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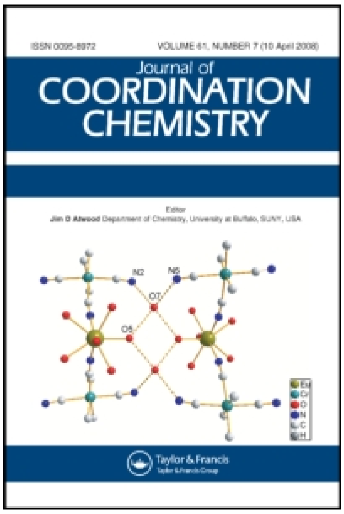

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Synthesis and crystal structure determination of the triflate salt of diacetonitrile(2,2'-bipyridine)platinum(II)

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SYNTHESIS AND CRYSTAL STRUCTURE DETERMINATION OF THE TRIFLATE SALT OF DIACETONITRILE(2,2′-BIPYRIDINE)PLATINUM(II)

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Reaction of [Pt(bipy)Cl_2] (bipy = 2,2′-bipyridine) with an excess of silver triflate in refluxing acetonitrile readily affords [Pt(bipy)$(MeCN)_2$]$(CF_3SO_3)_2$ as a yellow, crystalline solid. A single crystal X-ray diffraction study shows that the cations are arranged in a zig-zag manner in rows parallel to the *b* axis of the monoclinic unit cell. Consideration of the crystal structures of related bipyridyl ligand complexes of platinum(II), leads to the conclusion that a stacked structure with intermolecular Pt···Pt interactions for the title compound is prevented by the electrostatic repulsion between adjacent cations that are doubly charged.

Keywords: Bipyridyl; Platinum(II); Crystal structure

INTRODUCTION

2,2′-Bipyridyl (bipy) and 2,2′ : 6′,2″-terpyridyl (terpy) complexes of platinum(II) continue to be investigated with regard to their photophysical properties [1, 2]. Of relevance here are the *solid state* emission properties of compounds of this type, in particular emission from an excited state that has its origin in a $d\sigma^*(Pt) \rightarrow \pi^*(bipy)$ charge-transfer transition [3–5]. Emission of this type is only possible if $d_z^2(Pt)–d_z^2(Pt)$ interactions are present in the solid. For this to occur the complexes must stack parallel to each other in the solid with intermolecular Pt···Pt distances that are shorter than *ca.* 3.5 Å [6]. Connick and co-workers [7] have discussed the factors that promote parallel stacking and the formation of linear chain structures for planar bipyridyl ligand complexes of platinum(II). They conclude that the most important factor in stabilising the stack is the $d_z^2(Pt)–d_z^2(Pt)$ interaction, but note that $\pi(bipy)–\pi(bipy)$ interactions and steric factors also play a role.

Noteworthy in this context is that all the platinum bipyridyls with stacked structures and interacting platinum atoms that have been reported to date are *neutral* compounds

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e.g., [Pt(bipy)Cl_2] [4,8] and [Pt(bipy)$(CN)_2$] [9]. Thus the title compound provides a rare example of a dicationic bipyridyl ligand complex of platinum(II), where the third and fourth ligands (the acetonitriles) provide no steric barrier to the formation of a stacked linear chain arrangement for the cations. We wished to establish whether the stabilisation brought about by d_z^2(Pt)–d_z^2(Pt) interactions is sufficient to overcome the electrostatic repulsion between adjacent doubly charged cations. To this end the synthesis and crystal structure of [Pt(bipy)$(MeCN)_2$]$(CF_3SO_3)_2$ is reported here [10].

EXPERIMENTAL

Analysis and Physical Measurements

Microanalyses were performed by Galbraith Laboratories Inc., Knoxville, Tennessee, USA. ^{1}H NMR (200 MHz) spectra were recorded on a Varian Gemini 200 spectrometer at 25°C with chemical shifts referenced to $SiMe_4$. Infrared spectra were recorded using KBr discs on a Shimadzu FTIR-4300 spectrophotometer.

Reagents

[Pt(bipy)Cl_2] was prepared according to the method of Morgan and Burnstall [11]. $AgCF_3SO_3$ was obtained from Aldrich and used as received. Acetonitrile was purified using the method described by Carlsen *et al.* [12].

