APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2002; **16**: 331–336
DOI:10.1002/aoc.305

Synthesis and single crystal X-ray determination of the Schiff base 1-[(2-isopropyl-5-methylphenoxy)hydrazono] ethyl ferrocene

Ahmad O. Baghlaf*, M. Ishaq, Khalid H. Bakhiswein and Adil H. Al-Harbi

Department of Chemistry, Faculty of Science, King Abdulaziz University, PO Box 80203, Jeddah 21589, Kingdom of Saudi Arabia

Received 29 August 2001; Accepted 18 February 2002

The reaction of acetylferrocene [Fe(η-C_5H_5)(η-$C_5H_4COCH_3$)] (1) with (2-isopropyl-5-methylphenoxy) acetic acid hydrazide [$CH_3C_6H_3CH(CH_3)_2OCH_2CONHNH_2$] (2) in refluxing ethanol gives the stable light-orange–brown Schiff base 1-[(2-isopropyl-5-methylphenoxy)hydrazono] ethyl ferrocene, [$CH_3C_6H_3CH(CH_3)_2OCH_2CONHN{=}C(CH_3)Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4)$] (3). Complex 3 has been characterized by elemental analysis, IR, ^{1}H NMR and single crystal X-ray diffraction study. It crystallizes in the monoclinic space group $P2_1/n$, with $a = 9.6965(15)$, $b = 7.4991(12)$, $c = 29.698(7)$ Å, $\beta = 99.010(13)°$, $V = 2132.8(7)$ Å^3, $D_{calc} = 1.346$ Mg m^{-3}; absorption coefficient, 0.729 mm^{-1}. The crystal structure clearly shows the characteristic [N–H···O] hydrogen bonding between the two adjacent molecules of 3. This acts as a bidentale ligand, which, on treatment with $[Ru(CO)_2Cl_2]_n$, gives a stable bimetallic yellow–orange complex (4). Copyright © 2002 John Wiley & Sons, Ltd.

KEYWORDS: acetylferrocene; carboxylic acid; Schiff base; X-ray structure

INTRODUCTION

Transition-metal complexes show remarkable biological activity against certain microbes, viruses and tumours.[1] In some cases the highest activity is found with the metal complex rather than the free ligand.[2] Hydrazones, produced from the reaction of hydrazides with aldehydes or ketones, have very active sites for transition-metal atoms to coordinate with C=N and C=O groups. In previous examples, such Schiff bases have shown varied behaviour, depending on the involvement of active coordination sites.[3–5] We have already reported that Schiff bases such as acetylferrocene thiosemicarbazone or acetylferrocene semicarbazone can act as bidentate ligands with Ru(II).[6] We now report on the preparation of another Schiff base, 1-[(2-isopropyl-5-methylphenoxy)hydrazono] ethyl ferrocene (**3**), and its X-ray structure. Furthermore, complex[3] has been shown to act as a parent bidentate ligand, which on treatment with $[Ru(CO)_2Cl_2]_n$ in refluxing ethanol gave a yellow–orange solid complex.[4] The IR spectra of this complex showed characteristic two terminal metal carbonyl ν(Ru–CO) bands where the CO ligands appear to have a cis disposition.[6] The decrease in the frequencies of ν(C=N) and ν(C=O) in complex[4] probably arises from the direct metal–ligand coordination of the hydrazinic nitrogen and oxygen atoms respectively.

