

Note

Double cyclometallation of bridging 3,6-bis(2-thienyl)-1,2,4,5-tetrazine in a dinuclear mesityl(dimethylsulfoxide)platinum(II) complex: Structure and properties

Biprajit Sarkar^a, Thilo Schurr^a, Ingo Hartenbach^a, Thomas Schleid^a,
Jan Fiedler^b, Wolfgang Kaim^{a,*}

^a Institut für Anorganische Chemie, Universität Stuttgart, Pfaffenwaldring 55, D-70550 Stuttgart, Germany

^b J. Heyrovský Institute of Physical Chemistry, v.v.i., Academy of Sciences of the Czech Republic, Dolejškova 3, CZ-18223 Prague, Czech Republic

Received 28 September 2007; received in revised form 24 October 2007; accepted 24 October 2007

Available online 1 November 2007

Abstract

3,6-Bis(2-thienyl)-1,2,4,5-tetrazine (bttz) reacts with *trans*-Pt(dmsO)₂(mes)₂, mes = mesityl = 2,4,6-trimethylphenyl, under twofold cyclometallation to yield structurally characterized (μ-bttz-2H⁺)[Pt(dmsO)(mes)]₂ with uncoordinated thiophene sulfur atoms and bttz deprotonated in the 3,3' positions. The structural features include *cis*-positioned carbanionic ligands, twisted mesityl substituents, *S*-coordinated dmsO ligands with the S=O bonds lying in the molecular plane, shortened inter-ring bonds, and rather short Pt–C bonds at 1.998(9)/2.00(1) Å (Pt–C_{mes}) and 1.985(9)/1.99(1) Å (Pt–C_{bttz-2H+}). Reversible reduction to {(μ-bttz-2H⁺)[Pt(dmsO)(mes)]₂}⁻ causes a high-energy shift of the charge transfer bands and the appearance of an unresolved EPR signal at *g* = 1.9905.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Crystal structure; Cyclometallation; EPR spectroscopy; Heterocyclic ligand; Platinum complex

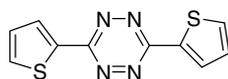
1. Introduction

The cumulation of four electronegative nitrogen atoms in a benzenoid six-membered ring to form 1,2,4,5-tetrazines has a number of remarkable consequences. In addition to their high nitrogen content [1] 1,2,4,5-tetrazines are distinguished by a very low-lying π* molecular orbital centered on the N atoms which is responsible for facile reduction (electron transfer and hydrogenation) [2] and low-energy electronic transitions [3], observable in absorption and emission [3]. Typically, the low-energy transitions of 1,2,4,5-tetrazines are of internal π–π* or *n*–π* character [3], however,

with electron rich metals coordinated via the N lone pairs [4] it is also possible to observe intense metal-to-ligand charge transfer (MLCT, d–π*) transitions at rather long wavelengths. Most metal complexes of tetrazines have involved derivatives with coordinating groups in 3,6-position [4]. Among the potentially bis-chelating tetrazine acceptor ligands the 3,6-bis(2-thienyl)-1,2,4,5-tetrazine (bttz) [5–7] has occupied a special position (Scheme 1). The dinuclear redox systems {(μ-bttz)[M(bpy)₂]₂}⁺⁺, M = Ru or Os, with unusually different features of the mixed-valent intermediates were initially assumed to involve S-bonded thienyl rings [5] but have now been identified as bis-cyclometallated species [7] following C–H activation. On the other hand, [Ru(acac)₂(CH₃CN)₂] reacts with bttz under reductive ring-opening of the tetrazine to yield a complex {(μ-dih-Th)[Ru(acac)₂]₂} with diH-Th²⁻ = 1,2-bis(2-thienylimino)-hydrazido(2-), i.e. with uncoordinated thiophene [8].

* Corresponding author. Tel.: +49 711 685 4170/71; fax: +49 711 685 4165.

E-mail address: kaim@iac.uni-stuttgart.de (W. Kaim).



3,6-bis(2-thienyl)-1,2,4,5-tetrazine
(bttz)

Scheme 1.