[Pt(bipy)$(MeCN)_2$]$(CF_3SO_3)_2$

A suspension of [Pt(bipy)Cl_2] (100 mg, 0.24 mmol) in acetonitrile (10 mL) was treated with a four-fold excess of $AgCF_3SO_3$ (243 mg, 0.96 mmol) dissolved in acetonitrile (5 mL). The reaction mixture was heated under reflux for 24 h and the precipitated AgCl removed by filtration. The volume of the filtrate was decreased under reduced pressure, resulting in the precipitation of [Pt(bipy)$(MeCN)_2$]$(CF_3SO_3)_2$. The material isolated was washed with acetone then by diethyl ether and dried *in vacuo*. Yield: 150 mg (85%). Anal. Calcd. for $C_{16}H_{14}F_6N_4O_6PtS_2$(%): C, 26.20; H, 2.20; N, 7.64. Found: C, 26.07; H, 1.87; N, 7.39.

Crystal Structure Determination

Yellow block-shaped crystals of [Pt(bipy)$(MeCN)_2$] were grown by slow evaporation at room temperature of a saturated solution of the compound in acetonitrile. Crystal data and details of the crystallographic study are reported in Table I. Intensity data were obtained on an Enraf-Nonius CAD4 diffractometer, using graphite-monochromated Mo Kα radiation and the ω–2θ scan technique. Unit cell parameters were obtained by least-squares fitting of 25 reflections monitored in the range $3° < \theta < 12°$ while the diffraction data were collected in the range $2° < \theta < 30°$. Corrections for Lorentz, polarisation, and absorption (χ scans of nine reflections) effects were applied. The intensities of three standard reflections showed no variations greater than those predicted by counting statistics. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares using SHELXS-97 [13] with all non-hydrogen

TABLE I Crystal data and structure refinement details for [Pt(bipy)(MeCN)$_2$](CF$_3$SO$_3$)$_2$

Formula	$C_{22}H_{14}F_6N_4O_6PtS_2$
Formula weight (g mol^{-1})	321.50
Crystal size (mm)	0.35 × 0.35 × 0.40
Crystal system	Monoclinic
Space group	$P2_1/m$
a (Å)	9.501(2)
b (Å)	12.464(3)
c (Å)	10.252(2)
β (°)	110.38(1)
V (Å^3)	1138(1)
Z	2
D_{calc} (g cm^{-3})	2.13
Temperature (K)	293(2)
μ (mm^{-1})	6.439
F (000)	700
Total no. of reflections measured	6909
No. of independent reflections	3461 [$R_{\text{int}} = 0.0188$]
No. of reflections observed [$I > 2\sigma(I)$]	3099
Refinement type	F^2
R_1^a, wR_2^b [$I > 2\sigma(I)$]	0.0194, 0.0618
R_1^a, wR_2^b (all data)	0.0258, 0.0700
No. of refined parameters	176
(Shift/esd)$_{\text{max}}$	0.001
Max, min $\Delta\rho$ (e Å^{-3})	0.65 (Pt), – 0.70 (Pt)

[a] $R_1 = \Sigma \| F_o| - |F_c \| / \Sigma |F_o|$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (0.1P)^2]$ and $P = (F_o^2 + 2F_c^2)/3$.

TABLE II Atomic coordinates and equivalent isotropic displacement parameters (Å^2 × 10^3).

	x/a	y/b	z/c	U_{eq}
Pt	0.54814(4)	0.25	0.31991(1)	0.0312(1)
S(1)	0.0336(1)	0.25	0.1229(1)	0.0364(2)
S(2)	0.4140(1)	0.25	0.7466(1)	0.0463(2)
F(1)	−0.1041(4)	0.1636(3)	0.2776(3)	0.083(1)
F(2)	−0.2483(4)	0.25	0.1033(5)	0.071(1)
F(3)	0.1481(4)	0.1642(4)	−0.3543(5)	0.126(2)
F(4)	0.1848(6)	0.25	−0.1694(5)	0.094(1)
O(1)	0.0049(3)	0.1528(2)	0.0424(3)	0.052(1)
O(2)	0.1692(4)	0.25	0.2426(4)	0.052(1)
O(3)	0.4624(4)	0.1526(3)	0.8203(4)	0.084(1)
O(4)	0.4216(6)	0.25	0.6083(5)	0.073(1)
N(1)	0.6568(1)	0.1461(2)	0.4682(3)	0.034(1)
N(2)	0.4434(3)	0.1402(3)	0.1789(2)	0.040(1)
C(1)	0.7388(3)	0.1915(2)	0.5915(3)	0.036(1)
C(2)	0.8177(4)	0.1294(3)	0.7050(3)	0.044(1)
C(3)	0.8118(5)	0.0186(3)	0.6927(4)	0.051(1)
C(4)	0.7276(4)	−0.0272(3)	0.5665(4)	0.051(1)
C(5)	0.6514(4)	0.0387(2)	0.4562(4)	0.044(1)
C(6)	0.3745(3)	0.0831(3)	0.0591(3)	0.040(1)
C(7)	0.2861(5)	0.0091(3)	−0.0099(4)	0.051(1)

