

Identification of a (H₂O)₈ cluster in a supramolecular host of a charge transfer platinum(II) complex

SUTANUVA MANDAL^a, IPSITA CHATTERJEE^a, ALFONSO CASTIÑEIRAS^{b,*} and SREEBRATA GOSWAMI^{a,*}

^aDepartment of Inorganic Chemistry, Indian Association for the Cultivation of Science, Kolkata 700 032, India

^bDepartamento de Química Inorgánica, Universidade de Santiago de Compostela, Campus Universitario Sur, 15782, Santiago de Compostela, Spain

e-mail: icsg@iacs.res.in; alfonso.castineiras@usc.es

MS received 22 March 2014; revised 9 April 2014; accepted 15 April 2014

Abstract. The chemical reaction of Pt^{II}(L¹)Cl₂ [L¹ = 2-(phenylazo)pyridine] with a bidentate N,S-donor atom ligand, 2-phenylthioaniline, (HL²) in alkaline acetonitrile yielded a mixed ligand donor acceptor complex, [Pt^{II}(L¹)(L²)⁻]Cl, [1]Cl. The complex has been characterized by using a host of physical methods: X-ray crystallography, nuclear magnetic resonance, cyclic voltammetry, absorption spectroscopy, electron paramagnetic resonance. The complex showed intense interligand charge transfer (ILCT) transition in the long wavelength region of UV-vis spectrum at 785 nm. The single-crystal X-ray structure of complex, [1]Cl·2.6H₂O is reported. The cationic complex upon crystallization from aqueous methanol solvent produces an assembly of three dimensional (H₂O)₈ guest moiety within the host lattice of reference Pt-complex. The water assembly showed a unique type of aggregation of two trigonal pyramids hydrogen bonded with three chloride anions. The complex displayed two reversible responses at -0.34 and -1.05 V along with one irreversible anodic response at 0.91 V *versus* Ag/AgCl reference electrode. The redox processes are characterized by examination of EPR spectra of the electrogenerated complexes.

Keywords. Platinum complex; X-ray structure; electrochemistry; ILCT transition; water cluster.

1. Introduction

Square-planar platinum(II) complexes of diimine ligands have generated much interest in recent years because of their rich spectroscopic properties as well as potential applications in materials science and biomedical fields.^{1–7} The square planar configuration of these complexes could facilitate electron delocalization and thus lead to various intramolecular charge transfer transition phenomena.^{8–10} In this field a series of charge transfer platinum complexes having donor 2-aminothioether and acceptor ligands were reported by us.^{1,11} In logical continuation of our ongoing research, a cationic mixed ligand platinum(II) complex having 2-(phenylazo)pyridine (pap, L¹) and 2-phenylthioaniline (HL²) as the acceptor and donor ligand, respectively, has been synthesized and thoroughly characterized. It shows an intense intramolecular charge transfer ($\epsilon = 9780 \text{ M}^{-1} \text{ cm}^{-1}$) band at 785 nm. This lowest

energy charge transfer transition is attributed to interligand charge transfer. Beside the rich spectroscopic property, the single crystal X-ray structural analysis showed the existence of a novel assembly of three dimensional (H₂O)₈ guest moiety surrounded by three chloride anions within the reference inorganic host lattice. Interestingly, the (H₂O)₈ cluster shows a unique type of arrangement of two trigonal pyramids in a single geometry. Only ice-like, cyclic morphology of (H₂O)₈ cluster in the solid-state structure of an organic supramolecular complex has been known in the literature.¹² Notably, in the past few decades, attention has been paid extensively to theoretical and experimental studies of discrete or small water clusters.^{13–16} A variety of one-dimensional (1D)^{17–21} water chains, tapes, and some two-dimensional (2D)^{22–24} water/ice layers containing large water rings have been identified but three-dimensional (3D) water clusters have been rare²⁵ type. Recently an unusual 3D (H₂O)₂₀ water cluster having aggregation of a distorted cube encapsulated by hydrogen bonded network of a twelve-water ring in the similar type of inorganic host lattice has been reported by us.¹

*For correspondence

2. Experimental

2.1 Materials

The starting Pt^{II}-salt, K₂PtCl₄ was collected from Arora-Matthey, Kolkata. The ligand 2-phenylthioaniline was purchased from Fluka. The ligand 2-(phenylazo)pyridine²⁶ the compound Pt(L¹)Cl₂^{27,28} and tetraethylammonium perchlorate (TEAP)²⁹ were prepared following published procedures. *Caution! perchlorate salts have to be handled with care and appropriate safety precautions.* Solvents and chemicals used for syntheses were of analytical grade and used as received.

