

Contribution from the Department of Chemistry, University of Rochester, Rochester, New York 14627, Department of Chemistry and Materials Science Center, Cornell University, Ithaca, New York 14853, and Département de Chimie, Université de Sherbrooke, Sherbrooke (Québec), Canada J1K 2R1

Spectroscopic and Theoretical Studies on the Excited State in Diimine Dithiolate Complexes of Platinum(II)

Juan A. Zuleta,¹ Joanne M. Bevilacqua,¹ Davide M. Proserpio,^{2a} Pierre D. Harvey,^{2b} and Richard Eisenberg^{*1}

Received February 19, 1992

The photophysical properties of a series of Pt(N-N)(S-S) complexes have been studied where (N-N) is either an α,α' -diimine or saturated diamine chelating ligand and (S-S) is either a dithiolate chelating ligand or two monothiolate ligands in order to determine the orbital composition of the excited state. The solvent dependence of the absorption spectra of these complexes and the temperature dependence of their emission intensities and lifetimes have been examined while the ligands have been systematically varied. The electronic spectra are found to be dependent on whether or not the nitrogen chelating ligand is unsaturated (contains a vacant π^* orbital). All of the unsaturated diimine complexes show an intense solvatochromic band in the visible region of their electronic spectra which shifts to higher energy with increasing solvent polarity. In the related complexes in which a saturated diamine chelating ligand replaces the unsaturated diimine chelating ligand, no solvatochromism is observed. On the basis of the spectroscopic data, the lowest energy absorption band in the diimine complexes is assigned as a metal-dithiolate to π^* (diimine) transition, whereas in the diamine complexes it is assigned as a metal-to-dithiolate MLCT transition. The only room-temperature emissive complexes are those that contain an α,α' -diimine chelating ligand. The nature of the emission in these complexes at all temperatures depends on the dithiolate ligand, and the temperature dependence of the emission spectra has been examined. When (S-S) is the 1,2-dithiolate maleonitriledithiolate (mnt), the emission in rigid glass is structured and shows single exponential behavior with both emission intensity and lifetime, increasing with decreasing temperature. For the other (S-S) complexes studied, the emission in rigid glass shows evidence of multiple emitting states based on the observation that lifetimes increase while emission quantum yields decrease as the temperature is lowered. The nature of the HOMO and LUMO has been examined experimentally using cyclic voltammetry. On the basis of the electrochemical and spectroscopic data, the emission from all of the Pt(diimine)(S-S) complexes except those of mnt is assigned as a $^3d(\text{Pt})/p(\text{S})-\pi^*$ (diimine) transition, while, for the mnt complexes, it corresponds to a $^3d(\text{Pt})/p(\text{S})-\pi^*$ (mnt) transition. These assignments are supported by extended Hückel molecular orbital calculations.

Introduction

Essential to the development of transition metal complex photochemistry is the elucidation of electronic excited states of metal complexes through a systematic variation of the donor and acceptor properties of the ligands. During the past two decades, much effort has been expended in this direction, most notably with d^6 complexes of octahedral geometry having heteroaromatic chelating ligands including $\text{Ru}(\text{bpy})_3^{2+}$, $\text{IrCl}_2(\text{phen})_2^+$, $\text{ReCl}(\text{bpy})(\text{CO})_3$, and their analogues, to name a few.³ In recent years, interest in luminescent d^8 square planar complexes has increased as a number of examples have been reported, including $\text{MLL}'(\text{mnt})^n$ ($n = 1, M = \text{Ir, Rh}; n = 0, M = \text{Pt}; L, L' = \text{PR}_3, \text{P}(\text{OR})_3, \text{CO}; \text{mnt} = \text{maleonitriledithiolate}$),⁴ orthometalated Pt(II) arylpyridine complexes,⁵ Ir(bis(diphenylphosphino)ethane)₂⁺ and related analogues,⁶ Ir(diene)(diimine)⁺ systems,⁷ Pt(biphenyl)(CH_3CN)₂,⁸ and Pt(diimine)(dithiolate) complexes,^{9,10} which are

the subjects of the present paper. Particularly notable are the recent reports of square planar Pt(II) complexes which emit in fluid solution.^{5a,c,8-10}

An interesting class of square planar complexes is those containing two different unsaturated chelating ligands in which one is more easily reduced and the other more easily oxidized. An example of this class was described by Miller and Dance, who synthesized and studied square planar nickel complexes containing an α,α' -diimine and an unsaturated dithiolate chelating ligand.¹¹ They observed that these complexes exhibited an intense solvatochromic band in the visible region of their electronic spectra and assigned it to an interligand $\pi-\pi^*$ charge transfer (LLCT) from the dithiolate to the diimine ligand. This work was later extended to analogous Pd and Pt systems by Vogler, who observed the solvatochromic band to be independent of the nature of the metal, supporting the LLCT assignment.^{12,13} In one case, that of Pt(bpy)(tdt) (tdt = 3,4-toluenedithiolate), emission was observed in a rigid medium at 77 K.¹² A similar type of electronic transition was proposed by Koester for the absorption band in the electronic spectrum of d^{10} Zn(diimine)(tdt) complexes of pseudotetrahedral geometry.¹⁴ Low-temperature luminescence studies were performed on these and related Zn(thiolate)₂ complexes both in rigid glasses and in the solid state by Crosby and coworkers.¹⁵

Previously we reported a series of Pt(diimine)(dithiolate) complexes where dithiolate = 1-(ethoxycarbonyl)-1-cyanoethylene-2,2-dithiolate (ecda), 1,1-dicyanoethylene-2,2-dithiolate (*i*-mnt), and maleonitriledithiolate (mnt) and diimine = 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), and the substituted derivatives 4,4'-Me₂bpy (dmbpy), 4,4'-Ph₂bpy (dppbpy), and 4,7-Ph₂phen (dpphen).^{9,10} These complexes were observed to be highly

- (1) University of Rochester.
- (2) (a) Cornell University. (b) Université de Sherbrooke.
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solvatochromic in their absorption spectra and to exhibit the remarkable property of being luminescent in fluid solution. While the solvatochromic absorption was found to be a common feature of all of these complexes, the emission behavior of these systems was seen to differ depending on whether (S-S) was mnt or a 1,1-dithiolate. On the basis of these results, we tentatively assigned the solvent-dependent absorption to be MLCT or LLCT in nature and the emission to arise from a MLCT $d-\pi^*$ state involving the dithiolate ligand.

Recently, the emission spectra of a number of these complexes have been investigated as a function of temperature, and the ecda systems have been found to exhibit evidence of multiple emitting states including an intraligand $\pi-\pi^*$ state and a charge-transfer state having spin-orbit split components.¹⁶ We describe herein a study of these complexes involving systematic ligand variation that provides a basis for analysis and assignment of their absorption and emission spectra. Our experimental results, which were obtained from diimine and saturated diamine complexes as well as systems containing O and Se analogues of the thiolate donors, are supported by extended Hückel molecular orbital calculations and electrochemical measurements.

Experimental Section

Materials, Methods, and Preparations. The compounds K_2PtCl_4 (Johnson Matthey), (\pm)-*trans*-diaminocyclohexane (tdach), phenyl mercaptan (PhSH), 2-mercaptoethanol (H_2meo) (Aldrich), ethanedithiol (H_2edt), sodium ethanethiolate (NaEtS) (Fluka), and benzeneselenol (PhSeH) (Alfa) were used as received without further purification. Potassium 1-(ethoxycarbonyl)-1-cyanoethylene-2,2-dithiolate, $K_2(ecda)$, sodium 1,2-dicyanoethylene-1,2-dithiolate, $Na_2(mnt)$, and the complexes $Pt(dmbpy)Cl_2$ and $Pt(dpphen)Cl_2$ were prepared according to literature procedures.¹⁷⁻²¹ The complexes $Pt(dmbpy)(mnt)$ (**1a**), $Pt(dpphen)(mnt)$ (**1b**), and their ecda analogues (**2a,b**) were prepared by previously described methods.¹⁰ The phosphine complexes, $Pt(chpe)(mnt)$, $Pt(P(OEt)_2)_2(mnt)$, and $Pt(chpe)(ecda)$, were prepared according to literature procedures.²² Syntheses were performed under N_2 using standard Schlenk and inert-atmosphere techniques. All solvents used were of spectral grade quality. For luminescence measurements the solvents were dried, distilled, and rigorously degassed before use.

$Pt(tdach)Cl_2$. A sample of 1.25 g (3 mmol) of K_2PtCl_4 was dissolved in 30 mL of distilled H_2O , and the mixture was heated to $\sim 60^\circ C$. A solution of 0.5 mL (4.2 mmol) of (\pm)-*trans*-diaminocyclohexane (tdach) in 20 mL of water was added. A yellow-green precipitate readily formed. The reaction was continued for 30 min to ensure complete precipitation. The precipitate was collected by filtration and washed with water and ethanol. IR (KBr, cm^{-1}): 3210, 3194, 2984, 2863, 1564, 1159, 758. 1H NMR (DMSO- d_6): δ 5.55 (d, 2 H), 5.01 (t, 2 H), 2.11 (s, 2 H), 1.83 (s, 2 H), 1.42 (d, 2 H), 1.20 (q, 2 H), 0.93 (t, 2 H).

