Molecule (IV) crystallized in the orthorhombic system; space group *Pnma* or *Pn*2_1*a* from the systematic absences. Both possibilities were examined in considerable detail and *Pnma* eventually selected after refinement in *Pn*2_1*a* led to various non-sensible parameters. The anion lies on a mirror plane; the N atom of the $[NEt_4]^+$ cation is on a crystallographic centre of symmetry which requires that the ethyl groups be disordered equally over two sites with 0.5 occupancy. Detailed inspection of successive difference-map plots showed clearly that two of the terminal methyl groups of the cation were each further disordered unequally over at least two sites. Sites for these groups were located from a difference Fourier plot and restrained to maintain sensible geometry using appropriate *DFIX* instructions during the *SHELXL*97 (Sheldrick, 1997) refinement. Site occupancies for these disordered methyl C atoms refined to 0.317 (9) (for C12 and C24) and 0.183 (9) (for C15 and C25). All non-H atoms of the anion and the N atom of the cation were allowed anisotropic displacement parameters. The partial-occupancy C atoms of the cation were only allowed isotropic motion. A view of the conformation of the cation is deposited. H atoms were treated as riding atoms (C—H 0.96–0.97 Å), but no allowance was made for the H atoms of the minor components of the cation.

Data collection: *CAD*-4-*PC* (Enraf–Nonius, 1992). Cell refinement: *SET*4 and *CELDIM* in *CAD*-4-*PC*. Data reduction: *DATRD*2 in *NRCVAX*96 (Gabe *et al.*, 1989). Program(s) used to solve structure: *NRCVAX*96 *via* Patterson heavy-atom method. Program(s) used to refine structure: *NRCVAX*96 and *SHELXL*97. Molecular graphics: *NRCVAX*96, *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 1998). Software used to prepare material for publication: *NRCVAX*96, *SHELXL*97 and *WordPerfect* macro *PRPCIF*97 (Ferguson, 1997).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1200). Services for accessing these data are described at the back of the journal. A simplistic view of the cation which does not show the disorder introduced by the inversion centre at the N atom has also been deposited.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.

Aupers, J. H., Cox, P. J., Doidge-Harrison, S. M. S. V., Howie, R. A., Khan, A., Spencer, G. M. & Wardell, J. L. (1998). *Polyhedron*. In the press.

Buchanan, H., Howie, R. A., Khan, A., Spencer, G. M., Wardell, J. L. & Aupers, J. H. (1996). *J. Chem. Soc. Dalton Trans.* pp. 541–548.

Chohan, Z. H., Howie, R. A., Wardell, J. L., Wilkens, R. & Doidge-Harrison, S. M. S. V. (1997). *Polyhedron*, **16**, 2689–2696.

Doidge-Harrison, S. M. S. V., Howie, R. A., Irvine, J. T. S., Spencer, G. M. & Wardell, J. L. (1991). *J. Organomet. Chem.* **414**, C5–C8.

Doidge-Harrison, S. M. S. V., Howie, R. A., Irvine, J. T. S., Spencer, G. M. & Wardell, J. L. (1992). *J. Organomet. Chem.* **463**, 23–33.

Doidge-Harrison, S. M. S. V., Howie, R. A., Irvine, J. T. S. & Wardell, J. L. (1992). *Polyhedron*, **11**, 2223–2229.

Doidge-Harrison, S. M. S. V., Irvine, J. T. S., Khan, A., Spencer, G. M., Wardell, J. L. & Aupers, J. H. (1996). *J. Organomet. Chem.* **516**, 199–205.

Enraf–Nonius (1992). *CAD-4-PC Software*. Version 1.1. Enraf–Nonius, Delft, The Netherlands.

Ferguson, G. (1997). *PRPCIF97. A WordPerfect-5.1 Macro to Merge and Polish CIF Format Files from NRCVAX and SHELXL97 Programs.* University of Guelph, Canada.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Huheey, J. E., Keiter, E. A. & Keiter, R. L. (1993). In *Inorganic Chemistry*, 4th ed. New York: Harper Collins.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Khan, A., Low, J. N., Wardell, J. L. & Ferguson, G. (1998). *Acta Cryst.* **C54**, 1399–1401.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.

