

## Luminescence Properties of Platinum(II) Dithiooxamide Compounds

Giuseppe Rosace,<sup>†</sup> Gaetano Giuffrida,<sup>†</sup> Marcello Saitta,<sup>‡</sup> Giovanni Guglielmo,<sup>†</sup>  
 Sebastiano Campagna,<sup>\*,†</sup> and Santo Lanza<sup>\*,†</sup>

Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica and Dipartimento di Chimica Organica e Biologica, Università di Messina, via Sperone 31, I-98166 Messina, Italy

Received October 30, 1995<sup>⊗</sup>

Tight contact ion pairs of general formula  $\{\text{Pt}(\text{H}_2\text{-R}_2\text{-dto})_2^{2+}, (\text{X}^-)_2\}$  have been prepared, and their absorption spectra and luminescence properties (at room temperature in dichloromethane fluid solution and at 77 K in butyronitrile rigid matrix) have been studied (dto = dithiooxamide; R = methyl, X = Cl (1); R = butyl, X = Cl (2); R = benzyl, X = Cl (3); R = cyclohexyl, X = Cl (4); R = cyclohexyl, X = Br (5); R = cyclohexyl, X = I (6)). The absorption spectra of all the compounds are dominated by moderately strong Pt(dπ)/S(p) to dithiooxamide ( $\pi^*$ ) charge transfer (Pt/S → dto CT) bands in the visible region ( $\epsilon$  in the  $10^4\text{--}10^5 \text{ M}^{-1} \text{ cm}^{-1}$  range). Absorption features are also present at higher energies, due to  $\pi\text{-}\pi^*$  transitions centered in the dto ligands (ligand centered, LC). All the compounds exhibit a unstructured luminescence band in fluid solution at room temperature, with the maximum centered in the 700–730 nm range. The luminescence bands are blue-shifted about  $4000 \text{ cm}^{-1}$  on passing to the rigid matrix at 77 K. Luminescence lifetimes are on the  $10^{-8}\text{--}10^{-7}$  s time scale at room temperature and 1 order of magnitude longer at 77 K. Luminescence is assigned to triplet Pt/S → dto CT excited states in all cases. Compounds 3–6 also exhibit a second higher-energy luminescence band at room temperature, centered at about 610 nm, attributed to a LC excited state. Charge transfer interactions between halides and dto ligands destabilize dto-centered orbitals, affecting the energy of Pt/S → dto CT transitions and states. The X counterions and X → dto CT levels are proposed to play a role in promoting excited state conversion between LC and Pt/S → dto CT levels. The R substituents on the nitrogen atoms of the dto ligands influence the absorption and photophysical properties of the compounds, by affecting proximity of the ion pairs. The possibility to functionalize the R substituents may open the way to interface these luminescent compounds with desired substrates and to construct supramolecular assemblies.

### Introduction

Design of luminescent transition metal complexes is a topic of interest for both theoretical and applicative reasons. For example, luminescent metal complexes are at the basis of supramolecular systems that can be involved in light energy conversion schemes and/or light-driven information devices<sup>1–7</sup> and can play the role of luminescent probes and sensors.<sup>1,8</sup>

In spite of the high number of d<sup>6</sup> transition metal complexes which exhibit room-temperature emission,<sup>9–12</sup> only few d<sup>8</sup> metal complexes are known to be emissive in fluid solution at room-temperature. In particular, room-temperature luminescence has been reported only for a limited number of platinum(II) compounds. Room-temperature metal-to-ligand charge transfer

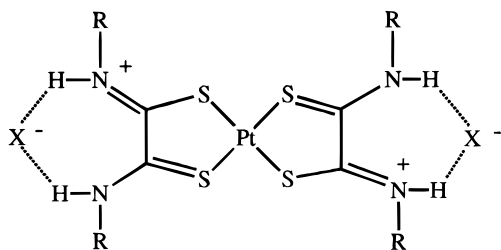
(MLCT) luminescence has been found in cyclometalated compounds<sup>13</sup> and in complexes containing polypyridine ligands with extended conjugation,<sup>14</sup> whereas ligand-centered (LC) luminescence has been reported for compounds containing ligands with strong ligand field strength such as carbonyls and cyanides.<sup>15</sup> Excimer emission has also been detected.<sup>16</sup> Finally,

<sup>†</sup> Dipartimento di Chimica Inorganica, Chimica Analitica e Chimica Fisica.

<sup>‡</sup> Dipartimento di Chimica Organica e Biologica.

<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, September 1, 1996.

- (1) Balzani, V.; Scandola, F. *Supramolecular Photochemistry*; Horwood: Chichester, U.K., 1991.
- (2) Balzani, V.; Credi, A.; Scandola, F. In *Transition Metals in Supramolecular Chemistry*, Fabbri, L., Poggi, A., Eds., Kluwer: Dordrecht, The Netherlands, 1994; p 1.
- (3) (a) Meyer, T. J. *Acc. Chem. Res.* **1989**, *22*, 163. (b) Worl, L. A.; Strouse, G. F.; Younathan, J. N.; Baxter, S. M.; Meyer, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 7571. (c) Opperman, K. A.; Mecklenburg, S. L.; Meyer, T. J. *Inorg. Chem.* **1994**, *33*, 5295.
- (4) (a) O'Regan, B.; Graetzel, M. *Nature* **1991**, *353*, 737. (b) Graetzel, M. *Comments Inorg. Chem.* **1991**, *12*, 93.
- (5) (a) Heimer, T. A.; Bignozzi, C. A.; Meyer, G. J. *J. Phys. Chem.* **1993**, *97*, 11987. (b) Bignozzi, C. A.; Schoonover, J. R.; Scandola, F. *Prog. Inorg. Chem.*, in press.
- (6) (a) Molnar, S. M.; Nallas, G.; Bridgewater, J. S.; Brewer, K. J. *J. Am. Chem. Soc.* **1994**, *116*, 5206. (b) Farid, R. S.; Chang, I.-J.; Winkler, J. R.; Gray, H. B. *J. Phys. Chem.* **1994**, *98*, 5176.
- (7) Goulle, V.; Harriman, A.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* **1993**, 1034.
- (8) For some representative examples of luminescent transition metals as probes and sensors, see: (a) Pyle, A. M.; Rehmann, J. P.; Meshoyer, R.; Kumar, C. V.; Turro, N. J.; Barton, J. K. *J. Am. Chem. Soc.* **1988**, *111*, 3051. (b) Tossi, A. B.; Kelly, J. M. *Photochem. Photobiol.* **1989**, *49*, 545. (c) Friedman, A. E.; Chambron, J.-C.; Sauvage, J.-P.; Turro, N. J.; Barton, J. K. *J. Am. Chem. Soc.* **1990**, *112*, 2695. (d) Lecomte, J. P.; Kirsch-De Mesmaeker, A.; Orellana, G. *J. Phys. Chem.* **1994**, *98*, 5382. (e) Carraway, E. R.; Demas, J. N.; DeGraff, B. A.; Bacon, J. R. *Anal. Chem.* **1991**, *63*, 337. (f) Preininger, C.; Klimant, I.; Wolfbeis, O. S. *Anal. Chem.* **1994**, *66*, 1841. (g) Di Marco, G.; Lanza, M.; Campagna, S. *Adv. Mater.* **1995**, *7*, 468. (h) Hartmann, P.; Leiner, M. J. P.; Lippitsch, M. E. *Anal. Chem.* **1995**, *67*, 88.
- (9) (a) Crosby, G. A.; Watts, R. J.; Carstens, D. H. W. *Science* **1970**, *170*, 1195. (b) Crosby, G. A. *Acc. Chem. Res.* **1975**, *8*, 231.
- (10) Meyer, T. J. *Pure Appl. Chem.* **1986**, *58*, 1193.
- (11) (a) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, *84*, 85. (b) Kalyanasundaram, K. *Photochemistry of Polypyridine and Porphyrin Complexes*; Academic Press: London, 1992.
- (12) Scandola, F.; Indelli, M. T.; Chiorboli, C.; Bignozzi, C. A. *Top. Curr. Chem.* **1990**, *158*, 73.
- (13) Maestri, M.; Balzani, V.; Deuschel-Cornioley, C.; von Zelewsky, A. *Adv. Photochem.* **1992**, *17*, 1 and references therein.
- (14) (a) Bailey, J. A.; Miskowski, V. M.; Gray, H. B. *Inorg. Chem.* **1993**, *32*, 369. (b) Chan, C.-W.; Lai, T.-F.; Che, C.-M.; Peng, S.-M. *J. Am. Chem. Soc.* **1993**, *115*, 11245. (c) Aldridge, T. K.; Stacy, E. M.; McMillin, D. R. *Inorg. Chem.* **1994**, *33*, 722.
- (15) (a) Blanton, C. B.; Rillema, D. P. *Inorg. Chim. Acta* **1990**, *168*, 145. (b) Wan, T. O.; Che, C.-M. *J. Chem. Soc., Chem. Commun.* **1990**, 140. (b) Monsù Scolaro, L.; Alibrandi, G.; Romeo, R.; Ricevuto, V.; Campagna, S. *Inorg. Chem.* **1992**, *31*, 2074.
- (16) Kunkely, H.; Vogler, A. *J. Am. Chem. Soc.* **1990**, *112*, 5625.



