Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Tris[bis(1-methyl-1*H*-imidazol-2-yl)methanone-κ^2N^3]iron(II) dichloride 5.5-hydrate, *cis*-bis[bis(1-methyl-1*H*-imidazol-2-yl)methanone-κ^2N^3]dichloroiron(II) (*ca* 153 K) and di-μ-chloro-bis{[bis(1-methyl-1*H*-imidazol-2-yl)methanone-κ^2N^3]chloroiron(II)} methanol disolvate (*ca* 300 K)

Michael P. Batten,[a] Allan J. Canty,[a] Kingsley J. Cavell,[a]‡ Thomas Rüther,[a]§ Brian W. Skelton[b]* and Allan H. White[b]

[a]Department of Chemistry, University of Tasmania, Hobart, Tasmania 7001, Australia, and [b]Chemistry, University of Western Australia, 35 Stirling Highway, Crawley, WA 6009, Australia
Correspondence e-mail: bws@crystal.uwa.edu.au

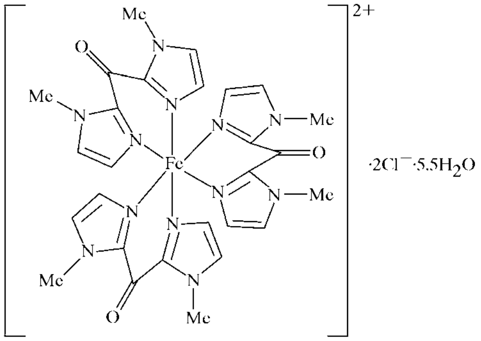
Received 24 March 2004
Accepted 4 May 2004
Online 22 June 2004

The first of the title compounds, $[Fe(C_9H_{10}N_4O)_3]Cl_2\cdot5.5H_2O$, is the first structurally characterized homoleptic tris[bis(imidazol-2-yl) ketone]–metal complex to be structurally defined. In the second of the title compounds, $[FeCl_2(C_9H_{10}N_4O)_2]$, a pair of monodentate donors supplants one of the bidentate ligands. In the third complex, $[Fe_2Cl_4(C_9H_{10}N_4O)_2]\cdot2CH_3OH$, a centrosymmetric binuclear compound with a pair of bridging chloride ligands, the introduction of a third chloro ligand results in five-coordination about each of the metal atoms; the environments of the latter are square pyramidal, with a chloro ligand at the apex and the two bidentate arrays about the base of the pyramid.

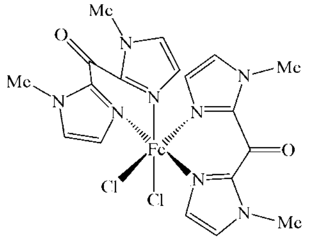
Comment

Metal chelate complexes of *N*,*N*′-bidentate ligands with aromatic heterocyclic donors have long been prominent features in coordination chemistry. Many of these are derivatives of 2,2′-bipyridyl, but more recently the chelate ring size and flexibility have been increased by the introduction of diverse linking groups between the two rings. Thus, bis(2-pyridyl) ketone complexes have been widely explored, with, in turn, further modifications by the incorporation of other heterocycles, some of different ring size, bis(imidazol-2-yl) ketone being of particular relevance here. Structurally characterized chelate complexes of ligands of the latter type have been restricted to arrays of metals with coordination number four, with the exception of chromium(III) (Rüther *et al.*, 2002), ruthenium (Elgafi *et al.*, 1997), copper(I) (Gorun *et al.*, 1996) and copper(II) complexes (Byers *et al.*, 1985). Some of these are homoleptic bis(ligand)–metal ion complexes with diversely substituted ligands, those of particular interest in the context of the present ligands being the complexes with Zn^{II} (Chen *et al.*, 1995), Cu^{II} (Stange & Kaim, 1996; McMaster *et al.*, 1996) and Cu^{I} (McMaster *et al.*, 1996); homoleptic arrays of the unsubstituted ligand are also recorded for these metals (Long *et al.*, 2001; Place *et al.*, 1998).