Olk, R.-M., Dietzsch, W., Kohler, K., Kirmse, R., Reinhold, J., Hoyer, E., Golic, L. & Olk, B. (1988). *Z. Anorg. Allg. Chem.* **567**, 131–144.

Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Spek, A. L. (1998). *PLATON. Molecular Geometry Program.* Version of March 1998. University of Utrecht, The Netherlands.

Sun, S. Q., Zhang, B., Wu, P. J. & Zhu, D. B. (1997). *J. Chem. Soc. Dalton Trans.* pp. 277–281.

Vicente, R., Ribas, J., Alvarez, S., Segui, A., Solans, X. & Verdaguer, M. (1987). *Inorg. Chem.* **26**, 4004–4009.

Vicente, R., Ribas, J., Zanchini, C., Gatteschi, D., Legros, J.-P., Faulmann, C. & Cassoux, P. (1988). *Z. Naturforsch. Teil B*, **43**, 1137–1143.

Yang, X., Freeman, G. K. W., Rauchfuss, T. B. & Wilson, S. R. (1991). *Inorg. Chem.* **30**, 3034–3038.

Zeltner, S., Dietzsch, W., Olk, R.-M., Kirmse, R., Richter, R., Schroder, U., Olk, B. & Hoyer, E. (1994). *Z. Anorg. Allg. Chem.* **620**, 1768–1776.

Acta Cryst. (1998). C54, 1403–1406

Deca-μ-acetato-di-μ_4-oxo-tetra(pyridine-*N*)-dimanganese(III)tetramanganese(II) Pyridine Solvate

PETER KARSTEN AND JOACHIM STRÄHLE

Institute of Inorganic Chemistry, University of Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany. E-mail: joachim.straehle@uni-tuebingen.de

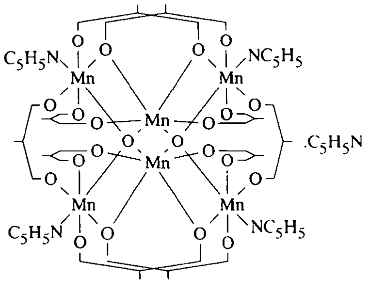
(*Received 30 October 1997; accepted 21 April 1998*)

Abstract

The title compound, $[Mn_6O_2(C_2H_3O_2)_{10}(C_5H_5N)_4]$.$C_5H_5N$, consists of well separated $[Mn_6O_2(OAc)_{10}py_4]$ complex units (OAc is acetate and py is pyridine) and pyridine solvent molecules. Six Mn atoms with distorted octahedral coordination spheres are connected by bridging oxo and acetato ligands. The Mn—O distances are between 1.892 (2) and 2.318 (3) Å, and the Mn—N distances are 2.287 (3) and 2.302 (4) Å. The magnetic moment at 300 K amounts to $\mu_{exp} = 5.66\ \mu_B$.

Comment

The complex $[Mn_6O_2(OAc)_{10}py_4]$.py (OAc is acetate and py is pyridine), (I), was obtained as a by-product in an attempt to prepare a manganese complex incorporating the N_3S_2-chelate ligand pyridine-2,6-diacetylbis(2-mercaptoanil). It can also be prepared by crystallizing $Mn^{II}(OAc)_2$ from aqueous pyridine.



(I)

An *ZORTEP* (Zsolnai, 1994) plot of the structure of the hexanuclear complex $[Mn_6O_2(OAc)_{10}py_4]$ with the atomic numbering scheme is shown in Fig. 1. The central Mn1 and Mn2 atoms occupy the special position $(0,y,\frac{1}{4})$ with C_2 symmetry. These two central Mn atoms exhibit a distorted octahedral coordination of O atoms from bridging oxo and acetato ligands. Both octahedra are connected by a common edge of O1 and O1^{i} oxo ions [symmetry code: (i) $-x$, y, $\frac{1}{2}-z$]. This results in a relatively short Mn1···Mn2 distance of 2.8243 (11) Å, indicating a possible Mn···Mn interaction [the sum of the Mn covalent radii is 2.78 Å (Huheey, 1978)]. The oxo ions have relatively short Mn—O1 distances of 1.892 (2) Å to the central Mn atoms, while the average Mn—O distances to the bridging acetate O2 and O5 atoms, and to the O3 and O4 atoms are 1.97 and 2.25 Å, respectively.