2.2 Instrumentation

UV-vis-NIR absorption spectra were recorded either on a Perkin-Elmer Lambda 950 UV/vis spectrophotometer or on a J&M TIDAS instrument. The IR spectrum was recorded with a Perkin-Elmer 783 spectrophotometer. Cyclic voltammetry was carried out in 0.1 M TEAP solutions using a three-electrode configuration (platinum working electrode, Pt counter electrode, Ag/AgCl reference electrode) and a PC-controlled PAR model 273A electrochemistry system. The $E_{1/2}$ for the ferrocenium-ferrocene couple under our experimental conditions was 0.39 V. EPR spectra in the X band were recorded with a JEOL JES-FA200 spectrometer. A Perkin-Elmer 240C elemental analyzer was used to collect micro analytical data (C, H, N). ¹H NMR spectrum was taken on a Bruker Avance DPX 300 spectrometer, and SiMe₄ was used as the internal standard. ESI mass spectrum was recorded on a micro mass Q-TOF mass spectrometer (serial no. YA 263).

2.3 Synthesis of [Pt(L¹)(L²)⁻]Cl

To a solution of 50 mg (0.11 mmol) Pt(L¹)Cl₂ in 30 mL of acetonitrile, 22 mg (0.11 mmol) 2-phenylthioaniline (HL²) was added followed by the addition of 2 drops of NEt₃. The colour of the solution changed from dark red to intense green instantaneously. The mixture was then stirred for 30 min. at room temperature. The crude mixture, obtained after evaporation of the solvent, was purified on a preparative alumina TLC plate. Toluene-methanol solvent mixture (10:1) was used as the eluent. The compound [Pt(L¹)(L²)⁻]Cl, ([1]Cl) was separated on a TLC plate as a major green band. The residue, obtained by solvent evaporation, was recrystallized using aqueous methanol as solvent. Highly crystalline [1]Cl was obtained in 90% yield. Anal. Calcd for C₂₃H₁₈N₄PtSCl: C, 45.06; H, 2.94; N, 9.14. Found:

Table 1. Crystallographic data of complex [1]₃Cl₃·8H₂O.^a

| Parameter | [1] ₃ Cl ₃ ·8H ₂ O |
|---|---|
| Empirical formula | C ₆₉ H ₇₃ N ₁₂ Pt ₃ S ₃ O ₈ Cl ₃ |
| Formula weight | 1986.19 |
| Crystal system | Trigonal |
| Space group | R-3 |
| <i>a</i> /Å | 28.2837(12) |
| <i>b</i> /Å | 28.2837(12) |
| <i>c</i> /Å | 15.5139(7) |
| α /° | 90 |
| β /° | 90 |
| γ /° | 120 |
| <i>V</i> /Å ³ | 10747.9(12) |
| <i>Z</i> | 6 |
| <i>D</i> _{calcd} /g cm ⁻³ | 1.837 |
| Cryst dims/mm ³ | 0.20 × 0.20 × 0.20 |
| θ range for data collection/° | 1.4 - 32.0 |
| GOF on <i>F</i> ² | 1.03 |
| Reflections collected | 7903 |
| Unique reflection | 295 |
| Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] | 0.0281 |
| <i>T</i> /K | 293 |

^aChemical formula of the reference compound.

C, 45.11; H, 2.91; N, 9.12. IR (KBr disk, cm⁻¹): 1332 (N=N). ESI-MS: *m/z* 577 amu, [1]⁺.