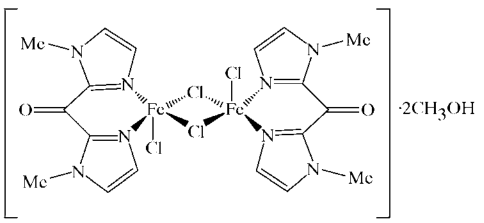
The intention of the present work was to explore the nature of complexes formed with a metal ion system inherently capable of yielding complexes in which the coordination number about the metal is intrinsically higher. Iron(II) is such a system; other studies recorded in an accompanying paper (Batten *et al.*, 2004*a*, and references therein) have shown the possibility of forming homoleptic bis(ligand)–metal arrays with tris-imidazolyl donors by the reaction of the ligand with the metal chloride. We turned our attention to such a possibility with the bis(1-methyl-1*H*-imidazolyl) ketone ligand, obtaining the three title complexes, which have been characterized by diffraction studies.



(I)



(II)



(III)

The results of the single-crystal X-ray studies are consistent in stoichiometry and connectivity with the formulation of the

---

‡ Present address: Department of Chemistry, University of Cardiff, Wales.
§ Present address: IDT Australia, Boronia, Victoria 3155, Australia.

DOI: 10.1107/S0108270104010881

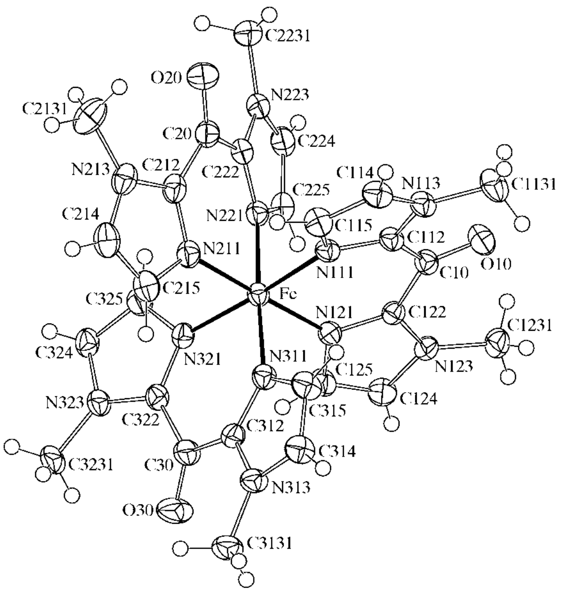


Figure 1
The cation of (I), projected down its quasi-3-axis. Displacement ellipsoids of 50% probability are shown for the non-H atoms, the H atoms having arbitrary radii of 0.1 Å.

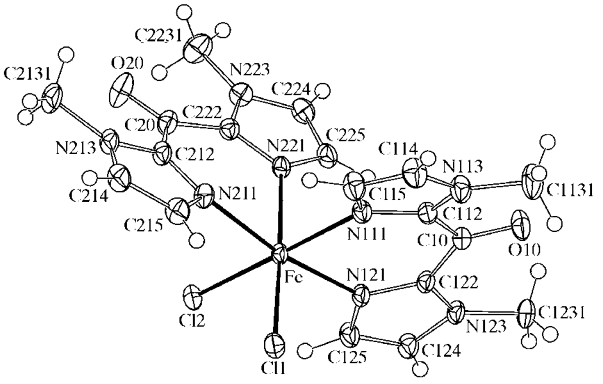


Figure 2
A single molecule of (II). Displacement ellipsoids of 50% probability are shown for the non-H atoms, the H atoms having arbitrary radii of 0.1 Å.

three title complexes, (I), (II) and (III), respectively. In (I) and (II), one mononuclear formula unit, devoid of crystallographic symmetry, composes the asymmetric unit of each structure; in (III), the asymmetric unit comprises one-half of the centrosymmetric binuclear unit. In (I), layers of cations, normal to **a***, are interleaved by layers of anions and solvent moieties; displacement parameters of the latter are high, diminishing the precision of the determination. A similar comment applies to (III), where despite good quality data, solvent disorder again militates against optimal precision in the determination.