Atoms Mn3 and Mn4 are each octahedrally coordinated by five O atoms and one pyridine N atom. Their polyhedra are connected to the central Mn1 and Mn2 octahedra by a common edge. The distances of Mn3 and Mn4 to the μ_4-oxo ion are 2.197 (2) and 2.196 (2) Å, respectively, and the distances to the O atoms of the acetato ligands are in the range 2.097 (3)–2.318 (3) Å. The sixth coordination sites are occupied by a pyridine N atom, with an average distance of 2.29 Å.

The acetato ligands are coordinated in two distinct patterns, bridging either two or three metal centers. In the latter case, one of the two O atoms coordinates to two metal atoms and so has longer Mn—O distances [2.236 (2)–2.318 (3) Å].

The neutral complex formally consists of two Mn^{3+} and four Mn^{2+} ions. The magnetic susceptibility has been measured between 5 and 300 K. In the range between 45 and 300 K, the susceptibility follows the Curie–Weiss law. An antiferromagnetic coupling with a Néel temperature of 10 K is observed, which may be

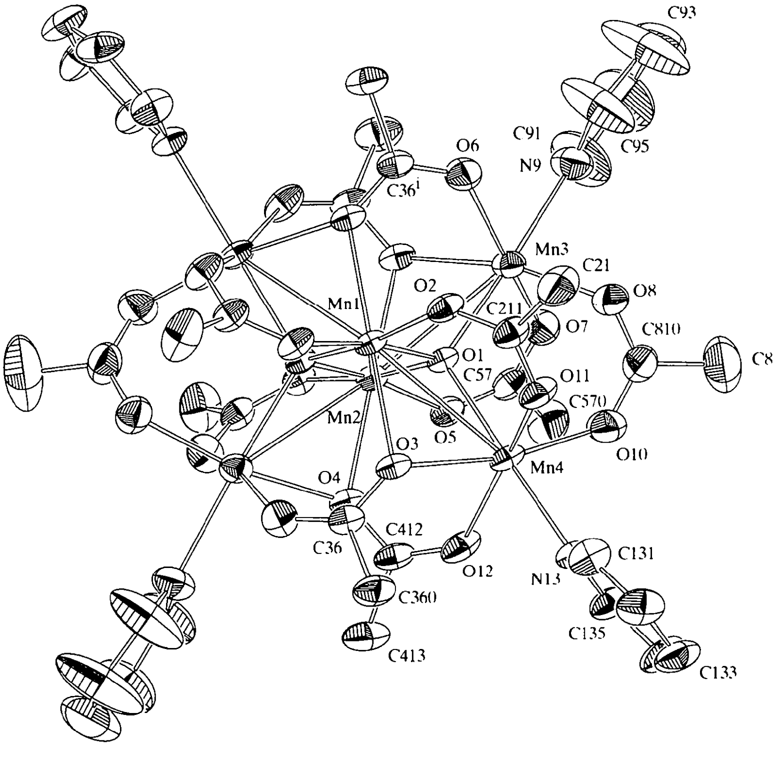


Fig. 1. *ZORTEP* plot (Zsolnai, 1994) of $[Mn_6O_2(OAc)_{10}py_4]$ with the atomic numbering scheme and 50% probability ellipsoids. The symmetry code is as given in Table 1.

mediated by a superexchange or a direct interaction of the central Mn1 and Mn2 atoms. The magnetic moment at 300 K amounts to $\mu_{\rm exp}$ = 5.66 $\mu_{\rm B}$, which compares well with the expected average magnetic moment of $\mu_{\rm s.o.}$ = 5.58 $\mu_{\rm B}$.

Experimental

The synthesis of the title compound was carried out by dissolving manganese(II) acetate in dry pyridine, adding traces of water and covering the solution with a layer of hexane. After several weeks, purple crystals of $[Mn_6O_2(OAc)_{10}py_4].py$ were obtained.