In the course of further studies on compounds between bttz and platinum metal containing complex fragments we have now been able to obtain a doubly cyclometallated compound for structural analysis and electron transfer studies. The precursor compound $[\text{Pt}(\text{dmsO})_2(\text{mes})_2]$ which exists in a *trans* configuration [9] and not in a *cis* arrangement as earlier believed [10] reacts with bttz to form the dinuclear bis-cyclometallated species $(\mu\text{-bttz-2H}^+)[\text{Pt}(\text{dmsO})(\text{mes})_2]$ as evident from a crystal structure determination and from spectroscopy (NMR, EPR of the reduced form), cyclic voltammetry and spectroelectrochemistry.

Whereas mononuclear cyclometallated platinum(II) complexes are well known [11], not in the least due to their photophysical properties [12], there are but a few reports of dinuclear such compounds [13] in which the potential for π conjugatively mediated metal–metal interaction exists. Dinuclear platinum(II) compounds have been discussed in connection with cytostatic behaviour [14], and organometallic compounds containing conjugated bridging ligands were investigated with respect to reduction and oxidation, establishing radical and mixed-valent intermediates [15]. Considering the stabilization of the Pt(III) state by two mesityl substituents [16] and the coordination ambivalence of the bttz ligand [5,7] we have reacted these components in order to probe the coordination behaviour of that ligand.

2. Results and discussion

Reaction of bttz with 2 equiv. of $\text{Pt}(\text{dmsO})_2(\text{mes})_2$ for 5 days in refluxing toluene produced $(\mu\text{-bttz-2H}^+)[\text{Pt}(\text{dmsO})(\text{mes})_2]$ in 28% isolated yield. In addition to elemental and crystal structure analysis (see below) the IR

Table 1
Selected bond lengths (Å) and angles (°) for $\{(\mu\text{-bttz-2H}^+)[\text{Pt}(\text{dmsO})(\text{mes})_2]\}$

Bond lengths			
Pt1–N1	2.091(7)	C1–C2	1.406(13)
Pt1–C3	1.985(9)	N1–N2	1.316(10)
Pt1–C6	1.998(9)	C1–N1	1.363(11)
Pt1–S2	2.274(3)	C1–N2A	1.362(11)
Bond angles			
C3–Pt1–C6	91.1(4)	S2–Pt1–N1	97.6(2)
C3–Pt1–N1	80.3(3)	C2–C3–Pt1	113.5(7)
C3–Pt1–S2	176.7(3)	C3–C2–C1	118.5(8)
C6–Pt1–S2	91.0(3)	C2–C1–N1	114.3(8)
C6–Pt1–N1	171.4(3)	C1–N1–Pt1	113.4(6)

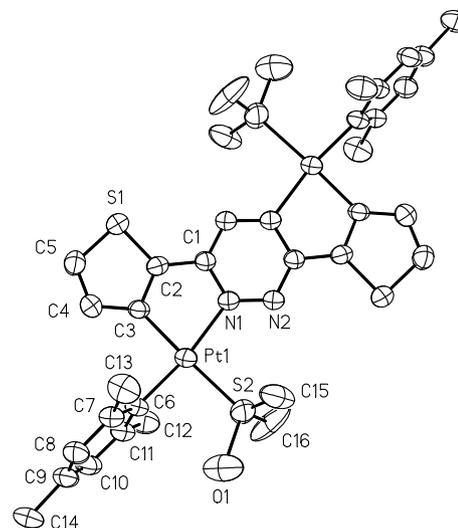


Fig. 1. Molecular structure of $\{(\mu\text{-bttz-2H}^+)[\text{Pt}(\text{dmsO})(\text{mes})_2]\}$ in the crystal.

and ^1H NMR spectrum clearly point to the composition indicated, the C–H activation of thienyl rings to effect cyclometallation is a known kind of reactivity [11–13].

Crystallization of the greenish-brown compound gave single crystals of suitable quality for X-ray diffraction. Table 1 contains the bond parameters and Fig. 1 shows a representation of the molecule in the crystal.

The crystal structure analysis confirms the binding of both equivalent platinum(II) centers to the 3 or 3' positions of the thienyl rings, leaving the sulfur atoms uncoordinated. Whereas the doubly deprotonated bttz bridge and the C,C,N,S donor sets around the platinum centers are largely coplanar, the mesityl ligand is almost orthogonally positioned, reflecting the steric repulsion of the *ortho*-methyl substituents [16]. The dmsO ligand is bound through the sulfur atom in such a way that the S=O bond comes to lie within the main molecular plane [17]. Expectedly, the carbanionic ligands at each platinum center are oriented in *cis* position, the Pt–C bond lengths are rather similar and relatively short at about 1.99 Å (Table 1).