2.4 Crystallography

Crystallographic data for the compound [Pt(L¹)(L²)⁻]₃Cl₃·8H₂O is collected in table 1. Suitable X-ray quality crystals of this compound are obtained by slow evaporation of aqueous methanolic solution of the compound. The data was collected on a Bruker SMART APEX-II diffractometer, equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å), and was corrected for Lorentz-polarization effects. A total of 7903 reflections were collected, of which 295 were unique ($R_{\text{int}} = 0.046$), satisfying the ($I > 2(I)$) criterion, and were used in subsequent analysis. The structure was solved by employing the SHELXS-97 program package³⁰ and was refined by full-matrix least-squares based on *F*² (SHELXL-97).³¹ The hydrogen atoms of the complex were added in calculated positions and that of water molecules are located.

3. Result and Discussion

3.1 Synthesis

A chemical reaction of the molecular compound Pt^{II}(L¹)Cl₂ with 2-phenylthioaniline (HL²) in acetonitrile

in presence of NEt₃ (base) at room temperature produced a green coloured mixed ligand cationic complex, [Pt(L¹)(L²)⁺]Cl, ([1]Cl) in nearly quantitative yield. The reaction involves simple substitution of two labile Cl⁻ ions by a deprotonated 2-phenylthioanilide ligand. The synthetic reaction is depicted in scheme 1.

The complex gave satisfactory elemental analyses (*cf.*, Experimental section). Electrospray mass spectrum of the complex corroborates with its formulation as [1]⁺ and showed an intense peak at *m/z* 577 amu. Notably, the experimental spectral feature of the complex corresponds very well with the simulated isotopic pattern for the given formulation. The spectrum and its simulated spectra are submitted as supplementary information (figure S1). The diamagnetic compound [1]Cl showed resolved ¹H NMR spectrum in methanol-*d*₄ solvent. Due to the presence of phenyl moiety overlapping signal appeared in the aromatic region of the spectrum and makes the NMR spectrum complex. However, the NH proton resonance appeared at δ, 4.50 ppm and disappeared on D₂O shake. The ¹H NMR spectrum of [1]Cl is submitted as supplementary information (figure S2). The complex showed a relatively broad band in the FTIR spectroscopic study at 3369 cm⁻¹, which is attributed to the O-H stretching frequency of the water cluster (figure S3).

3.2 X-ray crystal structure of [Pt(L¹)(L²)⁺]Cl·2.6H₂O

The complex [1]Cl forms dark green crystals, whose structure has been solved by single crystal X-ray diffraction. An Oak Ridge thermal-ellipsoid plot (ORTEP) and atom numbering scheme of the above complex is shown in figure 1, and selected bond parameters are collected in table 2. X-ray structure solution of the compound [1]Cl reconfirms its formulation as well as its geometry. The central platinum atom in the compound is coordinated to a neutral pap and a deprotonated 2-phenylthioanilide ligand in a square planar geometry (figure 1). The complex as a whole is monocationic and the crystallographic asymmetric

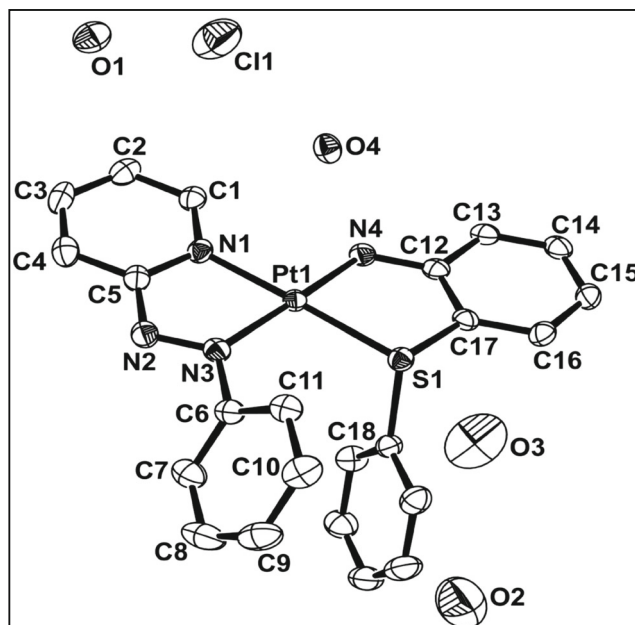
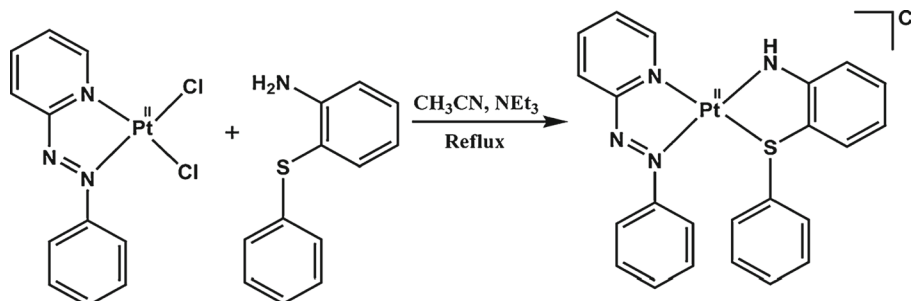