**Figure 1.** Structural formulas of compounds **1–6**. Only one of the possible resonance forms is shown.

$\sigma$ – $\sigma^*$  luminescence has been reported for metal–metal-bonded dinuclear systems.<sup>17</sup> In recent times, CT luminescence was reported by Eisenberg and co-workers for systems quite related to the present ones, namely Pt(II)–dithiolate compounds.<sup>18</sup> In the latter compounds, a  $\sigma$ -bond orbital–involving Pt( $d\pi$ ) and S(p) orbitals—has been proposed to be the donor orbital in the transition leading to the excited states responsible for the emission, and these excited states have been described as triplet Pt( $d\pi$ )/S(p)  $\rightarrow$  thiolate ( $\pi^*$ ) charge transfer excited states.<sup>18b</sup> Quite similar  $\sigma$ -bond to ligand charge transfer luminescence (SBLCT) has been reported for Rh(III)- and Ir(III)-cyclometalated systems.<sup>19,20</sup> It should be considered, however, that most of the Pt( $d\pi$ )/S(p)  $\rightarrow$  thiolate ( $\pi^*$ ) CT and of the Rh- and Ir-based SBLCT excited states reported in literature could be classified as examples of ligand-to-ligand charge transfer (LLCT) excited states as defined by Vogler and Kunkely.<sup>21</sup>

Here we report the synthesis, characterization, absorption spectra, and luminescence properties of a series of Pt(II)–dithiooxamide compounds which exhibit room-temperature emission in fluid solution. The compounds are tight contact ion pairs of general formula  $\{\text{Pt}(\text{H}_2\text{-R}_2\text{-dto})_2^{2+}, (\text{X}^-)_2\}$  (dto = dithiooxamide; R = methyl, X = Cl (**1**); R = butyl, X = Cl (**2**); R = benzyl, X = Cl (**3**); R = cyclohexyl, X = Cl (**4**); R = cyclohexyl, X = Br (**5**); R = cyclohexyl, X = I (**6**). Figure 1 shows the structural formula of the compounds. Luminescence properties have been investigated both at room-temperature in fluid solution and at 77 K in a rigid matrix. In some cases, dual luminescence has been found.

For comparison purposes, also corresponding neutral rubeanate compounds of general formula  $[\text{Pt}(\text{H-R}_2\text{-dto})_2]$  (R = methyl, **8**; R = butyl, **9**; R = benzyl, **10**; R = cyclohexyl, **11**) as well as the monodehydrogenated compound  $\{(\text{H}-(n\text{-butyl})_2\text{-dto})\text{Pt}(\text{H}_2-(n\text{-butyl})_2\text{-dto})^{2+}, \text{Cl}^-\}$  (**7**) and the free  $\text{H}_2\text{-R}_2\text{-dto}$  ligands have been prepared and characterized.

One point that deserves to be noted is that the R alkyl substituents on the nitrogen atoms of the dto ligands (see Figure 1) can be easily functionalized. This may open the way to interface the studied luminescent compounds with desired substrates and to construct supramolecular assemblies.

## Experimental Section

**Materials and Methods.** The starting sulfoxide platinum complexes, *cis*-[PtL<sub>2</sub>X<sub>2</sub>] (L = Me<sub>2</sub>SO; X = Cl, Br, I), were synthesized according to literature procedures.<sup>22a</sup> *cis*-[Pt(COD)MeCl] was a commercial product. The secondary dithiooxamides H<sub>2</sub>–R<sub>2</sub>–dto, where R is methyl (abbreviated as Me), benzyl (Bz), *n*-butyl (Bu), and cyclohexyl (Cy), were prepared according to Hurd.<sup>22b</sup> The other chemicals were commercially available and were used without further purification. Solvents for spectroscopic and photophysical measurements were of the best fluorimetric grade. NMR experiments were performed with a Bruker AMX 300 MHz spectrometer. Infrared spectra were obtained using a Perkin-Elmer FT-IR 1720 X spectrophotometer, electron impact (EI) mass spectra were recorded with a Finnigan MAT 90 reverse-geometry double-focusing mass spectrometer. Samples were introduced into the EI source by a heated direct inlet probe. Ion source conditions: ionization energy, 70 eV; acceleration voltage, 5 kV; temperature, 220 °C. A Kontron Uvikon 860 spectrophotometer was employed for recording UV–visible absorption spectra. Luminescence spectra and lifetimes were measured with a Perkin-Elmer LS-5B spectrofluorimeter equipped with a red-sensitive Hamamatsu R 928 photomultiplier and with an Edinburgh FL 900 single-photon-counting spectrometer, respectively. Luminescence quantum yields were obtained with the optically dilute method,<sup>23</sup> calibrating the fluorimeter with a standard lamp and using [Os(bpy)<sub>3</sub>](PF<sub>6</sub>)<sub>2</sub> (bpy = 2,2'-bipyridine) in deaerated aqueous solution as a quantum yield reference ( $\Phi = 0.0066$ ).