$Pt(tdach)(mnt)$ (1c**).** A 0.090-g sample of $Pt(tdach)Cl_2$ was dissolved in 30 mL of degassed DMSO/acetone (1:2 v/v). To this was added 0.05 g of $Na_2(mnt)$ in 40 mL of degassed MeOH. The solution turned bright yellow, and a fine yellow precipitate formed after ~ 5 min. The precipitate was washed with water, ethanol, and ether. The IR spectrum (KBr, cm^{-1}) shows peaks due to coordinated tdach (by comparison with $Pt(tdach)Cl_2$) and to mnt: 2203 ($C\equiv N$), 1446 ($C=C$), 1154 ($C-S$). 1H NMR (DMSO- d_6): δ 5.96 (d, 2 H), 5.27 (t, 2 H), 2.21 (s, 2 H), 1.89 (d, 2 H), 1.50 (d, 2 H), 1.29 (q, 2 H), 1.03 (t, 2 H). Anal. Calcd for $PtC_{10}H_{14}N_4S_2$: C, 26.72; H, 3.14; N, 12.76. Found: C, 26.41; H, 3.26; N, 11.76.

$Pt(tdach)(ecda)$ (2c**).** A 0.20-g sample of $Pt(tdach)Cl_2$ (0.53 mmol) was dissolved in 15 mL of degassed DMSO. In another flask, 0.18 g (0.7 mmol) of $K_2(ecda)$ was dissolved in MeOH, and the mixture was degassed by purging with N_2 . The methanol solution was then added slowly via cannula to the DMSO solution containing $Pt(tdach)Cl_2$. A fine yellow precipitate formed readily. When the solution was heated at $80^\circ C$ for 30 min, the precipitate dissolved, yielding a yellow-orange solution. The reaction was continued for 2 h. Addition of 20 mL of water yielded a yellow precipitate, which was washed with water, ethanol, and ether and recrystallized from methylene chloride as a yellow powder. The IR

spectrum (KBr, cm^{-1}) showed peaks due to coordinated tdach (by comparison with $Pt(tdach)Cl_2$) and to ecda: 2199 ($C\equiv N$), 1676 ($C=O$), 1143 ($C-S$). 1H NMR (acetone- d_6): δ 5.11 (d, 2 H), 4.20 (t, 2 H), 4.08 (q, 5.5 Hz, 2 H), 2.70 (s, 2 H), 2.13 (d, 2 H), 1.61 (d, 2 H), 1.47 (q, 2 H), 1.25 (t, 2 H), 1.20 (t, 5.5 Hz, 3 H). Anal. Calcd for $PtC_{12}H_{19}N_3S_2O_2$: C, 29.02; H, 3.85; N, 8.46. Found: C, 28.60; H, 3.86; N, 8.13.

$Pt(dmbpy)(edt)$ (3a**).** A 0.11-g sample of $Pt(dmbpy)Cl_2$ (0.244 mmol) was dispersed in 20 mL of degassed acetone. In another flask, 0.05 mL (0.6 mmol) of ethanedithiol (H_2edt) was dissolved in a solution of 0.08 g of NaOH in 30 mL of degassed ethanol; the mixture was stirred until a clear solution was obtained and then added to the above solution via cannula under N_2 . The yellow dispersion immediately turned brick red. After 1 h of stirring, a clear red solution was obtained. The solvent was evaporated under reduced pressure to ~ 20 mL. Addition of 50 mL of ether yielded a bright red precipitate, which was washed twice with water, ethanol, and ether and recrystallized from hot acetone. 1H NMR (DMSO- d_6): δ 8.81 (t, $J_{H-H} = 5.46$ Hz, $J_{Pt-H} = 51.60$ Hz, 2 H), 8.44 (s, 2 H), 7.53 (d, 5.46 Hz, 2 H), 3.39 (s, 6 H), 2.41 (br s, 4 H).

$Pt(dpphen)(edt)$ (3b**).** This complex was prepared by following a procedure analogous to that for $Pt(dmbpy)(edt)$ (**3a**) using 0.15 g of $Pt(dpphen)Cl_2$ (0.25 mmol) and 0.05 mL (0.6 mmol) of ethanedithiol (H_2edt). The clear dark red solution obtained was evaporated under reduced pressure to ~ 15 mL, and a red solid was precipitated by addition of 50 mL of ether. The precipitate was washed twice with water, ethanol, and ether and recrystallized from acetone. 1H NMR (DMSO- d_6): δ 9.38 (t, 5.95 Hz, 2 H), 8.07 (s, 2 H), 8.04 (d, 5.95 Hz, 2 H), 7.55-7.78 (m, 10 H), 2.28 (broad singlet with Pt satellites, $J_{Pt-H} = 54.12$ Hz, 4 H).

$Pt(dmbpy)(EtS)_2$ (4a**).** A 0.20-g sample of $Pt(dmbpy)Cl_2$ (0.44 mmol) and 0.13 g of Na(EtS) (1.3 mmol) were placed in a round-bottom flask, and 30 mL of degassed acetone was added. The dispersion was stirred until a red solution was obtained. The solution was then filtered into another flask via cannula. The remaining solid was washed in situ with 20 mL of acetone, and the resulting solution was again filtered into a flask via cannula. The two solutes were combined, the solvent was reduced under vacuum to ~ 5 mL, and a red solid precipitated upon the addition of 20 mL of pentane to the solution. Washing with water resulted in partial decomposition of the sample. Thus, after recrystallizing from acetone, the sample was repeatedly washed with dry ethanol and pentane and vacuum-dried. 1H NMR (acetone- d_6): δ 9.85 (t, $J_{H-H} = 5.87$ Hz, $J_{Pt-H} = 32.27$ Hz, 2 H), 8.34 (s, 2 H), 7.60 (d, 5.87 Hz, 2 H), 2.65 (q, $J_{H-H} = 7.04$ Hz, $J_{Pt-H} = 46.95$ Hz, 4 H), 1.31 (t, 7.04 Hz, 6 H).

$Pt(dpphen)(EtS)_2$ (4b**).** A 0.20-g sample of $Pt(dpphen)Cl_2$ (0.44 mmol) was placed in a round-bottom flask, and 30 mL of degassed acetone was added. A solution of 0.15 g of Na(EtS) (1.3 mmol) in 20 mL of acetone was added, and the solid was extracted with 30 mL of acetone. The solution obtained was again filtered, the volume reduced to ~ 5 mL under reduced pressure, and a purple solid precipitated upon the addition of 10 mL of pentane. The precipitate was then washed with dry ethanol and pentane and dried under vacuum. 1H NMR ($CDCl_3$): δ 10.33 (d, $J_{Pt-H} = 31.90$ Hz, 2 H), 7.80 (s, 2 H), 7.73 (d, $J_{H-H} = 5.55$ Hz, 2 H), 7.5-7.6 (m, 10 H), 2.89 (q, $J_{H-H} = 6.94$ Hz, $J_{Pt-H} = 45.47$ Hz, 4 H), 1.48 (t, 6.94 Hz, 6 H).

$Pt(dmbpy)(PhS)_2$ (5**).** A 0.235-g sample of $Pt(dmbpy)Cl_2$ (0.52 mmol) was stirred in 40 mL of degassed acetone until a uniform suspension was obtained. In a separate flask, 0.23 g (2 mmol) of phenyl mercaptan (PhSH) dissolved in 10 mL of methanol was added to a flask containing 0.6 g of KOH. The mixture was stirred under N_2 until the KOH dissolved, and the solution was then added slowly to the suspension of the complex via cannula. A red color appeared after ~ 5 s. The resulting red solution was stirred for 2 h and the solvent evaporated to dryness under reduced pressure. The red product was extracted with two 15-mL portions of methylene chloride, and the extract was filtered. The solvent was then evaporated to 10 mL. Addition of 30 mL of pentane yielded a red solid, which was washed with pentane and vacuum-dried. 1H NMR (DMSO- d_6): δ 9.44 (d, $J_{H-H} = 5.87$ Hz, 2 H), 8.54 (s, 2 H), 7.62 (d, 5.87 Hz, 2 H), 7.48 (d, 6.46 Hz, 4 H), 6.92 (t, $J_{H-H} = 7.04$ Hz, 6 H), 6.81 (t, $J_{H-H} = 6.46$ Hz, 4 H), 2.46 (s, 6 H). Anal. Calcd for $PtC_{24}H_{22}N_2S_2$: C, 48.23; H, 3.71. Found: C, 47.59; H, 3.70.

