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2,6-Bis(azaindole)pyridine: reactivity with iron(III) and copper(II) salts

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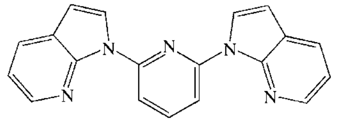
1-[6-(1*H*-Pyrrolo[2,3-*b*]pyridin-1-yl)pyridin-2-yl]-1*H*-pyrrolo-[2,3-*b*]pyridin-7-ium tetrachloridoferrate(III), $(C_{19}H_{14}N_5)[FeCl_4]$, (II), and [2,6-bis(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl-κN^7)-pyridine-κN]bis(nitrato-κO)copper(II), $[Cu(NO_3)_2(C_{19}H_{13}N_5)]$, (III), were prepared by self-assembly from $FeCl_3{\cdot}6H_2O$ or $Cu(NO_3)_2{\cdot}3H_2O$ and 2,6-bis(1*H*-pyrrolo[2,3-*b*]pyridin-1-yl)-pyridine [commonly called 2,6-bis(azaindole)pyridine, bap], $C_{19}H_{13}N_5$, (I). Compound (I) crystallizes with $Z' = 2$ in the $P\overline{1}$ space group, with both independent molecules adopting a *trans–trans* conformation. Compound (II) is a salt complex with weak C—H···Cl interactions giving rise to a zigzag network with π-stacking down the *a* axis. Complex (III) lies across a twofold rotation axis in the *C*2/*c* space group. The Cu^{II} center in (III) has an N_3O_2 trigonal–bipyramidal environment. The nitrate ligand coordinates in a monodentate fashion, while the bap ligand adopts a twisted tridentate binding mode. C—H···O interactions give rise to a ribbon motif.

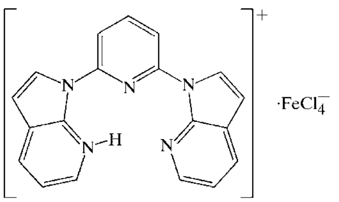
Comment

Organometallic supramolecular structures and materials remain a popular area of interest because of their spectral and electrochemical properties, and are thus potentially useful as molecular devices, sensors and catalysts (James, 2003; Braga, 2003; Blake *et al.*, 1999; Balzani & Juris, 2001). A plethora of geometric frameworks, dependent on the coordination preferences of the metal ion and the nature of the bridging ligand, have been reported (Moulton & Zaworotko, 2001). We were further inspired by the inorganic crystal engineering work reported by Mukherjee and coworkers (Mukherjee *et al.*, 2003; Balamurugan *et al.*, 2004), where C—H···Cl hydrogen bonding interactions proved a useful tool in forming supramolecular networks composed of $[(L^3)MnCl_2(EtOH)]$ and $[(L^6)FeCl_3]$ {L^3 is 2[3-(2-pyridyl)pyrazol-1-ylmethyl]pyridine and L^6 is methyl[2-(2-pyridyl)ethyl](2-pyridylmethyl)amine}.

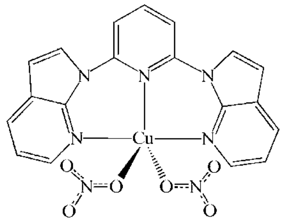
Our continuing research effort focuses on cyclometallating aryldiamine and polypyridyl ligands (i) as a mechanism to tune the electronic structure of square-planar platinum(II) and palladium(II) (Jude *et al.*, 2005; Tastan *et al.*, 2006), and (ii) as potential bridges to form more elaborate molecular architectures, such as triangles or larger polygons (Schweiger *et al.*, 2001, 2002). Thus, an ongoing effort is to synthesize a library of appropriate ligands. The synthesis and structural characterization of 2,6-bis(azaindole)pyridine (bap), (I), is described here. Furthermore, in addition to complexes with Pt^{II} and Pd^{II}, we would like to expand our studies to include other transition metals. In this report, we present our findings when Fe^{III} and Cu^{II} salts are reacted with (I).