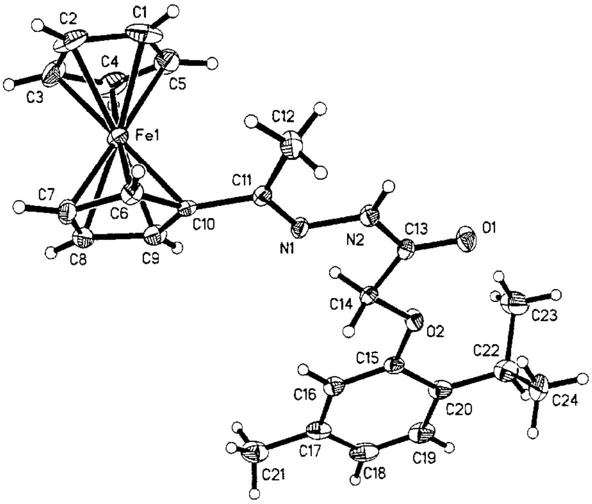
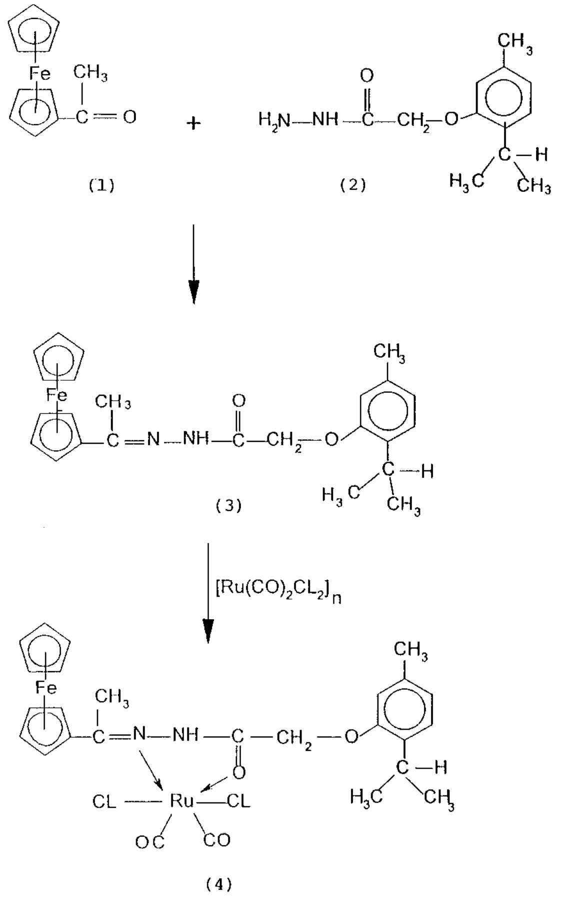


Figure 1. Molecular structure of **3**.

---

*Correspondence to: A. O. Baghlaf, Department of Chemistry, Faculty of Science, King Abdulaziz University, PO Box 80203, Jeddah 21589, Kingdom of Saudi Arabia.
E-mail: baghlaf@hotmail.com



Scheme 1.

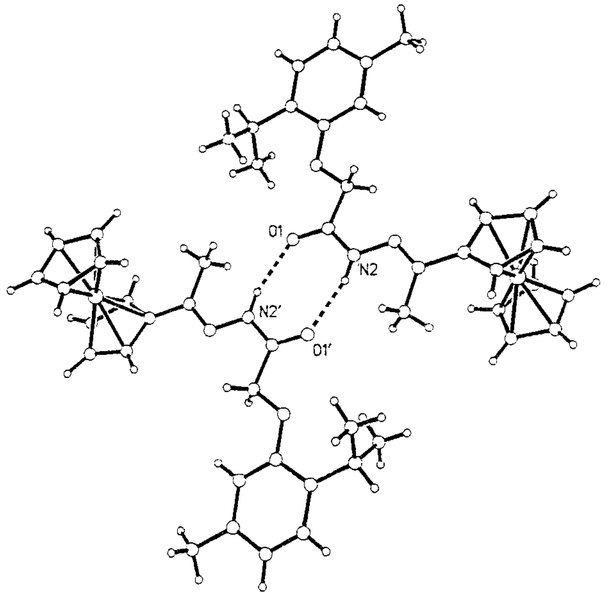


Figure 2. Structure of complex **3** showing hydrogen bonding interaction between adjacent molecules.

EXPERIMENTAL

The complex acetylferrocene was purchased from N.T. Ltd, UK, and 2-isopropyl-5-methylphenoxyacyl hydrazide was kindly provided by Dr S.A. Rahman (personal communication). The IR spectra were measured as KBr pellets using Pye–Unicam model 1100 and FTIR model 8101 IR spectrophotometers. The ^{1}H NMR spectra were recorded on a Varian EM 390–90 MHz spectrometer. Elemental analyses were carried out by the Microanalysis Laboratory of King Abdulaziz University, Jeddah. The X-ray crystal structure determination was carried out by the X-ray Crystallography Department, University of Leicester, UK.