$Pt(dmbpy)(PhSe)_2$ (6**).** This complex was prepared by a procedure analogous to that for $Pt(dmbpy)(PhS)_2$ (**5**). However, the sample was observed to decompose after extraction with CH_2Cl_2 . Attempts to extract with and recrystallize from $CHCl_3$ also resulted in decomposition. The best result was obtained by several rapid precipitations with THF/ether. Due to the inherent instability of the sample in solution, it was not possible to obtain good elemental analyses for the complex. Nevertheless the IR, NMR, and electronic spectra are consistent with the phenyl mercaptan analogue. 1H NMR (DMSO- d_6): δ 9.44 (d, $J_{H-H} = 5.87$ Hz, 2 H), 8.49 (s, 2 H), 7.62 (d, 5.87 Hz, 2 H), 7.50 (d, 6.46 Hz, 4 H), 7.16

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Table I. Parameters for Extended Hückel Calculations

atom	s		p		d ^a			ref
	H_{ii}	ζ	H_{ii}	ζ	H_{ii}	ζ_1	ζ_2	
Pt	-3.08	2.554	-5.57	2.554	-12.59	6.013 (0.6336)	2.696 (0.5518)	24
C	-21.4	1.625	-11.40	1.625				24
N	-26.0	2.95	-13.40	1.95				24
O	-32.3	2.275	-14.80	2.275				24
S	-20.0	1.817	-13.30	1.817				23
Se	-20.49	2.44	-14.44	2.07				25

^aContracted d orbitals. Coefficients for the two Slater exponential functions are given in parentheses.

(t, $J_{H-H} = 7.04$ Hz, 4 H), 6.75 (t, $J_{H-H} = 6.75$ Hz, 6 H), 2.42 (s, 6 H).

Pt(dmbpy)(meo) (7). A 0.11-g sample of Pt(dmbpy)Cl₂ (0.244 mmol) was dispersed in 20 mL of degassed acetone. In another flask, 0.05 mL (0.6 mmol) of 2-mercaptoethanol (H₂meo) was dissolved in a solution of 0.08 g of NaOH in 30 mL of degassed ethanol, and the resulting solution was added to the above solution via cannula under N₂. The yellow dispersion immediately turned brick red. After 1 h of stirring, a clear red solution was obtained. The solvent was evaporated under reduced pressure to ~20 mL. Addition of 50 mL of ether yielded a bright red precipitate, which was washed twice with water, ethanol, and ether and recrystallized from hot acetone. ¹H NMR (DMSO-*d*₆): δ 9.11 (d, 5.87 Hz, 1 H), 8.92 (d, 5.87 Hz, 1 H), 7.74 (s, 1 H), 7.67 (s, 1 H), 7.36 (d, 5.87 Hz, 1 H), 7.01 (d, 5.87 Hz, 1 H), 3.60 (d, 2 H), 2.42 (s, 3 H), 2.37 (s, 3 H), 2.21 (d, 2 H).

Spectroscopic Characterization. Infrared spectra were obtained from KBr pellets on a Mattson Sirius 100 FTIR spectrophotometer. ¹H NMR spectra (400 MHz) were recorded on a Bruker AMX-400 spectrometer. Chemical shifts are reported relative to internal solvent peaks (DMSO-*d*₆, $\delta = 2.49$; acetone-*d*₆, $\delta = 2.04$; CDCl₃, $\delta = 7.24$). Absorption spectra were recorded on a Hewlett Packard diode array UV-visible spectrophotometer interfaced to an IBM PC computer. Solution emission measurements were performed on deoxygenated samples using a Spex Fluorolog fluorescence spectrophotometer. Low-temperature measurements were performed using a Janis liquid-helium cryostat equipped with Lake Shore Cryotronics DRC-82C temperature controller. Low-temperature lifetimes were measured by transient digitization. The instrumental setups have been described elsewhere.⁹

Low-temperature emission spectra were recorded in DMM glasses (DMF/CH₂Cl₂/MeOH, 1:1:1 v/v/v) in which the samples were excited with the 442-nm line of a He-Cd laser. The emission signal was passed through a Corning 3-72 filter and a Cary monochromator with 0.2-mm slits and was detected with a Tektronix 762 photomultiplier tube. The signal was processed through a PAR 117 differential preamplifier and an EG&G 5208 two-phase lock-in amplifier. Spectra were recorded using a Hewlett Packard HP 9122 computer.

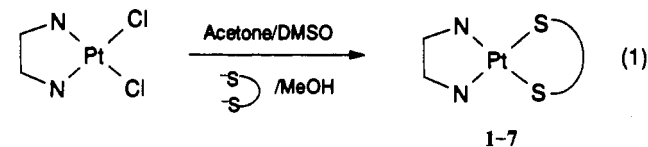
Electrochemical Measurements. Electrochemical measurements were made with a PAR Model 173 potentiostat, a Model 175 voltage programmer, and a Model 176 current follower and were recorded on an EG&G Princeton Research Model RE 0089 X-Y recorder. Cyclic voltammograms were recorded in 0.1 M (TBA)PF₆ (TBA = tetra-*n*-butylammonium) in CH₂Cl₂. Typically, cyclic voltammograms were obtained at concentrations less than 1 mM. The Pt-disk electrodes (0.5-mm diameter) were polished with alumina (0.3- μ m size) for 15 min in distilled water before use. The experiments were done under an atmosphere of N₂(g) and carried out using a Pt disk as the working electrode, Pt gauze as the auxiliary electrode, and a SSCE reference electrode. The SSCE electrode was filled with a 3% agar-agar solution (0.5-mm thickness) at the fritted junction to minimize solvent and water diffusion. The cell was a three-electrode cell, and no IR compensation was applied. The electrolyte (TBA)PF₆ (Aldrich Chemical Co.) was recrystallized three times from ethanol. CH₂Cl₂ was dried, distilled, and rigorously degassed prior to use.

Molecular Orbital Calculations. Extended Hückel (EH) calculations were performed on an AST 386/33 computer using a variation of the ICON-8 software package originally developed by Hoffmann²³ and modified by Mealli and Proserpio.²⁴ Because of limitations in the size of the molecules handled by the program, bpy, phen, and ethylenediamine (en) were used as the nitrogen donors and mnt, *i*-mnt, edt, meo, and bis(benzenethiolate) were used as the sulfur donors. In one calculation bis(benzeneselenolate) was used in place of the sulfur donors. The s and p orbitals of all the main group atoms as well as of Pt were approximated by Slater type orbitals. The contracted d orbitals are a linear combi-

nation of two Slater type wave functions. The H_{ii} 's obtained from the valence-orbital ionization potentials (VOIP) for H, C, N, and S were included in the program and are compiled from the original work by Hoffmann.²⁵ For Pt, the H_{ii} 's used are charge-iterated for square planar complexes.²⁶ The parameters for Se were obtained from the work by Hinze and Jaffe.²⁷ A complete list of parameters is shown in Table I. Bond lengths and angles were obtained from published X-ray data on similar compounds.²⁸⁻³¹ Pictorial representation of the orbitals was obtained using the CACAO graphics package included in the software.²⁴

Results

The mnt complexes **1a,b** and the ecda complexes **2a,b** were prepared as previously reported.⁹ All of the other complexes were readily prepared by slow addition of a methanolic solution of the thiolate ligand to a DMSO or acetone solution of the Pt(N-N)Cl₂ complex as shown in eq 1.



	N-N	S-S		N-N	S-S
1a	dmbpy	mnt	3b	dpphen	edt
1b	dpphen	mnt	4a	dmbpy	EtS
1c	tdach	mnt	4b	dpphen	EtS
2a	dmbpy	ecda	5	dmbpy	PhS
2b	dpphen	ecda	6	dmbpy	PhSe
2c	tdach	ecda	7	dmbpy	meo
3a	dmbpy	edt			

dmbpy = 4,4'-dimethyl-2,2'-bipyridine

dpphen = 4,7-diphenyl-1,10-phenanthroline

tdach = (\pm)-*trans*-diaminocyclohexane

mnt = maleonitriledithiolate = 1,2-dicyano-1,2-ethylenedithiolate

ecda = 1-(ethoxycarbonyl)-1-cyanoethylene-2,2-dithiolate

edt = 1,2-ethanedithiolate

EtS = ethanethiolate

PhS = benzenethiolate

PhSe = benzeneselenolate

meo = 2-mercaptoethanolate(2-)

The resulting complexes are air stable as solids. In solution, complexes containing a chelating dithiolate (mnt, ecda) are stable, while the nonchelated bis(thiolate) complexes show reduced stability, which correlates with the transition energy of the solvatochromic band (vide infra). The latter complexes are also less stable in halogenated solvents (CH₂Cl₂ and CHCl₃) than in acetone or THF. Characterization was done by electronic, infrared, and ¹H NMR spectroscopies. The ¹H NMR spectra of the Pt(diimine)(dithiolate) complexes are consistent with the structure being monomeric and square planar.