Figure 1. ORTEP and atom numbering scheme of the compound [1]Cl. Hydrogen atoms are omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°) of ([1]Cl)₃·8H₂O.

| Parameter | ([1]Cl) ₃ ·8H ₂ O |
|-----------------|---|
| Pt(1)-S(1) | 2.2776(7) |
| Pt(1)-N(1) | 2.018(2) |
| Pt(1)-N(3) | 1.968(2) |
| Pt(1)-N(4) | 1.952(2) |
| N(2)-N(3) | 1.295(3) |
| S(1)-C(17) | 1.774(3) |
| N(4)-C(12) | 1.371(4) |
| S(1)-C(18) | 1.798(3) |
| S(1)-Pt(1)-N(3) | 99.21(7) |
| S(1)-Pt(1)-N(4) | 84.36(8) |
| N(1)-Pt(1)-N(3) | 77.77(10) |
| N(1)-Pt(1)-N(4) | 98.77(10) |

unit contains one chloride anion as a counter ion and water molecules as solvate. The average Pt-N(pap) and



Scheme 1. Synthesis of complex [1]Cl.

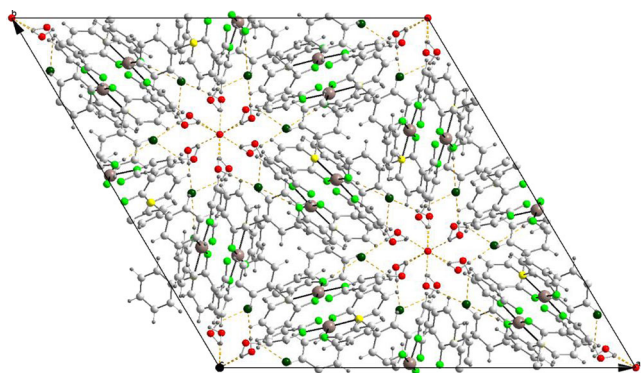


Figure 2. Packing diagram of $([1]Cl)_3 \cdot 8H_2O$ viewed down the crystallographic c axis showing various inter- and intramolecular hydrogen-bonding interactions.

Pt-N(anilido) distances are 1.993(2) and 1.952(2) Å, respectively.

Interestingly, the crystal structure reveals in crystals of $[Pt(L^1)(L^2)]_3Cl_3 \cdot 8H_2O$ (figure 2), $[Pt(L^1)(L^2)]^+$ cation form pairs (figure 3), each member of which is linked to two other pairs *via* an $(H_2O)_8$ cluster surrounded by three chloride anions (figure 4), each chloride forming an N-H...Cl⁻ hydrogen bond with a cation and two O-H...Cl bonds with the water cluster (table 3). The crystallographic unique part of the $(H_2O)_8$ cluster consists of two-third-occupancy water molecules on a 3-fold rotation axis (O1 and O2) and two total-occupancy water molecules (O3 and O4). The entire cluster is generated from these units by C_3 symmetry and the overall is two trigonal pyramids, (O1/O3/O3a/O3b) and (O2/O4/O4a/O4b) (a: $1/3+x, -1/3+x, 2/3-z$; b: $1/3-x, -1/3+y, 2/3-z$), with their bases facing each other in a staggered arrangement (O3-O1-O2-O4 = 77.2°) on either side of the plane of the chloride anions; each base atom forms an O-H...O