Preparation of 1-[(2-Iisopropyl-5-methylphenoxy)hydrazono] ethyl ferrocene

To a three-necked round-bottom (100 ml) flask fitted with nitrogen gas inlet and water condenser was added acetylferrocene (0.5 g, 2.2 mmol) dissolved in ethanol (25 ml). To this was added 2-isopropyl-5-methylphenoxyacyl hydrazide (0.5 g, 2.2 mmol) and a few drops of glacial acetic acid. The solution was heated at reflux for 2 h. The solution was concentrated under reduced pressure and on cooling gave a light-orange–brown solid, 1-[2-isopropyl-5-methylphenoxy)hydrazono] ethyl ferrocene (^{3}; Scheme 1). This was washed twice with petroleum ether (b.p. 30–40 °C) and dried under vacuum. Yield 90%. Anal. Found: C, 66.5; H, 6.6; N, 6.6. Calc. for $C_{24}H_{28}FeN_2O_2$: C, 66.6; H, 6.5; N, 6.5%. M.p. 172–173 °C. Recrystallization of^3 from MeOH–CH_2Cl_2 produced crystals suitable for single crystal X-ray determination (Figs 1 and 2).

Preparation of 1-[(2-isopropyl-5-methylphenoxy)hydrazono] ethyl ferrocene dichloro-dicarbonylruthenium(II)

To a three-necked round-bottom (100 ml) flask fitted with nitrogen gas inlet and water condenser was added 1-[(2-isopropyl-5-methylphenoxy)hydrazono] ethyl ferrocene (200 mg, 0.4 mmol) in absolute ethanol (15 ml). To this was added $[RuCl_2(CO)_2]_n$ (100 mg, 0.4 mmol). The mixture was heated to reflux for 1.5 h with stirring. The yellow solution was reduced to minimum volume, which on cooling gave the yellow-orange solid 1-[(2-isopropyl-5-methylphenoxy)-hydrazono] ethyl ferrocene dichloro-dicarbonylruthenium-(II) complex (**4**; Scheme 1). This was washed twice with petroleum ether, b.p. 30–40 °C, and dried under vacuum. Yield 90%; m.p. 164 °C. Elemental analyses for complex **4** were found to be satisfactory.

RESULTS AND DISCUSSION

Treatment of the acetylferrocene complex^1 with 2-isopropyl-5-methylphenoxyacyl hydrazide^2 in 1:1 mole ratio in ethanol gave a stable orange–brown solid of Schiff base 1-[(2-

Table 1. ^{1}H NMR and IR[a] spectra of 1-[(2-isopropyl-5-methylphenoxy)hydrazono] ethyl ferrocene complexes **3** and **4b**

Chemical shift δ (ppm)	Relative intensity	Multiplicity	Assignment	$\nu(C{=}O)/\nu(Ru(CO)_2)$	$\nu(C{=}N)$	Other bands
9.4	1	broad	NH	1694	1507	
(7.8)				(1678)[d]		3090, 2951, 2878, 1600–1700, 1400–1460[b], 1261, 1180, 1142, 1108, 1076, 819
6.7–7.3	1	m	Ph group	(1647)[g]	1500[f]	
4.5	2	s	$O-CH_2$ (2075)[e]			
(4.6)[c]				(2005)[e]		
4.8(centre)	2	m	η-C_5H_4			
4.2	5	s	η-C_5H_5			
4.0	2	broad	$-NH_2$			
3.4	1	m	$-CH$			
(3.3)[c]						
2.3	2	s	$-CH_3$			
2.4						
1.3	2	s	$-CH_3$			
(1.2)[c]						
1.4	2	s	$-CH_3$			
(1.3)[c]						

[a] KBr pellet.
[b] In $CDCl_3$ using tetramethylsilane as internal reference.
[c] The values in parentheses are for the free ligand.
[d] Value of $\nu(C{=}O)$ group in complex.[2]
[e] Terminal $\nu(Ru(CO)_2)$ of complex.[4]
[f] $\nu(C{=}N)$ in complex.[4]

isopropyl-5-methylphenoxy)hydrazono] ethyl ferrocene complex (**3**; Scheme 1). The complex is soluble in common organic solvents, such as chloroform and acetone, but sparingly soluble in petroleum ether and benzene.