(I)



(II)



(III)

Compound (I) (Fig. 1) crystallizes with two independent molecules in the asymmetric unit. Both molecules adopt a *trans–trans* conformation (see Table 1). Similar torsion angles are observed for the monoclinic (Bowes *et al.*, 2005) and orthorhombic forms (Bessel *et al.*, 1992) of 2,2′:6′,2″-terpyridine (tpy) and 2,6-bis(5,6,7,8-tetrahydroquinol-2-yl)pyridine (the torsion angles about the $C_{quinolyl}—C_{pyridine}$ bond are −168.5 and 165.7°; Sasaki *et al.*, 1998). On the other hand, 1,3-bis(7-azaindolyl)benzene (bab; Wu *et al.*, 2001) and 1-bromo-3,5-bis(7-azaindolyl)benzene (babBr; Song *et al.*, 2001) crystallize with noncoplanar azaindolyl rings, giving rise to a curved conformation (the torsion angles about the $N_{azaindolyl}—C_{benzene}$ bonds are in the 20–45° range).

Self-assembly of $FeCl_3{\cdot}6H_2O$ with (I) forms the salt $(bapH)FeCl_4$, (II) (Fig. 2). The $bapH^+$ cation is protonated at atom N1. A typical intramolecular N—H···N hydrogen bond occurs between atoms N1 and N5 [N1···N5 = 2.873 (3) Å]. The through-space separations N1···N3 and N5···N3 are 2.722 (3) and 2.832 (2) Å, respectively. The presence of the intramolecular hydrogen bond causes a conformational change in the bap molecule, giving rise to a *cis–cis* conformation [the torsion angles about the $N_{azaindolyl}—C_{pyridine}$ bonds

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are 3.8 (3) and 0.3 (3)°] with the azaindolyl rings essentially coplanar [the dihedral angles between the azaindolyl and pyridine rings are 3.32 (1) and 1.29 (1)°]. The Cl—Fe—Cl angles (Table 2) are consistent with tetrahedral geometry about the Fe^{III} center. The Fe—Cl distances are comparable to those in related complexes containing the $FeCl_4^-$ anion (Zora *et al.*, 1990; Chan & Baird, 2004; Lewis *et al.*, 2002).

Weak C—H···Cl interactions (Aullón *et al.*, 1998, Brammer *et al.*, 2001), forming a zigzag network, are observed between the bapH$^+$ cation and the $FeCl_4^-$ anion (see Table 3). π-Stacked interactions between neighboring cations run down the *a* axis; the interleaved layers are separated by ~3.4 Å [every second layer is aligned with a separation of 6.6695 (1) Å (the *a* axis cell length)]. Typical π–π interactions in organic compounds are less than 3.8 Å (Janiak, 2000).

Focused on forming square-planar complexes where (I) adopts a tridentate binding motif, we turned our attention to Ru^{III} and Cu^{II} salts. Attempts to react (I) with $RuCl_3\cdot nH_2O$ failed to yield a product. However, reaction of $Cu(NO_3)_2\cdot3H_2O$ with (I) resulted in the formation of $(bap)Cu(NO_3)_2$, (III) (Fig. 3*a*). The molecule crystallizes such that molecular and crystallographic twofold rotation symmetry coincide. The geometry about the Cu^{II} center is trigonal–bipyramidal, with an N_3O_2 environment. Both nitrate ions coordinate in a monodentate fashion through an O atom [Cu—O2 = 2.1746 (14) Å and Cu···O1 = 2.636 (2) Å]. Bond lengths and angles (see Table 4) are typical and comparable to those in $[(phtpy)Cu(OH)(NO_3)][(phtpy)Cu(NO_3)_2]$ [phtpy is 4′-(2-pyridyl)-2,2′:6,2″-terpyridine; Padhi & Manivannan, 2006] and $(tpyBr_2)Cu(NO_3)_2$ (Lam *et al.*, 2006). C—H···O interactions (see Table 5) give rise to a ribbon motif.

The bap ligand in (III) adopts a twisted, tridentate binding mode [C8—N3—Cu—N1 = 23.0 (1)°; Fig. 3*b*]. Perusal of the literature shows that the related structures $[(tpyOH)Cu(OH_2](ClO_4)_2$ (Jeitler & Turnbull, 2005), $[(phtpy)Cu(OH)(NO_3)][(phtpy)Cu(NO_3)_2]$ (Padhi & Manivannan, 2006) and $(tpyBr_2)Cu(NO_3)_2$ (Lam *et al.*, 2006) sport a tridentate-bound tpy ligand; however, the tpy rings are nearly planar (the C—N—*M*—N torsion angles are less than 6°). The chelate distortion from planarity in bap is echoed by the closely related bab and bab*R* ligands in (bab)*M*Cl and (babBr)*M*Cl (*M* = Pd and Pt) (with twisted geometry, having C—N—*M*—N torsion angles in the range 20–34°; Song *et al.*,

