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Inorganica Chimica Acta 345 (2003) 340–344

Inorganica Chimica Acta

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Luminescent η^5-pentamethylcyclopentadienyl tantalum(V) complexes: synthesis, characterization, and emission spectroscopy

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Received 6 August 2002; accepted 24 September 2002

This paper is dedicated to Dick Schrock in recognition of his friendship over the years and his outstanding research which has transformed the way organometallic chemists view metal–carbon bonds and what they can do

Abstract

A series of η^5-pentamethylcyclopentadienyl tantalum(V) complexes have been prepared and their electronic and emission spectra examined. Compounds of the form Cp^*TaX_4 (where X = Cl, Br, OC_6F_5) and $Cp^*TaCl_2X_2$ (where X = OC_6Cl_5, 2,6-$OC_6H_3Cl_2$), as well as $CpTaX_4$, have been found to luminesce at 77 K in frozen glasses (only Cp^*TaCl_4, reported previously, luminesces at ambient temperature in both solid and fluid solution). The shifts in luminescence maxima with ligand variation lead to the conclusion that the emissive state is a ligand-to-metal charge transfer in which the highest occupied orbital is based on the donor atom of one of the monodentate ligands and the lowest unoccupied orbital is Ta-based.

Keywords: Luminescence; Tantalum complexes; Cyclopentadienyl ligands; Emission spectroscopy

1. Introduction

While the luminescence of late transition metal complexes has received a great deal of attention, the corresponding behavior of early metal systems is much more limited and has remained distinctly less explored [1–4]. Only a few examples of luminescent metal complexes having d^0 metal ion configurations have been reported including Cp_2ZrCl_2, $Cp^*_2ZrCl_2$ and their bis thiolate analogs [2], and Cp^*TaCl_4 and its monosubstituted derivatives containing either a triflate or a carboxylate in place of one chloride [1]. Other luminescent d^0 metal complexes contain ligands that form multiple bonds with the metal center such as the imido complexes $Ta(\equiv NR)X_3L_2$ [3–5]. In contrast with emissive late transition metal complexes that generally have metal-to-ligand charge transfer (MLCT) excited states, the early metal cyclopentadienyl derivatives have been assigned as having ligand-to-metal charge transfer (LMCT) luminescent states. For the Zr complexes studied by Yam et al. [2], the shift in emission energy with ligand substitution led to the notion, supported by calculations, that the HOMO in these complexes is primarily a chloride or thiolate-based p-orbital with an empty Zr d-orbital as the LUMO. On the other hand, in studies of the Cp^*TaX_4 complexes by Sullivan and coworkers [1], it was proposed that the HOMO for the LMCT excited state was mainly cyclopentadienyl-based rather than X-based.

In an examination of different heavy metal emitters for possible application in display technology utilizing OLED's, we were impressed by the intensity of the yellow emission from Cp^*TaCl_4 in the solid state at ambient temperature. In the earlier study by Sullivan, a series of luminescent derivatives was created by substitution of a single chloride ligand with a chelating carboxylate anion [1]. In the present study, we have endeavored to replace all of the chlorides of Cp^*TaCl_4 by other monodentate anionic ligands. The choice of X-type ligand was made based on both its electronic nature and its structure. Since Cp^*TaCl_4 hydrolyzes very readily under ambient conditions [6], the use of bulkier

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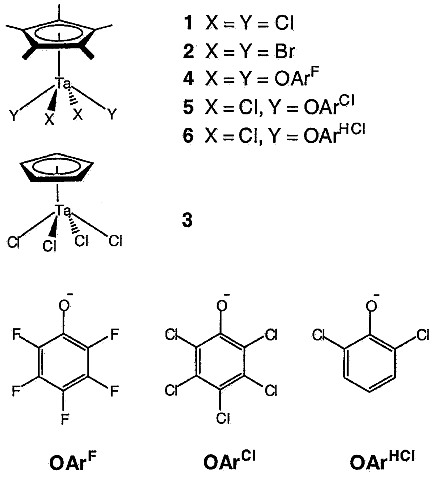
PII: S0020-1693(02)01276-8

ligands was considered to have the possibility of imparting some stability to the Cp*TaX_4 complexes. The ligands used in this study are phenoxides, and the resultant complexes shown in Scheme 1 have led to modification of the LMCT assignment made by Sullivan and co-workers [1].