The IR spectrum of acetylferrocene[1] showed the keto $\nu(C{=}O)$ bond at 1670 cm^{-1},[6] whereas the keto $\nu(C{=}O)$ of the free ligand 2-isopropyl-5-methylphenoxyacyl hydrazide complex[2] appeared as a strong band at 1678 cm^{-1}. On treatment of[1] with[2] the orange–brown 1-[(2-isopropyl-5-methylphenoxy)hydrazono] ethyl ferrocene complex[3] was obtained. Thus the keto group of acetylferrocene disappeared and a new sharp band at 1507 cm^{-1} appeared that can be attribtued to the $\nu(C{=}N)$ band.[7] However, the keto $\nu(C{=}O)$ of complex[3] was observed as a strong band at 1694 cm^{-1}. In complex[4] both $\nu(C{=}O)$ and $\nu(C{=}N)$ bands show a lowering in frequency on coordination with ruthenium(II), as expected. There are two distinct terminal carbonyl $\nu(Ru-CO)$ bands at 2074 and 2005 cm^{-1}, which appear to be in a cis position.[6] See Scheme 1. The IR spectra of complexes[1–4] showed the characteristic $\nu(C-H)$ stretches of cyclopentadienyls and phenyl groups (Table 1).

The ^{1}H NMR spectrum of complex[3] showed very distinctly the protons of the phenyl group in the range δ 6.7–7.3 (ppm) and of η-C_5H_5 and η-C_5H_4 groups in the range δ 4.6–5 (ppm). The protons of the two methyl groups of the isopropyl system are seen as two distinct singlets at δ 1.3 and δ 1.4 (ppm) and the single methyl group of the 5-methyl group at δ 2.3 (ppm). The single proton of the isopropyl group ($-CH$) appeared at δ 3.3 (ppm). The important IR absorption data and ^{1}H NMR spectrum for the ligand and the complexes are given in Table 1.

The present work closely relates to work came out on other ferrocene complexes acting as coordinating ligands, as materials for nonlinear optical applications and electrochemistry, and as receptor for electrochemical an ion sensing.[8–11]

X-ray crystal data

Crystals of complex $C_{24}H_{28}FeN_2O_2$ are monoclinic, $a = 9.6965(15)$ Å, $b = 7.4991(12)$ Å, $c = 29.698(7)$ Å, $\beta = 99.010(13)$°, space group $P2_1/n$ $D_{calc} = 1.346$ Mg m^{-3}, absorption coefficient 0.729 mm^{-1}. The X-ray structure clearly shows the characteristic $(N-H\cdots O)$ hydrogen bonding between adjacent pairs of molecules in complex[3]; for detailed X-ray data Figs 1 and 2 and Tables 2–4. Finally, the atomic coordinates and full lists of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. xxxxx. Copies of this information may be

Table 2. Crystal data and structure refinement for **3**

Identification code	9957
Empirical formula	$C_{24}H_{28}FeN_2O_2$
Formula weight	432.33
Temperature (K)	190 (2)
Wavelength (Å)	0.710 73
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 9.6965$ (15) Å $\alpha = 90°$ $b = 7.4991$ (12) Å $\beta = 99.010$ (13)° $c = 29.698$ (7) Å $\gamma = 90°$
Volume (Å^3), z	2132.8 (7), 4
Density (calc.) (Mg m^{-3})	1.346
Absorption coefficient (mm^{-1})	0.729
F (000)	912
Crystal size (mm^3)	0.47 × 0.46 × 0.09
θ range for data collection (deg)	2.13 to 26.00
Limiting indices	$-11 \leq h \leq 0$, $-1 \leq k \leq 9$, $-36 \leq l \leq 36$
Reflections collected	5125
Independent reflections	4172 ($R_{int} = 0.0758$)
Completeness to $\theta = 26.00°$ (%)	99.7
Absorption correction	Psi scan (XEMP, SHELXL-97)
Max. and min. transmission	0.624 and 0.515
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4172/0/266
Goodness-of-fit on F^2	1.027
Final R indices [$I > 2\sigma$ (I)]	$R_1 = 0.0601$, $wR_2 = 0.1161$
R indices (all data)	$R_1 = 0.1065$, $wR_2 = 0.1333$
Largest diff. peak and hole (e^- Å^{-3})	0.538 and −0.693