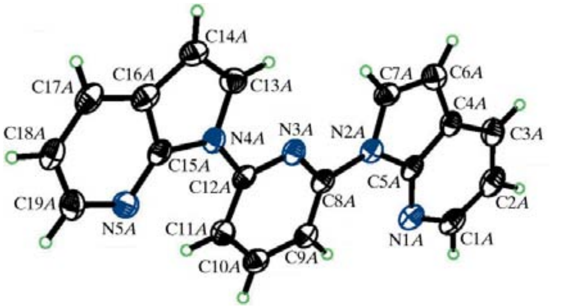

Figure 1
The structure of (I), showing the atomic labelling scheme and 50% probability displacement ellipsoids. Both independent molecules adopt similar conformations, therefore only molecule *A* is shown.

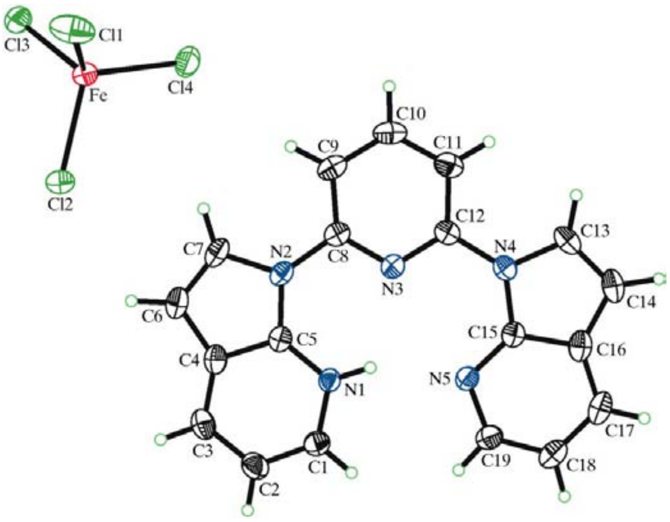

Figure 2
The structure of (II), showing the atomic labelling scheme and 50% probability displacement ellipsoids.

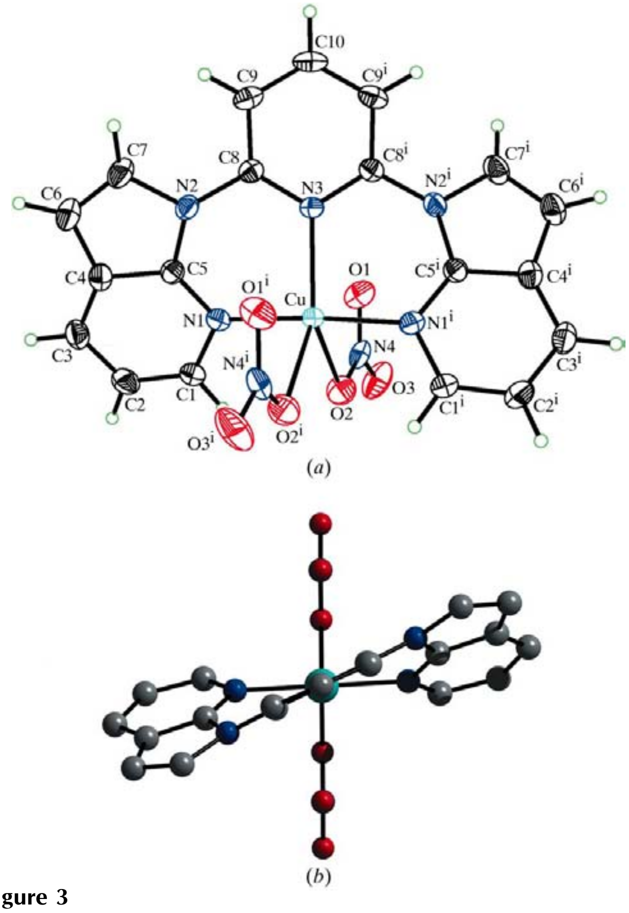

Figure 3
(*a*) The structure of (III), showing the atomic labelling scheme [symmetry code: (i) $-x+1, y, -z+\frac{1}{2}$] and 50% probability displacement ellipsoids. (*b*) A view down the Cu—N3—C10 axis, showing the ligand twist.