2. Results and discussion

Complexes **1**–**6** (see Scheme 1) were prepared and characterized by different spectroscopies and by elemental analyses (C, H). While all of the compounds appear to be pure by ^{1}H NMR spectroscopy, elemental analyses were only satisfactory for **4** and **6** and just slightly outside the acceptable limit for **5** (the crystalline sample of **5** may have had occluded solvent, thus explaining the slightly higher C result). For both **2** and **3**, however, multiple analyses from different recrystallized or reprecipitated samples yielded results that were unacceptably low in carbon. Difficulties of this type have been observed previously in analyzing other cyclopentadienyl complexes. The absorption spectrum and 77 K frozen glass emission spectrum were obtained for each complex with spectroscopic results provided in Table 1. In these measurements, the absorption spectroscopy was obtained in toluene, while the emission measurements were made in a toluene glass. Each of the complexes, except for **1**, displayed no room temperature luminescence in the solid state or fluid solution. Fig. 1 shows the emission of **2**, **4** and **5** in toulene glasses.

Compounds **2** and **3** were examined first because of their very similar electronic nature to **1**. Substitution of bromide for chloride in **2** and Cp for Cp* in **3** provided a simple means of gauging the effect of ligand substitution at each of these positions. The absorption spectrum for **1** and **2** shows two distinguishable features. Each compound exhibits a strong absorption around 28,300 cm^{-1} ($\varepsilon \sim 2000\ M^{-1}\ cm^{-1}$) and a weaker absorption in the visible region of the spectrum between 20,600 and 23,000 cm^{-1} ($\varepsilon \sim 500\ M^{-1}\ cm^{-1}$). On the other hand, the absorption spectrum of compound **3** shows a broad absorption between 20,600 and 30,600 cm^{-1}. The emission spectra of **1**–**3** at 77 K in frozen toluene each consist one band with that of compound **2** shifted to lower energy from the bands of **1** and **3** by approximately 1100 cm^{-1}. While the substitution of Cp for Cp* does not affect the emission energy significantly, the substitution of bromide for chloride clearly does. These initial results thus suggest that the emission in the Cp$^{(*)}$$TaX_4$ complexes may involve charge transfer from the X ligand to the metal rather than from Cp*, as proposed previously [1].



Scheme 1.

Table 1
Absorption and emission energies (cm^{-1}) for Cp*Ta(V) complexes

Complex	E_{abs} (M^{-1} cm^{-1}) [a]	E_{em} [b]
Cp*$TaCl_4$ (**1**)	28,800 (1870) 23,100 (670)	18,300
Cp*$TaBr_4$ (**2**)	28,400 (2010) 21,100 (250)	17,200
Cp$TaCl_4$ (**3**)	30,300 (1250)	18,300
Cp*$Ta(OC_6F_5)_4$ (**4**)	30,000 (4010)	19,000
Cp*$Ta(OC_6Cl_5)_2Cl_2$ (**5**)	27,100 (4010)	18,300
Cp*$Ta(OC_6H_3Cl_2)_2Cl_2$ (**6**)	28,100 (3090)	
Cp*$Ta(OPh)_4$	30,200 (2680)	

[a] Absorption spectra at 298 K.

[b] Emission spectra at 77 K in toluene glass.