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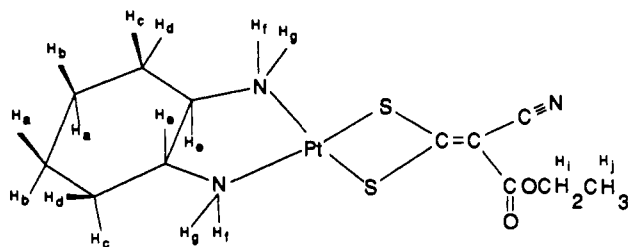
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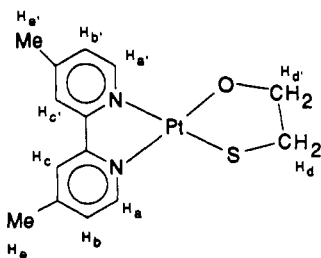
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Characterization of Compounds. For the diaminocyclohexane complexes, Pt(tdach)Cl₂ and Pt(tdach)(ecda) (**2c**), selective decoupling and 2D COSY spectroscopy led to detailed assignments of the tdach ¹H resonances consistent with a trans diequatorial orientation of the coordinated NH₂ groups and a cyclohexane boat conformation. For this conformation, Pt(tdach)Cl₂ possesses C₂ symmetry while Pt(tdach)(ecda) (**2c**) has nearly this symmetry, differing only in the CN and COOR substituent of the ecda ligand. For Pt(tdach)Cl₂, the two tdach resonances with the largest downfield chemical shifts (δ 5.55 and 5.01 ppm) are mutually coupled and correspond to protons on the amines labeled H_f and H_g shown in structure A for the related complex Pt(tdach)(ecda)



Structure A



Structure B

(**2c**); addition of D₂O results in their immediate disappearance. From decoupling and 2D COSY experiments, the resonance at δ 2.11 ppm is established as the protons H_e geminal to the amino donors. Selective irradiation of this resonance collapses the 5.01 ppm triplet to a doublet but has little effect on the 5.51 ppm resonance, leading to assignment of the triplet at 5.01 ppm as H_g, which is anti to H_e, and the resonance at 5.55 ppm as H_f. Irradiation of the δ 2.11 ppm resonance also collapses the quartet at δ 1.20 ppm to a triplet, thereby yielding assignment of the latter to H_c, the protons trans to H_e. Additional experiments show the protons at δ 1.42 ppm to be coupled to those at δ 0.93 ppm, leading to their assignment as H_d and H_a, respectively. On the basis of these results for Pt(tdach)Cl₂ and a COSY 2D experiment for Pt(tdach)(ecda) (**2c**), the tdach resonances for Pt(tdach)(ecda) (**2c**) are assigned as follows: H_g, 1.25 ppm; H_b, 1.47 ppm; H_c, 1.61 ppm; H_d, 2.13 ppm; H_e, 2.70 ppm; H_f, 5.11 ppm; H_g, 4.20 ppm; H_i, 4.08 ppm; H_j, 1.20 ppm.

The ¹H NMR spectrum of Pt(dmbpy)(meo) (**7**) shows two resonances at high field corresponding to the two sets of protons of the ethylene bridge in the mercaptoethanolate(2-) ligand. The signal at δ 3.60 ppm is assigned to the two protons closer to the oxygen donor (labeled H_k in structure B). In addition, each of the dmbpy resonances observed in the analogous Pt(dmbpy)(edt) (**3a**) complex is now split into two due to the asymmetry of the meo ligand. For each pair of resonances, the one at lower relative field is assigned to the bpy ring closer to the oxygen donor of meo as follows: H_a, 8.95 ppm; H_a, 8.92 ppm; H_b, 7.74 ppm; H_b, 7.67 ppm; H_c, 7.36 ppm; H_c, 7.01 ppm; H_d, 3.60 ppm; H_d, 2.21 ppm; H_e, 2.42 ppm; H_e, 2.37 ppm.

Solvent Dependence of Absorption Spectroscopy. The low-energy electronic absorption spectra show marked differences between the α,α' -diimine complexes and the saturated diamine analogues containing tdach. All of the diimine complexes as solids are highly colored and in solution show several intense absorptions at higher energies ($\lambda > 350$ nm, 33.3×10^3 cm⁻¹) as well as an intense absorption band in the 450–600 nm ($(22.2\text{--}16.7) \times 10^3$ cm⁻¹) region of the spectrum ($\epsilon > 10000$). The energy of the

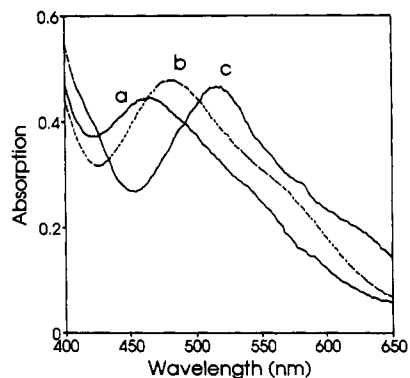


Figure 1. Absorption spectra of Pt(dmbpy)(PhS)₂ (**5**) in (a) MeCN, (b) CH₂Cl₂, and (c) C₆H₆.

long-wavelength absorption band in different solutions increases directly with solvent polarity, as shown for Pt(dmbpy)(PhS)₂ (**5**) in Figure 1. An excellent correlation of absorption band energy with solvent polarity was found using Lee's E^*_{MLCT} scale,³² which is based on a reference charge-transfer transition.¹⁰

In contrast, the complexes containing tdach as the nitrogen donor are pale yellow solids possessing several absorption bands in the 250–350 nm ($(40.0\text{--}28.6) \times 10^3$ cm⁻¹) region of their solution spectra with only a weak shoulder in the visible portion of the spectrum. None of the bands show dependence on solvent polarity. However, both the energy and intensity of the low-energy transition are dependent on the dithiolate ligand.

Even though the band shape and solvatochromic behavior of the low-energy absorption band are similar for a given Pt(diimine), there are two trends worth noting. The first is that the energy of the lowest electronic transition decreases in the order ecda > edt \approx meo > (EtS)₂ > mnt > (PhS)₂ > (PhSe)₂. Second, the absorption energy is higher for dmbpy complexes than for the dpphen analogues for a given dithiolate.

In all of the complexes studied, the higher energy transitions ($\lambda_{abs} < 350$ nm, 28.6×10^3 cm⁻¹) are similar to those observed in either the free ligands or the parent Pt(diimine)Cl₂ complexes and are not solvatochromic. These high-energy bands are assigned to intraligand diimine, intraligand dithiolate, or Pt(diimine) MLCT transitions and are not considered further in this report.

Temperature Dependence of Emission Spectroscopy. Emission spectra for all complexes depend on the nature of both the N-donor and the S-donor ligands. All of the Pt(diimine)(S-S) complexes except those where (S-S) is mnt exhibit broad, asymmetric emission in the 600–650 nm ($(16.7\text{--}15.4) \times 10^3$ cm⁻¹) region in fluid solution. In contrast with the energy of the solvent-dependent absorption bands, the emission energy is virtually independent of solvent polarity, although it does shift to lower energy upon glassing of the DMM (DMF/CH₂Cl₂/MeOH, 1:1:1 v/v/v) solvent mixture. Also, the emission intensity decreases with decreasing temperature below ~ 80 K, as shown in Figure 2 for Pt(dmbpy)(edt) (**3a**) and Pt(dmbpy)(EtS)₂ (**4a**). Those complexes that contain mnt as the sulfur-donor ligand are an exception to this pattern in that their fluid solution emission is highly structured, the emission does not shift in energy upon glassing of the DMM solvent, and the emission intensity *increases* with decreasing temperature, in contrast with that shown by all of the other Pt(diimine)(dithiolate) and Pt(diimine)(thiolate)₂ compounds.

In comparison, the Pt(diamine)(S-S) complexes are different from the diimine analogues in that they emit only at low temperature in rigid media. As with the diimine complexes, the energy and shape of the emission band vary with the nature of the dithiolate as shown in Figure 3 for Pt(tdach)(mnt) (**1c**) and Pt(tdach)(ecda) (**2c**). The emission of Pt(tdach)(ecda) (**2c**) is broad and asymmetric, resembling that observed for Pt(diimine)(ecda) complexes, although the emission maximum ($\lambda_{max} = 520$ nm, 19.2×10^3 cm⁻¹) is significantly blue-shifted (~ 3000 cm⁻¹) with respect to the diimine analogues ($\lambda_{max} \approx 620$ nm, 16.1×10^3 cm⁻¹). In

Table II. Absorption and Emission Maxima for Pt(N-N)(S-S) Complexes

complex	no.	λ_{abs} nm (10^3 cm^{-1})			λ_{em} nm (10^3 cm^{-1}) 77 K, DMM glass
		C ₆ H ₆	CH ₂ Cl ₂	CH ₃ CN	
Pt(dmbpy)(mnt)	1a	518 (19.3)	492 (20.3)	458 (21.8)	610 (16.4)
Pt(dpphen)(mnt)	1b	552 (18.1)	520 (19.2)	492 (20.3)	630 (15.9)
Pt(tdach)(mnt)	1c	a	a	440 (22.7)	610 (16.4)
Pt(dmbpy)(ecda)	2a	460 (21.7)	434 (23.0)	410 (24.4)	620 (16.1)
Pt(dpphen)(ecda)	2b	474 (21.1)	454 (22.0)	434 (23.0)	650 (15.4)
Pt(tdach)(ecda)	2c	a	a	424 (23.6)	540 (18.5)
Pt(dmbpy)(edt)	3a	510 (19.6)	482 (20.7)	466 (21.4)	624 (16.0)
Pt(dpphen)(edt)	3b	516 (19.3)	488 (20.5)	468 (21.4)	667 (15.0)
Pt(dmbpy)(EtS) ₂	4a	512 (19.5)	482 (20.7)	466 (21.4)	632 (15.8)
Pt(dpphen)(EtS) ₂	4b	520 (19.2)	488 (20.5)	472 (21.2)	678 (14.7)
Pt(dmbpy)(PhS) ₂	5	524 (19.1)	498 (20.1)	476 (21.0)	615 (16.3)
Pt(dmbpy)(PhSe) ₂	6	536 (18.6)	514 (19.4)	498 (20.1)	646 (15.4)
Pt(dmbpy)(meo)	7	500 (20.0)	458 (21.8)	448 (22.3)	610 (16.4)

^a Not soluble in C₆H₆ or CH₂Cl₂.

