4262 *Inorg. Chem.* **1999,** *38,* 4262−4267

Spectroscopic Properties of Luminescent Platinum(II) Complexes Containing 4,4′,4″-Tri-*tert*-butyl-2,2′:6′,2″-terpyridine ($^tBu_3$tpy). Crystal Structures of [Pt($^tBu_3$tpy)Cl]ClO_4 and [Pt($^tBu_3$tpy){$CH_2C(O)Me$}]ClO_4

Siu-Wai Lai, Michael C. W. Chan, Kung-Kai Cheung, and Chi-Ming Che*

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong

Received April 26, 1999

The 77 K emission spectrum of [Pt($^tBu_3$tpy)Cl]ClO_4, **1**(ClO_4) ($^tBu_3$tpy = 4,4′,4″-tri-*tert*-butyl-2,2′:6′,2″-terpyridine), in a 10^{-3} mol dm^{-3} MeOH/EtOH glassy solution exhibits a 625 nm band attributed to $^tBu_3$tpy $\pi-\pi$ interactions, whereas a dilute solution (10^{-6} mol dm^{-3}) shows a vibronic intraligand emission at λ_{max} 467 nm. By comparing the UV−vis spectra of **1** with the ^{1}IL-dominated spectrum of [Au($^tBu_3$tpy)Cl]$^{2+}$ (**4**) in CH_3CN, the moderately intense absorption band at λ_{max} 373−386 nm for the former is ascribed to a ^{1}MLCT [(5d)Pt → π^*($^tBu_3$tpy)] transition. The absorption spectrum of **1** contains a weak shoulder at 465 nm (ϵ = 57 dm^3 mol^{-1} cm^{-1}) which obeys Beer's law in the concentration range 5×10^{-4} to 1×10^{-2} mol dm^{-3}, and a ^{3}MLCT assignment is proposed. Ketonyl platinum(II) complexes [Pt($^tBu_3$tpy){$CH_2C(O)R$}]ClO_4 (R = Me, **2** and R = Ph, **3**) have been prepared from **1**(ClO_4) in the presence of aqueous NaOH and the corresponding methyl ketone. The molecular structures of **1**(ClO_4) and **2**(ClO_4)·C_2H_5OH reveal π-stacking orientations for the $^tBu_3$tpy ligands with interplanar separations of ca. 3.8 and 3.6 Å, respectively. Complexes **2** and **3** are luminescent in solution at room temperature, and ^{3}MLCT excited states are assigned, while **1** is nonemissive. The superior photophysical properties of **2** and **3** are ascribed to the stronger σ-donating ability of the ketonyl ligands. Like **1**, complexes **2** and **3** also display low-energy emission at ca. 620 nm in 10^{-3} mol dm^{-3} MeOH/EtOH glass at 77 K. Complex **1**(ClO_4) is emissive in crystalline form at 77 K only (λ_{max} 560 nm). Solid-state emissions of **2**(ClO_4) and **3**(ClO_4) at room temperature (λ_{max} 607 and 615 nm, respectively) are derived from weak stacking interactions between $^tBu_3$tpy groups, while their emission maxima are red-shifted at 77 K.

Introduction

The propensity for platinum(II) diimine solids to engage in intermolecular interactions has been extensively studied.[1] Anisotropic spectroscopic properties and low-energy absorptions arising from metal−metal-to-ligand charge transfer (MMLCT) transitions are often the result of such solid-state stacking interactions.[2] The 2,2′:6′,2″-terpyridine (tpy) derivative [Pt(tpy)Cl]$^+$, which was established as an important DNA intercalator[3,4] and protein probe,[5] has been reported by Lippard[6] and Gray[7,8] to oligomerize in solution. Hence investigations into its photophysical properties and in particular the metal-to-ligand charge transfer (MLCT) transition are often complicated by this aggregation process.[9−11] In this context, the judicious employment of 4,4′,4″-tri-*tert*-butyl-2,2′:6′,2″-terpyridine ($^tBu_3$tpy) can simplify such endeavors because the bulky *tert*-butyl groups should discourage oligomerization interactions in this system.

Metalated ketones are important reagents in organic synthesis.[12] Several platinum(II) and palladium(II) derivatives have been reported,[13] including the cationic monoacetonyl species [Pt{$CH_2C(O)Me$}(PPh_3)$_3$]BF_4[14] and the diacetonyl complex [Pt{$CH_2C(O)Me$}$_2$(bpy)].[15] Nevertheless, accounts of their photophysical behavior are sparse. Herein, the preparation and molecular structures of cationic chloro and ketonyl Pt(II) complexes bearing the tridentate $^tBu_3$tpy ligand are described. Detailed investigations are undertaken to probe and elucidate

---

* Author to whom correspondence should be addressed. Fax: (852) 2857 1586. E-mail: cmche@hkucc.hku.hk.

(1) (a) Miller, J. S.; Epstein, A. J. *Prog. Inorg. Chem.* **1976**, *20*, 1. (b) *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum Press: New York, 1982; Vol. 1. (c) Schindler, J. W.; Fukuda, R. C.; Adamson, A. W. *J. Am. Chem. Soc.* **1982**, *104*, 3596. (d) Novoa, J. J.; Aullón, G.; Alemany, P.; Alvarez, S. *J. Am. Chem. Soc.* **1995**, *117*, 7169.

(2) For example, see: (a) Houlding, V. H.; Miskowski, V. M. *Coord. Chem. Rev.* **1991**, *111*, 145. (b) Miskowski, V. M.; Houlding, V. H. *Inorg. Chem.* **1991**, *30*, 4446. (c) Miskowski, V. M.; Houlding, V. H.; Che, C. M.; Wang, Y. *Inorg. Chem.* **1993**, *32*, 2518. (d) Che, C. M.; He, L. Y.; Poon, C. K.; Mak, T. C. W. *Inorg. Chem.* **1989**, *28*, 3081.

(3) (a) Lippard, S. J. *Acc. Chem. Res.* **1978**, *11*, 211. (b) Barton, J. K.; Lippard, S. J. *Biochemistry* **1979**, *18*, 2661. (c) Howe-Grant, M.; Lippard, S. J. *Biochemistry* **1979**, *18*, 5762. (d) Dewan, J. C.; Lippard, S. J.; Bauer, W. R. *J. Am. Chem. Soc.* **1980**, *102*, 858. (e) McFadyen, W. D.; Wakelin, L. P. G.; Roos, I. A. G.; Hillcoat, B. L. *Biochem. J.* **1987**, *242*, 177.