Compounds **4**–**6** were synthesized to explore further ligand effects on the excited state of the formally d^0 Ta(V) Cp*TaX_4 system and to attempt to overcome hydrolysis tendencies arising from the oxophilicity of tantalum [7,8]. The complexes were prepared from compound **1** by reaction with the desired phenol in the presence of triethylamine. The pentafluoro- and pentachlorophenoxide ligands were chosen because of their lack of hydrogen atoms. In addition to **4**–**6**, other Cp*TaX_4 phenoxide complexes with X = OPh, *p*-OC_6H_4OMe, *p*-OC_6H_4-i-Pr were synthesized, but these complexes were found not to be photo-emissive. The lack of luminescence from any of the Cp*TaX_4 systems containing C–H bonds may relate to the involvement of these bonds in facile non-radiative decay pathways. For complex **4**, the fluorine atoms provided a convenient NMR handle in the characterization of the complex, but for complex **5**, a similar ease of NMR characterization was missing. Previously, it had been reported that steric hindrance from groups located in the 2 and 6 positions of the phenol ring interfered with the formation of a tetra-substituted complex [8], and therefore, it was not evident whether complete substitution of pentachlorophenoxide had occurred. To examine this question more closely, compound **6** was synthesized and found by ^{1}H NMR spectroscopy to contain two phenoxide and two

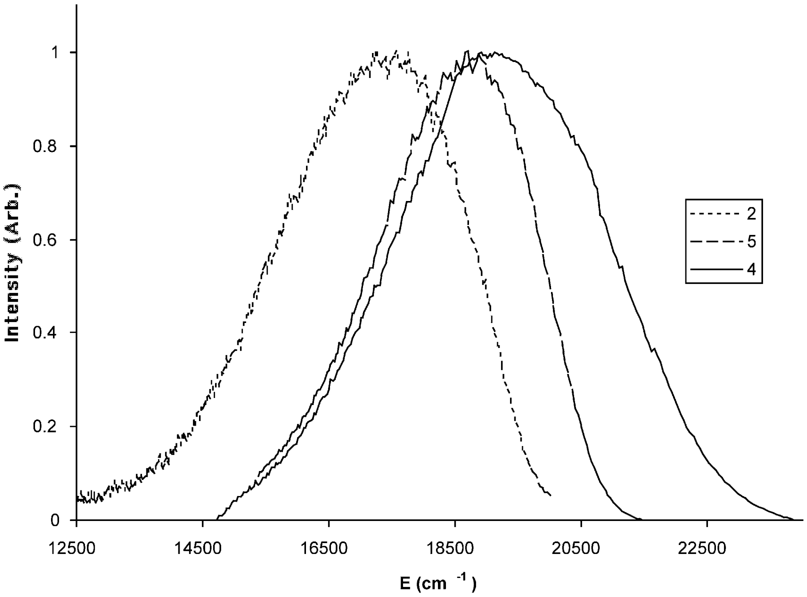


Fig. 1. Emission spectra of Cp^*TaBr_4 (**2**), $Cp^*Ta(OC_6F_5)_4$ (**4**) and $Cp^*Ta(OC_6Cl_5)_2Cl_2$ (**5**) in a toluene frozen glass at 77 K. Excitation energies are 22,200 cm^{-1} (450 nm) for **2**, 26,700 cm^{-1} (375 nm) for **4** and 24,100 cm^{-1} (415 nm) for **5**.

chloride ligands. The two pairs of phenoxide ligands in **5** and **6** are presumably in a *trans* relationship due to steric reasons. Additionally, each compound showed only one Cp* resonance in the NMR spectrum indicating that only a single isomer of each $Cp^*TaCl_2(OAr)_2$ complex (**5** and **6**) was present.

The absorption spectrum of compound **4** displays an intense band around 30,000 cm^{-1}, similar to those of compounds **1** and **2**, but lacks the lower energy band found for those complexes. The absorption spectrum of $Cp^*Ta(OPh)_4$ is similar to that of **4** with only one band around 30,000 cm^{-1}. The absence of the lower energy absorption band accounts for the colorless nature of **4** and $Cp^*Ta(OPh)_4$ in solution, whereas both of the chloride-containing complexes **5** and **6** are yellow in solution. The results from the electronic spectra of the different Cp*Ta complexes suggest that absorption in the visible region of the spectrum involves a chloride ligand and associated ligand-to-metal charge transfer. For **5** and **6**, the absorption spectra each show only one very broad band with a maximum around 28,000 cm^{-1}, unlike the spectra for **1** and **2** that exhibit two distinct absorptions, but the single bands are broad enough to encompass the lower energy chloride-based transitions.