2001). For (bab*R*)Re(CO)$_3$ (*R* = H, F, CF$_3$ and MeO) complexes, the chelate takes on a folded butterfly geometry (Tani *et al.*, 2004). Characteristic of these structures is the increased nonplanarity of the tridentate ligand (twist or butterfly conformations) as the progression tpy, tpyOH, tpyO, phtpy $\simeq$ tpyBr$_2$ < bap, bab, bap*R* is made, consistent with a direct relationship between increased steric effects near the metal coordination plane and the degree of nonplanarity.

Experimental

Compound (I) was prepared by a modified procedure based on the synthesis of bab (Wu *et al.*, 2001). 2,6-Dibromopyridine (8.6 mmol, 2.0407 g), 7-azaindole (18 mmol, 2.1415 g), potassium carbonate (14.8 mmol, 2.0526 g) and cupric sulfate (1.75 mmol, 0.2792 g) were added to a flask under an argon atmosphere. The mixture was heated with stirring for 4 h at 483 K. After cooling to room temperature, the resulting mixture was extracted with methylene chloride and water. The organic layer was separated, dried with MgSO$_4$ and filtered, and the solvent volume was reduced. Hexanes were added to precipitate (I) as a white crystalline solid (2.1 mmol, 0.6700 g, 25% yield). Colorless crystals suitable for X-ray analysis were grown by slow evaporation of a methanol–methylene chloride solution.

FeCl$_3$·6H$_2$O in methanol was layered over a solution of (I) in methylene chloride (1:1 molar ratio of reactants, 5 ml of each solvent) in a test tube. The test tube was covered with Parafilm. Crystallite formation occurred within a few hours at room temperature. Yellow X-ray quality crystals of (II) were harvested after 1–2 weeks.

In an analogous fashion, equimolar amounts of Cu(NO$_3$)$_2$·3H$_2$O and (I) in methanol and methylene chloride, respectively, were allowed to react. Light-green X-ray quality crystals of (III) were obtained after 1–2 weeks.

Compound (I)

Crystal data

$C_{19}H_{13}N_5$
M_r = 311.34
Triclinic, $P\overline{1}$
a = 6.6377 (2) Å
b = 10.1397 (3) Å
c = 21.9214 (6) Å
α = 76.609 (1)°
β = 86.563 (10)°
γ = 90.004 (1)°
V = 1432.56 (7) Å^3
Z = 4
Cu *Kα* radiation
μ = 0.72 mm^{-1}
T = 150 (2) K
0.35 × 0.10 × 0.05 mm

Data collection

Bruker SMART 6000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.787, T_{max} = 0.965
11609 measured reflections
4847 independent reflections
4215 reflections with $I > 2\sigma(I)$
R_{int} = 0.026

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.122
S = 1.06
4847 reflections
434 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.24 e Å^{-3}

Table 1
Selected torsion angles (°) for (I).

C5*A*—N2*A*—C8*A*—N3*A*	176.4 (2)	C5*B*—N2*B*—C8*B*—N3*B*	176.1 (2)
C15*A*—N4*A*—C12*A*—N3*A*	−178.4 (2)	C15*B*—N4*B*—C12*B*—N3*B*	−179.4 (2)

Compound (II)

Crystal data

$(C_{19}H_{14}N_5)[FeCl_4]$
M_r = 510.00
Monoclinic, $P2_1/n$
a = 6.6695 (1) Å
b = 23.2657 (4) Å
c = 13.3959 (2) Å
β = 100.312 (1)°
V = 2045.07 (6) Å^3
Z = 4
Cu *Kα* radiation
μ = 10.86 mm^{-1}
T = 150 (2) K
0.19 × 0.04 × 0.02 mm

Data collection

Bruker SMART 6000 CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.232, T_{max} = 0.812
17199 measured reflections
3653 independent reflections
3210 reflections with $I > 2\sigma(I)$
R_{int} = 0.041

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.075
S = 1.04
3653 reflections
266 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.34 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}

Table 2
Selected geometric parameters (Å, °) for (II).