The bond parameters *within* the heterocycles of $(\mu\text{-bttz-2H}^+)[\text{Pt}(\text{dmsO})(\text{mes})_2]$ can be compared with those of free bttz [5c,7]: The main differences are the shortened inter-ring distance (1.448(3) Å \rightarrow 1.406(13) Å) and the diminished intra-chelate angle N1–C1–C2 (117.9(2)° \rightarrow 114.3(8)°). Whereas the latter is caused by the formation of the short C3–Pt bond, the increased inter-ring bond order reflects the charge shift from the deprotonated thienyl rings to the strongly [4a] electron accepting tetrazine.

Electron acceptance is also obvious from electrochemical experiments: The reversible reduction of the diplatinum(II) complex as determined by cyclic voltammetry occurs at -0.76 V vs. ferrocenium/ferrocene, i.e. at distinctly less negative values than the reduction of the free bttz ligand at -1.26 V [5,7]. This result, observed in spite of the double deprotonation of the bridging ligand, confirms

the efficient compensation of that negative charge by Pt^{II}–C bonding, leaving even sufficient acceptor strength at the metal to withdraw electron density from the ligand. The second reduction at –2.15 V and the oxidation at about +0.56 V were found irreversible in the cyclic voltammetry experiment.

EPR spectroscopy of the one-electron reduced form showed an unresolved broad line at $g = 1.9905$ which did not exhibit any g component splitting in frozen solution (4 K) under X-band conditions (9.5 GHz). In the absence of detectable ¹⁹⁵Pt satellite lines the peak-to-peak linewidth of about 5 mT suggests an upper limit of 5 mT for the metal isotope hyperfine coupling which, together with the small g anisotropy and the isotropic g close to the free electron value of 2.0023, indicates [18] very little participation of the heavy metals at the singly occupied MO. We attribute this comparatively [15,16,19] small metal contribution to the carbanion coordination of Pt^{II} while the spin is probably localized in the tetrazine ring [4a]; formally, the bridge functions as a radical trianion in that state.

Monitoring the reversible one-electron reduction by spectroelectrochemistry in the UV–Vis region reveals a decrease of the long-wavelength charge transfer bands at 560(sh), 434(9550), 395(8970), 340(sh) nm (molar extinction coefficients in M⁻¹ cm⁻¹) while new bands emerge at 381(8600), 363(8800), 308(6800) nm (Fig. 2).

The decrease of the absorption bands in the visible follows from the partial occupation of the low-lying tetrazine-centered π^* LUMO during reduction and has been similarly observed for metal-to-ligand charge transfer (MLCT) bands of reduced dinuclear tetrazine complexes [4a,15b]. Further transitions including ligand-to-ligand charge transfer are conceivable, however, a detailed assignment is precluded at this stage by the low symmetry of the chromophore. At ambient temperatures the neutral precursor compound does not emit as a solid or in solution, most likely due to energy dissipation through rotation and vibration of the non-chelate ligands dmsO and mes [16].

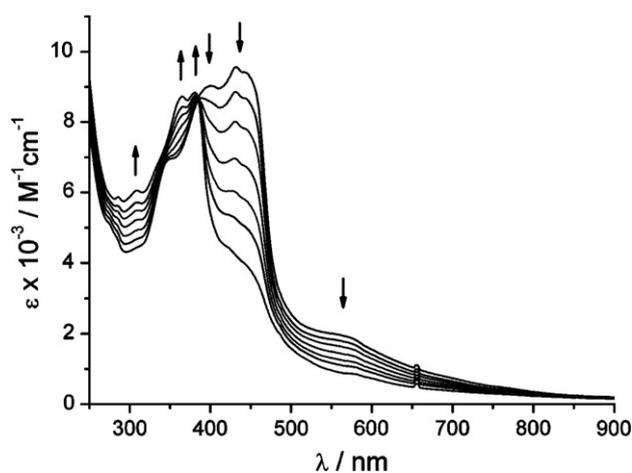


Fig. 2. Spectroelectrochemical reduction of $\{(\mu\text{-bttz-2H}^+)[\text{Pt}(\text{dmsO})(\text{mes})_2]\} \rightarrow \{(\mu\text{-bttz-2H}^+)[\text{Pt}(\text{dmsO})(\text{mes})_2]\}^-$ in $\text{CH}_2\text{Cl}_2/0.1 \text{ M Bu}_4\text{NPF}_6$.