(4) (a) Arena, G.; Monsú Scolaro, L.; Pasternack, R. F.; Romeo, R. *Inorg. Chem.* **1995**, *34*, 2994. (b) Peyratout, C. S.; Aldridge, T. K.; Crites, D. K.; McMillin, D. R. *Inorg. Chem.* **1995**, *34*, 4484.

(5) Ratilla, E. M. A.; Brothers, H. M., II; Kostić, N. M. *J. Am. Chem. Soc.* **1987**, *109*, 4592.

(6) Jennette, K. W.; Gill, J. T.; Sadownick, J. A.; Lippard, S. J. *J. Am. Chem. Soc.* **1976**, *98*, 6159.

(7) Bailey, J. A.; Hill, M. G.; Marsh, R. E.; Miskowski, V. M.; Schaefer, W. P.; Gray, H. B. *Inorg. Chem.* **1995**, *34*, 4591.

(8) Hill, M. G.; Bailey, J. A.; Miskowski, V. M.; Gray, H. B. *Inorg. Chem.* **1996**, *35*, 4585.

(9) Yip, H. K.; Cheng, L. K.; Cheung K. K.; Che, C. M. *J. Chem. Soc., Dalton Trans.* **1993**, 2933.

(10) (a) Aldridge, T. K.; Stacy, E. M.; McMillin, D. R. *Inorg. Chem.* **1994**, *33*, 722. (b) Büchner, R.; Field, J. S.; Haines, R. J.; Cunningham, C. T.; McMillin, D. R. *Inorg. Chem.* **1997**, *36*, 3952. (c) Crites, D. K.; Cunningham, C. T.; McMillin, D. R. *Inorg. Chim. Acta* **1998**, *273*, 346.

(11) Arena, G.; Calogero, G.; Campagna, S.; Monsú Scolaro, L.; Ricevuto, V.; Romeo, R. *Inorg. Chem.* **1998**, *37*, 2763.

(12) (a) Masamune, S.; Choy, W.; Petersen, J. S.; Sita, L. R. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 1. (b) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1624.

10.1021/ic990446k CCC: $18.00

their excited-state properties. The synthesis and spectroscopic characterization of the isoelectronic gold(III) congener [Au(^{t}Bu$_3$-tpy)Cl]$^{2+}$ are also reported to provide an additional probe of the electronic structure in these d^8 systems.

Experimental Section

General Procedures. All reagents were obtained from commercial sources and used as received. 4,4′,4″-Tri-*tert*-butyl-2,2′:6′,2″-terpyridine (^{t}Bu$_3$tpy) was prepared by the literature method.[16] (**CAUTION**: Perchlorate salts are potentially explosive and should be handled with care and in small amounts.) Acetonitrile for photophysical measurements was distilled over potassium permanganate and calcium hydride. All other solvents were of analytical grade and purified according to conventional methods.[17]

Physical Measurements and Instrumentation. Fast atom bombardment (FAB) mass spectra were obtained on a Finnigan Mat 95 mass spectrometer. ^{1}H (300 MHz) and ^{13}C (126 MHz) spectra were recorded on DPX 300 and 500 Bruker FT-NMR spectrometers, respectively, with chemical shifts (in ppm) relative to tetramethylsilane. Elemental analysis was performed by the Institute of Chemistry at the Chinese Academy of Sciences, Beijing. Infrared spectra were recorded as Nujol mulls on a BIO RAD FT-IR spectrometer. UV−vis spectra were recorded on a Perkin-Elmer Lambda 19 UV/vis spectrophotometer.

Emission and Lifetime Measurements. Steady-state emission spectra were recorded on a SPEX 1681 Fluorolog-2 series F111AI spectrophotometer. Low-temperature (77 K) emission spectra for glasses and solid-state samples were recorded in 5 mm diameter quartz tubes which were placed in a liquid nitrogen Dewar equipped with quartz windows. The emission spectra were corrected for monochromator and photomultiplier efficiency and for xenon lamp stability. Details of emission quantum yield determinations using the method of Demas and Crosby[18] have been provided.[19]

Emission lifetime measurements were performed with a Quanta Ray DCR-3 pulsed Nd:YAG laser system (pulse output 355 nm, 8 ns). The emission signals were detected by a Hamamatsu R928 photomultiplier tube and recorded on a Tektronix model 2430 digital oscilloscope. Errors for λ values ($\pm$1 nm), τ ($\pm$10%), and ϕ ($\pm$10%) are estimated.

Syntheses. [Pt(^{t}Bu$_3$tpy)Cl]ClO$_4$, 1(ClO$_4$). A stirred mixture of K$_2$-PtCl$_4$ (0.20 g, 0.48 mmol) and ^{t}Bu$_3$tpy (0.19 g, 0.48 mmol) in CH$_3$-CN/H$_2$O (15/15 mL) was heated at reflux for 24 h to give a yellow solution, and this was filtered into an aqueous solution of sodium perchlorate. Upon cooling, the resultant yellow precipitate was collected and washed with dilute hydrochloric acid (0.1 M), water, and diethyl ether. The solid was recrystallized by vapor diffusion of diethyl ether into an acetonitrile solution of the crude product to afford yellow crystals: yield 0.23 g, 65%. Anal. Calcd for $C_{27}H_{35}N_3O_4Cl_2Pt$: C, 44.33; H, 4.82; N, 5.74. Found: C, 44.25; H, 4.86; N, 5.80. FAB-MS: *m/z* 632 [M$^+$]. IR (Nujol): $\nu = 1616$ cm^{-1}. ^{1}H NMR (CD$_3$CN): 1.46 (s, 18H, ^{t}Bu), 1.54 (s, 9H, ^{t}Bu), 7.82 (dd, 2H, $^3J_{HH} = 6.1$ Hz, $^4J_{HH} = 2.2$ Hz, H(5)), 8.31 (m, 4H, H(3, 3′)), 8.89 (d with broad ^{195}Pt satellites, 2H, $^3J_{HH} = 6.1$ Hz, H(6)). ^{13}C{^{1}H} NMR (CD$_3$CN): 30.3; 30.6 (C*Me*$_3$), 37.2; 38.2 (*C*Me$_3$), 122.7, 124.3, 126.5, 151.8, 155.5, 159.5, 168.5, 168.6.