Fe—Cl4	2.1895 (7)	Fe—Cl2	2.1970 (6)
Fe—Cl3	2.1949 (6)	Fe—Cl1	2.1985 (7)
Cl4—Fe—Cl3	108.65 (3)	Cl4—Fe—Cl1	109.79 (3)
Cl4—Fe—Cl2	110.34 (3)	Cl3—Fe—Cl1	108.45 (3)
Cl3—Fe—Cl2	110.85 (3)	Cl2—Fe—Cl1	108.73 (3)

Table 3
Hydrogen-bond geometry (Å, °) for (II).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H20···N5	0.89 (3)	2.04 (3)	2.873 (3)	156 (2)
C3—H3···Cl1^{i}	0.95	2.87	3.692 (2)	146
C19—H19···Cl1^{ii}	0.95	2.88	3.718 (2)	147
C13—H13···Cl2^{iii}	0.95	2.85	3.676 (2)	146
C9—H9···Cl4	0.95	2.73	3.660 (2)	168

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{3}{2}, z - \frac{1}{2}$; (ii) $x, y, z - 1$; (iii) $-x + \frac{1}{2}, y - \frac{1}{2}, -z + \frac{3}{2}$.

Compound (III)

Crystal data

$[Cu(NO_3)_2(C_{19}H_{13}N_5)]$
M_r = 498.90
Monoclinic, *C*2/*c*
a = 17.3858 (12) Å
b = 12.8324 (8) Å
c = 8.4011 (6) Å
β = 94.726 (2)°
V = 1867.9 (2) Å^3
Z = 4
Synchrotron radiation
λ = 0.77490 Å
μ = 1.55 mm^{-1}
T = 193 (2) K
0.06 × 0.04 × 0.04 mm

Data collection

Bruker Platinum 200 diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
T_{min} = 0.913, T_{max} = 0.941
10400 measured reflections
2319 independent reflections
2155 reflections with $I > 2\sigma(I)$
R_{int} = 0.105

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.134
S = 1.01
2319 reflections
151 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.65 e Å^{-3}
$\Delta\rho_{min}$ = −0.59 e Å^{-3}

Table 4
Selected geometric parameters (Å, °) for (III).

Cu—N1	1.963 (2)	Cu—O2	2.1746 (14)
Cu—N3	2.117 (2)		
$N1—Cu—N1^{i}$	176.05 (8)	$N1^{i}—Cu—O2$	86.84 (6)
N1—Cu—N3	91.97 (4)	N3—Cu—O2	136.42 (4)
N1—Cu—O2	90.30 (6)	$O2^{i}—Cu—O2$	87.16 (8)

Symmetry code: (i) $-x+1, y, -z+\frac{1}{2}$.

Table 5
Hydrogen-bond geometry (Å, °) for (III).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
$C9—H9\cdots O1^{ii}$	0.95	2.39	3.249 (3)	150
$C6—H6\cdots O3^{iii}$	0.95	2.53	3.277 (3)	136
$C7—H7\cdots O3^{iv}$	0.95	2.39	3.141 (2)	135

Symmetry codes: (ii) $-x+1, -y+1, -z$; (iii) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (iv) $x-\frac{1}{2}, y+\frac{1}{2}, z$.

Initial refinement of (I) in $P\overline{1}$ yielded a structure solution with $R1 \simeq 19\%$. Subsequent refinements included the twin law ($\overline{1}00$, 010, $01\overline{1}$) obtained from *ROTAX* (Parsons & Gould, 2001) as implemented in *CRYSTALS* (Betteridge *et al.*, 2003). The twin fraction ratio is 42:58. The N-bound H atom in (II) was located directly; the position and isotropic displacement parameters were refined. All remaining H atoms were either located or calculated and treated as riding (C—H = 0.95 Å); the isotropic displacement parameters were defined as $1.2U_{eq}$(C).

For (I) and (II), data collection: *SMART* (Bruker, 2003); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT* (Bruker, 2003). For (III), data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT* (Bruker, 2005). For all compounds, program(s) used to solve structure: *SHELXTL* (Sheldrick, 2003); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL* for (I), and *SHELXTL* and *DIAMOND* (Brandenburg, 2007) for (II) and (III); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3124). Services for accessing these data are described at the back of the journal.

References

Aullón, G., Bellamy, D., Brammer, L., Bruton, E. A. & Orpen, G. A. (1998). *J. Chem. Soc. Chem. Commun.* pp. 653–654.

Balamurugan, V., Jacob, W. & Mukherjee, J. (2004). *CrystEngComm*, **6**, 396–400.

Balzani, V. & Juris, A. (2001). *Coord. Chem. Rev.* **211**, 97–115.