From Table 1, it is seen that the three emissive compounds that contain chloride as a ligand, including the dichloride complex **5**, have approximately the same energy (18,300 cm^{-1}) whereas for the bromide complex **2**, the emission shifts to lower energy and for the pentafluorophenoxide complex **4** the emission is blue-shifted, as seen in Fig. 1. (In Fig. 2, the emission and excitation spectra of **5** are shown.) The results are consistent with an LMCT excited state in which an X ligand orbital acts as the highest occupied molecular orbital (HOMO). This assignment agrees with that made by Yam for the Cp_2ZrX_2 systems, but differs from that made by Sullivan in which the Cp ligand was proposed to be involved in the transition as the origin of the HOMO. While low temperature lifetime measurements were not performed for the complexes in the present study, the previous assignment of a triplet excited state to the Cp^*TaCl_4 complex [1] gives credence to the notion that in these Ta complexes, the excited state is in fact a triplet.

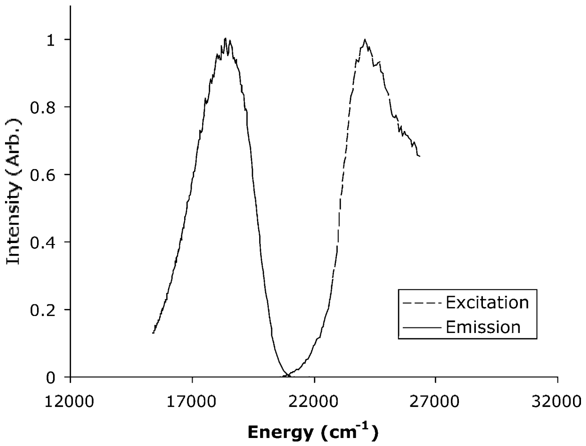


Fig. 2. Emission and excitation spectra of $Cp^*Ta(OC_6Cl_5)_2Cl_2$ (**5**) in a toluene frozen glass at 77 K. Excitation was at 24,100 cm^{-1} (415 nm) and emission was monitored at 18,700 cm^{-1} (535 nm).

3. Conclusion

Derivatives of Cp^*TaCl_4 have been synthesized and examined by emission spectroscopy. The phenoxide derivatives appear to be sensitive to steric hindrance in the 2, 6 positions of the aromatic ring, but appear somewhat more robust than the Cp*TaX_4 complexes. Based on 77 K emission measurements, the luminescence from the Cp*TaX_4 derivatives appears to arise from a ligand-to-metal charge transfer excited state (LMCT) involving orbitals based on the X-type ligands, in contrast with an earlier assignment for related Cp*Ta complexes.

4. Experimental

4.1. General procedures

All reactions were carried out under an inert atmosphere in a Vacuum Atmospheres glove-box or using standard Schlenck line techniques. Solvents were degassed and passed through activated alumina prior to use. NMR solvents were dried over Linde molecular sieves and referenced to the residual solvent peak in the case of ^{1}H and ^{13}C NMR spectra or to trifluorotoluene in the case of ^{19}F NMR spectra. Cp*H, trimethylsilyl chloride (TMSCl), pentachlorophenol, 2,6-dichlorophenol and pentafluorophenol were purchased from Aldrich and used as received. $TaCl_5$ and $TaBr_5$ were purchased from Strem and TMSCl was purchased from Acros and used as received.

4.2. Measurements

Absorption spectra were recorded in $C_6H_5CH_3$ in resealable quartz cuvettes. Measurements were taken on a Hitachi U2000 vis/uv spectrophotometer. Emission spectra were recorded in $C_6H_5CH_3$ glasses at 77 K in sealed EPR tubes. The measurements were taken on a SPEX Fluorolog-3 flourometer with a low temperature Dewar apparatus.