[Pt(^{t}Bu$_3$tpy){CH$_2$C(O)Me}]ClO$_4$, 2(ClO$_4$). To a yellow suspension of **1**(ClO$_4$) (0.20 g, 0.27 mmol) in deionized H$_2$O (20 mL) was added 6 M NaOH (1 mL), and the mixture was stirred at 40 °C for 30 min. Acetone (10 mL) was added to give a clear yellow solution, which was further stirred for 12 h at room temperature. Evaporation of acetone and addition of excess aqueous LiClO$_4$ yielded a yellow solid. This was collected and recrystallized by vapor diffusion of *n*-pentane into an ethanol/acetone solution of the solid to afford yellow crystals: yield 0.12 g, 60%. Anal. Calcd for $C_{30}H_{40}N_3O_5ClPt$: C, 47.84; H, 5.35; N, 5.58. Found: C, 47.94; H, 5.21; N, 5.52. FAB-MS: *m/z* 653 [M$^+$], 596 [M$^+$ − CH$_2$COCH$_3$]. IR (Nujol): $\nu = 1651$ (C═O), 1611 cm^{-1}. ^{1}H NMR (acetone-*d*$_6$): 1.50 (s, 18H, ^{t}Bu), 1.53 (s, 9H, ^{t}Bu), 2.20 (s, 3H, COCH$_3$), 3.13 (s with ^{195}Pt satellites, 2H, $^2J_{PtH} = 104$ Hz, CH$_2$CO), 8.00 (dd, 2H, $^3J_{HH} = 6.1$ Hz, $^4J_{HH} = 2.2$ Hz, H(5)), 8.73 (d, 2H, $^4J_{HH} = 2.1$ Hz, H(3)), 8.78 (s, 2H, H(3′)), 9.29 (d with broad ^{195}Pt satellites, 2H, $^3J_{HH} = 6.1$ Hz, H (6)). ^{13}C{^{1}H} NMR (CD$_3$CN): 29.4 (*C*H$_2$CO, $^1J_{PtC} = 635$ Hz), 30.3; 30.7 (C*Me*$_3$), 30.8 (CO*Me*), 37.0; 38.0 (*C*Me$_3$), 122.2, 124.2, 126.4, 153.0, 153.9, 160.5, 167.6, 168.0, 213.9 (C═O).

[Pt(^{t}Bu$_3$tpy){CH$_2$C(O)Ph}]ClO$_4$, 3(ClO$_4$). The procedure for **2**(ClO$_4$) was adopted using acetophenone (10 mL) to afford a yellow crystalline solid: yield 0.14 g, 64%. Anal. Calcd for $C_{35}H_{42}N_3O_5ClPt$: C, 51.56; H, 5.19; N, 5.15. Found: C, 51.32; H, 5.34; N, 5.22. FAB-MS: *m/z* 715 [M$^+$]. IR (Nujol): $\nu = 1678$ (C═O), 1618 cm^{-1}. ^{1}H NMR (acetone-*d*$_6$): 1.49 (s, 18H, ^{t}Bu), 1.51 (s, 9H, ^{t}Bu), 3.69 (s with ^{195}Pt satellites, 2H, $^2J_{PtH} = 106$ Hz, CH$_2$CO), 7.38 (m, 3H, H$_{m/p}$ of Ph), 8.01 (m, 4H, H$_o$ of Ph and H(5)), 8.70 (d, 2H, $^4J_{HH} = 1.9$ Hz, H(3)), 8.75 (s, 2H, H(3′)), 9.32 (d with broad ^{195}Pt satellites, 2H, $^3J_{HH} = 6.1$ Hz, H(6)). ^{13}C{^{1}H} NMR (CD$_3$CN): 24.6 (*C*H$_2$CO, $^1J_{PtC} = 637$ Hz), 30.3; 30.6 (C*Me*$_3$), 37.0; 38.0 (*C*Me$_3$), 122.2, 124.1, 126.2, 128.5, 129.3, 132.3, 142.1, 152.9, 153.9, 160.4, 167.7, 168.0, 208.5 (C═O).

[Au(^{t}Bu$_3$tpy)Cl](CF$_3$SO$_3$)$_2$, 4(CF$_3$SO$_3$)$_2$. This procedure is modified from that described by Hollis and Lippard for [Au(tpy)Cl]Cl$_2$·3H$_2$O.[20] A stirred solution of KAuCl$_4$ (0.32 g, 0.85 mmol) and AgCF$_3$SO$_3$ (0.44 g, 1.71 mmol) in acetonitrile was heated at reflux for 3 h. After cooling to room temperature, the resultant mixture was filtered to remove the insoluble AgCl. ^{t}Bu$_3$tpy (0.34 g, 0.85 mmol) was added to the filtrate, which was refluxed for 24 h to yield a red solution. This was filtered and concentrated to ca. 5 mL, and addition of diethyl ether gave an orange solid. This was recrystallized by vapor diffusion of diethyl ether into an acetonitrile solution to afford yellow crystals: yield 0.50 g, 63%. Anal. Calcd for $C_{29}H_{35}N_3O_6AuClF_6S_2$: C, 37.37; H, 3.78; N, 4.51. Found: C, 37.18; H, 3.66; N, 4.57. FAB-MS: *m/z* 633 [M$^+$]. IR (Nujol): $\nu = 1621$ cm^{-1}. ^{1}H NMR (CD$_3$CN): 1.50 (s, 18H, ^{t}Bu), 1.58 (s, 9H, ^{t}Bu), 8.00 (dd, 2H, $^3J_{HH} = 6.4$ Hz, $^4J_{HH} = 2.2$ Hz, H(5)), 8.56 (m, 4H, H(3, 3′)), 8.96 (d, 2H, $^3J_{HH} = 6.4$ Hz, H(6)). ^{13}C{^{1}H} NMR (CD$_3$CN): 29.1; 29.5 (C*Me*$_3$), 37.1; 38.2 (*C*Me$_3$), 125.0, 127.0, 127.4, 151.0, 152.6, 158.7, 172.5, 174.0.