U_{eq} is defined as one-third of the trace of the orthogonalised U_{ij} tensor.

atoms assigned anisotropic temperature factors and with the hydrogen atoms (in calculated positions) assigned a single overall isotropic temperature factor. Final atomic positions and equivalent isotropic thermal parameters for the non-hydrogen atoms are listed in Table II.

RESULTS AND DISCUSSION

Initial attempts at synthesising the title compound were based on the substitution by 2,2′-bipyridine of two acetonitrile molecules in the tetrakisacetonitrile species, $[Pt(MeCN)_4]^{2+}$ [14]. However, the selective addition of one equivalent of 2,2′-bipyridine proved very difficult to achieve because of the concomitant formation the disubstituted product $[Pt(bipy)_2]^{2+}$. A more successful approach made use of the previously reported complex $[Pt(bipy)Cl_2]$ as the precursor [11]. Thus, treatment of a refluxing solution of $[Pt(bipy)Cl_2]$ in acetonitrile with an excess of $AgCF_3SO_3$ afforded the desired product in solution and silver chloride as a precipitate. Separation of the latter by filtration and slow evaporation of the filtrate afforded light-yellow crystals of $[Pt(bipy)_2(MeCN)_2](CF_3SO_3)_2$ in yields of *ca.* 85%.

The infrared spectrum of $[Pt(bipy)_2(MeCN)_2](CF_3SO_3)_2$ recorded in KBr exhibits two peaks at 2328 and 2306 cm^{-1} in the C≡N stretching region of the spectrum. Similar C≡N stretching frequencies at 2330 and 2302 cm^{-1} have been reported for the solid-state infrared spectrum of $[Pt(terpy)(MeCN)](SbF_6)_2$ [15]. The *cis*-$[Pt(MeCN)_2Cl_2]$ complex exhibits peaks at 2333 and 2305 cm^{-1} in its solid-state infrared spectrum that are also attributed to C≡N stretches of the coordinated acetonitrile [16]. It is noteworthy that the C≡N stretching frequencies for coordinated acetonitrile are shifted to slightly higher values than the 2266 cm^{-1} reported for free acetonitrile [17]. This implies that the C≡N bond is strengthened slightly on coordination. The ^{1}H NMR spectrum recorded in CD_3CN exhibits three low-field multiplets at δ 8.86 ($H_{6,6'}$), 8.48 ($H_{3,3'}$ and $H_{4,4'}$) and 7.88 ($H_{2,2'}$) assigned as indicated to the protons of the bipyridyl ligand. Also present in the ^{1}H NMR spectrum is a high field peak at δ 2.20 that integrates for six protons and which is assigned to the methyl protons of coordinated acetonitrile molecules.

Crystal Structure of $[Pt(bipy)(MeCN)_2](CF_3SO_3)_2$

Figure 1 gives a perspective view of the cation drawn using the program ORTEP [18]. Selected interatomic distances and angles are listed in Table III.