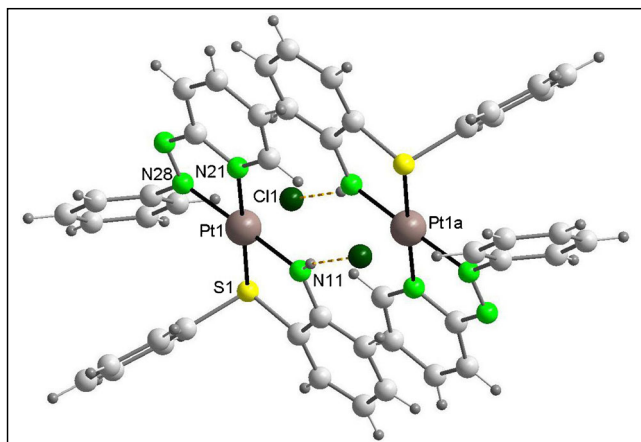


Figure 3. A view of a pair of cationic $[Pt(L^1)(L^2)]^+$ complex moiety.

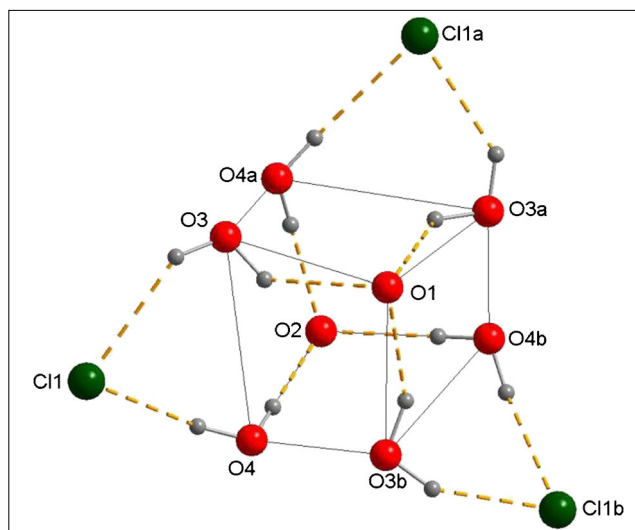


Figure 4. Topology of supramolecular $(H_2O)_8$ cluster H-bonded with three chloride anions.

bond with the corresponding apex, and an OH...Cl bond with one of the chloride anions, which thus link the two pyramids (figure 4). The ClH_3 unit formed by each chloride and the hydrogens of its hydrogen bonds is flat but asymmetric, with an H3-Cl-H4 angle of 85.756(2)° and, H3A-Cl1-H11 and H4A-Cl1-H11 angles of 97.818(2)° and 175.055(2)°, respectively. The distance O3-O3 between the base atoms of one water pyramid is 4.289(6) Å, the distance O4-O4 4.226(6) Å, and the distance O1-O2 between apices 4.9886(2) Å; the apical angles O3-O1-O3 are 93.832(1)°, and the O4-O2-O4 angles 98.040(2)°. The vanderWaals volume of the water cluster is 1389.1 Å³, which is 12.9% of the unit cell volume, 10747.9 Å³. When compared with the O-O distances found in ice, liquid water and water vapour (2.74, 2.85 and 2.98 Å, respectively), the distances between water clusters in the c direction, 2.755(10) Å (O1-O1) and 2.786(11) Å (O2-O2), suggest that strong between-cluster hydrogen bonds complete a highly compact, stable three-dimensional structure.

3.3 Cyclic voltammetry and EPR

Cyclic voltammogram (CV) of the complex $[Pt^{II}(L^1)(L^2)]Cl$ was recorded in CH_3CN solvent containing 0.1 (M) Et_4NClO_4 as a supporting electrolyte using platinum as the working electrode. The potentials are referenced to the saturated Ag/AgCl electrode and the data are collected in table 4. Segmented voltammograms (cathodic sweep) of the two representative compounds are displayed in figure 5 and their full range (+1.5 to -1.5 V) voltammograms are

Table 3. Hydrogen bonds (Å / °) for [Pt(L¹)(L²)⁻]₃Cl₃·8H₂O.