X-ray Crystallography. Crystal data and details of collection and refinement for complexes **1**(ClO$_4$) and **2**(ClO$_4$)·C$_2$H$_5$OH are summarized in Table 1. For **1**(ClO$_4$), intensity data were collected at 28 °C on a Rigaku AFC7R diffractometer with graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å) using $\omega{-}2\theta$ scans. For **2**(ClO$_4$)·C$_2$H$_5$OH, intensity data were collected at 28 °C on a MAR diffractometer with a 300 mm image plate detector using graphite-monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by Patterson methods, expanded by Fourier methods (PATTY),[21] and refined by full-matrix least squares using the software package TeXsan[22] on a Silicon Graphics Indy computer. For **1**(ClO$_4$), one crystallographic asymmetric unit consists of one formula unit. In the least-squares refinement, all 37 non-H atoms were refined anisotropically and 35 H atoms at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. For **2**(ClO$_4$)·C$_2$H$_5$OH, one

---

(13) (a) Yamamoto, H.; Suzuki, K. *J. Organomet. Chem.* **1974**, *71*, C38. (b) Cairns, M. A.; Dixon, K. R.; Smith, M. A. R. *J. Organomet. Chem.* **1977**, *135*, C33. (c) Appleton, T. G.; Bennett, M. A. *Inorg. Chem.* **1978**, *17*, 738. (d) Bennett, M. A.; Yoshida, T. *J. Am. Chem. Soc.* **1978**, *100*, 1750. (e) Arnold, D. P.; Bennett, M. A. *J. Organomet. Chem.* **1980**, *199*, 119. (f) Almeida, J. F.; Pidcock, A. *J. Organomet. Chem.* **1981**, *209*, 415. (g) Bertani, R.; Castellani, C. B.; Crociani, B. *J. Organomet. Chem.* **1984**, *269*, C15. (h) Suzuki, K.; Yamamoto, H. *Inorg. Chim. Acta* **1993**, *208*, 225.

(14) Pregosin, P. S.; Favez, R.; Roulet, R.; Boschi, T.; Michelin, R. A.; Ros, R. *Inorg. Chim. Acta* **1980**, *45*, L7.

(15) Vicente, J.; Abad, J. A.; Chicote, M.-T.; Abrisqueta, M.-D.; Lorca, J.-A.; Ramírez de Arellano, M. C. *Organometallics* **1998**, *17*, 1564.

(16) Hadda, T. B.; Bozec, H. L. *Inorg. Chim. Acta* **1993**, *204*, 103.

(17) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon: Oxford, 1980.

(18) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991.

(19) Chan, C. W.; Lai, T. F.; Che, C. M.; Peng, S. M. *J. Am. Chem. Soc.* **1993**, *115*, 11245.

(20) Hollis, L. S.; Lippard, S. J. *J. Am. Chem. Soc.* **1983**, *105*, 4293.

(21) PATTY: Beurskens, P. R.; Admiraal, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. The DIRDIF program system. Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1992.

(22) TeXsan: *Crystal Structure Analysis Package*; Molecular Structure Corporation: The Woodlands, TX, 1985 and 1992.

Table 1. Crystal Data

	1(ClO_4)	**2**(ClO_4)·C_2H_5OH
formula	$C_{27}H_{35}N_3Cl_2O_4Pt$	$C_{30}H_{40}N_3ClO_5Pt \cdot C_2H_5OH$
fw	731.59	799.27
color	yellow	yellow
cryst size, mm	0.15 × 0.15 × 0.25	0.35 × 0.15 × 0.05
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	13.046(5)	16.524(3)
b, Å	17.044(7)	11.152(2)
c, Å	13.194(7)	19.006(3)
β, deg	91.37(4)	91.69(2)
V, Å^3	2932(2)	3500.8(9)
Z	4	4
D_c (g cm^{-3})	1.657	1.516
μ, cm^{-1}	49.83	41.12
F(000)	1448	1608
$2\theta_{max}$, deg	45	51
no. of unique data	3994	6635
no. of obsd data for $I > 3\sigma(I)$	2711	4938
no. of variables	334	353
R,[a] R_w[b]	0.031, 0.031	0.048, 0.067
residual ρ, e Å^{-3}	+0.73, −0.51	+1.59, −1.78

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

crystallographic asymmetric unit consists of one formula unit. In the least-squares refinement, the 4 O atoms of the perchlorate anion and the 3 non-H atoms of the ethanol solvent molecule with large thermal parameters were refined isotropically, the other 36 non-H atoms were refined anisotropically, and 45 H atoms at calculated positions were not refined.

Results and Discussion

Synthesis and Characterization. Considerable attention has been granted toward the synthesis and spectroscopic properties of the $[Pt(tpy)X]^{n+}$ systems.[3−11] The $^tBu_3$tpy ligand in this work was prepared according to the published method of Hadda and Bozec.[16] An important feature of metal complexes bearing $^tBu_3$-tpy is their high solubility, which results from the presence of the hydrophobic ^{t}Bu groups. Thus $[Pt(^tBu_3tpy)Cl]^+$ (**1**), formed by refluxing K_2PtCl_4 and $^tBu_3$tpy in CH_3CN/H_2O, is soluble in acetonitrile up to a concentration of 10^{-2} mol dm^{-3}, whereas $[Pt(tpy)Cl]^+$ exhibits low solubility in dichloromethane and acetonitrile.[7] In addition, the bulky nature of the ^{t}Bu substituents is expected to minimize intermolecular interactions in solution and solid states. The gold(III) analogue $[Au(^tBu_3tpy)Cl](CF_3SO_3)_2$, **4**$(CF_3SO_3)_2$, is similarly generated from $KAuCl_4$, $AgCF_3SO_3$, and $^tBu_3$tpy in CH_3CN.