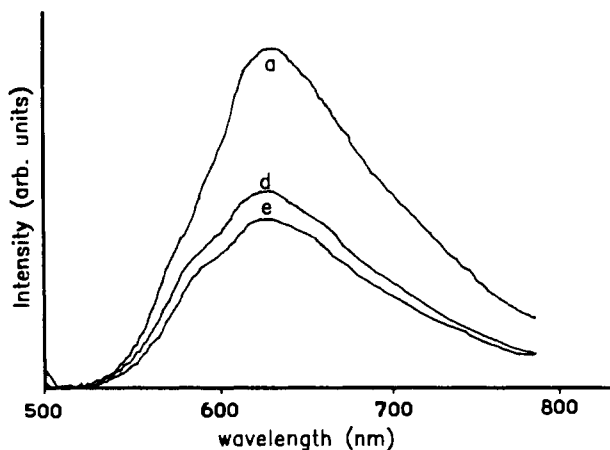
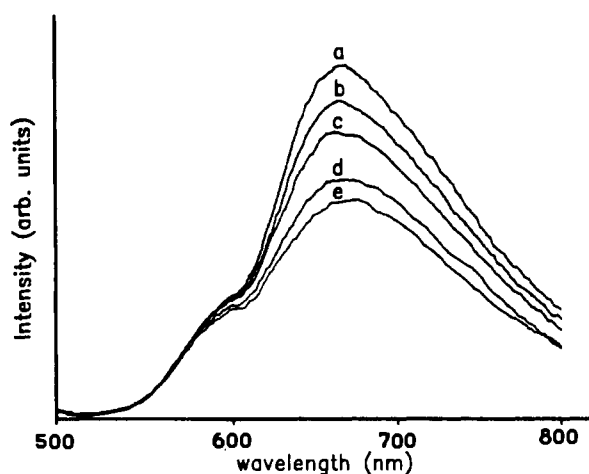


Figure 2. Emission spectra of Pt(dmbpy)(edt) (3a) (top) and Pt(dmbpy)(EtS)₂ (4a) (bottom) in DMM glass at (a) 25 K, (b) 16 K, (c) 12 K, (d) 10 K, and (e) 6 K.

marked contrast, the 1,2-dithiolate complex Pt(tdach)(mnt) (1c) exhibits a structured emission ($\lambda_{\text{max}} = 610 \text{ nm}$, $16.4 \times 10^3 \text{ cm}^{-1}$) reminiscent of those observed for Pt(diimine)(mnt) complexes and for other M(LL')(mnt) analogues,⁴ although the vibrational structure is somewhat less resolved than that of the dmbpy and dpphen complexes. The emissions of both Pt(tdach)(mnt) (1c) and Pt(tdach)(ecda) (2c) increase in relative intensity with decreasing temperature. This temperature dependence was expected for Pt(tdach)(mnt) (1c) but not for Pt(tdach)(ecda) (2c) because the diimine ecda complexes showed a decrease in emission intensity with decreasing temperature. A complete list of the electronic absorption and emission energies is given in Table II.

For complexes containing the same dithiolate ligand, the emission energy is higher for the dmbpy system than for the corresponding dpphen derivative, which is consistent with the trend

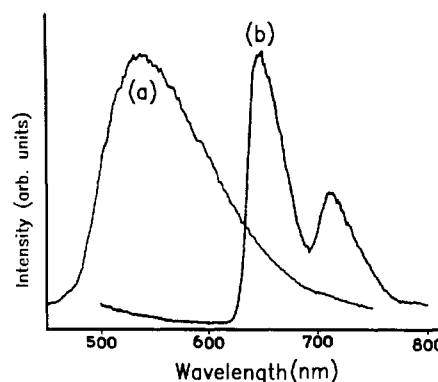


Figure 3. Emission spectra of (a) Pt(tdach)(ecda) (2c) and (b) Pt(tdach)(mnt) (1c) at 77 K.

Table III. Electrochemical Measurements^a

complex	no.	$E^{0/-}$, V ^b	Δ , mV ^c	rev ^d	$E^{+/0}$, V ^b	Δ , mV ^c	rev ^d
Pt(dmbpy)(mnt)	1a	-1.17	60	qr	1.22	70	qr
Pt(dpphen)(mnt) ^e	1b	-1.09	110 ^e	qr	1.18	150	qr
Pt(chpe)(mnt)					1.33	100	qr
Pt(P(OEt) ₃) ₂ (mnt)					1.45	130	qr
Pt(dmbpy)(ecda)	2a	-1.21	90	qr	0.81	230	irr
Pt(dpphen)(ecda) ^e	2b	-1.24	80	qr	1.30 ^f		irr
Pt(chpe)(ecda)					1.54 ^f		irr

^a In CH₂Cl₂ solutions containing 0.1 M (TBA)PF₆ at 298 K. All potentials are reported for scan rates of 100 mV/s (unless stated otherwise); experimental error is estimated to be $\pm 0.02 \text{ V}$. ^b Potentials are reported versus SSCE. ^c Δ is the difference between the anodic and cathodic waves of the electrochemical process in absolute value. ^d The reversibility conditions are defined by the ratio of the anodic over the cathodic wave area being ~ 1 and only indicate that the processes are chemically reversible, not necessarily electrochemically reversible (qr = quasi-reversible, irr = irreversible). ^e Scan rate = 1000 mV/s. ^f The oxidation process is completely irreversible. The potential is the one for the anodic peak only.

in the absorption energy for these complexes. For a given diimine ligand, the emission energy decreases in the order $\text{ecda} \approx \text{mnt} > (\text{PhS})_2 > \text{edt} > (\text{EtS})_2 > (\text{PhSe})_2$. For the ecda complexes, new emission bands appear at higher energy as the temperature is lowered below 140 K. These new bands have been discussed and analyzed previously.¹⁶

Electrochemical Measurements. As a further means of examining the highest occupied and lowest unoccupied molecular orbitals of the complexes, electrochemical measurements and, in particular, cyclic voltammograms were obtained. Table III summarizes the electrochemical results. The diimine dithiolate complexes 1a,b and 2a,b exhibit both an oxidation and a reduction in the range of -1.5 to $+2.0 \text{ V}$ vs SSCE. All of the reductions are quasi-reversible whereas the oxidation process differs depending on the nature of the dithiolate ligand, being quasi-reversible for the mnt complexes and irreversible for the ecda systems. For comparison, cyclic voltammetry was also performed on the phosphine and phosphite complexes Pt(chpe)(mnt), Pt(chpe)(ecda), and Pt(P(OEt)₃)₂(mnt). These systems showed only an oxidation process over the same potential range which was qua-

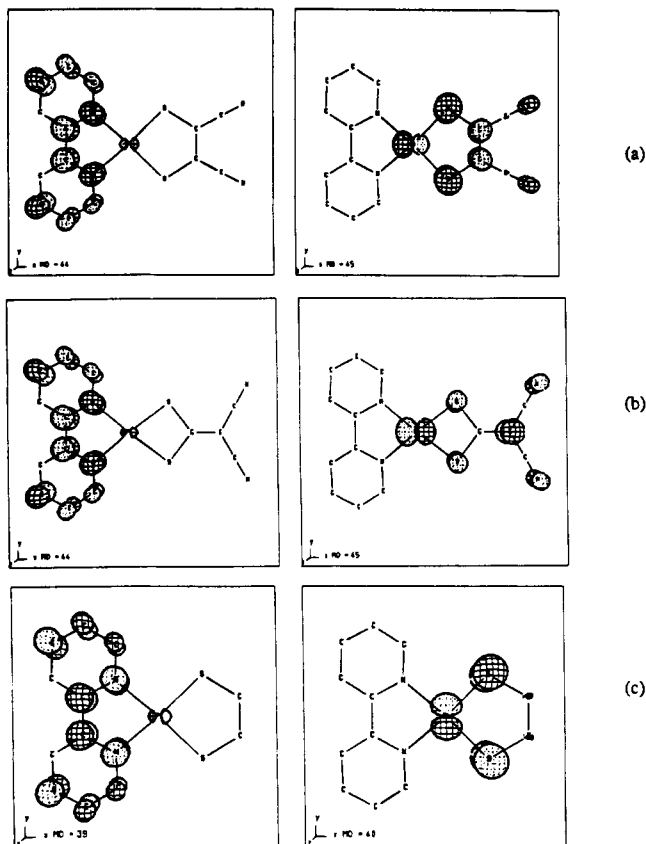


Figure 4. Molecular orbital representation for the HOMO (right) and LUMO (left) of (a) Pt(bpy)(mnt), (b) Pt(bpy)(i-mnt), and (c) Pt(bpy)(edt).

si-reversible for the mnt complexes and irreversible for the ecda system. On the basis of the separation between anodic and cathodic peak potentials for all of the quasi-reversible waves in dichloromethane, the electrochemical processes are all assumed to be one-electron transfers.