| D-H...A | d(D-H) | d(H...A) | d(D...A) | ∠(DHA) |
|----------------------|--------|----------|-----------|--------|
| O1 - O1#2 | | | 2.755(10) | |
| O1 - O3 | | | 2.929(5) | |
| O1 - O3#3 | | | 2.929(5) | |
| O1 - O3#4 | | | 2.929(5) | |
| O2 - O2#1 | | | 2.786(11) | |
| O2 - O4 | | | 2.805(5) | |
| O2 - O4#3 | | | 2.805(5) | |
| O2 - O4#4 | | | 2.805(5) | |
| N(4)-H(4')...Cl(1)#5 | 0.74 | 2.62 | 3.348(3) | 168.3 |
| O(3)-H(3A)...Cl(1) | 0.91 | 2.47 | 3.182(3) | 135.0 |
| O(3)-H(3B)...O(1) | 0.92 | 2.22 | 2.930(5) | 133.3 |
| O(4)-H(4A)...Cl(1) | 0.85 | 2.40 | 3.224(4) | 152.5 |
| O(4)-H(4B)...O(2) | 0.85 | 1.96 | 2.805(5) | 179.4 |

Symmetry transformations used to generate equivalent atoms: #1 -x, -y, -z; #2 -x, -y, 1-z; #3 -y, x-y, z; #4 -x+y, -x, z; #5 1/3-x, 2/3-y, 2/3-z

Table 4. Cyclic voltammetric^a and UV-vis spectral data^d of the complex [1]Cl.

| Compound | Cyclic voltammetric data ^a | | UV-vis spectral data ^d |
|--|--|--|--|
| | Reduction E _{2/1} ^b V (ΔE _p , mV) | Oxidation E _{2/1} ^b V (ΔE _p , mV) | λ _{max} ^d (ε) |
| [Pt(L ¹)(L ²) ⁻]Cl | -0.34 (89), -1.05 (88) | 0.91 ^c | 785 (9780), 365(9135) 230 ^e (28520) |

^aIn acetonitrile solution supporting electrolyte Et₄NClO₄, reference electrode Ag/AgCl. ^bE_{1/2} = 0.5(E_{pa} + E_{pc}) where E_{pa} and E_{pc} are anodic and cathodic peak potentials respectively, ΔE_p = E_{pa} - E_{pc}, scan rate 50 mV S⁻¹. ^cIrreversible. ^dWavelength in nm, molar extinction coefficients in M⁻¹ cm⁻¹ in methanol solvent. ^eShoulder.

submitted as supplementary information (figure S4). The complex [1]Cl displayed three electrochemical responses at -0.34, -1.05 and 0.91 V. The two responses at cathodic potentials are reversible while the oxidative response is irreversible. The one-electron stoichiometry of the reversible response was confirmed by constant-potential coulometry. Irreversibility in the oxidative waves may result from dissociation of the thioether sulfur atom from the Pt center in the oxidized form of the complex while the cathodic wave formally correspond to the reduction of the azo chromophore of ligand L¹ (figure 5 and S4).¹¹

To have further insight into the reversible redox process, the electrogenerated complexes were studied by EPR at 120 K and UV-vis-NIR spectroelectrochemistry at 300 K in CH₃CN/0.1 M Et₄NClO₄. The one electron reduced species, [Pt^{II}(L^{1•-})(L²)⁻] was generated by exhaustive electrolysis of [Pt^{II}(L¹)(L²)⁻]⁺ at -0.6 V which showed a single line EPR signal (figure 5) with strong hyperfine coupling¹⁶ constants of 7.3 and 2.9 mT (for ¹⁹⁵Pt, I = 1/2, natural abundance = 33%) at g = 2.001 confirming some metal participation to the SOMO. Expectedly the second electron reduced species remains EPR silent due to the second reduction at the same ligand center, (L¹)^{•-}. Unfortunately,