The monoketonyl complexes $[Pt(^tBu_3tpy)\{CH_2C(O)R\}]^+$ (R = Me, **2**; Ph, **3**) have been prepared in ca. 60% yield by warming mixtures of **1**(ClO_4) and NaOH in the presence of the corresponding methyl ketone (Scheme 1). These reactions did not proceed at an appreciable rate at room temperature; this is partly due to the insoluble nature of **1**(ClO_4) in aqueous basic medium. On the basis of previous accounts,[13b,f] the acetonyl ligands are proposed to be generated in situ by base-deprotonation of the ketone, and subsequent displacement of the chloride group affords the observed products **2** and **3**.

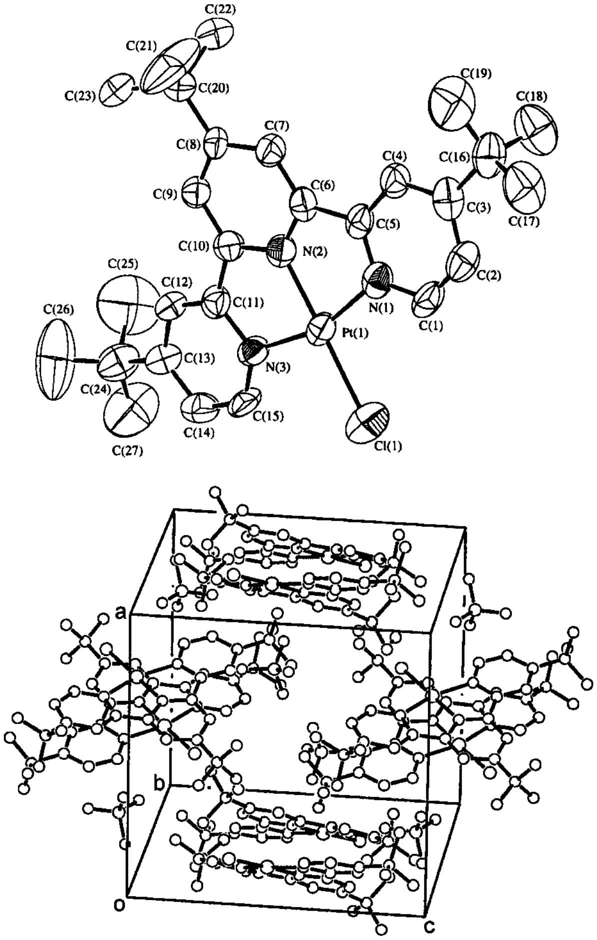
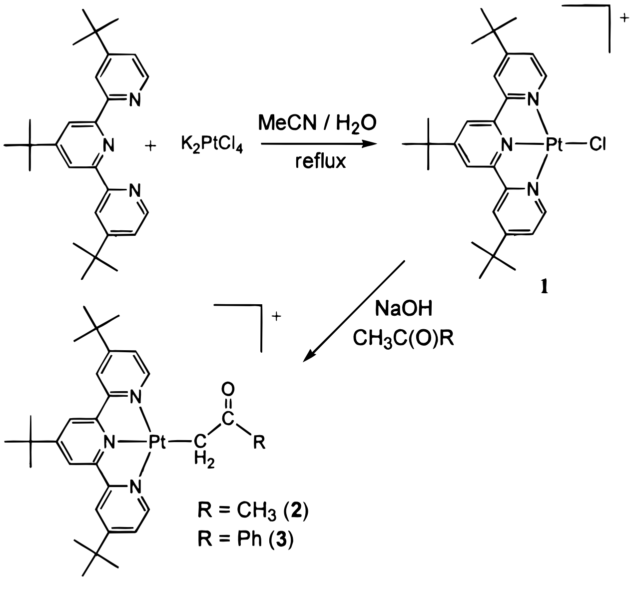


Figure 1. Top: Perspective view of cation in **1**(ClO_4) (50% probability ellipsoids, hydrogen atoms omitted for clarity). Bottom: Crystal packing diagram showing head-to-tail orientations of cation pairs.

Scheme 1



The ^{1}H and $^{13}C\{^1H\}$ NMR spectra of the $^tBu_3$tpy complexes contain the anticipated peaks. The ^{1}H NMR resonances of **2** and **3** at 3.13 ($^2J_{PtH}$ = 104 Hz) and 3.69 ($^2J_{PtH}$ = 106 Hz) ppm, respectively, in acetone-d_6 are attributed to the ketonyl CH_2 groups. In the $^{13}C\{^1H\}$ NMR spectra, the CH_2 signals appear at 29.4 ($^1J_{PtC}$ = 635 Hz) and 24.6 ($^1J_{PtC}$ = 637 Hz) ppm, respectively; the magnitudes of the $^1J_{PtC}$ coupling constants are consistent with sp^3-hybridized methylene carbons. The IR spectra of the ketonyl complexes show strong ν(CO) absorptions at 1651 and 1678 cm^{-1} for **2** and **3**, respectively.

Crystal Structures. The molecular structures of **1**(ClO_4) and **2**(ClO_4)·C_2H_5OH have been established by X-ray crystallography (Figures 1 and 2), and selected bond lengths and angles are listed in Table 2. The platinum atom in **1**(ClO_4) resides in

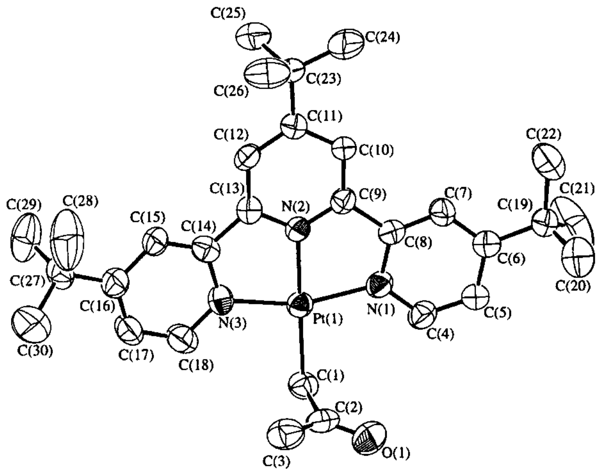


Figure 2. Perspective view of cation in **2**(ClO_4)·C_2H_5OH (50% probability ellipsoids, hydrogen atoms omitted for clarity).