**Syntheses. (a) Compounds 1–6.** As a general method, *cis*-[PtL<sub>2</sub>X<sub>2</sub>] species (1 mmol) was dissolved (or suspended) in chloroform (30 mL), and a 2-fold amount of the desired H<sub>2</sub>–R<sub>2</sub>–dto ligand was added. The solution became purple in a few minutes and was allowed to stand without any particular precaution for 30 min. Finally, hexane was added and  $\{\text{Pt}(\text{H}_2\text{-R}_2\text{-dto})_2^{2+}, (\text{X}^-)_2\}$  compounds precipitated as purple powders. The new compounds were obtained in virtually quantitative yields. Anal. Found (calcd) for **1**, C<sub>8</sub>H<sub>16</sub>N<sub>4</sub>S<sub>4</sub>Cl<sub>2</sub>Pt: C, 16.86 (17.08); H, 2.89 (2.87); N, 10.36 (9.96); Cl, 13.00 (12.61). Found (calcd) for **2**, C<sub>20</sub>H<sub>40</sub>N<sub>4</sub>S<sub>4</sub>Cl<sub>2</sub>Pt: C, 33.81 (32.87); H, 5.83 (5.52); N, 7.91 (7.67); Cl, 10.10 (9.70). EI-MS: M<sup>+</sup> = 729. Found (calcd) for **3**, C<sub>32</sub>H<sub>32</sub>N<sub>4</sub>S<sub>4</sub>Cl<sub>2</sub>Pt: C, 44.49 (44.34); H, 3.71 (3.72); N, 6.40 (6.46); Cl, 8.20 (8.08). Found (calcd) for **4**, C<sub>28</sub>H<sub>48</sub>N<sub>4</sub>S<sub>4</sub>Cl<sub>2</sub>Pt: C, 40.33 (40.28); H, 5.79 (5.79); N, 6.73 (6.71); Cl, 8.50 (8.49). Found (calcd) for **5**, C<sub>28</sub>H<sub>48</sub>N<sub>4</sub>S<sub>4</sub>Br<sub>2</sub>Pt: C, 36.28 (36.40); H, 5.22 (5.24); N, 6.03 (6.06); Br, 17.31 (17.30). Found (calcd) for **6**, C<sub>28</sub>H<sub>48</sub>N<sub>4</sub>S<sub>4</sub>I<sub>2</sub>Pt: C, 33.00 (33.04); H, 4.73 (4.75); N, 5.60 (5.50); I, 25.00 (24.94).

**(b) Compound 7.** A chloroform solution of [Pt(COD)MeCl] (1 mmol) was treated with a 2-fold amount of H<sub>2</sub>–(*n*-butyl)<sub>2</sub>–dto. The solution became purple within a few minutes. It was allowed to stand without particular precautions for 30 min. Finally, the compound was precipitated on addition of hexane as a deep red powder. Anal. Found (calcd) for **7**, C<sub>20</sub>H<sub>39</sub>N<sub>4</sub>S<sub>4</sub>ClPt: C, 33.94 (34.62); H, 5.60 (5.66); N, 8.15 (8.07); Cl, 4.83 (5.11).

**(c) Compounds 8–11.** As a general method, compounds **1–4** were dissolved in the minimum amount of chloroform and column-chromatographed (silica gel, chloroform as eluant). The red-orange eluates were concentrated by rotary evaporation under vacuum, and **8–11** precipitated as red (**9–11**) or yellow-brown (**8**) crystals. Anal. Found (calcd) for C<sub>8</sub>H<sub>14</sub>N<sub>4</sub>S<sub>4</sub>Pt: C, 19.75 (19.63); H, 2.88 (2.88); N, 11.18 (11.44). EI-MS: M<sup>+</sup> = 489.0. Found (calcd) for **9**, C<sub>20</sub>H<sub>38</sub>N<sub>4</sub>S<sub>4</sub>Pt: C, 36.40 (36.51); H, 5.70 (5.82); N, 8.25 (8.52). EI-MS: M<sup>+</sup> = 657.1. Found (calcd) for **10**, C<sub>32</sub>H<sub>30</sub>N<sub>4</sub>S<sub>4</sub>Pt: C, 48.49 (48.41); H, 3.66 (3.81); N, 6.85 (7.06). Found (calcd) for **11**, C<sub>28</sub>H<sub>46</sub>N<sub>4</sub>S<sub>4</sub>Pt: C, 43.95 (44.13); H, 6.08 (6.08); N, 7.15 (7.35). EI-MS: M<sup>+</sup> = 761.3.

## Results

The reaction of platinum complexes of formula *cis*-PtL<sub>2</sub>X<sub>2</sub> (L = Me<sub>2</sub>SO, 1/2 COD; X = Cl, Br, I) with secondary

- (17) For some examples, see: (a) Rounhill, D. M.; Gray, H. B.; Che, C.-M. *Acc. Chem. Res.* **1989**, *22*, 55. (b) Che, C.-M.; Yam, V. W. W.; Wong, W. T.; Lai, T. F. *Inorg. Chem.* **1989**, *104*, 3596. (c) Shin, Y. K.; Miskowski, V. M.; Nocera, D. G. *Inorg. Chem.* **1990**, *29*, 2303. (d) Nocera, D. G. *Acc. Chem. Res.* **1995**, *28*, 209.
- (18) (a) Zuleta, J. A.; Chesta, C. A.; Eisenberg, R. *J. Am. Chem. Soc.* **1989**, *111*, 8916. (b) Zuleta, J. A.; Bevilacqua, J. M.; Eisenberg, R. *Coord. Chem. Rev.* **1991**, *111*, 237. (c) Zuleta, J. A.; Bevilacqua, J. M.; Proserpio, D. M.; Harvey, P. D.; Eisenberg, R. *Inorg. Chem.* **1992**, *31*, 2396. (d) Bevilacqua, J. M.; Eisenberg, R. *Inorg. Chem.* **1994**, *33*, 2913. (e) Cummings, S. D.; Eisenberg, R. *Inorg. Chem.* **1995**, *34*, 2007.
- (19) (a) Didier, P.; Ortmans, L.; Kirsch-De Mesmaeker, A.; Watts, R. J. *Inorg. Chem.* **1993**, *32*, 5239. (b) Ortmans, L.; Didier, P.; Kirsch-DeMesmaeker, A. *Inorg. Chem.* **1995**, *34*, 5239.
- (20) Serroni, S.; Juris, A.; Campagna, S.; Venturi, M.; Denti, G.; Balzani, V. *J. Am. Chem. Soc.* **1994**, *116*, 9086.
- (21) Vogler, A.; Kunkely, H. *Comments Inorg. Chem.* **1989**, *9*, 201.

- (22) (a) Kukushkin, Y. N.; Viaz'menskii, Y. E.; Zorina, L. I. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1968**, 835. (b) Hurd, R. N.; De La Mater G.; McElheny, G. C.; Turner, R. J.; Wallingford, V. H. *J. Org. Chem.* **1961**, *26*, 3980.
- (23) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.

**Table 1.**  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR Spectral Data<sup>a</sup> for  $[\text{Pt}(\text{H}_2\text{-R}_2\text{-dto})^{2+}, (\text{X}^-)_2]$  Complexes **1–6** and  $\{\text{Pt}(\text{H-Bu}_2\text{-dto})(\text{H}_2\text{-Bu}_2\text{-dto})^+, \text{Cl}^-$  (**7**)

R	X	$^1\text{H}$ NMR <sup>b</sup>	$^{13}\text{C}\{^1\text{H}\}$ NMR <sup>b</sup>
1	Me	Cl NH, nd; N-CH <sub>3</sub> , 3.40 s	
2	Bu	Cl NH, 13.51, s; N-CH <sub>2</sub> -, 3.89 t, $J_{\text{vic}} = 7.35$ ; N-CH <sub>2</sub> -CH <sub>2</sub> -, 1.97, m; N-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -, 1.49, m; CH <sub>3</sub> , 0.99, t, $J_{\text{vic}} = 7.35$	CS, 186.49; N-CH <sub>2</sub> -, 50.14; N-CH <sub>2</sub> -CH <sub>2</sub> -, 28.25; N-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -, 20.49; -CH <sub>3</sub> , 13.45
3	Bz	Cl NH, 13.45, s; C <sub>6</sub> H <sub>5</sub> , 7.42, m; N-CH <sub>2</sub> -, 4.99, s	CS, 186.38; C <sub>6</sub> H <sub>5</sub> , 132.32, 129.34, 129.06, 128.85; N-CH <sub>2</sub> -, 52.84
4	Cy	Cl NH, 13.47, s; N-CH=, 4.12, m; (CH <sub>2</sub> ) <sub>5</sub> , 1.71, m	CS; 184.85; N-CH=, 61.68; (CH <sub>2</sub> ) <sub>5</sub> , 31.71, 25.46, 24.52
5	Cy	Br NH, 12.57, s; N-CH=, 4.14, m; (CH <sub>2</sub> ) <sub>5</sub> , 1.71, m	
6	Cy	I NH, 12.33, s; N-CH=, 4.17, m; (CH <sub>2</sub> ) <sub>5</sub> , 1.71, m	
7	Bu	Cl NH, 12.92; N-CH <sub>2</sub> -, 3.70, t, $J_{\text{vic}} = 7.35$ ; N-CH <sub>2</sub> -CH <sub>2</sub> -, bm, 1.87; N-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -, m, 1.47; -CH <sub>3</sub> , 0.99 t, $J_{\text{vic}} = 7.35$	CS, 182.21; N-CH <sub>2</sub> -, 49.48; N-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -, 20.51; -CH <sub>3</sub> , 13.6