Bessel, C. A., See, R. F., Jameson, D. L., Churchill, M. R. & Takeuchi, K. J. (1992). *J. Chem. Soc. Dalton Trans.* pp. 3223–3228.

Betteridge, P. W., Carruthers, J. R., Cooper, R. I., Prout, K. & Watkin, D. J. (2003). *J. Appl. Cryst.* **36**, 1487.

Blake, A. J., Champness, N. R., Hubberstey, P., Li, W.-S., Withersby, M. A. & Schröder, M. (1999). *Coord. Chem. Rev.* **183**, 117–138.

Bowes, K. F., Clark, I. P., Cole, J. M., Gourlay, M., Griffin, A. M. E., Mahon, M. F., Ooi, L., Parker, A. W., Raithby, P. R., Sparkes, H. A. & Towrie, M. (2005). *CrystEngComm*, **7**, 269–275.

Braga, D. (2003). *J. Chem. Soc. Chem. Commun.* pp. 2751–2753.

Brammer, L., Bruton, E. A. & Sherwood, P. (2001). *Cryst. Growth Des.* **1**, 277–290.

Brandenburg, K. (2007). *DIAMOND*. Version 3.1e. Crystal Impact GbR, Bonn, Germany.

Bruker (2003). *SMART* (Version 5.631) and *SAINT* (Version 6.45A). Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2005). *APEX2* (Version 2.0-2) and *SAINT* (Version 7.23A). Bruker AXS Inc., Madison, Wisconsin, USA.

Chan, B. C. K. & Baird, M. C. (2004). *Inorg. Chim. Acta*, **357**, 2776–2782.

James, S. L. (2003). *Chem. Soc. Rev.* **32**, 276–288.

Janiak, C. (2000). *J. Chem. Soc. Dalton Trans.* pp. 3885–3896.

Jeitler, J. R. & Turnbull, M. M. (2005). *Acta Cryst.* E**61**, m1846–m1848.

Jude, H., Krause Bauer, J. A. & Connick, W. B. (2005). *Inorg. Chem.* **44**, 1211–1220.

Lam, A. K. Y., Abrahams, B. F., Grannas, J. J., McFadyen, W. D. & O'Hair, R. A. J. (2006). *J. Chem. Soc. Dalton Trans.* pp. 5051–5061.

Lewis, G. R., Hubberstey, P. & Sampson, C. L. (2002). *Acta Cryst.* E**58**, m331–m333.

Moulton, B. & Zaworotko, M. J. (2001). *Chem. Rev.* **101**, 1629–1658.

Mukherjee, J., Balamurugan, V., Gupta, R. & Mukherjee, R. (2003). *Dalton Trans.* pp. 3686–3692.

Padhi, S. K. & Manivannan, V. (2006). *Inorg. Chem.* **45**, 7994–7996.

Parsons, S. & Gould, R. (2001). *ROTAX*. Version 26. University of Edinburgh, Scotland.

Sasaki, I., Daran, J. C., Aït-Haddou, H. & Balavoine, G. G. A. (1998). *Inorg. Chem. Commun.* **1**, 354–357.

Schweiger, M., Seidel, S. R., Arif, A. M. & Stang, P. J. (2001). *Angew. Chem. Int. Ed.* **40**, 3467–3469.

Schweiger, M., Seidel, S. R., Arif, A. M. & Stang, P. J. (2002). *Inorg. Chem.* **41**, 2556–2559.

Sheldrick, G. M. (2003). *SADABS* (Version 2.10) and *SHELXTL* (Version 6.14). Bruker AXS Inc., Madison, Wisconsin, USA.

Song, D., Wu, Q., Hook, A., Kozin, I. & Wang, S. (2001). *Organometallics*, **20**, 4683–4689.

Tani, K., Sakurai, H., Fujii, H. & Hirao, T. (2004). *J. Organomet. Chem.* **689**, 1665–1674.

Tastan, S., Krause, J. A. & Connick, W. B. (2006). *Inorg. Chim. Acta*, **359**, 1889–1898.

Wu, Q., Lavigne, J. A., Tao, Y., D'Iorio, D. & Wang, S. (2001). *Chem. Mater.* **13**, 71–77.

Zora, J. A., Sneddon, K. R., Hitchcock, P. B., Lowe, C. B., Shum, D. P. & Carlin, R. L. (1990). *Inorg. Chem.* **29**, 3302–3308.