Table 2. Selected Bond Lengths (Å) and Angles (deg)

Complex **1**(ClO_4)			
Pt(1)−N(1)	2.020(7)	Pt(1)−N(3)	2.025(7)
Pt(1)−N(2)	1.935(6)	Pt(1)−Cl(1)	2.288(3)
N(1)−Pt(1)−N(3)	161.8(3)	N(1)−Pt(1)−Cl(1)	99.9(2)
N(1)−Pt(1)−N(2)	80.3(3)	Cl(1)−Pt(1)−N(2)	178.8(2)
Complex **2**(ClO_4)·C_2H_5OH			
Pt(1)−N(1)	2.033(7)	Pt(1)−C(1)	2.099(8)
Pt(1)−N(2)	1.979(6)	C(1)−C(2)	1.49(1)
Pt(1)−N(3)	2.022(6)	O(1)−C(2)	1.24(1)
N(1)−Pt(1)−N(3)	160.2(3)	N(2)−Pt(1)−C(1)	179.2(3)
N(1)−Pt(1)−N(2)	79.9(2)	Pt(1)−C(1)−C(2)	108.4(5)
N(1)−Pt(1)−C(1)	99.5(3)	O(1)−C(2)−C(1)	119.9(8)

a distorted square planar environment with a N(1)−Pt(1)−N(3) bite angle of 161.8(3)°. The bond distances of Pt(1)−N(*i*) (*i* = 1−3) range from 1.935(6) to 2.025(7) Å, which are comparable to related platinum(II) terpyridine complexes.[3−11,23] In the crystal lattice (bottom of Figure 1), pairs of complex cations are stacked in head-to-tail orientations. However, a large interplanar separation between the ^{t}Bu$_3$tpy ligands (ca. 3.8 Å, defined by ^{t}Bu$_3$tpy mean planes) and a distant Pt−Pt contact (3.838(1) Å) are observed; hence appreciable intermolecular interactions are not apparent.

The molecular structure of **2**(ClO_4)·C_2H_5OH is shown in Figure 2. The geometry around the platinum center is distorted square planar (e.g. N(1)−Pt(1)−N(3) 160.2(3)°). The Pt(1)−N(2) distance of 1.979(6) Å (trans to ketonyl moiety) is slightly longer than that in **1** (1.935(6) Å) which is trans to the chloro group. The Pt(1)−C(1) bond length (2.099(8) Å) is comparable to those in [Pt{$CH_2C(O)Me$}$_2$(bpy)] (2.088(4) Å)[15] and in derivatives bearing the Pt−$CH_2C(sp^2)$ unit (mean 2.067 Å).[24] The trigonal geometry of the ketonyl carbon atom and the C(2)−O(1) bond length are unremarkable. The packing diagram of **2** reveals displaced head-to-tail stacking between cation pairs (see Supporting Information). The $\pi-\pi$ interplanar separation of ca. 3.5 Å and the Pt−Pt distance of 3.5841(6) Å are shorter than in **1**. While this clearly implies negligible metal−metal communication, solid-state ligand−ligand ($\pi-\pi$) interactions in **2** are evidently more significant than in **1**.

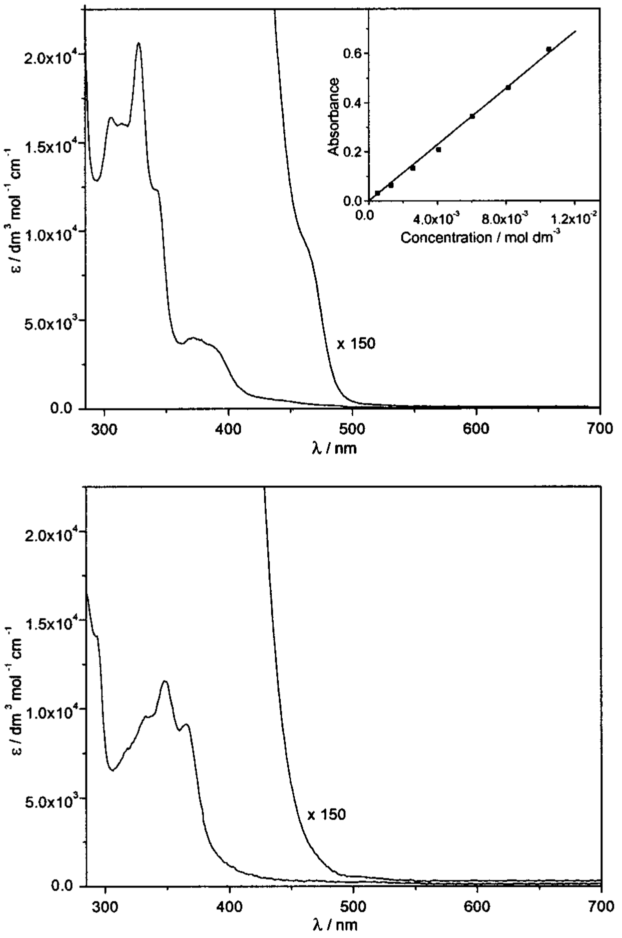


Figure 3. UV−vis absorption spectra of ^{t}Bu$_3$tpy complexes in CH_3CN at 298 K. Top: [Pt(^{t}Bu$_3$tpy)Cl]$^+$, **1** (Inset: plot of absorbance at 465 nm versus concentration, R = 0.99). Bottom: [Au(^{t}Bu$_3$tpy)-Cl]$^{2+}$, **4**.

Absorption and Emission Spectroscopy. In previous studies by Gray and co-workers,[7,8] [Pt(tpy)Cl]$^+$ was reported to undergo oligomerization in solution to yield low-energy visible absorptions at 460−550 nm which were attributed to MMLCT transitions. In this work, complex **1**(ClO_4) bearing bulky *tert*-butyl groups on the terpyridine ligand is expected to disfavor oligomerization processes in solution.