4.3. Potassium pentamethylcyclopentadienide, KCp*

A slurry of 2.56 g (0.064 mol) of potassium hydride in 40 ml of THF was chilled at −30 °C for 1 h. To this slurry was added drop-wise 10 ml (0.064 mole) of cold Cp*H. The mixture was allowed to warm to room temperature (r.t.) and then heated at 70 ° for 2 h during which time vigorous gas evolution occurred. After heating, 20 ml of hexanes was added and the reaction mixture filtered. The filtered product was dried in vacuo, yielding 9.94 g (89% yield) of a white powder.

4.4. (Trimethylsilyl)pentamethylcyclopentadiene, TMSCp*

To a slurry of 3.50 g (0.020 mol) of KCp* in 50 ml of THF at 0 ° was added, drop-wise, 2.8 ml (0.022 mol) of TMSCl. The reaction was stirred at r.t. for 12 h, and then filtered through celite. The solvent was removed in vacuo giving 4.45 g (97% yield) of a pale yellow oil. ^{1}H NMR (CD_2Cl_2): δ 1.75 (s, 15H); δ −0.15 (d, 9H) [9].

4.5. η^5-Pentamethylcyclopentadienyl tantalum tetrachloride, Cp*$TaCl_4$

The previously reported complex [10] was prepared via a slightly modified procedure reported here. A slurry of 7.64 g (0.021 mol) of $TaCl_5$ in 50 ml of $C_6H_5CH_3$ was chilled at −30 °C for 30 min. In a separate vial, 4.45 g (0.021 mol) of TMSCp* was dissolved in 15 ml of $C_6H_5CH_3$ and the solution chilled to −30 °C. The cold TMSCp* solution was added drop-wise to the slurry of $TaCl_5$, and the resulting red reaction mixture stirred for 12 h at r.t. While stirring, a bright orange–yellow precipitate formed in the reaction flask. The precipitate was collected by filtration and dried in vacuo, yielding 7.79 g (80% yield) of an orange–yellow powder. ^{1}H NMR (CD_2Cl_2): δ 2.71 (s). ^{13}C NMR (CD_2Cl_2): δ 133.8 (C_5Me$_5$); δ 14.5 (C$_5$$Me_5$) [10].

4.6. η^5-Pentamethylcyclopentadienyl tantalum tetrabromide, Cp*$TaBr_4$

The bromide complex was prepared by an analogous route as the chloride starting from 1.99 g (0.0034 mol) of $TaBr_5$. The complex was isolated as 1.71 g (80% yield) of an orange powder. ^{1}H NMR (CD_2Cl_2): δ 2.92 (s). Elemental analysis results were unsatisfactory, suggesting the possible presence of unreacted $TaBr_5$ but the compound appeared pure by NMR spectroscopy. *Anal*. Calc. for $C_5H_{15}Br_4Ta$: C, 18.89; H, 2.38. Found: C, 7.98; H, 1.70%.

4.7. η^5-Cyclopentadienyl tantalum tetrachloride, Cp$TaCl_4$

The Cp analog of Cp*$TaCl_4$ was prepared according to a slightly modified literature procedure beginning with 2.15 g (0.0060 mol) of $TaCl_5$ and 1.0 ml (0.0060 mol) of commercial TMSCp [11]. The reaction produced 1.55 g (67% crude yield) of a brown powder that was recrystallized from CH_2Cl_2 giving pink crystalline needles. ^{1}H NMR (CD_2Cl_2): δ 7.07 (s).