Table 3. Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å^2 × 10^3) for **3**

	x	y	z	U_{eq}[a]
Fe (1)	5178 (1)	3533 (1)	7905 (1)	27 (1)
O (1)	6553 (3)	857 (4)	10284 (1)	39 (1)
O (2)	9047 (3)	2148 (4)	10297 (1)	36 (1)
N (1)	6391 (3)	1301 (4)	9110 (1)	26 (1)
N (2)	5979 (3)	888 (5)	9522 (1)	31 (1)
C (1)	3167 (5)	4174 (7)	7952 (2)	56 (1)
C (2)	3450 (5)	4481 (8)	7503 (2)	59 (2)
C (3)	4528 (5)	5740 (7)	7528 (2)	52 (1)
C (4)	4913 (5)	6203 (6)	7986 (2)	49 (1)
C (5)	4089 (5)	5257 (7)	8250 (2)	51 (1)
C (6)	5394 (4)	850 (5)	7865 (1)	28 (1)
C (7)	6109 (4)	1705 (6)	7547 (1)	36 (1)
C (8)	7136 (4)	2842 (6)	7788 (1)	38 (1)
C (9)	7053 (4)	2700 (6)	8260 (1)	33 (1)
C (10)	5968 (3)	1443 (5)	8311 (1)	23 (1)
C (11)	5523 (4)	942 (5)	8744 (1)	25 (1)
C (12)	4129 (4)	61 (6)	8737 (1)	40 (1)
C (13)	6888 (4)	1183 (5)	9911 (1)	28 (1)
C (14)	8293 (4)	1911 (5)	9851 (1)	27 (1)
C (15)	10 423 (4)	2641 (5)	10 336 (1)	29 (1)
C (16)	11 091 (4)	3032 (5)	9971 (1)	32 (1)
C (17)	12 489 (4)	3505 (6)	10 029 (2)	38 (1)
C (18)	13 209 (4)	3570 (7)	10 473 (2)	48 (1)
C (19)	12 541 (4)	3173 (6)	10 837 (2)	46 (1)
C (20)	11 149 (4)	2683 (6)	10 788 (1)	38 (1)
C (21)	13 200 (4)	3947 (6)	9626 (2)	50 (1)
C (22)	10 479 (5)	2189 (8)	11 198 (1)	54 (2)
C (23)	9306 (5)	3476 (9)	11 274 (2)	75 (2)
C (24)	9996 (5)	255 (9)	11 192 (2)	68 (2)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table 4. Bond lengths (Å) and angles (°) for **3**