The UV−visible spectral data of the d^8 substituted terpyridine derivatives **1**−**4** are listed in Table 3. The comparison in Figure 3 between the UV−vis spectra of **1** (top) and the corresponding gold(III) complex [Au(^{t}Bu$_3$tpy)Cl]$^{2+}$, **4** (bottom), evidently assists the excited-state assignments. For **4**, the vibronically structured absorption centered at λ_{max} 350 nm (ϵ = 11 400 dm^3 mol^{-1} cm^{-1}) can be attributed to an intraligand $\pi-\pi^*$ transition because an MLCT assignment can be discounted due to the electrophilicity of the gold(III) center. Ligand-to-metal charge transfer (LMCT) transitions are possible for Au(III) species and may contribute to the λ < 300 nm region,[25] but can be excluded for the ~350 nm band because its energy and vibronic structure are diagnostic for the lowest energy $^1(\pi \rightarrow \pi^*)$ transition of the aromatic ligand.[2,3,7,8] For **1**, in contrast, a broad band at λ_{max} 373−386 nm (ϵ = 3530−3990 dm^3 mol^{-1} cm^{-1}) is evident in addition to the vibronically structured ^{1}IL absorption centered

---

[23] (a) Bailey, J. A.; Miskowski, V. M.; Gray, H. B. *Inorg. Chem.* **1993**, *32*, 369. (b) Yip, H. K.; Che, C. M.; Zhou, Z. Y.; Mak, T. C. W. *J. Chem. Soc., Chem. Commun.* **1992**, 1369. (c) Ratilla, E. M. A.; Scott, B. K.; Moxness, M. S.; Kostić, N. M. *Inorg. Chem.* **1990**, *29*, 918.

[24] Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

[25] (a) Wong, K. H.; Cheung, K. K.; Chan, M. C. W.; Che, C. M. *Organometallics* **1998**, *17*, 3505. (b) Mansour, M. A.; Lachicotte, R. J.; Gysling, H. J.; Eisenberg, R. *Inorg. Chem.* **1998**, *37*, 4625. (c) Chan, C. W.; Wong, W. T.; Che, C. M. *Inorg. Chem.* **1994**, *33*, 1266.

Table 3. UV−Vis Absorption Data in Acetonitrile at 298 K

complex	λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1})
$[Pt(^{t}Bu_3tpy)Cl]ClO_4$, **1**(ClO_4)	215 (46 000), 256 (45 100), 282 (33 700), 306 (16 400), 328 (20 600), 343 (12 300), 373 (3990), 386 (3530), 465 (57)
$[Pt(^{t}Bu_3tpy)\{CH_2C(O)Me\}]ClO_4$, **2**($ClO_4$)	254 (27 100), 281 (19 000), 305 (9200), 330 (11 500), 371 (2050), 387 (1390), 464 (87)
$[Pt(^{t}Bu_3tpy)\{CH_2C(O)Ph\}]ClO_4$, **3**($ClO_4$)	247 (39 100), 313 (14 400), 331 (15 400), 347 (8700), 374 (3170), 387 (3350), 464 (63)
$[Au(^{t}Bu_3tpy)Cl](CF_3SO_3)_2$, **4**($CF_3SO_3$)$_2$	230 (68 200), 264 (28 400), 294 (14 300), 318 (7700), 333 (9320), 349 (11 430), 366 (9050)

Table 4. Emission Data for $[Pt(^{t}Bu_3tpy)(X)]ClO_4$ (350 nm Excitation)

fluid (concn 5 × 10^{-5} M)	298 K:[a] λ_{max}/nm; τ_o/μs; ϕ_o	77 K:[b] λ_{max}/nm
X = Cl, **1**(ClO_4)	nonemissive	467 (max), 500, 538
X = $CH_2C(O)Me$, **2**(ClO_4)	595; 0.58; 3.26 × 10^{-4}	464 (max), 498, 534
X = $CH_2C(O)Ph$, **3**(ClO_4)	596; 0.60; 6.44 × 10^{-4}	464 (max), 497, 532

solid state	298 K: λ_{max}/nm; τ_o/μs	77 K: λ_{max}/nm
X = Cl, **1**(ClO_4)	nonemissive	560
X = $CH_2C(O)Me$, **2**(ClO_4)	607; 3.38	608
X = $CH_2C(O)Ph$, **3**(ClO_4)	615; 0.71	631

[a] Measured in acetonitrile. [b] Measured in MeOH/EtOH (1:1); additional emission bands observed in ≥10^{-4} M glasses at λ_{max} 625 (**1**), 623 (**2**), and 617 (**3**) nm, respectively.

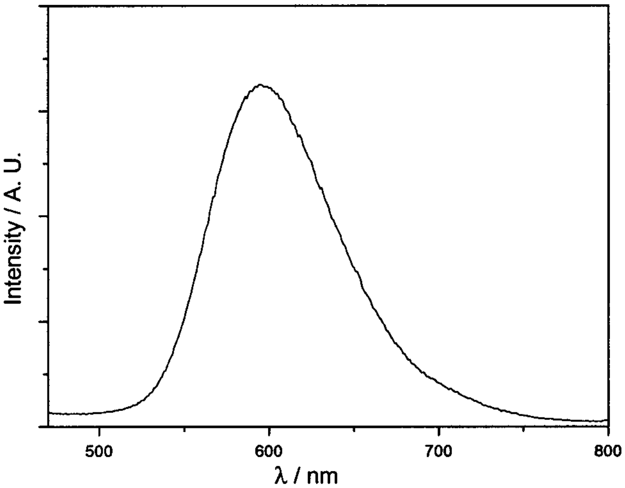


Figure 4. Emission spectra of **2** in CH_3CN (5 × 10^{-5} M) at 298 K (λ_{ex} 350 nm).

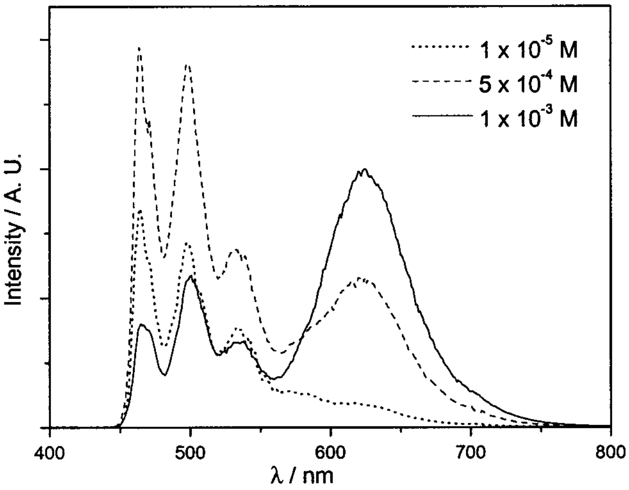


Figure 5. Emission spectra of **2** at different concentrations in MeOH/EtOH (1:1) at 77 K (λ_{ex} 350 nm).