The cation is situated on a special position of mirror symmetry with the mirror plane bisecting the N(1)–Pt–N(1′) and N(2)–Pt–N(2′) angles and passing through the mid-point of the C(1)–C(1′) bond. The geometry at the platinum atom is approximately

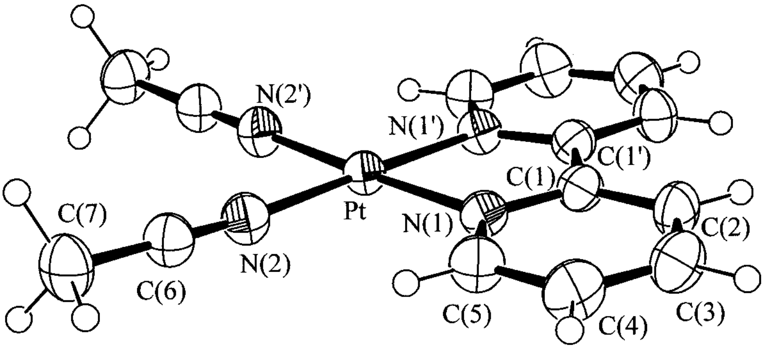

FIGURE 1 Perspective view of the cation in $[Pt(bipy)(MeCN)_2](CF_3SO_3)_2$. Ellipsoids are drawn at the 50% probability level for the non-hydrogen atoms. Hydrogen atoms are drawn as spheres of arbitrary radius.

TABLE III Selected interatomic distances (Å) and angles (°) for [Pt(bipy)-$(MeCN)_2](CF_3SO_3)_2$

Pt–N(1)	1.990(2)	Pt–N(2)	1.988(3)
N(1)–C(1)	1.357(4)	N(1)–C(5)	1.344(4)
C(1)–C(1′)	1.458(6)	C(1)–C(2)	1.381(4)
C(2)–C(3)	1.386(5)	C(3)–C(4)	1.385(6)
C(4)–C(5)	1.380(5)	N(2)–C(6)	1.132(4)
C(6)–C(7)	1.444(4)		
N(1)–Pt–N(1′)	81.2(1)	N(1)–Pt–N(2)	95.9(1)
N(2)–Pt–N(2′)	87.0(1)	N(1)–Pt–N(2′)	177.1(1)
Pt–N(2)–C(6)	174.6(3)	N(2)–C(6)–C(7)	178.9(4)
C(1)–N(1)–C(5)	119.5(3)	N(1)–C(1)–C(2)	121.2(3)
N(1)–C(1)–C(1′)	114.7(2)	C(2)–C(1)–C(1′)	124.1(2)
C(1)–C(2)–C(3)	119.3(3)	C(2)–C(3)–C(4)	119.2(3)
C(3)–C(4)–C(5)	119.2(3)	C(4)–C(5)–N(1)	121.7(3)

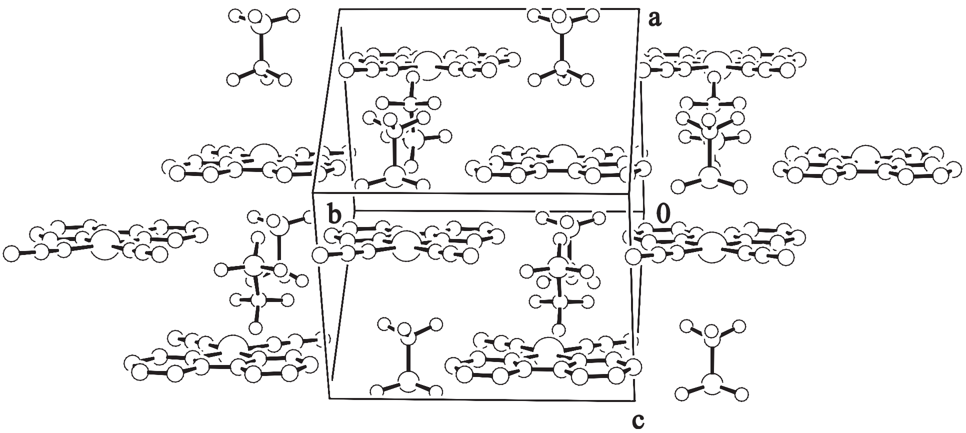

FIGURE 2 A view of the packing of the cations and anions in $[Pt(bipy)(MeCN)_2](CF_3SO_3)_2$. Atoms are drawn as spheres of arbitrary size with the hydrogen atoms omitted for clarity.