Fe (1) – C (6)	2.028 (4)	Fe (1) – C (2)	2.028 (4)
Fe (1) – C (7)	2.031 (4)	Fe (1) – C (1)	2.035 (4)
Fe (1) – C (4)	2.038 (4)	Fe (1) – C (3)	2.042 (5)
Fe (1) – C (5)	2.044 (4)	Fe (1) – C (8)	2.049 (4)
Fe (1) – C (9)	2.050 (4)	Fe (1) – C (10)	2.051 (4)
O (1) – C (13)	1.227 (4)	O (2) – C (15)	1.371 (5)
O (2) – C (14)	1.421 (4)	N (1) – C (11)	1.294 (4)
N (1) – N (2)	1.380 (4)	N (2) – C (13)	1.357 (4)
C (1) – C (5)	1.412 (7)	C (1) – C (2)	1.422 (7)
C (2) – C (3)	1.402 (7)	C (3) – C (4)	1.395 (6)
C (4) – C (5)	1.398 (7)	C (6) – C (7)	1.409 (5)
C (6) – C (10)	1.427 (5)	C (7) – C (8)	1.418 (6)
C (8) – C (9)	1.420 (6)	C (9) – C (10)	1.438 (5)
C (10) – C (11)	1.467 (5)	C (11) – C (12)	1.502 (5)
C (13) – C (14)	1.504 (5)	C (15) – C (16)	1.379 (5)
C (15) – C (20)	1.415 (5)	C (16) – C (17)	1.386 (5)
C (17) – C (18)	1.394 (6)	C (17) – C (21)	1.507 (6)
C (18) – C (19)	1.378 (6)	C (19) – C (20)	1.384 (6)
C (20) – C (22)	1.512 (6)	C (22) – C (24)	1.523 (8)
C (22) – C (23)	1.536 (7)		
C (6) – Fe (1) – C (2)	113.4 (2)	C (6) – Fe (1) – C (7)	40.64 (15)
C (2) – Fe (1) – C (7)	108.79 (19)	C (6) – Fe (1) – C (1)	110.33 (19)
C (2) – Fe (1) – C (1)	41.0 (2)	C (7) – Fe (1) – C (1)	134.8 (2)
C (6) – Fe (1) – C (4)	176.20 (19)	C (2) – Fe (1) – C (4)	67.4 (2)
C (7) – Fe (1) – C (4)	143.0 (2)	C (1) – Fe (1) – C (4)	67.6 (2)
C (6) – Fe (1) – C (3)	142.89 (18)	C (2) – Fe (1) – C (3)	40.3 (2)
C (7) – Fe (1) – C (3)	112.59 (18)	C (1) – Fe (1) – C (3)	68.2 (2)
C (4) – Fe (1) – C (3)	39.98 (18)	C (6) – Fe (1) – C (5)	136.4 (2)
C (2) – Fe (1) – C (5)	68.2 (2)	C (7) – Fe (1) – C (5)	175.2 (2)
C (1) – Fe (1) – C (5)	40.52 (19)	C (4) – Fe (1) – C (5)	40.05 (19)
C (3) – Fe (1) – C (5)	67.8 (2)	C (6) – Fe (1) – C (8)	68.44 (17)
C (2) – Fe (1) – C (8)	133.7 (2)	C (7) – Fe (1) – C (8)	40.67 (17)
C (1) – Fe (1) – C (8)	174.1 (2)	C (4) – Fe (1) – C (8)	113.9 (2)
C (3) – Fe (1) – C (8)	109.1 (2)	C (5) – Fe (1) – C (8)	144.1 (2)
C (6) – Fe (1) – C (9)	68.72 (16)	C (2) – Fe (1) – C (9)	173.5 (2)
C (7) – Fe (1) – C (9)	68.47 (17)	C (1) – Fe (1) – C (9)	145.0 (2)
C (4) – Fe (1) – C (9)	110.93 (18)	C (3) – Fe (1) – C (9)	134.5 (2)
C (5) – Fe (1) – C (9)	114.92 (19)	C (8) – Fe (1) – C (9)	40.53 (16)
C (6) – Fe (1) – C (10)	40.95 (14)	C (2) – Fe (1) – C (10)	144.3 (2)
C (7) – Fe (1) – C (10)	68.73 (15)	C (1) – Fe (1) – C (10)	114.44 (19)
C (4) – Fe (1) – C (10)	136.39 (17)	C (3) – Fe (1) – C (10)	175.16 (19)
C (5) – Fe (1) – C (10)	111.30 (17)	C (8) – Fe (1) – C (10)	68.68 (15)
C (9) – Fe (1) – C (10)	41.06 (15)	C (15) – O (2) – C (14)	117.7 (3)
C (11) – N (1) – N (2)	117.2 (3)	C (13) – N (2) – N (1)	118.6 (3)
C (5) – C (1) – C (2)	107.4 (5)	C (5) – C (1) – Fe (1)	70.1 (3)
C (2) – C (1) – Fe (1)	69.3 (3)	C (3) – C (2) – C (1)	108.1 (4)
C (3) – C (2) – Fe (1)	70.4 (3)	C (1) – C (2) – Fe (1)	69.8 (3)
C (4) – C (3) – C (2)	107.6 (5)	C (4) – C (3) – Fe (1)	69.9 (3)
C (2) – C (3) – Fe (1)	69.3 (3)	C (3) – C (4) – C (5)	109.4 (5)
C (3) – C (4) – Fe (1)	70.2 (3)	C (5) – C (4) – Fe (1)	70.2 (3)
C (4) – C (5) – C (1)	107.5 (5)	C (4) – C (5) – Fe (1)	69.8 (3)
C (1) – C (5) – Fe (1)	69.4 (3)	C (7) – C (6) – C (10)	108.7 (4)
C (7) – C (6) – Fe (1)	69.8 (2)	C (10) – C (6) – Fe (1)	70.4 (2)

Table 4. continued.

