplatinum(II) has already been suggested [2].

The X-ray photoelectron spectral data of N(1s), Pt(4d<sub>5/2</sub>), Cl(2p), Br(3p), and I(3d) in the platinum(II) complexes containing halide ions are given in Table IV. The measured binding energies can be correlated in terms of an electronegativity difference between the platinum and donor atoms of the ligands and metal → ligand π-bonding [15–17]. The Pt(4d<sub>5/2</sub>) binding energies of the [Pt(DCHEDA)Cl<sub>2</sub>], [Pt(DCHEDA)Br<sub>2</sub>] and [Pt(DCHEDA)I<sub>2</sub>] complexes increase in the same order from Cl → Br → I. This order is contrary to the decrease of Pt–halogen bond polarities from Cl → Br → I. This suggests that as the Pt–halogen bond polarities decrease, the platinum → halogen π-bonding dominates on the overall charge of platinum. The N(1s) binding energies of the halide complexes shift slightly toward the high energy side as the halide ion is changed from Cl → Br → I and is again due to the increasing influence of platinum → halogen π-bonding from Cl → Br → I. The lower energies of Cl(2p) (197.5 eV) Br(3p) (187.6 eV) and I(3d) (619.0 eV) in their platinum complexes as compared to the respective values of halide ions [Cl(2p) (200.0 eV), Br(3p) (189.0 eV) and I(3d) (620.0 eV)] suggest that there are electron drifts towards halogen in these complexes.

Several platinum(II) complexes of *N,N'*-dicyclohexylethylenediamine with various anionic ligands (X) of the general formula [Pt(DCHEDA)X<sub>2</sub>] have been synthesized and characterized. The modes of binding of DCHEDA and anions to platinum have been deduced.

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