<sup>a</sup> All spectra were recorded at room-temperature in CDCl<sub>3</sub> solutions at 300 MHz ( $^1\text{H}$  NMR) and 75 MHz ( $^{13}\text{C}\{^1\text{H}\}$  NMR). <sup>b</sup> Chemical shifts are given in ppm, relative to TMS resonance = 0.00. Key: s, singlet; t, triplet; m, multiplet; b m, broad multiplet; nd, not detected. Coupling constants ( $J$ ) are in Hz.

**Table 2.**  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR Spectral Data<sup>a</sup> for  $[\text{Pt}(\text{H-R}_2\text{-dto})_2]$  Complexes **8–11**

R	$^1\text{H}$ NMR <sup>b</sup>	$^{13}\text{C}\{^1\text{H}\}$ NMR <sup>b</sup>
8	Me N-CH <sub>3</sub> , 3.38, s	
9	Bu N-CH <sub>2</sub> -, t, 3.66; $J_{\text{vic}} = 7.35$ ; N-CH <sub>2</sub> -CH <sub>2</sub> -, m, 1.75; N-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -, m, 1.43; -CH <sub>3</sub> , t, $J_{\text{vic}} = 7.35$	CS, 179.65; N-CH <sub>2</sub> -, 49.15; N-CH <sub>2</sub> -CH <sub>2</sub> -, 30.82; N-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -, 20.51; -CH <sub>3</sub> , 13.70
10	Bz C <sub>6</sub> H <sub>5</sub> , 7.36, m; N-CH <sub>2</sub> -, 4.84, s	CS, 180.70; C <sub>6</sub> H <sub>5</sub> , 136.55, 128.78, 128.22, 127.82; N-CH <sub>2</sub> -, 53.40
11	Cy N-CH=, 3.99, m; (CH <sub>2</sub> ) <sub>5</sub> , 1.63 m	CS, 177.70; N-CH=, 57.77; (CH <sub>2</sub> ) <sub>5</sub> , 29.93, 24.81, 24.52

<sup>a</sup> All spectra were recorded at room temperature in CDCl<sub>3</sub> solutions at 300 MHz ( $^1\text{H}$  NMR) and 75 MHz ( $^{13}\text{C}\{^1\text{H}\}$  NMR). <sup>b</sup> Chemical shifts are given in ppm, relative to TMS resonance = 0.00. Key: s, singlet, t, triplet; m, multiplet. Coupling constants ( $J$ ) are in Hz.

**Table 3.**  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR Spectral Data<sup>a</sup> for H<sub>2</sub>-R<sub>2</sub>-dto Ligands **12–15**

R	$^1\text{H}$ NMR <sup>b</sup>	$^{13}\text{C}\{^1\text{H}\}$ NMR <sup>b</sup>
12	Me NH, 10.36; N-CH <sub>3</sub> , 3.3, d, $J_{\text{vic}} = 5.14$	CS, 185.59; N-CH <sub>3</sub> , 34.10
13	Bu NH, 10.36; N-CH <sub>2</sub> -, dt, 3.695, $J_{\text{vic}}(\text{CH}_2\text{-CH}_2) = 7.35$ ; $J_{\text{vic}}(\text{NH-CH}_2) = 5.88$ ; N-CH <sub>2</sub> -CH <sub>2</sub> -, m, 1.75; N-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -, m, 1.46; CH <sub>3</sub> , t, 0.98, $J_{\text{vic}} = 7.35$	CS, 184.36; N-CH <sub>2</sub> -, 47.22; N-CH <sub>2</sub> -CH <sub>2</sub> -, 29.48; N-CH <sub>2</sub> -CH <sub>2</sub> -CH <sub>2</sub> -, 20.24; -CH <sub>3</sub> , 13.66
14	Bz NH, 10.54, s; C <sub>6</sub> H <sub>5</sub> , 7.38, m; N-CH <sub>2</sub> -, 4.90, d, $J_{\text{vic}} = 5.51$	CS, 184.56; C <sub>6</sub> H <sub>5</sub> , 134.99, 129.02, 128.26, 129.10; N-CH <sub>2</sub> -, 51.52
15	Cy NH, 10.34, s; N-CH=, 4.24, m; (CH <sub>2</sub> ) <sub>5</sub> , 1.65, m	CS, 182.96; N-CH=, 55.73; (CH <sub>2</sub> ) <sub>5</sub> , 30.55, 25.37, 24.33

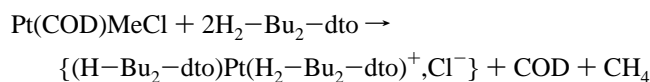
<sup>a</sup> All spectra were recorded at room temperature in CDCl<sub>3</sub> solutions at 300 MHz ( $^1\text{H}$  NMR) and 75 MHz ( $^{13}\text{C}\{^1\text{H}\}$  NMR). <sup>b</sup> Chemical shifts are given in ppm, relative to TMS resonance = 0.00. Key: s, singlet; d, doublet; t, triplet; dt, double triplet; m, multiplet. Coupling constants ( $J$ ) are in Hz.

dithiooxamides (RHN-C(=S)-)<sub>2</sub> in a 1:2 molecular ratio readily affords the compounds **1–6** in good yield. The NMR data for **1–6**, as well as those for the corresponding rubeanate compounds **8–11** and of the free dto ligands **12–15**, are reported in Tables 1–3. As far as the purity of **1–6** is concerned, it was tested by analytical data and NMR experiments. However, these methods are not able to detect traces of impurities, which can disturb photophysical experiments. TLC experiments on alumina or silica gel (chloroform/hexane mixtures as eluants) failed to exclude that these compounds contain traces of the corresponding dehydrohalogenated compounds **8–11**, since both alumina and silica gel cause dehydrohalogenation of **1–6**. However, compounds **8–11** are not luminescent both in rigid matrix and in fluid solution at room-temperature, so that double emission of **1–6** (see later) cannot be attributed to **8–11** as impurities.