C (6) – C (7) – C (8)	108.4 (3)	C (6) – C (7) – Fe (1)	69.6 (2)
C (8) – C (7) – Fe (1)	70.4 (2)	C (7) – C (8) – C (9)	108.0 (4)
C (7) – C (8) – Fe (1)	69.0 (2)	C (9) – C (8) – Fe (1)	69.8 (2)
C (8) – C (9) – C (10)	108.0 (4)	C (8) – C (9) – Fe (1)	69.7 (2)
C (10) – C (9) – Fe (1)	69.5 (2)	C (6) – C (10) – C (9)	106.9 (3)
C (6) – C (10) – C (11)	127.6 (3)	C (9) – C (10) – C (11)	125.5 (3)
C (6) – C (10) – Fe (1)	68.6 (2)	C (9) – C (10) – Fe (1)	69.4 (2)
C (11) – C (10) – Fe (1)	125.3 (3)	N (1) – C (11) – C (10)	116.1 (3)
N (1) – C (11) – C (12)	124.7 (3)	C (10) – C (11) – C (12)	119.1 (3)
O (1) – C (13) – N (2)	120.5 (3)	O (1) – C (13) – C (14)	123.6 (3)
N (2) – C (13) – C (14)	115.9 (3)	O (2) – C (14) – C (13)	106.1 (3)
O (2) – C (15) – C (16)	124.1 (3)	O (2) – C (15) – C (20)	114.8 (4)
C (16) – C (15) – C (20)	121.1 (4)	C (15) – C (16) – C (17)	121.9 (4)
C (16) – C (17) – C (18)	117.5 (4)	C (16) – C (17) – C (21)	121.2 (4)
C (18) – C (17) – C (21)	121.3 (4)	C (19) – C (18) – C (17)	120.6 (4)
C (18) – C (19) – C (20)	123.0 (4)	C (19) – C (20) – C (15)	116.0 (4)
C (19) – C (20) – C (22)	121.0 (4)	C (15) – C (20) – C (22)	123.0 (4)
C (20) – C (22) – C (24)	113.2 (4)	C (20) – C (22) – C (23)	112.7 (4)
C (24) – C (22) – C (23)	111.5 (5)		

obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposut@ccdc.cam.ac.uk; or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

Mr Khalid H. Bakhiswein and Adel H. Al-Harbi thank the King Abdulaziz University for financial support and Dr S. A. Rahman for the supply of 2-isopropyl-5-methylphenoxyacyl hydrazide.

REFERENCES

1. Padhye S and Kaufman GB. *Coord. Chem. Rev.* 1985; **63**: 123.
2. Levinson WE. *Antibiot. Chemother.* 1980; **27**: 288.
3. Kulkarni VH. *Asian J.f Chem.* 1975; **7**: 50.
4. Zhao G, Li F, Xie J and Ma XY. *Polyhedron* 1988; **7**: 393.
5. Ma XY and Zhao G. *Polyhedron* 1988; **7**: 1101.
6. Baghlaf AO, Ishaq M, Rahman SA, Al-Tahir AB, Zaidon A and Kabli RA. *Polyhedron* 1988; **7**: 219 and references cited therein.
7. Bellamy LJ. *The Infrared Spectra of Complex Molecules*. Chapman and Hall: London; 1975.
8. Benito A, Cano J, Martinez-Manez R, Soto J, Tendero MJL, Paya J and Sinn E. *Inorg. Chim. Acta* 1993; **210**: 233.
9. Cano J, Benito A, Martinez-Manez R, Soto J, Paya J, Lloret F, Julve M, Marcos MD and Sinn E. *Inorg. Chim. Acta* 1995; **231**: 45.
10. Benito A, Cano J, Martinez-Manez R, Paya J, Soto J, Julve M, Lloret F, Marcos MD and Sinn E. *J. Chem. Soc. Dalton Trans.* 1993; 1999.
11. Lloris JM, Martinez-Manez R, Padilla-Tosta ME, Pardo T, Soto J, Garcia-Espana E, Ramirez JA, Burguete MY, Luis SV and Sinn E. *J. Chem. Soc. Dalton Trans.* 1999; 1779.