Compound (I) is the first structurally characterized tris[bis(imidazolyl) ketone]–metal ion system; like all such systems, the complex is inherently chiral (Fig. 1), although the crystal overall is racemic. The environment about the metal atom is close to octahedral; the mean Fe—N distance is 1.983 (12) Å, consistent with low-spin iron(II) with the maximum (*cis* angle) deviation from orthogonality [85.75 (15)°; Table 1]. The cation departs from ideal 32 symmetry by distortion of the chelate rings; comparison with the other two complexes suggests the distortion to be a concomitant of the Fe—N distance. The driver of this distortion may just as well be close contacts at the periphery between the carbonyl and the methyl substituents to either side; these should be most widely spaced in (I) where the Fe—N distance is short, but here the distortion is largest, the interplanar dihedral angles between the heterocycle planes for the three ligands being 18.0 (2), 24.5 (2) and 16.5 (2)°, with Fe-atom deviations from the individual planes of 0.075 (6), 0.125 (6), 0.064 (6), 0.301 (6), 0.101 (6) and 0.307 (6) Å. The On0$\cdots$Cn131/Cn231 distances lie in the range 2.806 (5)–2.896 (6) Å.

In (II) (Fig. 2), one of the ligands is supplanted by a pair of chloride donors, *cis* in the coordination sphere, resulting in a neutral molecule in which the Fe–donor distances (Table 2) are consistent with a high-spin rather than a low-spin electronic state. The interplanar dihedral angles between the heterocycle moieties for the two ligands are 14.62 (8) and 9.42 (8)°. The Fe-atom deviations from the individual planes are very large, *viz*. 0.276 (3), 0.301 (3), 0.563 (3) and 0.597 (3) Å; the C10/C20 deviations are much less [0.048 (3) Å maximum], so that the rings have envelope conformations. The On0$\cdots$Cn131/Cn231 distances are generally smaller than those in (I), a concomitant of the 'flatter' ligand profile [range 2.782 (3)–2.817 (3) Å]. Angular distortions from orthogonality about the metal atom are greater in (II) than in (I), most notably in the bidentate 'bite' angles [89.68 (14), 88.95 (13) and 89.9 (14) in (I), and 82.17 (6) and 82.33 (6)° in (II)], in keeping with increased Fe—N distances. Furthermore, in (I), the N$\cdots$N intraligand distances are 2.801 (4), 2.763 (4) and 2.807 (4) Å, while in (II) they are 2.868 (2) and 2.881 (2) Å.

In (III) (Fig. 3), with the displacement of a further bidentate ligand, the coordination number contracts to five, with concomitant formation of a centrosymmetric di-μ-chloro-bridged binuclear complex and a (chelate-N_2)FeCl(μ-Cl)$_2$

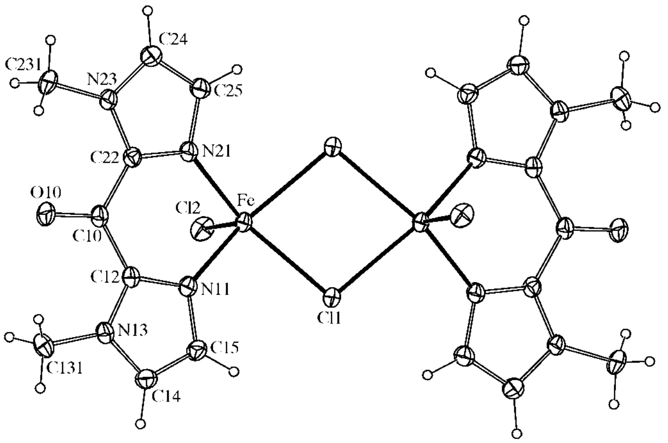


Figure 3
The dimeric structure of (III); displacement ellipsoids are shown at the 20% probability level.

coordination environment. This five-coordinate array can be contrasted with the mononuclear (chelate-N_2)Fe(HOMe)Cl_2 compound, (IV), described by Batten *et al.* (2004*b*), which exhibits a similar bite angle [2.864 (10) Å in (III), *cf.* 2.855 (3) Å in (IV)]. In (IV), the Fe-atom environment is quasi-trigonal bipyramidal; in (III), it is quasi-square pyramidal, with the pyramid apex occupied by the monodentate Cl atom and the base composed of the pair of bidentate ligands. The Fe—N distances for the two complexes are similar [2.146 (6) and 2.148 (10) Å in (III) (Table 3), *cf.* 2.108 (2) (equatorial) and 2.149 (2) Å (axial) in (IV)]; the terminal Fe—Cl distance in (III) is 2.282 (3) Å and the bridging distances are 2.455 (4) and 2.470 (3) Å [*cf.* 2.3246 (7) and 2.3290 (6) Å in (IV)]. The present ligand is more nearly planar than in (IV) [the interplanar dihedral angle between the pair of heterocycles is 5.0 (4)°], but the Fe-atom deviations are again large [0.43 (1) and 0.36 (1) Å], so that the chelate ring again has an envelope conformation.