Complexes of group 10 metals containing neutral secondary dithiooxamides as chelate ligands were known as dicationic species of formula  $[\text{M}(\text{H}_2\text{-R}_2\text{-dto})\text{X}_2]$ .<sup>24</sup> We have recently demonstrated that they are extensively associated tight contact ion pairs (Beer's law holds in the concentration range  $5 \times 10^{-6}$ – $2 \times 10^{-5}$  M), in which the interaction N-H...X plays an important role in the stabilization of  $\{\text{Pt}(\text{H}_2\text{-R}_2\text{-dto})^{2+}, (\text{X}^-)_2\}$  species.<sup>25a</sup> A similar stabilizing effect of halide ions has been

also recognized in strong tight contact ion pairs such as  $\{\text{H}_4\text{TPP}^{2+}, (\text{Cl}^-)_2\}$  ( $\text{H}_4\text{TPP}^{2+}$  is the deprotonated 5,10,15,20-tetraphenylporphyrin).<sup>25b</sup>

Compounds **1–6** can be easily dehydrohalogenated to give neutral rubeanate complexes  $[\text{Pt}(\text{H-R}_2\text{-dto})_2]$  (**8–11**) in a pure form, by means of a double-phase reaction with water or by column chromatography (alumina or silica gel). The acid-base process *ion pair–neutral rubeanate complex* can be monitored via UV-vis spectrophotometry by adding increasing amounts of a nitrogen base to a chloroform solution of the ion pairs. As an example, the spectral changes obtained upon titration of **2** by *n*-butylamine are shown in the Supporting Information. Two successive processes can be noted in the titration, each of them being characterized by well-defined isosbestic points. The final spectrum of the first process is coincident with that of an authentic sample of the monochlorohydrated uni-univalent ion pair  $\{(\text{H-Bu}_2\text{-dto})\text{Pt}(\text{H}_2\text{-Bu}_2\text{-dto})^+, \text{Cl}^-\}$ , independently prepared by the reaction



Both the two spectral families of the titration process can be obtained by adding increasing amounts of HCl to a chloroform solution of the neutral rubeanate complex  $[\text{Pt}(\text{H-Bu}_2\text{-dto})_2]$ ;

(24) (a) Peyronel, G.; Pellacani G. G. *Inorg. Chim. Acta* **1974**, *9*, 189. (b) Hoffmans, H. C.; Desseyen, H. O.; Dommissse, R.; Herman, M. A. *Bull. Chim. Soc. Belg.* **1982**, *91*, 175. (c) Antolini, L.; Fabretti, A. C.; Franchini, G.; Menabue, L.; Pellacani G. C.; Desseyen, H.; Dommissse, R.; Hoffmans, H. C. *J. Chem. Soc., Dalton Trans.* **1987**, 1921.

(25) (a) Rosace, G.; Bruno, G.; Monsù Scolaro, L.; Nicolò, F.; Sergi, S.; Lanza, S. *Inorg. Chim. Acta* **1993**, *208*, 59. (b) Karaman, R.; Bruce, T. C. *Inorg. Chem.* **1992**, *31*, 2455.

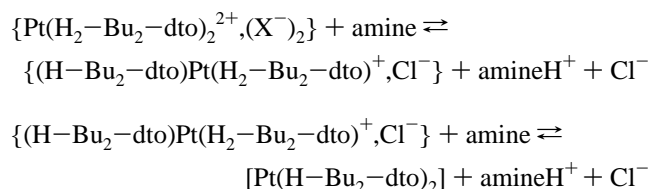
**Table 4.** Absorption Spectra and Luminescence Properties of the New Compounds 1–6<sup>a</sup>

compd	formula	absorption		luminescence <sup>b</sup>				
		298 K		298 K		77 K		
		$\lambda_{\max}$ , nm	$(\epsilon, 10^{-3} \text{ M}^{-1} \text{ cm}^{-1})$	$\lambda_{\max}$ , nm	$\tau$ , ns	$\Phi$	$\lambda_{\max}$ , nm	$\tau$ , ns
1	{Pt(H <sub>2</sub> -Me <sub>2</sub> -dto) <sub>2</sub> <sup>2+</sup> , (Cl <sup>-</sup> ) <sub>2</sub> }	507 (10.0)		700	20	$9 \times 10^{-4}$	640	485
2	{Pt(H <sub>2</sub> -Bu <sub>2</sub> -dto) <sub>2</sub> <sup>2+</sup> , (Cl <sup>-</sup> ) <sub>2</sub> }	513 (12.0)		716	25	$10 \times 10^{-4}$	640	425
3	{Pt(H <sub>2</sub> -Bz <sub>2</sub> -dto) <sub>2</sub> <sup>2+</sup> , (Cl <sup>-</sup> ) <sub>2</sub> }	518 (13.0)	620 <sup>c</sup>	60 <sup>c</sup>	$2 \times 10^{-4}$	645	345	
			720	23				
4	{Pt(H <sub>2</sub> -Cy <sub>2</sub> -dto) <sub>2</sub> <sup>2+</sup> , (Cl <sup>-</sup> ) <sub>2</sub> }	520 (12.8)	610 <sup>c</sup>	<i>d</i> <sup>c</sup>	$8 \times 10^{-4}$	650	510	
			725	18				
5	{Pt(H <sub>2</sub> -Cy <sub>2</sub> -dto) <sub>2</sub> <sup>2+</sup> , (Br <sup>-</sup> ) <sub>2</sub> }	520 (12.5)	620 <sup>c</sup>	<i>d</i> <sup>c</sup>		645	480	
			730	20				
6	{Pt(H <sub>2</sub> -Cy <sub>2</sub> -dto) <sub>2</sub> <sup>2+</sup> , (I <sup>-</sup> ) <sub>2</sub> }	520 (13.8)		730	18		645	490

<sup>a</sup> Solvent used: dichloromethane (room temperature) or butyronitrile (77 K). For the absorption spectra, only visible maxima are reported.

<sup>b</sup> Excitation wavelength 500 nm except as otherwise noted. <sup>c</sup> Excitation wavelength 450 nm. <sup>d</sup> Luminescence too low to measure lifetime.

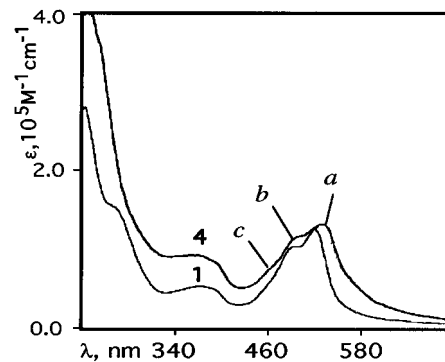
this confirms that the electronic spectra refer to the following two reversible acid–base processes:



As a consequence, the ion pairs 1–7 have the same coordination as the rubeanate complexes 8–11, for which the PtS<sub>4</sub> square planar environment has been shown by an X-ray analysis.<sup>25a</sup>

Mass spectrometry affords further useful information for the full characterization of 1–11. Rubeanate compounds 8, 9, and 11 show intense molecular peaks of  $M^+ = 657.1$  (9), 489.0 (8), 761.3 (11), characterized by the typical isotopic pattern of platinum-containing compounds. As far as ion pairs 1–7 are concerned, only 2 shows a low intensity (<1%) but a significant molecular peak of  $M^+ = 729$ , characterized by the usual platinum isotopomer pattern. The other hydrohalogenated compounds, except 3, exhibit the molecular peaks of the corresponding neutral rubeanate complexes, together with an intense peak of HX, which was absent in the mass spectra of 8, 9, and 11. Finally, both benzyl derivatives 3 and 10 decompose under the actual experimental conditions and do not provide reliable mass spectra.