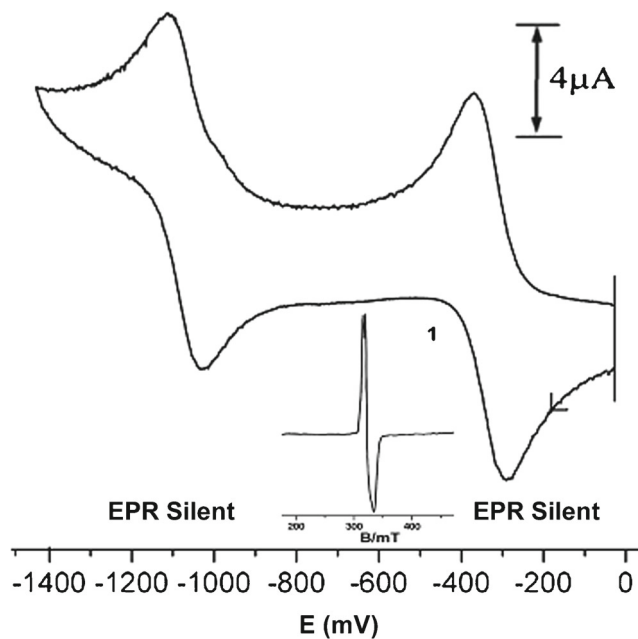


Figure 5. Cyclic voltammogram of the compound [1]Cl and EPR spectrum of the electrogenerated compound [1] in CH₃CN/0.1 M Et₄NClO₄.

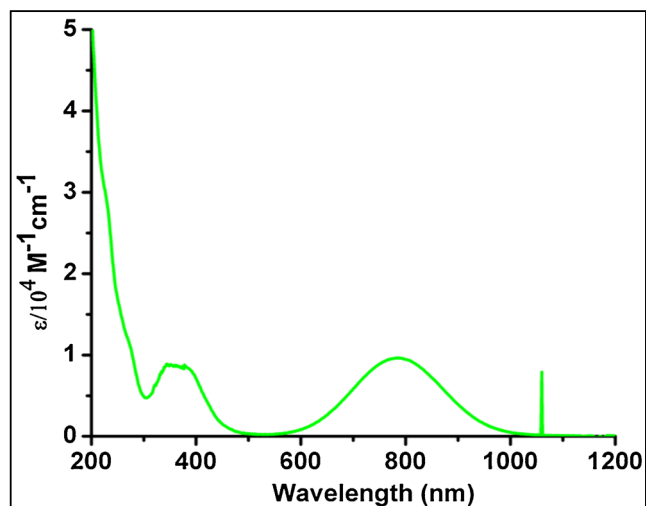


Figure 6. UV-vis-NIR absorption spectra of the compound [1]Cl in 10^{-4} M acetonitrile solution.

we are unable to record spectra of the electrogenerated reduced species because these are not sufficiently stable for meaningful measurements.

3.4 UV-vis spectrum

The electronic spectra of the cationic mixed chelate [1]Cl has been recorded in the range 240–1200 nm in CH_3CN solvent. It exhibited a single allowed low energy intense transition at 785 nm (table 4, figure 6). Cyclic voltammetry and EPR results, as discussed before, suggested that both HOMO and the LUMO are primarily localized on the two ligand centers; HOMO on the ligand L^1 and LUMO on the ligand $(\text{L}^2)^-$.^{1,11} The lowest energy transition can thus be described as a interligand charge transfer (ILCT) transition (figure 6).^{1,11} Notably the colour of the solution of the above complex faded considerably upon reduction. This is not unexpected since the acceptor character of $(\text{L}^2)^-$ centre diminishes upon reduction, resulting in disappearance of the above ILCT transition.

4. Conclusion

We have introduced an intense green coloured platinum(II) complex exhibiting intramolecular interligand charge transfer transition in the long wavelength part of visible spectrum. Elucidation of X-ray structure analysis confirmed the presence of a novel $(\text{H}_2\text{O})_8$ water cluster in the supramolecular host lattice of the reference inorganic complex. The present mode of association of eight water molecules, as far as we know, has not been predicted theoretically or previously found experimentally. The understanding of three dimensional

structures of water clusters has profound effects in several areas like molecular self-assembly or protein structures. Attempts should thus be made to simulate water crystallization in restricted environments such as inorganic host lattices.

Supplementary Information

The electronic supporting information can be seen at www.ias.ac.in/chemsci.

Acknowledgements

Financial support received from the Council of Scientific and Industrial Research, New Delhi (Project 01/2714/13/EMR-II) is gratefully acknowledged. S G thanks DST for a J C Bose fellowship. Crystallography was performed at the DST-funded National Single Crystal Diffractometer Facility at the Department of Inorganic Chemistry, IACS. I C thanks the Council of Scientific and Industrial Research for her fellowship.