Concluding, we have described a dinuclear complex $(\mu\text{-bttz-2H}^+)[\text{Pt}(\text{dmsO})(\text{mes})_2]$ in which 2 equiv. diorganoplatinum(II) centers are connected by a potentially π conjugated bridge, the 3,3' bis-deprotonated and bis-cyclo-metallated bttz ligand. The compound with two carbanionic ligands in *cis* position at each metal center exhibits reversible reduction to a radical anion complex, formally containing a radical trianion bridge. EPR and UV/Vis spectroelectrochemical studies suggest very little metal participation at the singly occupied MO. As preliminary studies have indicated, the substitution of the dmsO ligand by nitrogen bases is possible and may be exploited to form other dinuclear compounds or extended systems (coordination polymers) (Scheme 1).

3. Experimental

3.1. Instrumentation

EPR spectra in the X-band were recorded with a Bruker System ESP 300 equipped with a HP frequency counter 5350B, a Bruker ER035M gaussmeter for g -value determination and a continuous flow cryostat ESR 900 of Oxford Instruments for measurements at liquid helium temperatures (4 K). ¹H NMR spectra were taken on a Bruker AC 250 spectrometer. IR spectra were obtained using Perkin Elmer FTIR 684 and 283 instruments. UV–Vis–NIR absorption spectra were recorded on J&M TIDAS and Shimadzu UV 3101 PC spectrophotometers. Cyclic voltammetry was carried out in 0.1 M Bu₄NPF₆ solutions using a three-electrode configuration (glassy carbon working electrode, Pt counter electrode, Ag/AgCl reference) and a PAR 273 potentiostat and function generator. The ferrocene/ferrocenium (Fc/Fc⁺) couple served as internal reference. Spectroelectrochemistry was performed using an optically transparent thin-layer electrode (OTTLE) cell. A two-electrode capillary served to generate intermediates for X-band EPR studies.

3.2. Synthesis of $(\mu\text{-bttz-2H}^+)[\text{Pt}(\text{dmsO})(\text{mes})_2]$

A mixture containing 307 mg (0.520 mmol) Pt(dmsO)₂(mes)₂ and 64 mg (0.260 mmol) bttz in 110 ml toluene was heated to reflux in toluene for 5 days. The solution changed its colour from orange-red to dark green during this time. After removal of the solvent, the product was recrystallised from dichloromethane/heptane (1/3). Yield: 150 mg (0.146 mmol, 28%). Anal. Calc. for C₃₂H₃₈N₄O₂Pt₂S₄ (1039.08 g/mol): C, 37.35; H, 3.72; N, 5.44. Found: C, 36.83; H, 3.55; N, 5.02%. ¹H NMR (CD₂Cl₂): $\delta = 2.28$ (s, 6H, *p*-CH₃, mes), 2.41 (s, 12H, *o*-CH₃, mes, ⁴J (Pt–H) = 6.41 Hz), 3.08 (s, 12H, CH₃, dmsO, ³J (Pt–H) = 13.67 Hz), 6.42 (d, 2H, 4' (bttz), ³J (H–H) = 4.8 Hz, ³J (Pt–H) = 28.6 Hz), 6.79 (s, 4H, C–H, mes, ⁴J (Pt–H) = 14.7 Hz), 7.58 (d, 2H, 5' (bttz), ³J (H–H) = 4.6 Hz, ⁴J (Pt–H) = 19 Hz). UV/Vis (CH₂Cl₂):

λ_{\max}/nm ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$) = 565(1.99), 434(9.55), 395(8.97), 341(6.9).