Dithiooxamides as neutral chelate ligands bear one hydrogen atom on each amidic nitrogen, and this implies that the two NCS moieties are twisted toward each other. The torsional angle (about 40°) seems to be independent of the central metal (Zn, Cu, Sn, and Bi) and coordination geometry (square planar, tetrahedral, octahedral, bipyramidal),<sup>24c,26</sup> and therefore it is probably a structural feature of neutral chelating dithiooxamides. Notwithstanding, R alkyl substituents on nitrogen in 1–7 are magnetically equivalent in the <sup>1</sup>H NMR spectra; in particular, N-CH<sub>3</sub> and N-CH<sub>2</sub>-Ph resonances appear in the <sup>1</sup>H NMR spectrum as a unique, sharp singlet at room-temperature and N-CH<sub>2</sub>-*n*-propyl, as a unique, sharp triplet. These signals become broad at low temperatures, and in the case of the butyl derivative, the triplet of N-CH<sub>2</sub>- coalesces at 180 K. Since a high barrier torsional angle in 1–7 should result in complicated ABX<sub>*n*</sub> (*n* = 0, 2) patterns in the <sup>1</sup>H NMR spectra, a fast-exchange mechanism should be invoked. This can be obtained by either Cl<sup>-</sup> or HCl exchange. However, chloride exchange may be ruled out since the <sup>1</sup>H NMR spectrum of 7 exhibits a



**Figure 2.** Absorption spectra of compounds 1 and 4 in dichloromethane solution. The visible maxima or shoulders labeled as a, b, and c are discussed in the text.

single butylic pattern, and this can be only explained by a rapid HCl exchange through the various nitrogen sites. The fast HCl exchange makes it difficult to draw a molecular formula for compounds 1–6. We had previously observed that for the organoplatinum complex {(Me)ClPt(H<sub>2</sub>-Bz<sub>2</sub>-dto)<sup>+</sup>, Cl<sup>-</sup>}, N-H...Cl signals at about 13.5 ppm appear in the <sup>1</sup>H NMR spectrum as two broad coalescing singlets at room-temperature; these singlets become sharp and well separated below 240 K.<sup>27</sup> In other words, when the hydrogen atoms are fixed on amidic nitrogens, each of them is engaged in a strong N-H...Cl interaction. On these bases, we can provide the molecular formula {Pt(H<sub>2</sub>-R<sub>2</sub>-dto)<sub>2</sub><sup>2+</sup>, (X<sup>-</sup>)<sub>2</sub>} (Figure 1) for the complexes with neutral dithiooxamides linked to platinum(II).

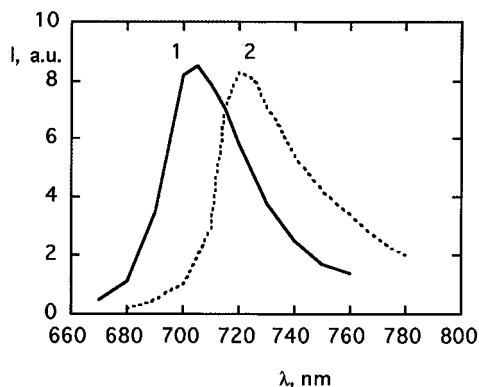
All the studied complexes are fairly stable in low-polarity solvents such as dichloromethane or chloroform, as shown by the constancy of their absorption and emission spectra after a few days, whereas they rapidly decompose in methanol or acetone to yield the neutral species [Pt(H-R<sub>2</sub>-dto)<sub>2</sub>]. The same neutral species are also obtained by shaking a chloroform solution of 1–6 with water. Interestingly, 1–6 can be rapidly restored by double-phase reactions of [Pt(H-R<sub>2</sub>-dto)<sub>2</sub>] in chloroform with aqueous HX. This permits a convenient and easy route to efficiently exchange X in these compounds.

The spectroscopic and photophysical spectral data for 1–6 are gathered in Table 4. Figure 2 shows absorption spectra of 1 and 4 in dichloromethane solution, Figure 3 shows luminescence spectra of 1 and 2 at room-temperature, Figure 4 shows emission spectra of 3 at two different excitation wavelengths, and luminescence spectra (at room-temperature) of 4–6 are shown in Figure 5.

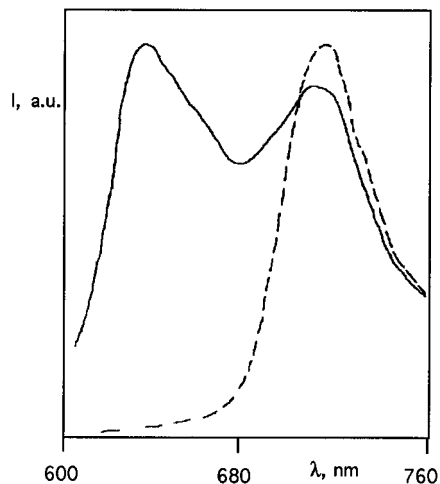
Absorption spectra of 1–6 in dichloromethane (Table 4, Figure 2) are dominated by moderately intense bands in the

(26) Drew, M. G. B.; Kisenyi, J. M.; Willey, G. R. *J. Chem. Soc., Dalton Trans.* **1984**, 1723.

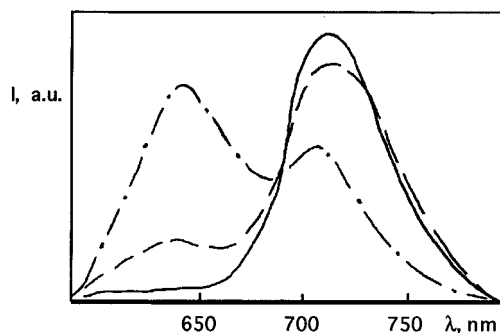
(27) Lanza, S.; Monsù Scolaro, L.; Rosace, G. *Inorg. Chim. Acta* **1994**, *227*, 63.



**Figure 3.** Room-temperature luminescence spectra of compounds **1** and **2** in dichloromethane solution. Excitation wavelength: 500 nm.



**Figure 4.** Room-temperature luminescence spectra of compound **3** in dichloromethane solution: solid line, excitation wavelength 450 nm; dashed line, excitation wavelength 500 nm.



**Figure 5.** Room-temperature luminescence spectra of compounds **4** (— · —), **5** (---), and **6** (—) in dichloromethane solution. Excitation wavelength is 450 nm in all cases.

visible region, with a maximum in the 500–530 nm range ( $\epsilon$  in the range  $10^4$ – $10^5$   $M^{-1} \text{ cm}^{-1}$ ) and by an absorption feature lower in intensity at about 350 nm ( $\epsilon$  in the range  $10^3$ – $10^4$   $M^{-1} \text{ cm}^{-1}$ ). More intense absorption bands appear at much higher energies. The Lambert–Beer law holds for all the compounds studied in dichloromethane within the concentration range investigated ( $2 \times 10^{-5}$ – $2 \times 10^{-4}$  M), indicating that no aggregation (e.g., dimerization) occurs in this concentration range.

All of the compounds exhibit luminescence both at 77 K in a rigid matrix and at room-temperature in fluid solution (Table 4). Room-temperature luminescence spectra are unstructured and centered at about 720 nm. Their shapes do not depend on concentration of the compounds within the concentration range investigated. For the chloride-containing compounds, the

emission energy decreases in the series **1**, **2**, **3**, and **4**. Compounds **5** and **6** exhibit very similar luminescences at slightly lower energies. Compounds **3**–**5** also exhibit a second luminescence band at higher energies. Emission spectra are independent of excitation wavelength for **1** and **2** whereas they are dependent on the wavelength of the excitation light for **3**–**5**. In particular, excitation at 500 nm (the maximum of the absorption spectra in the visible region) maximizes low-energy emission, while excitation at 450 nm (corresponding to a shoulder at the blue side of the main absorption band; see later) maximizes high-energy emission. Luminescence lifetimes are on the  $10^{-8}$ – $10^{-7}$  s time scale. At 77 K in a rigid matrix, only one luminescence band is found for all the complexes, for each excitation wavelength; 77 K luminescence lifetimes are on the  $10^{-7}$ – $10^{-6}$  s time scale.