Experimental

For the synthesis of (I), a solution of bis(1-methylimidazol-2-yl)methanone (0.233 g, 1.23 mmol) in methanol (40 ml) was added to a stirred solution of iron(II) chloride (0.052 g, 0.410 mmol) in methanol (20 ml). The rose-coloured solution that formed initially became purple as the amount of ligand added exceeded ~0.25 equivalents. The solvent was removed under reduced pressure to give a dark-blue solid. This was recrystallized from methanol/dichloromethane, then from methanol/ether, and washed with light petroleum (3 × 7 ml) to give a blue microcrystalline solid, which was dried in a vacuum. The solid was dissolved in methanol (10 ml) and left to crystallize in a 50 ml Erlenmeyer flask capped with a small watch glass. A crop of dark-blue crystals suitable for X-ray work (0.06 g, 60%) was obtained. For the synthesis of (II), a solution of bis(1-methylimidazol-2-yl)methanone (0.7154 g, 3.761 mmol) in methanol (10 ml) was added dropwise to a stirred solution of iron(II) chloride (0.2383 g, 1.880 mmol) in methanol (16.5 ml). The rose-coloured solution that formed initially became purple as the amount of ligand added exceeded 1 equivalent. Diethyl ether (60 ml) was added to the dark-violet solution and the mixture was left to crystallize. Dark-blue crystals formed and were collected by cannula filtration, washed with diethyl ether (4 × 5 ml) and light petroleum (2 × 5 ml), and dried in a vacuum (yield 0.8214 g, 1.620 mmol, 86%). Analysis found: C 42.82, H 3.68, N 21.82%; $C_{18}H_{20}Cl_2FeN_8O_2$ requires: C 42.63, H 3.97, N 22.09%. For the synthesis of (III), a solution of bis(1-methylimidazol-2-yl)methanone (0.1069 g, 0.562 mmol) in methanol (5.0 ml) was added dropwise to a stirred solution of iron(II) chloride (0.1867 g, 1.473 mmol) in methanol (20 ml). The blood-red solution that formed initially became purple on completion of ligand addition, whereupon methanol (10 ml) was added to return some of the red colour to the solution. A layer of diethyl ether (60 ml) and a layer of light petroleum (17 ml) were added, and the reaction mixture was allowed to stand for 3 d. The resulting mixture was filtered and the solvent was removed under reduced pressure to give a purple solid that was recrystallized from dichloromethane (30 ml) and light petroleum (50 ml). A mixture of blue and red crystals formed, which were collected by cannula filtration; the red crystals were washed carefully with small portions of dichloromethane (40 ml) to remove the blue material and then dried in a vacuum (yield 0.0926 g, 0.133 mmol, 24%).

Compound (I)

Crystal data

$[Fe(C_9H_{10}N_4O)_3]Cl_2\cdot5.5H_2O$
$M_r = 796.54$
Monoclinic, $C2/c$
$a = 21.3036\ (10)$ Å
$b = 13.9936\ (7)$ Å
$c = 24.4634\ (10)$ Å
$\beta = 104.230\ (1)^\circ$
$V = 7069.1\ (6)$ Å^3
$Z = 8$
$D_x = 1.497$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6946 reflections
$\theta = 2.5$–28.5°
$\mu = 0.64$ mm^{-1}
$T = 153\ (2)$ K
Bar, dark blue
0.24 × 0.14 × 0.13 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.69$, $T_{max} = 0.86$
73 261 measured reflections
9402 independent reflections
6365 reflections with $I > 2\sigma(I)$
$R_{int} = 0.083$
$\theta_{max} = 29.0^\circ$
$h = -29 \rightarrow 28$
$k = -19 \rightarrow 19$
$l = -33 \rightarrow 33$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.062$
$wR(F^2) = 0.13$
$S = 1.22$
6365 reflections
460 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F^2) + 0.\ 60F^2]$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.16$ e Å^{-3}
$\Delta\rho_{min} = -1.06$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °) for (I).