3.3. Crystallography

Crystallographic data and refinement parameters of $(\mu\text{-bttz-2H}^+)[\text{Pt}(\text{dmsO})(\text{mes})_2]$: green needles, $0.2 \times 0.1 \times 0.05$ mm, $\text{C}_{32}\text{H}_{38}\text{N}_4\text{O}_2\text{Pt}_2\text{S}_4$, $M = 1029.08 \text{ g mol}^{-1}$, space group $P2_1/c$, monoclinic, $a = 15.9138(5) \text{ \AA}$, $b = 11.4844(3) \text{ \AA}$, $c = 11.9364(3) \text{ \AA}$, $\beta = 124.68(10)^\circ$, $V = 1793.81(9) \text{ \AA}^3$, $Z = 2$, $\rho_{\text{calc}} = 1.905 \text{ g cm}^{-3}$, μ (Mo $K\alpha$) = 0.71073 \AA , absorption coefficient 8.057 mm^{-1} , $T = 293(2) \text{ K}$, max. 2θ 55.98° , 4108 reflections collected and 3549 unique reflections, index ranges $-20 \leq h \leq 20$, $-14 \leq k \leq 14$, $-15 \leq l \leq 15$, 3549 data, 199 parameters, 0 restraints, $R_{\text{int}}/R_{\sigma} = 0.0774/0.0303$, $\text{GOF}/F^2 = 1.144$, $R_1 = 0.0676$ and $wR_2 = 0.1254$ for all data, $R_1 = 0.0577$ and $wR_2 = 0.1204$ for $I > 2\sigma(I)$, largest residual densities -1.083 and 1.514 e \AA^{-3} .

4. Supplementary material

CCDC 660655 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033.

Acknowledgements

This work was supported by the DFG, the FCI and the EU (COST D35). We also thank Johnson & Matthey for a generous loan of K_4PtCl_6 .