## Discussion

The spectroscopic and photophysical properties of transition metal complexes and of organometallic compounds are usually discussed with the assumption that the ground state as well as the excited states used to interpret the observed properties can be described by a localized molecular orbital configuration.<sup>28</sup> Within such an assumption, the various spectroscopic transitions (and the corresponding excited states) are classified as metal-centered (MC), ligand-centered (LC), or charge-transfer (metal-to-ligand, MLCT, ligand-to-metal, LMCT, or ligand-to-ligand, LLCT). This simplified picture, of course, is less applicable when a large degree of covalency exists in metal–ligand bonds.<sup>13,20,28</sup>

**Absorption Spectra.** We assign the strong absorption bands in the visible region exhibited by all the complexes (Table 4, Figure 2) to Pt( $d\pi$ )/S( $p$ )  $\rightarrow$  dithiooxamide ( $\pi^*$ ) CT transitions (this transition, and the corresponding excited state, will be hereafter named Pt/S  $\rightarrow$  dto CT), on the basis of (i) the sensitivity of the absorption band energy to the substituents of the dithiooxamide moieties (Table 4), (ii) the extinction coefficients of the bands (Table 4), (iii) the absence of any absorption feature in the visible region in the absorption spectra of the free ligands, and (iv) the structural and electronic similarities between the Pt(II)–dithiolate complexes<sup>18b,c,29</sup> and the Pt(II)–dithiooxamide compounds. The visible absorption maximum is in any case followed by a shoulder at slightly higher energy (e.g., see Figure 2 for **4**, where the dominant visible maximum *a* is followed by the shoulder *b*;  $\Delta E$  between the maxima  $\sim 1300$   $\text{cm}^{-1}$ ). This higher energy shoulder could be attributed to another Pt/S  $\rightarrow$  dto CT transition or to the vibrational progression of the main band. The energy difference is equivalent to the C=N and C=C stretching frequency, so that if the latter hypothesis is true, this frequency mode would be the dominant vibrational progression of the Pt/S  $\rightarrow$  dto CT excited state of **1**–**6**. It can be recalled that C=C and C=N stretching modes are the dominant vibrational modes of the ground and excited states of polypyridine metal complexes.<sup>9–11</sup> The fact that the same vibrational modes could also be the dominant modes in these complexes would suggest an interesting similitude between dithiooxamide and polypyridine metal compounds.

The Pt/S  $\rightarrow$  dto CT transition warrants further comments: the Pt(II) metal ion provides a large electronic coupling between the two chelating sulfur-containing ligands, as demonstrated in

(28) (a) Balzani, V.; Carassiti, V. *Photochemistry of Coordination Compounds*; Academic: London, 1970. (b) Lees, A. J. *Chem. Rev.* **1987**, *87*, 711.

(29) Pt(II)–dithiolate compounds exhibit typical Pt/S  $\rightarrow$  dto CT absorption bands peaking at wavelengths longer than 500 nm ( $\epsilon$  in the range  $10^4$ – $10^5$   $M^{-1} \text{ cm}^{-1}$ ).<sup>18</sup>

square-planar  $d^8$  complexes of Ni(II), Pd(II), and Pt(II).<sup>21,30</sup> The HOMO in the series of complexes **1–6** is therefore probably well described as delocalized on both the ligands, receiving contribution from the Pt( $d\pi$ ) and all the S( $p$ ) orbitals. On the other hand, depending on the electronic coupling between the ligands, the molecular LUMO will be centered on the amidic moiety of a single dto ligand or delocalized on the entire molecule (nevertheless, mainly centered on the amidic moieties of both the ligands). A definitive preference for one of the two hypotheses is impossible with the experimental data in our hands: however, due to the very small solvent sensitivity of the absorption band (solvents used: dichloromethane, chloroform, benzene), we believe that a  $\pi^*$  LUMO delocalized on the two dto ligands is more likely.<sup>31</sup> In this case, this electronic transition (and the excited state) should not have a net CT contribution, in that the overall electric dipole of the molecule does not change. However, because of the redistribution of the density of charge upon excitation (an electron is shifted from the center of the molecule, where the HOMO is essentially located, to the periphery, where the LUMO is centered), sensitivity to the environment (for example to the nature of the ion-paired anions; see later) is expected. From this discussion, it appears that the electronic transition under study is a particular type of CT transition. We will continue to call it (and the corresponding excited state) as Pt/S  $\rightarrow$  CT for the sake of simplicity.

Another electronic transition contributes to the strong absorption at about 500 nm, and it can be noticed in the blue side of the main band, clearly visible as a shoulder at 460 nm for **4** (Figure 2, shoulder *c*). Because of its intensity, this shoulder cannot be attributed to MC transitions, so that MLCT or LC transitions should be responsible for it. Similar absorption bands ( $\lambda_{\max}$  at about 450 nm) are present in the spectra of the neutral parent compounds [Pt(H–R–dto)<sub>2</sub>].<sup>26</sup> As a consequence, a LC assignment seems to be most likely. MLCT transitions, in fact, should be more sensitive to the different charge densities on the dto ligands in neutral [Pt(H–R–dto)<sub>2</sub>] and ion-paired {Pt-(H<sub>2</sub>–R–dto)<sub>2</sub><sup>2+</sup>, (X<sup>-</sup>)<sub>2</sub>} species (the possibility that the absorption shoulder *c* is a vibrational component of the main band (*a* + *b*) or that it is due to partial contamination of **1–6** owing to the presence of the parent neutral species can be excluded on the basis of the photophysical properties; see later).

It is interesting to note that, on the basis of the electron-donor power of the R substituents, the Pt/S  $\rightarrow$  dto CT bands could be expected to move to higher energies in the order **1** < **3**  $\leq$  **2** < **4** (**5** and **6** are left aside for simplicity). This order is not found in the absorption properties (see Table 4). The experimental order for the absorption band energies **4** < **3** < **2** < **1** is the reverse order of the steric hindrance of the R substituents. Such a result can be explained when one considers that, in tight ion pairs like the ones studied here, also CT interactions (and states) involving the paired ions (outer-sphere CT) may play important roles.<sup>32</sup> In our compounds, CT interactions between the chloride anions and dto can destabilize the  $\pi^*$  orbital of the dto ligands. These interactions depend on the proximity of chloride to dto, which in its turn can be governed by steric hindrance. Bulky substituents can prevent

or diminish ion-pair interactions, leading to decreased electron density on the dto ligands and moving the Pt/S  $\rightarrow$  CT transition to lower energies. The effect of the substituents of the dto nitrogens on the absorption (and emission; see later) energy should be therefore a consequence of the different steric hindrance.

The following alternative explanation could also be taken into account: It should be noted that substituents on nitrogen are essentially  $\sigma$ -donor groups. Donor ability could be transferred across the  $\sigma$ -backbone of the dto ligands to the Pt/S region, and its main effect would be destabilization of the HOMO. Destabilization of the LUMO (dto-centered  $\pi^*$  orbitals) could be less important. As a consequence, Pt/S  $\rightarrow$  CT transitions should move to lower energy with increased  $\sigma$ -donor ability of R, according to the experimental results. Nevertheless, a slight (although not definitive) preference for the former explanation is suggested from the differences in the LC shoulder intensity in the series **4–1** (Figure 2). In fact, intensity of the LC shoulder at about 460 nm decreases in the series **4**, **3**, **2**, **1**. This can be explained by considering that strong interactions between the ions in the tight contact ion pairs could lead to an increased distortion of the dto backbone, yielding different intensities of dto-centered transitions. This confirms that interpenetration of the ion pairs significantly modifies the electronic properties of the compounds under study.

**Luminescence Properties.** We assign luminescence of **1–6** at  $\sim$ 720 nm at room-temperature and at  $\sim$ 640 nm at 77 K to triplet Pt/S  $\rightarrow$  CT levels, on the basis of the following arguments: (i) matrix sensitivity of the emission energy (which tends to rule out LC and MC assignments); (ii) energy maximum dependence on the R substituents of the dto ligands; (iii) luminescence lifetimes, which are on the same time scale as luminescence lifetimes for Pt(II)–dithiolate emission, already assigned to Pt/S  $\rightarrow$   $\pi^*$ (thiolate) CT levels.<sup>18b</sup> The effect of the R substituents on excited state energy can be explained with the same arguments used to discuss absorption spectra (see above).