Fe—N111	1.986 (4)	Fe—N221	1.979 (3)
Fe—N121	1.979 (3)	Fe—N311	1.993 (3)
Fe—N211	1.961 (3)	Fe—N321	1.995 (4)
N111—Fe—N121	89.68 (14)	N121—Fe—N321	95.16 (14)
N111—Fe—N211	89.42 (15)	N211—Fe—N221	88.95 (13)
N111—Fe—N221	87.81 (14)	N211—Fe—N311	93.66 (13)
N111—Fe—N311	90.71 (14)	N211—Fe—N321	85.75 (15)
N111—Fe—N321	175.16 (13)	N221—Fe—N311	176.98 (14)
N121—Fe—N211	178.46 (15)	N221—Fe—N321	92.21 (14)
N121—Fe—N221	89.78 (13)	N311—Fe—N321	89.49 (14)
N121—Fe—N311	87.59 (13)		

Compound (II)

Crystal data

$[FeCl_2(C_9H_{10}N_4O)_2]$
$M_r = 507.17$
Monoclinic, $P2_1/c$
$a = 14.650\ (2)$ Å
$b = 9.1340\ (10)$ Å
$c = 16.180\ (2)$ Å
$\beta = 102.078\ (3)^\circ$
$V = 2117.2\ (5)$ Å^3
$Z = 4$
$D_x = 1.591$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5040 reflections
$\theta = 2.4$–34.5°
$\mu = 1.00$ mm^{-1}
$T = 153\ (2)$ K
Hexagonal plate, dark blue
0.44 × 0.41 × 0.28 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.81$, $T_{max} = 1$
42 826 measured reflections
9074 independent reflections
6873 reflections with $I > 2\sigma(I)$
$R_{int} = 0.044$
$\theta_{max} = 34.7^\circ$
$h = -23 \rightarrow 22$
$k = -14 \rightarrow 14$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.082$
$S = 1.04$
6873 reflections
280 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F^2) + 2.3F^2]$
$(\Delta/\sigma)_{\max} = 0.045$
$\Delta\rho_{\max} = 0.69$ e Å^{-3}
$\Delta\rho_{\min} = -0.54$ e Å^{-3}

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

Fe—Cl1	2.4345 (6)	Fe—N121	2.1713 (17)
Fe—Cl2	2.4729 (6)	Fe—N211	2.1719 (16)
Fe—N111	2.1961 (18)	Fe—N221	2.2069 (16)
Cl1—Fe—Cl2	95.40 (2)	Cl2—Fe—N221	85.51 (5)
Cl1—Fe—N111	88.99 (5)	N111—Fe—N121	82.17 (6)
Cl1—Fe—N121	94.93 (5)	N111—Fe—N211	94.13 (6)
Cl1—Fe—N211	94.33 (5)	N111—Fe—N221	90.28 (6)
Cl1—Fe—N221	176.52 (5)	N121—Fe—N211	169.96 (7)
Cl2—Fe—N111	174.63 (5)	N121—Fe—N221	88.34 (6)
Cl2—Fe—N121	94.34 (5)	N211—Fe—N221	82.33 (6)
Cl2—Fe—N211	88.63 (5)		

Compound (III)

Crystal data

$[Fe_2Cl_4(C_9H_{10}N_4O)_2]\cdot 2CH_4O$
$M_r = 693.97$
Triclinic, $P\overline{1}$
$a = 8.358$ (3) Å
$b = 9.215$ (3) Å
$c = 10.650$ (4) Å
$\alpha = 93.175$ (5)°
$\beta = 108.871$ (4)°
$\gamma = 113.923$ (4)°
$V = 692.8$ (4) Å^3
$Z = 1$
$D_x = 1.663$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2043 reflections
$\theta = 2.5$–27.4°
$\mu = 1.48$ mm^{-1}
$T = 300$ (2) K
Plate, red
0.25 × 0.22 × 0.10 mm

Data collection

Bruker SMART CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.82$, $T_{\max} = 1$
6649 measured reflections
3012 independent reflections
2200 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\max} = 27.0$°
$h = -11 \rightarrow 10$
$k = -12 \rightarrow 11$
$l = -14 \rightarrow 14$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.146$
$S = 1.06$
2085 reflections
170 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F^2) + 0.58F^2]$
$(\Delta/\sigma)_{\max} = 0.018$
$\Delta\rho_{\max} = 1.52$ e Å^{-3}
$\Delta\rho_{\min} = -0.40$ e Å^{-3}

Table 3
Selected geometric parameters (Å, °) for (III).