Crystal data

$[Mn_6O_2(C_2H_3O_2)_{10}$-
$(C_5H_5N)_4].C_5H_5N$
M_r = 1347.58
Monoclinic
$C2/c$
a = 25.601 (8) Å
b = 12.694 (3) Å
c = 18.153 (5) Å
β = 107.608 (12)°
V = 5623 (3) Å^3
Z = 4
D_x = 1.591 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 8–14°
μ = 1.386 mm^{-1}
T = 223 (2) K
Block
0.60 × 0.25 × 0.15 mm
Purple

Data collection

Enraf–Nonius CAD-4 diffractometer
ω scans
Absorption correction: ψ scans (North *et al.*, 1968)
$T_{\rm min}$ = 0.777, $T_{\rm max}$ = 0.812
6713 measured reflections
6129 independent reflections

4870 reflections with $F > 2\sigma(F)$
$R_{\rm int}$ = 0.023
$\theta_{\rm max}$ = 27.01°
$h = -32 \rightarrow 31$
$k = 0 \rightarrow 16$
$l = -1 \rightarrow 23$
3 standard reflections every 400 reflections intensity decay: 0.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.052$
$wR(F^2) = 0.128$
S = 1.104
6127 reflections
353 parameters
H atoms calculated at idealized positions
$w = 1/[\sigma^2(F_o^2) + (0.0770P)^2 + 10.9217P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max}$ = 1.046 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.797 e Å^{-3}
Extinction correction: *SHELXL*93
Extinction coefficient: 1×10^{-6}
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

Mn1—O1	1.892 (2)	Mn4—O3	2.318 (3)
Mn1—O2	1.967 (3)	Mn4—O10	2.097 (3)
Mn1—O3	2.262 (2)	Mn4—O11	2.154 (3)
Mn1···Mn2	2.8243 (11)	Mn4—O12	2.141 (3)
Mn1···Mn4	3.1954 (9)	Mn4—N13	2.287 (3)
Mn2—O1	1.895 (2)	O2—C211	1.273 (5)
Mn2—O4	2.236 (2)	O3—C36	1.260 (4)
Mn2—O5	1.968 (2)	O4—C412	1.280 (4)
Mn2···Mn3	3.1795 (11)	O5—C57	1.254 (5)
Mn3—O1	2.197 (2)	O6—C36$^{\rm i}$	1.248 (5)
Mn3—O4$^{\rm i}$	2.294 (3)	O7—C57	1.242 (5)
Mn3—O6	2.163 (3)	O8—C810	1.269 (5)
Mn3—O7	2.164 (3)	O10—C810	1.239 (5)
Mn3—O8	2.105 (3)	O11—C211	1.237 (5)
Mn3—N9	2.302 (4)	O12—C412	1.241 (5)
Mn4—O1	2.196 (2)		