Molecular Orbital Calculations. Extended Hückel molecular orbital calculations were carried out for model diimine dithiolate and bis(thiolate) complexes. For computational purposes, the 1,1-dithiolate *i*-mnt was used in place of ecda. This substitution does not affect the validity of the calculations, since spectroscopic evidence suggests there is very little difference between the electronic structures of Pt(diimine)(*i*-mnt) and Pt(diimine)(ecda) complexes.¹⁰ Likewise, Pt(en)(S-S) (en = 1,2-ethylenediamine) complexes were used for calculations involving a saturated diamine ligand rather than the larger tdach. The calculated energies for the different energy levels as well as the relative atomic contributions to the molecular orbitals for selected complexes are shown in Table IV.

The calculations show that the lowest unoccupied MO is almost exclusively π^* (diimine) for all the diimine dithiolate complexes examined, whereas the highest occupied MO is a combination of d(Pt) and p(S) atomic orbitals with some delocalization for the unsaturated S chelating ligands, the amount being larger for 1,2- than for 1,1-dithiolates. A pictorial representation of the HOMO and LUMO for Pt(bpy)(mnt), Pt(bpy)(*i*-mnt), and Pt(bpy)(edt) is shown in Figure 4. While the HOMO's and LUMO's for the different diimine dithiolates are very similar, the ordering and nature of the levels above the LUMO and below the HOMO change in going from the 1,2-dithiolate mnt to the 1,1-dithiolate *i*-mnt.

For the 1,2-dithiolate complex Pt(bpy)(mnt), the energy level immediately above the LUMO belongs to a π^* (mnt) orbital followed by a second π^* (diimine) orbital separated by ~ 0.1 eV (1100 cm^{-1}) and 0.9 eV (7300 cm^{-1}), respectively. The lowest unoccupied molecular orbital which is metal-based in character is located 1.4 eV above the LUMO. The results for Pt(phen)(mnt) are virtually the same as for Pt(bpy)(mnt). In contrast, for the

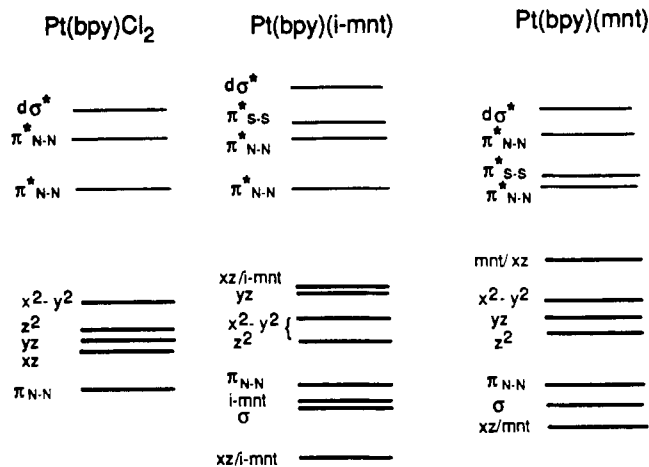


Figure 5. Energy level orderings (not to scale) of the relevant orbitals for Pt(bpy)Cl₂, Pt(bpy)(*i*-mnt), and Pt(bpy)(mnt).

i-mnt (and presumably ecda) complexes, while the two π^* (diimine) orbitals remain at nearly the same energy as in the mnt system, the first unoccupied π^* (dithiolate) orbital lies *above* the second π^* (diimine) level and is 0.86 eV higher in energy than the corresponding π^* (dithiolate) orbital in Pt(bpy)(mnt). The σ^* metal-d orbital is also raised in energy by 0.2 eV compared to the mnt analogue, indicating that *i*-mnt is a stronger field ligand than mnt, as has been assigned in other reports based on spectroscopic results.^{33,34} Figure 5 shows the relative orderings of the molecular orbitals for Pt(bpy)(mnt) and Pt(bpy)(*i*-mnt) along with that of Pt(bpy)Cl₂ for comparison.

For the Pt(diimine) complexes with saturated dithiolates, even though no vacant π^* (dithiolate) levels exist, the relative positions and energies of the antibonding diimine orbitals remain the same as for the unsaturated dithiolates. For the two complexes containing a saturated diamine ligand, i.e., Pt(en)(mnt) and Pt(en)(*i*-mnt), the nature of the HOMO shows very little change but the LUMO becomes exclusively π^* (dithiolate) in character.

While quantitative agreement between experimental transition energies and the calculated values from the EH MO calculations is only fair, the trend predicted by the calculations for the relative energies of the lowest absorption band and the assignment of excited states based on the energy level orderings are completely consistent with experimental results.

Discussion

The Pt(diimine)(dithiolate) complexes studied here have C_{2v} or lower symmetry and present a complicated problem in the assignment of the solvatochromic transition and the emissive excited states. The two different ligand systems necessarily have different oxidation and reduction potentials and possess delocalized π systems which can serve as donor and acceptor via an interligand charge-transfer transition (LLCT). In addition, the platinum d orbitals open up the possibility of ligand field (LF) states and metal-to-ligand (MLCT) and ligand-to-metal (LMCT) charge-transfer transitions. The specific states, of course, depend on the relative energies of the molecular orbitals of the system which in turn are influenced by relatively small changes in ligand substituents and structure.

The intense solvatochromic absorption band is present in all of the diimine complexes containing unsaturated or saturated dithiolates, as well as in bis(thiolate) complexes, but it is absent in complexes containing a *saturated* diamine and an unsaturated dithiolate. This indicates that, for the solvent-dependent transition, it is necessary to have a π system on the N donor ligand, but not necessarily on the dithiolate ligand. The conclusion is that the LUMO in these complexes is mainly of π^* (diimine) character. This conclusion is supported by the fact that the diimine dithiolate complexes all show a single quasi-reversible reduction over the

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Table IV. Relative Percent Atomic Contribution^a to the MO's

Pt(bpy)(mnt)															
energy of MO, eV	Pt	2S	C=C	2C(CN)	2N(CN)	2N(N-N)	10Cπ-(N-N)	energy of MO, eV	Pt	2S	C=C	2C(CN)	2N(CN)	2N(N-N)	10Cπ-(N-N)
-8.16	54	24				22		-11.48 ^b	27	38	22	4		8	
-8.30						2	98	-11.96	69	16	6	6		2	
-8.66						18	82	-12.12	72	12	4	2			4
-9.44	1	10	30	32	26			-12.23	77	2	2			10	6
-9.57	2					26	72	-12.46	4					4	92
Pt(bpy)(i-mnt)															
energy of MO, eV	Pt	2S	C=C	2C(CN)	2N(CN)	2N(N-N)	10Cπ-(N-N)	energy of MO, eV	Pt	2S	C=C	2C(CN)	2N(CN)	2N(N-N)	10Cπ-(N-N)
-7.95	50	24	2			20		-11.95 ^b	47	14	18	2	12		4
-8.29			1			2	94	-11.96	61	34				2	2
-8.58	5	14	50	16	10		4	-12.09	79	2	1			6	6
-8.66						18	82	-12.28	87		2			2	2
-9.59	3		1			26	70	-12.46	2					2	96
Pt(bpy)(edt)															
energy of MO, eV	Pt	2S	C-C	4H(C-C)	2N(N-N)	10Cπ-(N-N)	energy of MO, eV	Pt	2S	C-C	4H(C-C)	2N(N-N)	10Cπ-(N-N)		
-8.18	54	22			22		-11.60 ^b	41	44	4	8				
-8.29					2	98	-11.91	61	28		4		6		
-8.76					18	82	-11.93	67	18	8		2	2		
-9.57	2				28	70	-12.23	75	2	2		6	10		
Pt(bpy)(PhS) ₂															
energy of MO, eV	Pt	2S	12C(Ph)	2N(N-N)	10Cπ-(N-N)	energy of MO, eV	Pt	2S	12C(Ph)	2N(N-N)	10Cπ-(N-N)				
-8.32				2	98	-11.66	29	20	38		6				
-8.38	39	10	32	16	80	-11.82	53	32	12						
-8.67				18	70	-11.98	4	14	74		6				
-9.56	3			26	70	-12.18	65		10	4	12				
-11.60 ^b	41	46	12			-12.21	62		16	8	4				
Pt(bpy)(PhSe) ₂															
energy of MO, eV	Pt	2Se	12C(Ph)	4H(C-C)	N(N-N)	10Cπ-(N-N)	energy of MO, eV	Pt	2Se	12C(Ph)	4H(C-C)	N(N-N)	10Cπ-(N-N)		
-7.98	28	8	24	32	6	98	-10.52	2	30	56		4	4		
-8.32					2	98	-11.24	41	14	30		8			
-8.66					18	80	-11.79	67	16	14					
-9.52	3				28	68	-12.08	49	2	28		10	4		
-10.05 ^b	23	60				12									
Pt(bpy)(meo)															
energy of MO, eV	Pt	S	O	C-C	4H(C-C)	N(N-N)	10Cπ-(N-N)	energy of MO, eV	Pt	S	O	C-C	4H(C-C)	N(N-N)	10Cπ-(N-N)
-8.77	59	9	5			23		-11.90	31	28	6	27	4		
-9.58	3					27	70	-12.18	45	6	2	12	2	9	18
-11.76 ^b	51	36	0	2	6		2	-12.28	90	1	1			2	3
Pt(en)(mnt)															
energy of MO, eV	Pt	2S	C=C	C(CN)	N(CN)	N(N-N)	2C(N-N)	energy of MO, eV	Pt	2S	C=C	C(CN)	N(CN)	N(N-N)	2C(N-N)
-8.39	54	22				22	2	-11.73	18					12	68 ^c
-9.44	1	10	30	32	26			-12.02	71	18	6		2		
-11.44 ^b	28	38	22	4	8			-12.14	76	12	4		2	2	2
Pt(en)(i-mnt)															
energy of MO, eV	Pt	2S	C=C	C(CN)	N(CN)	N(N-N)	2C(N-N)	energy of MO, eV	Pt	2S	C=C	C(CN)	N(CN)	N(N-N)	2C(N-N)
-8.17	51	26	1			20		-11.92	49	16	18	2	12	2	
-8.59	6	14	52	18	10			-11.96	63	34					2
-11.55 ^b	14					12	74 ^c	-12.18	90	4	1				2