4.8. η^5-Pentamethylcyclopentadienyl tantalum tetrapentafluorophenoxide, Cp*$Ta(OC_6F_5)_4$

Cp*$TaCl_4$ (0.250 g, 0.546 mmol) and pentafluorophenol (0.412g, 2.24 mmol) were combined in a reaction vessel and 45 ml of $C_6H_5CH_3$ was transferred in vacuo at 77 K. The reaction was allowed to warm to 196 K and Et_3N (approximately 1 ml) was transferred in vacuo at which point the yellow reaction mixture became an orange solution. The reaction was then allowed to warm to r.t. and stir for 16 h during which time the orange solution became pale yellow and a precipitate formed. The reaction was filtered through celite and the volatiles removed in vacuo giving 0.220 g (38% yield) of a white powder which was recrystallized from Et_2O. ^1H NMR (CD_2Cl_2): δ 2.49 (s). ^{13}C NMR (CD_2Cl_2); δ 137.4 (m, OC_6F_5); δ 130.2 (C_5Me_5); δ 8.7 (C_5Me_5). ^{19}F NMR (C_6D_6): δ −97.03 (d, 8F) ($J_{F-F} = 18.8$ Hz); δ −102.12 (t, 8F) ($J_{F-F} = 20.7$ Hz); δ −104.16 (t, 8F) ($J_{F-F} = 22.5$ Hz). *Anal*. Calc. for $C_{34}H_{15}F_{20}O_4Ta$: C, 38.95; H, 1.44. Found: C, 38.80; H, 1.29.

4.9. *η^5-Pentamethylcyclopentadienyl tantalum bis(pentachlorophenoxide) dichloride, $Cp^*Ta(OC_6Cl_5)_2Cl_2$*

This compound was prepared in an analogous fashion to $Cp^*Ta(OC_6F_5)_4$ starting from 0.207 g of Cp^*TaCl_4 (0.452 mmol) and 0.484 g of pentachlorophenol (1.82 mmol). The resulting yellow residue was washed with Et_2O and filtered to give 0.322 g (78% yield) of a yellow powder that was recrystallized from $C_6H_5CH_3/C_5H_{12}$. ^1H NMR (CD_2Cl_2): δ 2.65 (s). *Anal*. Calc. for $C_{22}H_{15}Cl_{12}O_2Ta$: C, 28.79; H, 1.65. Found: C, 30.30; H, 1.60%.

4.10. *η^5-Pentamethylcyclopentadienyl tantalum bis(2,6-dichlorophenoxide) dichloride, $Cp^*Ta(OC_6H_3Cl_2)_2Cl_2$*

This compound was prepared in an analogous fashion to $Cp^*Ta(OC_6Cl_5)_2Cl_2$ starting from 0.110 g of Cp^*TaCl_4 (0.240 mmol) and 0.613 g of 2,6-dichlorophenol (1.00 mmol). The resulting yellow residue was washed with C_5H_{12} and filtered to give 0.095 g (56% yield) of a yellow powder. ^1H NMR (THF-d_8): δ 7.22 (d, 4H) ($J_{H-H} = 6.5$ Hz); δ 6.78 (t, 2H) ($J_{H-H} = 6.5$ Hz); δ 2.63 (s, 15H). *Anal*. Calc. for $C_{22}H_{21}Cl_6O_2Ta$: C, 37.16; H, 2.98. Found: C, 37.47 H, 3.14%.

4.11. *η^5-Pentamethylcyclopentadienyl tantalum tetraphenoxide, $Cp^*Ta(OPh)_4$*

This previously reported complex [12] was prepared by an alternate procedure analogous to $Cp^*Ta(OC_6F_5)_4$. A white powder was collected (0.103 g) in 33% yield starting from 0.200 g (0.437 mmol) of Cp^*TaCl_4 and 0.186 g (1.98 mmol) of phenol. The compound was recrystallized from Et_2O. ^1H NMR (C_6D_6): δ 7.06 (dd, 8H); δ 6.83 (d, 8H); δ 6.70 (t, 4H); δ 2.11 (s, 15H).

Acknowledgements

This work was carried out with financial support from the Eastman Kodak Company, for which we are grateful. Z.J.T. would also like to acknowledgement Thad Wadas and James McGarrah for assistance with spectroscopic measurements.

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