The second emission exhibited by **3–6** at room-temperature has the absorption counterpart in the absorption feature at  $\sim$ 450 nm, as clearly demonstrated by excitation spectroscopy (not shown), and is therefore assigned to excited states centered in the dto ligands.<sup>33</sup> Further support for such an assignment comes from the luminescence at 620 nm of the somewhat similar compound Zn(tdt)<sub>2</sub> (tdt<sup>2-</sup> = 3,4-toluenedithiolate),<sup>34</sup> a *bona fide* LC emitter.

An interesting point to be discussed here is the double emission exhibited by some of the complexes at room-temperature (Table 4). Multiple emission in mononuclear metal complexes is rare and usually occurs at low temperature.<sup>13,19,35–37</sup> In most of the cases, multiple emission originates from two closely-lying excited states which can equilibrate at room-

(30) (a) McCleverty, J. A. *Prog. Inorg. Chem.* **1968**, 10, 49. (b) Schrauzer, G. N. *Acc. Chem. Res.* **1969**, 2, 72. (c) Burns, R. P.; McAuliffe *Adv. Inorg. Chem. Radiochem.* **1979**, 22, 303.

(31) A complete study of the solvent sensitivity of the band is hampered because of the instability of the compounds in polar solvents.

(32) (a) Sexton, D. A.; Curtis, J. C.; Cohen, H.; Ford, P. C. *Inorg. Chem.* **1984**, 23, 49. (b) Pina, F.; Maestri, M.; Ballardini, R.; Mulazzani, Q. G.; D'Angelantonio, M.; Balzani, V. *Inorg. Chem.* **1986**, 25, 4249. (c) Billing, R.; Rehorek, D.; Hennig, H. *Top. Curr. Chem.* **1990**, 158, 151. (d) Reference 1, Chapter 8.

(33) This high-energy emission cannot be due to [Pt(H–R–dto)<sub>2</sub>] impurities, because the latter species are not luminescent under any conditions. On the other hand, the fact that excitation in the 455 nm shoulder gives different emission spectra than excitation at the other wavelengths in compounds **3–6** definitely rules out the assignment of this absorption shoulder (labeled as *c* in Figure 2 for compound **4**) to a vibrational component of the lowest energy CT band.

(34) Benedix, R.; Hennig, H.; Kunkely, H.; Vogler, A. *Chem. Phys. Lett.* **1990**, 175, 483.

(35) Colombo, M.; Hauser, A.; Güdel, H. U. *Top. Curr. Chem.* **1994**, 171, 143.

(36) A different situation is the case of multiple emissions in multinuclear metal complexes. In such multinuclear systems, in fact, multiple emissions can originate from inefficient energy transfer among the chromophores.<sup>37</sup>

(37) Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Serroni, S. *Chem. Rev.* **1996**, 96, 759.

temperature, while they are essentially independent at 77 K in rigid matrices. Inefficiency of direct conversion between excited states is attributed to high nuclear barriers. The behavior of compounds **3**–**6** is somewhat surprising, in that double emission is only found at room-temperature (Table 4). This somewhat puzzling behavior can be rationalized as follows.

The experimental results (Table 4) indicate that high-energy emission becomes more and more important on passing from **1** and **2** (for which high-energy 640 nm emission is totally absent) to **3** and **4**. This suggests that emission at 640 nm becomes dominant over the 720 nm emission when the steric hindrance of the R substituents increases (i.e., with decreased close proximity of the ions in the tight ion pairs). Therefore, a role of the halide counterions in promoting conversion between LC and Pt/S  $\rightarrow$  CT states can be envisaged. This role could be the efficient participation of a high-lying X  $\rightarrow$  CT level in mediating excited state conversion.<sup>38</sup>

It can be pointed out that conversion of a dto-centered ( $\pi \rightarrow \pi^*$ ) level into a Pt/S  $\rightarrow$  CT state corresponds to electron transfer from a Pt/S  $\sigma$ -bond orbital to a  $\pi$  orbital of dto. Significant distortions within the molecule structure are expected for such an electron transfer, due to the reduced strength of the Pt–S bond, so that nuclear barriers are indeed possible. Due to the tight contact ion pair nature of the compounds, the dto-centered level could be easily converted into a higher-lying X  $\rightarrow$  CT level (this would be a thermally activated process), which in its turn would afford the final Pt/S  $\rightarrow$  CT state by Pt/S to halide electron transfer. Significant distortions are also expected for this electron transfer, but the higher driving force could overcome the nuclear barriers. The above mentioned hypothesis is almost equivalent to considering that excited state conversion from LC and Pt/S  $\rightarrow$  CT levels can be promoted by mixing between LC and X  $\rightarrow$  CT levels. In this case, however, effective production of the X  $\rightarrow$  CT state is not necessary. The conclusion that can be inferred from both viewpoints is that the more the halides approach the dto ligands (e.g., in **1** and **2**), the more efficient would be the X  $\rightarrow$  CT level in promoting conversion between LC and Pt/S  $\rightarrow$  CT excited states.

At 77 K, the rate constants of the direct deactivations to the ground state of the LC level decrease, so that conversion to the

Pt/S  $\rightarrow$  CT level can efficiently compete with luminescence from LC levels even for **3** and **4**.

The proposed mechanisms could be confirmed by the results obtained for **5** and **6**, compared to **4**. In compounds **5** and **6**, in fact, we used bromide and iodide instead of chloride, respectively, to form tight contact ion pairs. Br  $\rightarrow$  and I  $\rightarrow$  CT levels are lower in energy than the Cl  $\rightarrow$  CT state, and the X  $\rightarrow$  CT level is expected to be more efficient in promoting interconversion between LC and Pt/S  $\rightarrow$  CT levels in **5** and **6** than in **4**. The fact that the ratio between LC and Pt/S  $\rightarrow$  CT emissions decreases in the series **4**, **5**, and **6** (Figure 5) is in full agreement with the proposed role for the X  $\rightarrow$  CT level.

It should be noted that, on the basis of the above considerations, one might expect a larger difference in the  $\lambda_{\text{max}}$  in the absorption and emission spectra of **4**–**6**, as also pointed out by one of the reviewers. However, it has been suggested that high-lying excited states can influence excited state dynamics without significantly affecting spectroscopic properties.<sup>39</sup> This seems also to be the case for the compounds studied here.

## Conclusion

Novel tight contact ion pairs of general formula  $\{\text{Pt}(\text{H}_2\text{R}_2\text{-dto})_2^{2+}, (\text{X}^-)_2\}$  have been prepared, and their absorption spectra and luminescence properties (at room-temperature in dichloromethane fluid solution and at 77 K in a butyronitrile rigid matrix) have been studied. The excited state properties of these compounds can be rationalized by taking into account Pt/S  $\rightarrow$  CT, LC, and X  $\rightarrow$  CT levels. Because of the fact that the alkyl substituents on the nitrogen atoms of the dto ligands can be easily functionalized, the compounds studied here can be considered as luminescent components of larger supramolecular assemblies. Work in this direction is underway in our laboratories.

**Acknowledgment.** We thank the MURST and the CNR for financial support.

**Supporting Information Available:** Figure 1S, showing spectral changes of **2** in chloroform upon successive addition of *n*-butylamine (1 page). Ordering information is given on any current masthead page.

IC9514004

(38) Charge transfer transitions involving halides as donors can play significant roles in the deactivation of excited states of metal complexes.<sup>21,32</sup>

(39) Guglielmo, G.; Ricevuto, V.; Giannetto, A.; Campagna, S. *Gazz. Chim. Ital.* **1989**, *119*, 457.