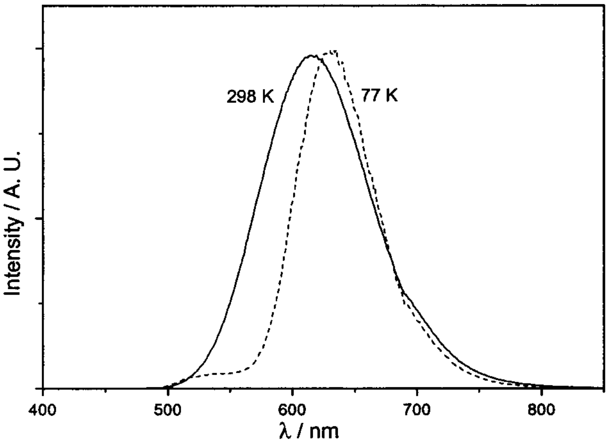


Figure 6. Solid-state emission spectra of **3**(ClO_4) at 77 and 298 K (λ_{ex} 350 nm, normalized intensities).

at λ_{max} 328 nm. The former absorption, with noticeably lower extinction coefficients compared to the ~328 nm band, is tentatively assigned as ^{1}MLCT [(5d)Pt → π^*(^{t}Bu$_3$tpy)], although mixing with the ^{t}Bu$_3$tpy ^{1}IL transition is likely in view of the distinct blue shift (1835 cm^{-1}) of the ^{1}IL band for **1** relative to the Au(III) complex **4**. The absorption spectra of **1** obey Beer's law at concentrations ranging from 5 × 10^{-4} to 1 × 10^{-2} mol dm^{-3}, as evidenced by the plot of the absorbance at 465 nm versus concentration (top of Figure 3: inset). We assign the 465 nm band (ϵ = 57 dm^3 mol^{-1} cm^{-1}) to ^{3}MLCT [(5d)Pt → π^*(^{t}Bu$_3$tpy)], since no significant absorption is seen in this region for the Au(III) analogue **4**. The ^{3}MLCT bands for **2** and **3** are cautiously assigned at 464 nm, with ϵ values of 87 and 63 dm^3 mol^{-1} cm^{-1}, respectively. This assignment is different from that for $[Pt(tpy)Cl]^+$, which displays MMLCT transitions at 460−550 nm in solution.[7]

The chloro derivatives **1** and **4** show no emission in fluid solution at room temperature, but the Pt(II) ketonyl derivatives **2** and **3** are luminescent in acetonitrile solution (Table 4, see Figure 4 for **2**). We suggest that the stronger ligand-field strengths of the ketonyl moieties lead to greater destabilization of the empty Pt(II) d(x^2−y^2) orbital. Hence the energy difference between the d−d and ^{3}MLCT [(5d)Pt → π^*(^{t}Bu$_3$tpy)] transitions increases and nonradiative deactivation via d−d states decreases. With reference to earlier reports,[9,10] the structureless 298 K emissions of **2** and **3** in CH_3CN at λ_{max} ca. 595 nm are tentatively ascribed to ^{3}MLCT in nature. An excimeric emission assignment is not preferred because the emission maxima are concentration-independent from 10^{-5} to 10^{-3} mol dm^{-3} at room temperature. Complexes **2** and **3** emit at λ_{max} 613 and 624 nm, respectively, at 77 K in frozen 10^{-5} mol dm^{-3} CH_3CN solutions.

The luminescent behavior of **1**−**3** at 77 K in glassy MeOH/EtOH (1:1) solutions has been examined (Table 4). The emissions are sensitive to the complex concentration in the range

$10^{-6}-10^{-3}$ mol dm^{-3}. At low concentrations ($<10^{-5}$ mol dm^{-3}), the emission spectra are highly structured with peak maxima at 464−467 nm and vibronic progressions of ca. 1400 cm^{-1}. This luminescence is very similar to those reported for $[Pt(bpy)(en)]^{2+}$ and $[Pt(bpy)_2]^{2+}$,[26] and a ^{3}IL ($\pi\pi^*$) assignment is clearly indicated. At higher concentrations ($\geq 10^{-4}$ mol dm^{-3}), the emissive profile changes and a broad unstructured band appears at λ_{max} ca. 620 nm (Figure 5 for **2**). This low-energy emission is attributed to an excimeric intraligand transition arising from $^{t}Bu_3$tpy $\pi-\pi$ interactions.[7]

The emission data of yellow microcrystalline samples of complexes **1**(ClO_4)−**3**(ClO_4) at 298 and 77 K are listed in Table 4. Solid **1**(ClO_4) exhibits no luminescence at room temperature, but upon cooling to 77 K, an emission band at λ_{max} 560 nm is detected which is tentatively assigned to a ^{3}MLCT excited state. In contrast, the solid-state emission of **2**(ClO_4) and **3**(ClO_4) at room temperature is composed of a structureless band centered at λ_{max} 607 and 615 nm, respectively. At 77 K, the bandwidths of the emissions are reduced and the emission maxima slightly red-shift to 608 and 631 nm, respectively (Figure 6 for **3**(ClO_4)). These low-energy bands are comparable to those observed in glassy MeOH/EtOH solutions and can also be ascribed to excimeric IL emissions resulting from $^{t}Bu_3$tpy π-stacking. It is pertinent to remark that such intermolecular interactions are indicated in the crystal lattice of **2** but not **1**.

Acknowledgments. We are grateful to The University of Hong Kong and the Research Grants Council of the Hong Kong SAR, China [HKU 7298/99P] for support. We thank Dr. V. M. Miskowski for helpful discussions and Mr. K. H. Wong for experimental assistance.

Supporting Information Available: Crystal packing diagrams and tables of crystal data, atomic coordinates, calculated coordinates, anisotropic displacement parameters, and bond lengths and angles for **1**(ClO_4) and **2**(ClO_4)·C_2H_5OH. This material is available free of charge via the Internet at http://pubs.acs.org.

IC990446K

---

(26) Miskowski, V. M.; Houlding, V. H. *Inorg. Chem.* **1989**, *28*, 1529.