^aNote: Atomic contributions do not add up to 100% in some instances, since atomic contributions in the MO's of less than 1% are neglected. ^bHighest occupied molecular orbital. ^c16% on H atoms of ethylene bridge of en ligand.

range -1.5 to +2.0 V vs SSCE, whereas ecda and mnt complexes with a diphosphine chelating ligand or two monophosphite ligands do not exhibit similar reduction.

The fact that Pt(dmbpy)Cl₂ does not show the intense solvatochromic band, whereas Pt(dmbpy)(edt) (3a) with a saturated sulfur chelating ligand does, suggests that the HOMO has sig-

nificant sulfur character. This is true for mnt and ecda complexes with delocalized π systems on the dithiolate and for edt and bis(thiolate) systems where no dithiolate π system exists, suggesting that the largest contribution to the HOMO originates from either an orbital located on the sulfur donor or a combination of metal-d and sulfur-p orbitals. This conclusion is supported by

the MO calculations which show that, for the Pt(diimine)(dithiolate) and Pt(diimine)(thiolate)₂ complexes, the HOMO possesses significant metal-d and sulfur-p character, while the LUMO is essentially π^* (diimine).

The fact that the same solvatochromic transition is present even in complexes containing nonchelating thiolate ligands such as Pt(dmbpy)(EtS)₂ (**4a**) and Pt(dmbpy)(PhS)₂ (**5**) lends further support to the assignment of this transition as $\{d(\text{Pt})/p(\text{S})-\pi^*(\text{diimine})\}$ charge transfer. Additional support is provided by the absorption spectra of O- and Se-containing analogues. In the case of the bis(benzeneselenolate) complex Pt(dmbpy)(PhSe)₂ (**5**), for example, the solvatochromic absorption band is red-shifted by $\sim 500 \text{ cm}^{-1}$ with respect to the benzenethiolate analogue, consistent with the proposal that the donor orbital is significantly localized on the S or Se donor. In addition, the complex Pt(dmbpy)(meo) (**7**), which contains only one sulfur atom, possesses the solvatochromic absorption band.

Our assignments for the solvatochromic transition are in general accord with that put forward by Dance and Vogler as LLCT although in our case the MO calculations show significant metal involvement in the HOMO. The basis of the solvent dependence of the transition is rationalized in terms of a large dipole moment change between the ground and excited states leading to increasingly different solvations of the two states in increasingly polar solvents. The fact that the solvatochromism is of the negative type—i.e., the transition shifts to higher energy with increasing solvent polarity—suggests that the ground state is highly polar and that upon excitation the dipole moment is greatly reduced or even reversed. This is also supported by the nature of the HOMO and LUMO obtained from the MO calculations (see Figure 4). For the related Zn(diimine)(thiolate)₂ complexes studied by Vogler, Koester, and Crosby,¹³⁻¹⁵ an interesting observation is the need for an aromatic thiolate to observe the LLCT band. The Pt complexes studied here exhibit similar transitions for aromatic (PhS, PhSe) and aliphatic (EtS) thiolates. The extinction coefficients reported for the tetrahedral Zn complexes are also significantly lower ($\epsilon = 50\text{--}200$) than those of the planar Pt systems described here.¹³

The solution stability of the Pt(diimine) complexes containing nonchelating thiolates decreases with decreasing energy of the solvatochromic electronic transition and is reduced in halogenated solvents. For the Pt(diimine)(RS)₂ complexes, the energy of the acceptor orbital (LUMO) remains essentially constant for a given diimine, so that the decrease in transition energy arises solely from an increase in the energy of the donor orbital (HOMO). The lower transition energy thus corresponds to the complex being more easily oxidized. For the Pt(diimine) complexes with mnt and ecda, an irreversible oxidation wave is observed by cyclic voltammetry, and these complexes are irreversibly oxidized when irradiated in the presence of electron acceptors.¹⁰ A similar complex, Pt(bpy)(tdt) (tdt = 3,4-toluenedithiolate), has been reported to undergo photochemical oxidation in chloroform, generating the CHCl_2^\bullet radical.¹⁰ Thus for the bis(thiolate) complexes, the decrease in stability with decrease in solvatochromic absorption energy and in halogenated solvents results from the increasing tendency of these systems toward irreversible oxidation.

The lack of solvatochromism in the Pt(tdach)(dithiolate) systems leads to a different assignment for their lowest energy absorption. As seen from the results of the MO calculations given in Table IV, the HOMO for the *i*-mnt system Pt(en)(*i*-mnt) is a combination of metal-d and N(amine)-p orbitals, while for Pt(en)(mnt) the energy and orbital percentage of the HOMO is essentially unchanged from that of Pt(bpy)(mnt). The absence of a π system in the N-donor ligand requires that the LUMO be either π^* (mnt) or $d\sigma^*$ (Pt) in character. Our calculations show that, for both mnt and *i*-mnt systems, the π^* (dithiolate) orbital is lower in energy than the antibonding metal orbital by 0.6 and 1.3 eV, respectively, and shows virtually no change from the corresponding π^* (dithiolate) orbitals in the diimine systems. Thus for the Pt(diimine)(dithiolate) systems, we assign the low-energy nonsolvatochromic absorption as a $d-\pi^*$ (dithiolate) MLCT. It is important to note that in all cases the π^* (mnt) levels are lower

in energy than those of $\pi^*(i\text{-mnt})$.

The emission spectra of the complexes depend on the nature of both the diimine and the dithiolate ligands. The Pt(diimine)(ecda) and Pt(diimine)(RS)₂ complexes show broad asymmetric emission bands in DMM glass at temperatures below 165 K. In addition, the Pt(diimine)(ecda) complexes show a red shift of the emission upon going from fluid solution to rigid glass and the emergence of two new high-energy emission bands separated by 1300 cm^{-1} at temperatures below 140 K.³³ Upon further cooling from 80 to 6 K, the original emission exhibits a decrease in its intensity relative to the high-energy bands. These observations, along with the temperature dependence of emission quantum yield and excited-state lifetimes of the ecda complexes, are inconsistent with the notion of a single emitting state and have led to a model based on multiple emitting states for all of the complexes except those of mnt. A detailed analysis has been described elsewhere.¹⁶ The present study makes possible a definitive assignment of the orbital parentage of these excited states.