O1—Mn1—O1$^{\rm i}$	83.60 (14)	O5—Mn2—O5$^{\rm i}$	86.57 (15)
O1—Mn1—O2	95.03 (10)	O1—Mn3—O4$^{\rm i}$	76.80 (9)
O1—Mn1—O2$^{\rm i}$	170.75 (10)	O1—Mn3—O6	97.63 (10)
O1$^{\rm i}$—Mn1—O2	170.74 (10)	O1—Mn3—O7	92.96 (10)
O1$^{\rm i}$—Mn1—O2$^{\rm i}$	95.03 (10)	O1—Mn3—O8	94.03 (11)
O1—Mn1—O3	84.71 (9)	O1—Mn3—N9	174.81 (13)
O1—Mn1—O3$^{\rm i}$	98.45 (10)	O4$^{\rm i}$—Mn3—O6	85.85 (10)
O1$^{\rm i}$—Mn1—O3	98.45 (9)	O4$^{\rm i}$—Mn3—O7	81.40 (10)
O2$^{\rm i}$—Mn1—O2	87.8 (2)	O4$^{\rm i}$—Mn3—O8	165.43 (10)
O2—Mn1—O3	90.52 (10)	O4$^{\rm i}$—Mn3—N9	98.64 (13)
O2$^{\rm i}$—Mn1—O3	86.45 (10)	O6—Mn3—O7	161.14 (12)
O2—Mn1—O3$^{\rm i}$	86.45 (10)	O6—Mn3—O8	106.81 (12)
O3—Mn1—O3$^{\rm i}$	175.80 (13)	O6—Mn3—N9	84.40 (12)
Mn1—O1—Mn2	96.46 (11)	O7—Mn3—O8	87.87 (12)
Mn1—O1—Mn3	120.25 (11)	O7—Mn3—N9	83.84 (12)
Mn1—O1—Mn4	102.55 (10)	O8—Mn3—N9	89.93 (14)
Mn1—O3—Mn4	88.48 (9)	O1—Mn4—O3	77.02 (9)
Mn2—O1—Mn3	101.75 (10)	O1—Mn4—O10	93.90 (11)
Mn2—O1—Mn4	118.32 (11)	O1—Mn4—O11	90.65 (9)
Mn2—O4—Mn3$^{\rm i}$	89.14 (9)	O1—Mn4—O12	99.14 (10)
Mn3—O1—Mn4	116.63 (10)	O1—Mn4—N13	175.02 (10)
O1—Mn2—O1$^{\rm i}$	83.49 (14)	O3—Mn4—O10	168.48 (10)
O1—Mn2—O5	95.60 (10)	O3—Mn4—O11	81.22 (10)
O1—Mn2—O5$^{\rm i}$	171.37 (10)	O3—Mn4—O12	85.09 (10)
O1$^{\rm i}$—Mn2—O5	171.37 (10)	O3—Mn4—N13	100.89 (10)
O1—Mn2—O4	99.67 (10)	O10—Mn4—O11	91.94 (12)
O1—Mn2—O4$^{\rm i}$	84.56 (10)	O10—Mn4—O12	103.56 (12)
O1$^{\rm i}$—Mn2—O4	84.56 (10)	O10—Mn4—N13	87.58 (12)
O4—Mn2—O4$^{\rm i}$	174.38 (13)	O11—Mn4—O12	160.95 (12)
O4—Mn2—O5	87.14 (10)	O11—Mn4—N13	84.54 (11)
O4—Mn2—O5$^{\rm i}$	88.77 (10)	O12—Mn4—N13	85.12 (11)
O4$^{\rm i}$—Mn2—O5	88.77 (10)		

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

H atoms were calculated at ideal positions with common isotropic displacement parameters ($U_{\rm iso}$ = 0.08 Å^2).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *SET*4 (de Boer & Duisenberg, 1984) in *CAD*-4 *Software*. Data reduction: *SDP* (Enraf–Nonius, 1985). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ZORTEP* (Zsolnai, 1994). Software used to prepare material for publication: *SHELXL*93. Computations were performed on a DEC VAX Station 3100, a CONVEX C3860 and a Pentium 120 PC.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1019). Services for accessing these data are described at the back of the journal.

References

Boer, J. L. de & Duisenberg, A. J. M. (1984). *Acta Cryst.* A**40**, C-410.
Enraf–Nonius (1985). *Structure Determination Package*. Version 3.0. Enraf–Nonius, Delft, The Netherlands.
Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Huheey, J. E. (1978). *Inorganic Chemistry, Principles of Structure and Reactivity*, 2nd ed., p. 232. New York: Harper & Row Publishers.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.
Zsolnai, L. (1994). *ZORTEP. Program for the Presentation of Thermal Ellipsoids.* University of Heidelberg, Germany.

Acta Cryst. (1998). C**54**, 1406–1408

Bis(1,8-diazabicyclo[5.4.0]undec-7-en-8-ium) *trans*-Dichlorotetra(pyridine-*N*)-iron(II) Dichloride

PETER KARSTEN AND JOACHIM STRÄHLE

Institute of Inorganic Chemistry, University of Tübingen, Auf der Morgenstelle 18, D-72076 Tübingen, Germany. E-mail: joachim.straehle@uni-tuebingen.de

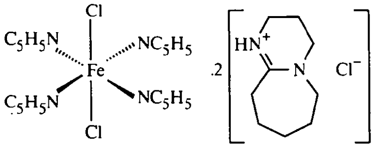
(*Received 31 October 1997; accepted 21 April 1998*)