References

- [1] (a) M.-H.V. Huynh, M.A. Hiskey, E.L. Hartline, D.P. Montoya, R. Gilardi, *Angew. Chem., Int. Ed.* 116 (2004) 5032; M.-H.V. Huynh, M.A. Hiskey, E.L. Hartline, D.P. Montoya, R. Gilardi, *Angew. Chem., Int. Ed.* 43 (2004) 4924; (b) M.H.V. Huynh, M.A. Hiskey, J.G. Archuleta, E.L. Roemer, R. Gilardi, *Angew. Chem., Int. Ed.* 116 (2004) 5776; M.H.V. Huynh, M.A. Hiskey, J.G. Archuleta, E.L. Roemer, R. Gilardi, *Angew. Chem., Int. Ed.* 43 (2004) 5658; (c) T.M. Klapötke, C. Kuffer, P. Mayer, K. Polborn, A. Schulz, H.J. Weigand, *Inorg. Chem.* 44 (2005) 5949.
- [2] A.-R. Katritzky, *Handbook of Heterocyclic Chemistry*, Pergamon Press, New York, 1986.
- [3] (a) R. Gleiter, V. Schehlmann, J. Spanget-Larsen, H. Fischer, F.A. Neugebauer, *J. Org. Chem.* 53 (1988) 5756; (b) P. Audebert, F. Miomandre, G. Clavier, M.-C. Vernières, S. Badré, R. Méallet-Renault, *Chem. Eur. J.* 11 (2005) 5667; (c) I. Janowska, F. Miomandre, G. Clavier, P. Audebert, J. Zakrzewski, K.H. Thi, I. Ledoux-Rak, *J. Phys. Chem. A* 110 (2006) 12971.
- [4] (a) W. Kaim, *Coord. Chem. Rev.* 230 (2002) 127; (b) S. Kohlmann, S. Ernst, W. Kaim, *Angew. Chem., Int. Ed.* 97 (1985) 698; S. Kohlmann, S. Ernst, W. Kaim, *Angew. Chem., Int. Ed. Engl.* 24 (1985) 684.
- [5] (a) B. Sarkar, W. Kaim, A. Klein, B. Schwederski, J. Fiedler, C. Duboc-Toia, G.K. Lahiri, *Inorg. Chem.* 42 (2003) 6172; (b) W. Kaim, G.K. Lahiri, *Angew. Chem., Int. Ed.* 119 (2007) 1808; W. Kaim, G.K. Lahiri, *Angew. Chem., Int. Ed.* 46 (2007) 1778; (c) B. Sarkar, Ph.D. Thesis, Universität Stuttgart, 2005.
- [6] P. Audebert, S. Sadki, F. Miomandre, G. Clavier, M.C. Vernières, M. Saoud, P. Hapiot, *New J. Chem.* 28 (2004) 387.
- [7] B. Sarkar, G.K. Lahiri, W. Kaim (in preparation).
- [8] S. Maji, B. Sarkar, S. Patra, J. Fiedler, S.M. Mobin, V.G. Puranik, W. Kaim, G.K. Lahiri, *Inorg. Chem.* 45 (2007) 1316.
- [9] A. Klein, T. Schurr, A. Knödler, D. Gudat, K.-W. Klinkhammer, V.K. Jain, S. Zális, W. Kaim, *Organometallics* 24 (2005) 4125.
- [10] C. Eaborn, K. Kundu, A. Pidcock, *J. Chem. Soc., Dalton Trans.* (1981) 933.
- [11] (a) I. Omae, *Chem. Rev.* 79 (1979) 287; (b) A.D. Ryabov, *Chem. Rev.* 90 (1990) 403; (c) T. Yagyu, J.-I. Ohashi, M. Maeda, *Organometallics* 26 (2007) 2383.
- [12] (a) B. Ma, P.I. Djurovich, M.E. Thompson, *Coord. Chem. Rev.* 249 (2005) 1501; (b) J.A.G. Williams, *Top. Curr. Chem.* 281 (2007) 205.
- [13] (a) A. Zucca, A. Doppiu, M.A. Cinellu, S. Stoccoro, G. Minghetti, M. Manassero, *Organometallics* 21 (2002) 783; (b) T.-C. Cheung, K.-K. Cheung, S.-M. Peng, C.-M. Che, *J. Chem. Soc., Dalton Trans.* (1996) 1645; (c) W. Lu, M.C.W. Chan, K.-K. Cheung, C.-M. Che, *Organometallics* 20 (2001) 2477.
- [14] (a) J. Kasparkova, N. Farrell, V. Brabec, *J. Biol. Chem.* 275 (2000) 15789; (b) S. Fakhir, W.C. Tung, D. Eierhoff, C. Mock, B. Krebs, Z. Anorg. Allg. Chem. 631 (2005) 1397; (c) H. Ertürk, A. Hofmann, R. Puchta, R. van Eldik, *Dalton Trans.* (2007) 2295.
- [15] (a) A. Klein, W. Kaim, J. Fiedler, S. Zalis, *Inorg. Chim. Acta* 264 (1997) 269; (b) A. Klein, S. Hasenzahl, W. Kaim, J. Fiedler, *Organometallics* 17 (1998) 3532.
- [16] (a) A. Klein, H.-D. Hausen, W. Kaim, *J. Organomet. Chem.* 440 (1992) 207; (b) W. Kaim, A. Klein, *Organometallics* 14 (1995) 1176.
- [17] (a) M. Calligaris, O. Carugo, *Coord. Chem. Rev.* 153 (1996) 83; (b) J.R.L. Priqueler, F.D. Rochon, *Inorg. Chim. Acta* 357 (2004) 2167.
- [18] W. Kaim, *Coord. Chem. Rev.* 76 (1987) 187.
- [19] (a) W. Kaim, A. Dogan, M. Wanner, A. Klein, I. Tiritiris, T. Schleid, D.J. Stufkens, T.L. Snoeck, E.J.L. McInnes, J. Fiedler, S. Zalis, *Inorg. Chem.* 41 (2002) 4139; (b) A. Dogan, B. Sarkar, A. Klein, F. Lissner, Th. Schleid, J. Fiedler, S. Zalis, V.K. Jain, W. Kaim, *Inorg. Chem.* 43 (2004) 5973; (c) C. Kavakli, A. Gabriellson, M. Sieger, B. Schwederski, M. Niemeyer, W. Kaim, *J. Organomet. Chem.* 692 (2007) 3151; (d) E. Bulak, M. Leboschka, B. Schwederski, O. Sarper, T. Varnali, J. Fiedler, F. Lissner, Th. Schleid, W. Kaim, *Inorg. Chem.* 46 (2007) 5562.