Fe—Cl1	2.455 (4)	Fe—N21	2.148 (10)
Fe—Cl2	2.282 (3)	Fe—Cl1$^{\rm i}$	2.470 (3)
Fe—N11	2.146 (6)		
Cl1—Fe—Cl2	104.48 (13)	Cl2—Fe—Cl1$^{\rm i}$	109.42 (10)
Cl1—Fe—N11	90.4 (2)	N11—Fe—N21	83.5 (3)
Cl1—Fe—Cl1$^{\rm i}$	80.68 (11)	N11—Fe—Cl1$^{\rm i}$	146.2 (2)
Cl2—Fe—N11	104.4 (2)	N21—Fe—Cl1$^{\rm i}$	88.0 (2)
Cl2—Fe—N21	105.6 (2)	Fe—Cl1—Fe$^{\rm i}$	99.32 (12)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

H atoms were located from difference Fourier maps, and placed at idealized positions [C—H = 0.95 Å, and $U_{\rm iso}({\rm H}) = 1.25U_{\rm eq}({\rm C_{CH}})$ and $1.5U_{\rm eq}({\rm C_{CH_3}})$] and not refined. For (I) and (III), the H atoms of the solvent molecules were not located. For (I), the site-occupancy factor of atom O6 was assigned a value of 0.5 after trial refinement. For (III), the largest peak in the final difference map was located close to the atoms of the disordered methanol molecule (0.60 Å from C1 and 0.48 Å from O1′).

For all three title compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *Xtal*3.5 (Hall *et al.*, 1995); program(s) used to refine structure: *CRYLSQ* in *Xtal*3.5; molecular graphics: *Xtal*3.5; software used to prepare material for publication: *BONDLA* and *CIFIO* in *Xtal*3.5.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1447). Services for accessing these data are described at the back of the journal.

References

Batten, M. P., Canty, A. J., Cavell, K. J., Rüther, T., Skelton, B. W. & White, A. H. (2004*a*). *Acta Cryst.* C**60**, m311–m313.

Batten, M. P., Canty, A. J., Cavell, K. J., Rüther, T., Skelton, B. W. & White, A. H. (2004*b*). *Acta Cryst.* C**60**, m314–m315.

Byers, P. K., Canty, A. J., Engelhardt, L. M., Patrick, J. M. & White, A. H. (1985). *J. Chem. Soc. Dalton Trans.* pp. 981–986.

Chen, X.-M., Xu, Z.-T. & Mak, T. C. W. (1995). *Polyhedron*, **14**, 319–322.

Elgafi, S., Field, L. D., Messerle, B. A., Hambley, T. W. & Turner, P. (1997). *J. Chem. Soc. Dalton Trans.* pp. 2341–2345.

Gorun, S. M., Stibrany, R. T., Katritzky, A. R., Slawinski, J. J., Faid-Allah, H. & Brunner, F. (1996). *Inorg. Chem.* **35**, 3–4.

Hall, S. R., King, G. S. D. & Stewart, J. M. (1995). *The Xtal3.5 User's Manual.* University of Western Australia: Lamb, Perth.

Long, L.-S., Ren, R.-P., Huang, R.-B., Zheng, L.-S., Chen, X.-M. & Ng, S. W. (2001). *Main Group Met. Chem.* **74**, 463–464.

McMaster, J., Beddoes, R. L., Collison, D., Eardley, D. R., Helliwell, M. & Garner, C. D. (1996). *Chem. Eur. J.* **2**, 685–693.

Place, C., Zimmerman, J.-L., Mulliez, E., Guillot, G., Bois, C. & Chottard, J.-C. (1998). *Inorg. Chem.* **37**, 4030–4039.

Rüther, T., Cavell, K. J., Brassaud, N. C., Skelton, B. W. & White, A. H. (2002). *J. Chem. Soc. Dalton Trans.* pp. 4684–4693.

Sheldrick, G. M. (1996). *SADABS.* University of Göttingen, Germany.

Siemens (1995). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Stange, A. F. & Kaim, W. (1996). *Z. Anorg. Allg. Chem.* **622**, 1118–1124.