The broad asymmetric band of the ecda complexes and of the other diimine complexes except those of mnt decreases in intensity with decreasing temperature, as noted above, and is attributed to two closely spaced spin-orbit components of a state of $\{d(\text{Pt})/p(\text{S})-\pi^*(\text{diimine})\}$ character. The emission thus has the same orbital parentage as the solvatochromic absorption, but on the basis on its lifetime, the emission is from a state with a multiplicity different from that of the ground state, i.e. $^3\{d(\text{Pt})/p(\text{S})-\pi^*(\text{diimine})\}$. This assignment is supported by the emission behavior of Pt(diimine) complexes with saturated dithiolate or bis(thiolate) systems in which no π^* (dithiolate) orbital is present. The similarity of emission from these complexes with the broad asymmetric emission of the Pt(diimine)(ecda) systems indicates that π^* (dithiolate) is not involved directly in that emitting state. For the diimine complexes containing ecda, the two higher energy emission bands, which emerge below 140 K, are separated by $\sim 1360 \text{ cm}^{-1}$ and possess a single, relatively long lifetime of 500 μs at 6 K. These higher energy emissions are assigned to an intraligand $^3(\pi-\pi)^*$ state of the diimine ligand.

In contrast, complexes containing the 1,2-dithiolate mnt show a significantly different type of emission, one that possesses a well-resolved vibrational progression of $\sim 1400 \text{ cm}^{-1}$ ($\lambda_{\text{max}} = 600 \text{ nm}$, $16.7 \times 10^3 \text{ cm}^{-1}$). At temperatures between 80 and 6 K, the emission intensity of the Pt(diimine)(mnt) complexes increases with decreasing temperature. The emission from these complexes is very similar to that observed from Pt(tdach)(mnt) (**1c**) and Pt(L)₂(mnt)⁴ (L = tertiary phosphine or phosphite, cyclooctadiene), which do not contain π^* (diimine) levels. The results, including the similarity of the structured emission, suggest that for the mnt systems there is a single emitting state of common origin. Johnson et al. have previously assigned the emission from analogous anionic complexes $\text{MLL}'(\text{mnt})^-$ (M = Ir, Rh; L, L' = CO, tertiary phosphine, tertiary phosphites) observed in rigid media to be $^3\{d-\pi^*(\text{mnt})\}$,⁴ and on the basis of the similarity of those emissions to what is observed for the mnt complexes here, we extend that assignment to the present systems.

The MO calculations for the Pt(diimine)(mnt) complexes are consistent with this assignment. While the LUMO in these complexes is a π^* (diimine) orbital, there exists a π^* (mnt) level which is immediately above the LUMO and is substantially lower in energy than the second unoccupied π^* (diimine) level. The calculation, however, does not take into account electron-electron correlation and spin. We therefore propose that, on the basis of the great similarity of all mnt complex emissions and the striking difference between emissions from mnt and ecda complexes, the lower state in the triplet manifold is $^3\{d(\text{Pt})/p(\text{S})-\pi^*(\text{mnt})\}$ rather than $^3\{d(\text{Pt})/p(\text{S})-\pi^*(\text{diimine})\}$. Thus, while the absorption in the Pt(diimine)(mnt) complexes is the same as that assigned above for the ecda and bis(thiolate) complexes, i.e. $\{d(\text{Pt})/p(\text{S})-\pi^*(\text{diimine})\}$, within the triplet manifold the state designated as $^3\{d(\text{Pt})/p(\text{S})-\pi^*(\text{mnt})\}$ lies lower and is the emissive state. This assignment is also appropriate for the emission from Pt(tdach)(mnt) (**1c**), which is similar in structure to that of the other mnt complexes.

For the Pt(tdach)(ecda) (**2c**) complex a different situation exists. While the emission band of Pt(tdach)(ecda) (**2c**) is broad and asymmetric, similar to that observed for the Pt(diimine)(ecda) systems, the absence of π^* (diimine) levels and a large blue shift in the emission maximum relative to the diimine analogues suggest a different orbital origin for its emission. The emission intensity for Pt(tdach)(ecda) (**2c**) also increases as the temperature is lowered, consistent with a single emitting state and contrasting with the behavior of the diimine analogues. Furthermore, the shape, energy, and temperature dependence of the emission are similar to those observed for PtL₂(ecda) complexes where L₂ is a chelating diolefin³⁵ or phosphine.²² From the MO calculation of the similar complex Pt(en)(i-mnt), it is found that the LUMO possesses mainly dithiolate character and is significantly higher in energy than the diimine-based LUMO of Pt(bpy)(i-mnt). Thus, the lowest energy transition for both absorption and emission in Pt(tdach)(ecda) (**2c**) is assigned as a metal-to-dithiolate charge transfer, with emission coming from the triplet manifold.

Conclusions

Complexes of the type Pt(diimine)(dithiolate) exhibit both an intense solvatochromic absorption and an intense emission which are observed at room temperature in fluid solution. The solva-

chromic absorption is present in Pt(diimine) systems containing saturated dithiolates but disappears when the diimine is substituted by a saturated diamine. This transition is in all cases ascribed to a {d(Pt)/p(S)- π^* (diimine)} charge transfer. For all of the diimine complexes except those of mnt, the broad asymmetric emission is assigned as having the same orbital parentage as the solvatochromic absorption but arising from a state of different multiplicity—i.e., ³{d(Pt)/p(S)- π^* (diimine)}. All of the mnt complexes exhibit emissions having similar types and degrees of structuring, leading to the conclusion that they possess a common emitting state. This state is assigned on the basis of systematic ligand variation and MO calculations as ³{d(Pt)/p(S)- π^* (mnt)}.

Acknowledgment. We wish to thank the Department of Energy, Division of Basic Chemical Sciences, and the Eastman Kodak Co., Inc., for support of this work. We are also grateful to Prof. R. Hoffmann for helpful discussions. A generous loan of platinum salts from Johnson Matthey Co., Inc., is also gratefully acknowledged. P.D.H. acknowledges le Ministère des Affaires Internationales (Programme de Coopération Québec/États-Unis) for funding.

Registry No. **1a**, 126929-37-1; **1b**, 126929-39-3; **1c**, 138678-00-9; **2a**, 123623-04-1; **2b**, 123623-05-2; **2c**, 138623-24-2; **3a**, 138678-01-0; **3b**, 138623-25-3; **4a**, 138623-22-0; **4b**, 138623-26-4; **5**, 138623-27-5; **6**, 141249-58-3; **7**, 141249-59-4.

(35) Bevilacqua, J. M.; Zuleta, J. A.; Eisenberg, R. Paper in preparation.

Contribution from the Department of Chemistry, University of Sassari, Via Vienna 2, 07100 Sassari, Italy, Department of Physical Chemistry, University of Padua, Via Loredan 2, 35131 Padua, Italy, and Istituto per l'Applicazione delle Tecniche Chimiche Avanzate ai Problemi Agrobiologici, CNR, Via Vienna 2, 07100 Sassari, Italy

Structural Information on Chromium(V) Complexes of 1,2-Diols in Solution, As Determined by Isotropic and Anisotropic ¹H ENDOR Spectroscopy

Mario Branca,^{*,1a} Giovanni Micera,^{1a} Ulderico Segre,^{1b} and Alessandro Dessi^{1c}

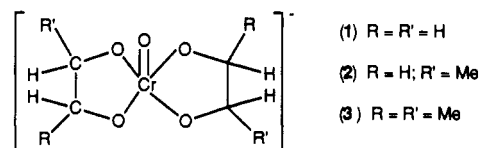
Received August 22, 1991

The ¹H ENDOR study of complexes formed by 1,2-diols, namely ethylene glycol, (S)-(+)-1,2-propanediol, and (2R,3R)-(-)-2,3-butanediol, has demonstrated the potential of this technique as a structural probe of Cr(V) complexes in solution. The spectra recorded in liquid CD₃OD solution demonstrate the ¹H superhyperfine (shf) interaction, which, except for the case of the glycolate complex, is not resolved in the EPR spectra. The comparative analysis provides unambiguous evidence for the presence of two classes of protons in the chelated ethylene bridge of the complexes. The analysis shows also that the single ¹H ENDOR coupling observed for the bis(ethylene glycolato(2-))oxochromate(V) complex is really an average signal due to a fast axial-equatorial interconversion. Crystallike ENDOR information has been obtained on the anisotropic spectra recorded in frozen solution by using both ⁵²Cr and ⁵³Cr isotopes. The complementary use of the isotropic and anisotropic couplings allow discrimination among all the protons of the ligands and calculation of their distances from the metal ion. The proton ENDOR analysis has been supported by a theoretical simulation of the spectra.

Introduction

Recently, attention has been paid to Cr(V) complexes of polyols or sugars, which are also stable in biological systems.²⁻⁶ Unfortunately, only limited information can be obtained on these complexes by use of EPR spectroscopy. We have tested the usefulness of complementary ENDOR studies, which, as is well-known, can resolve hyperfine splittings not observable by EPR and thus provide information about the interaction between a paramagnetic center and the neighboring magnetic nuclei.⁷⁻¹⁰

The only ENDOR study so far published on Cr(V) complexes reports the isotropic spectrum of the bis(ethylene glycolato(2-))oxochromate(V) species **1**.¹¹ The spectrum, recorded above



180 K, showed a single coupling between the metal ion and the methylene protons of the ligand. The same conclusion was reached by analysis of the EPR spectrum,¹² which was also observed earlier^{2,13} and exhibited nine shf components indicating the equivalence of the eight protons belonging to the two ligand molecules. Accordingly, almost coincident values were measured

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