square planar, the major deviation from regular square-planar coordination being the result of the restricted bite of the bipyridyl ligand, as evidenced by a N(1)–Pt–N(1′) angle of 81.4(2)°. The largest deviation of any one non-hydrogen atom from the mean plane through all the non-hydrogen atoms that comprise the cation is 0.091(3) Å for C(5). The Pt–N(bipy) distances of 1.990(3) Å are in good agreement with those of 2.001(6) and 2.001(1) Å determined for $[Pt(bipy)Cl_2]$ [8] and $[Pt(bipy)(CN)_2]$, [9] respectively. The Pt–N(MeCN) distances of 1.988(3) Å are very similar to those of 1.98(1) and 2.00(2) Å reported for *cis*-$[Pt(MeCN)_2Cl_2]$ [16] and $[Pt(terpy)(MeCN)](SbF_6)_2$ [15]. The C(6)–N(2) (C≡N) bond length of 1.132(4) Å is marginally shorter than the value of 1.16 Å reported for free acetonitrile in the gas phase [19]. This is consistent with the infrared data that also suggest that the C≡N bond is slightly strengthened on coordination to a transition metal. Other interatomic distances and angles internal to the cation are entirely as expected.

The packing of the cations and anions in crystals of $[Pt(bipy)(MeCN)_2](CF_3SO_3)_2$ is illustrated in the PLUTO plot [18] shown in Fig. 2. The cations are arranged in a zig-zag manner in rows that run parallel to the *b* axis. Successive cations are related by centres of inversion. Interpersed between the cations are pairs of triflate anions. The net result of this packing motif is that the platinum atoms are well separated, the shortest Pt···Pt distance being 7.461 Å. Nor is there face-to-face overlap between the bipyridyl moieties. In short, $[Pt(bipy)(MeCN)_2](CF_3SO_3)_2$ does not adopt a stacked structure that allows for either d_z^2(Pt)–d_z^2(Pt) or π(bipy)–π(bipy) interactions.

The question arises as to whether a stacked structure is expected and, if so, why one is not obtained. We first note that a fairly wide range of compounds of the type $[Pt(bipy)(L)_2]$, where L is a monodentate ligand, have been synthesised and their crystal structures reported. These are, with their colours given in brackets: L = Cl (yellow polymorph) [20], L = Cl (red polymorph) [4,8], L = CN (red) [9], L = C≡CPh (yellow) [21], L = NCS (N-bonded, red) [7], and L = NCO (blue) [22]. Of these, the red compounds as well as the blue cyanate complex exhibit stacked linear chain structures in which intermolecular Pt···Pt distances are shorter than 3.5 Å. No such stacking is observed for the two yellow compounds. In the case of $[Pt(bipy)(C{\equiv}CPh)_2]$ this is probably due to the additional steric constraint associated with the phenyl group of the acetylide ligand. As far as $[Pt(bipy)Cl_2]$ is concerned, the yellow polymorph is obtained by careful choice of crystallisation conditions that preclude the formation of the red polymorph with the stacked structure [20]. Secondly, we note that the space-filling requirements of the thiocyanate ligand are very similar to those of the acetonitrile ligand. This follows from a van der Waals radius of 1.85 Å for a sulfur atom that is close in value to that of 2.00 Å for a methyl group [23]. On this basis $[Pt(bipy)(MeCN)_2](CF_3SO_3)_2$, like $[Pt(bipy)(NCS)_2]$, might be expected to exhibit a crystal structure where the cations are stacked in parallel layers with interacting platinum atoms. Of course, acetonitrile is distinguished from the thiocyanate ion by being a *neutral* ligand, with the result that the platinum complex is ionic. We believe that it is the electrostatic repulsion between adjacent cations that prevents the formation of a stacked linear chain structure for $[Pt(bipy)(MeCN)_2](CF_3SO_3)_2$. In drawing this conclusion we note that stacked structures with intermolecular Pt···Pt interactions have been reported for ionic *terpyridyl* ligand complexes of platinum(II) such as $[Pt(terpy)Cl]ClO_4$ [24] and $[Pt\{4'\text{-}(o\text{-}Me\text{-}Ph)terpy\}Cl]SbF_6$ [25]. However, in all these cases there is a single positive charge on the cation. The only example of a *dicationic* terpyridyl ligand complex of platinum(II) for which a crystal structure has been reported is $[Pt(terpy)(MeCN)](SbF_6)_2$ [15]. Like $[Pt(bipy)(MeCN)_2](CF_3SO_3)_2$, this compound has the cations arranged in the crystal in such a way that they are in a monomeric environment. We conclude that stacked structures stabilised by d_z^2(Pt)–d_z^2(Pt) interactions are possible for bipyridyl ligand complexes of platinum(II) provided the complex is neutral or, if ionic, that the charge on the cation is not greater than one. As noted in the Introduction this has implications for the solid-state emission properties of compounds of this type [26].