References

- Mandal S, Castiñeiras A, Mondal T K, Mondal A, Chattopadhyay D and Goswami S 2010 *Dalton Trans.* **39** 9514
- Du Z, Luo Q, Yang L, Bing T, Li X, Guo W, K Wu W, Zhao Y, Xiong S, Shangguan D and Wang F 2014 *J. Am. Chem. Soc.* **136** 2948
- Patel M N, Patel C R, Joshi H N and Thakor K P 2014 *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **127** 261
- Ji Z, Li S, Li Y and Sun W 2010 *Inorg. Chem.* **49** 1337
- Shavaleev N M, Davies E S, Adams H, Best J and Weinstein J A 2008 *Inorg. Chem.* **47** 1532
- de Quadras L, Shelton A H, Kuhn H, Hampel F, Schanze K S and Gladysz J A 2008 *Organometallics* **27** 4979
- Eryazici I, Moorefield C N and Newkome G R 2008 *Chem. Rev.* **108** 1834
- Shao P, Li Y, Azenkeng A, Hoffmann M R and Sun W 2009 *Inorg. Chem.* **48** 2407
- Carli S, Casarin L, Bergamini G, Caramori S and Bignozzi C A 2014 *J. Phys. Chem. C*. doi: [10.1021/jp412758g](https://doi.org/10.1021/jp412758g)
- Petersen A R, Taylor R A, Vicente-Hernandez I, Heinzer J, White A J P and Britovsek G J P 2014 *Organometallics* **33** 1453
- (a) Mandal S, Paul N, Banerjee P, Mondal T K and Goswami S 2010 *Dalton Trans.* **39** 2717; (b) Mandal S, Samanta S, Mondal T K and Goswami S 2012 *Organometallics* **31** 5282
- Atwood J L, Barbour L J, Ness T J, Raston C L and Raston P L 2001 *J. Am. Chem. Soc.* **123** 7192
- Ghosh S J and Bharadwaj P K 2004 *Angew. Chem. Int. Ed.* **43** 3577
- Buck U and Huisken F 2000 *Chem. Rev.* **100** 3863

15. Chen K, Hirst J, Camba R, Bonagura C A, Stout C D, Burgess B K and Armstrong F A 2000 *Nature* **405** 814
16. Mahata P, Ramya K V and Natarajan S 2009 *Inorg. Chem.* **48** 4942
17. Cheng L, Lin J B, Gong J Z, Sun A P, Ye B H and Chen X M 2006 *Cryst. Growth Des.* **6** 2739
18. Ma B Q, Sun H L and Gao S 2005 *Chem. Commun.* 2336
19. Khatua S, Kang J, Huh J O, Hong C S and Churchill D G 2010 *Cryst. Growth Des.* **10** 327
20. Mahata P, Ramya K V and Natarajan S 2009 *Inorg. Chem.* **48** 4942
21. Yang G P, Wang Y Y, Liu P, Fu A Y, Zhang Y N, Jin J C and Shi Q Z 2010 *Cryst. Growth Des.* **10** 1443
22. Lakshminarayanan P S, Suresh E and Ghosh P 2005 *J. Am. Chem. Soc.* **127** 13132
23. Yang A H, Zhang H, Gao H L, Zhang W Q, He L and Cui J Z 2008 *Cryst. Growth Des.* **8** 3354
24. Janiak C and Scharmann T G 2002 *J. Am. Chem. Soc.* **124** 14010
25. Lakshminarayanan P S, Suresh E and Ghosh P 2006 *Angew. Chem. Int. Ed.* **45** 3807
26. Campbell N, Henderson W A and Taylor J D 1953 *J. Chem. Soc.* 1281
27. Panda M, Das S, Mostafa G, Castiñeiras A and Goswami S 2005 *Dalton Trans.* 1249
28. Rauth K G, Pal S, Das D, Sinha C, Slawin M Z A and Woollins D J 2001 *Polyhedron* **20** 363
29. Goswami S, Mukherjee R N and Chakravarty A 1983 *Inorg. Chem.* **22** 2825
30. Sheldrick G M 1990 *Acta Crystallogr., Sect. A: Found. Crystallogr.* **46** 467
31. Sheldrick G M 1997 *SHELXL 97. Program for the refinement of crystal structures* (Göttingen, Germany: University of Göttingen)