Abstract

The title compound, $(C_9H_{17}N_2)_2[FeCl_2(C_5H_5N)_4]Cl_2$, consists of well separated $[FeCl_2(NC_5H_5)_4]$ complex molecules, 1,8-diazabicyclo[5.4.0]undec-7-en-8-ium ($HDBU^+$) cations and Cl^- anions. The Fe atom, located at an inversion center, is octahedrally coordinated, with the two chloro ligands arranged *trans*. The Fe—Cl distance is 2.4067 (8) Å. The N atoms of the four pyridine ligands constitute the equatorial plane, with Fe—N distances in the range 2.273 (3)–2.279 (3) Å.

Comment

The $[FeCl_2(NC_5H_5)_4]$ complex was formed as a crystalline by-product in an attempt to synthesize an iron(III) complex of the tetradentate ligand glyoxal–bis(2-mercaptoanil). Mercapto groups are well known as reducing agents for trivalent iron compounds (Hagen *et al.*, 1981). 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) was used as an auxiliary base.



(I)

The structure of $[FeCl_2(NC_5H_5)_4].2[(HDBU)Cl]$, (I), is shown in Fig. 1, together with the atomic numbering scheme. In the structure, the Fe atom occupies the inversion center at (0,0,0). It is octahedrally coordinated

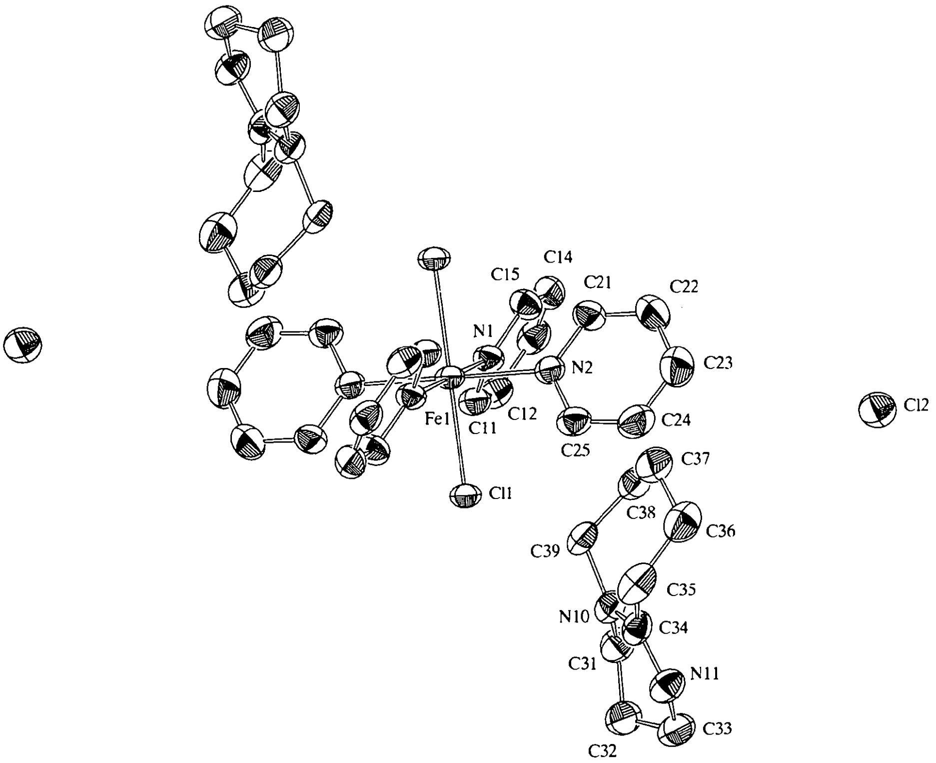


Fig. 1. *ZORTEP* plot (Zsolnai, 1994) of $[FeCl_2(NC_5H_5)_4].2[(HDBU)Cl]$ with the atomic numbering scheme and 50% probability ellipsoids.

Acta Crystallographica Section C
ISSN 0108-2701 © 1998