Acknowledgments

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References

[1] M. Kato, A. Omura, A. Toshikawa, S. Kishi and Y. Sugimoto, *Angew. Chem. Int. Ed.* **41**, 3183 (2002).

[2] V.W.-W. Yam, K.M.-C. Wong and N. Zhu, *J. Am. Chem. Soc.* **124**, 6506 (2002).

[3] M. Kato, C. Kosuge, K. Morii, J.S. Ahn, H. Kitagawa, T. Mitani, M. Matsushita, T. Kato, S. Yano and M. Kimura, *Inorg. Chem.* **38**, 1638 (1999).

[4] W.B. Connick, L.M. Henling, R.E. Marsh and H.B. Gray, *Inorg. Chem.* **35**, 6261 (1996).

[5] J.S. Field, R.J. Haines, D.R. McMillin and G.C. Summerton, *J. Chem. Soc., Dalton Trans.* 1369 (2002).

[6] D.S. Martin, In: *Extended Interactions between Metal Ions.* ACS Symp. Ser. 5. L.V. Interannte, ed. (American Chemical Society, Washington DC, 1974), p. 254.

[7] W.B. Connick, R.E. Marsh, W.B. Schaefer and H.B. Gray, *Inorg. Chem.* **36**, 913 (1997).

[8] R.J. Osbourn and D. Rogers, *J. Chem. Soc., Dalton Trans.* 1002 (1974).

[9] W.B. Connick, L.M. Henling and R.E. Marsh, *Acta Crystallogr.* **B52**, 817 (1996).

[10] We note in passing that the $[Pt(bipy)(MeCN)_2]^{2+}$cation is a useful synthon for the preparation of a wide range of bipyridyl ligand complexes of platinum(II).

[11] G.T. Morgan and F.H. Burnstall, *J. Chem. Soc.* 965 (1934).

[12] L. Carlsen, H. Egsgaard and J.R. Anderson, *Anal. Chem.* **51**, 1593 (1979).

[13] G.M. Sheldrick, SHELXS-97, A Program for Crystal Structure Determination and Refinement (University of Göttingen, Göttingen, Germany 1997).

[14] A. de Renzi, A. Pununzi and A. Vitagliano, *J. Chem. Soc., Chem. Commun.* **47** (1976).

[15] R. Büchner, J.S. Field, R.J. Haines, C.T. Cunningham and D.R. McMillin, *Inorg. Chem.* **36**, 3952 (1997).

[16] F.D. Rochon, R. Melanson, H.E. Howard-Lock, C.J.L. Lock and G. Turner, *Can. J. Chem.* **62**, 860 (1984).

[17] K.F. Purcell and R.S. Drago, *J. Am. Chem. Soc.* **88**, 919 (1966).

[18] L. Farrugia, *J. Appl. Crystallogr.* **30**, 565 (1997).

[19] M.D. Danford and R.L. Livingston, *J. Am. Chem. Soc.* **77**, 2944 (1955).

[20] A.J. Canty, B.W. Skelton, P.R. Traill and A.H. White, *Aust. J. Chem.* **45**, 417 (1992).

[21] H. Lang, A. del Villar and G. Rheinwald, *J. Organometallic Chem.* **587**, 284 (1999).

[22] M. Coyer, R.H. Herber and S. Cohen, *Inorg. Chim. Acta* **175**, 47 (1990).

[23] F.A. Cotton and G. Wilkinson, Basic Inorganic Chemistry (J. Wiley & Sons, New York, 1976).

[24] J.A. Bailey, M.G. Hill, R.E. Marsh, V.M. Miskowski, W.P. Schaefer and H.B. Gray, *Inorg. Chem.* **34**, 459 (1995).

[25] J.S. Field, R.J. Haines, D.R. McMillin and G.C. Summerton, *J. Chem. Soc., Dalton Trans.* 1369 (2002).

[26] The solid state emission exhibited by the title compound is of the intraligand (π–π^*) type, consistent with the crystal structure. Full details will be reported in a subsequent paper.