

Complexes of iron(III) with 1,2-dihydro-1,5-dimethyl-2-phenyl-4-formyl(benzhydrazide)-3H-pyrazol-3-one

P K Radhakrishnan* & K C Raju

School of Chemical Sciences, Mahatma Gandhi University,
Kottayam, Kerala, India
Email: pkrkn@sancharnet.in

Received 7 January 2005; revised 5 July 2005

Iron(III) complexes of the schiff base, 1,2-dihydro-1,5-dimethyl-2-phenyl-4-formyl(benzhydrazide)-3H-pyrazol-3-one, $[\text{Fe}(\text{DPFBP})_2\text{X}]_2$, (where $\text{X}=\text{ClO}_4$, or NO_3) and $[\text{Fe}(\text{DPFBP})_2\text{X}_2]\text{X}$ ($\text{X}=\text{SCN}$, Cl or Br) have been synthesized and characterized by elemental analyses, electrical conductance in non-aqueous solvents, infrared, and electronic spectra as well as magnetic susceptibility measurements. In these complexes, DPFBP acts as a neutral bidentate ligand coordinating through the azomethine nitrogen and the carbonyl oxygen of the pyrazolone ring. The molar conductance of the complexes in DMF, methanol and nitrobenzene are in the range suggested for 1:2 electrolytes for perchlorate and nitrate complexes while the thiocyanate, chloride and bromide complexes behave as 1:1 electrolytes. The electronic spectra of the complexes exhibit a band in the region $19,230\text{--}20,080\text{ cm}^{-1}$ due to ${}^6\text{A}_{1g} \rightarrow {}^4\text{T}_{1g}$ consistent with octahedral Fe(III) complexes. The molar magnetic moment of the complexes varies in the range 5.61-6.05 B.M., indicative of octahedral geometry.

IPC Code: Int. Cl.⁷ C07F15/00

The antibacterial¹, antiinflammatory² and antitumour³ activities of antipyrine-based ligands and their metal complexes have drawn the attention of many investigators. Iron complexes were the earliest metal complexes used in the treatment of hypochromic anaemia⁴. In view of this and as a continuation of our investigation on Schiff base metal complexes⁵⁻¹², we report here the synthesis and characterisation of the iron(III) complexes of a Schiff base, viz., 1,2-dihydro-1,5-dimethyl-2-phenyl-4-formyl(benzhydrazide)-3H-pyrazol-3-one (**I**).

Experimental

The metal salts were prepared from Analar ferric carbonate and the respective 50% acids and recrystallized out the salt by evaporating the solution on a steam bath. Ferric thiocyanate was prepared by the method reported earlier¹³.

Preparation of the ligand

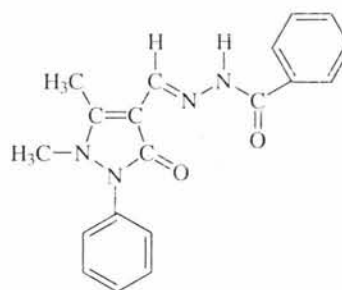
5 mmol (0.6850 g) of benzoylhydrazine was dissolved in 15 mL of ethanol and few drops of conc. HCl were added to maintain the pH at 6. The solution was boiled on a steambath. 5 mmol (1.08 g) of 4-antipyrine carboxaldehyde dissolved in 20 mL of ethanol was added to the hot solution slowly with stirring and refluxed for about 4 h. The solution was then concentrated. The pale yellow crystals formed on cooling were filtered and washed several times with cold ethanol and recrystallized from ethyl acetate. It was then dried under vacuum over phosphorous(V) oxide.

Perchlorate, thiocyanate, chloride and bromide complexes

One mmol of $\text{Fe}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$, $\text{Fe}(\text{SCN})_3 \cdot 6\text{H}_2\text{O}$, $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{FeBr}_3 \cdot 6\text{H}_2\text{O}$ in ethyl acetate (10 mL) was added to a boiling suspension of 2.2 mmol of DPFBP in ethyl acetate (100 mL). The mixture was refluxed for about 3 h on a steambath. The resulting solution was concentrated and cooled. The complexes, which precipitated on cooling, were filtered and washed several times with hot benzene to remove the excess ligand and recrystallised from methanol and dried under vacuum over phosphorous(V) oxide.

Nitrate complex

One mmol of $\text{Fe}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ in methanol (10 mL) was added to a boiling suspension of 2.2 mmol of DPFBP in ethyl acetate (100 mL). The mixture was refluxed for about 2 h on a steambath. The resulting solution was concentrated and cooled. The complex, which precipitated on cooling, was filtered and



1,2-Dihydro-1,5-dimethyl-2-phenyl-4-formyl(benz-hydrazide)-3H-pyrazol-3-one (DPFBP).
(**I**)

Table 1— Analytical data of the iron(III) complexes of DPFBP (calculated values in parentheses)

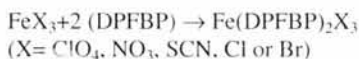
Complex	Molecular formula	Formula weight	Metal (%)	Anion (%)	C (%)	H (%)	N (%)	Yield (%)	M.pt. (°C)
DPFBP	C ₁₉ H ₁₈ N ₄ O ₂	334.39	-	-	67.98 (68.25)	5.58 (5.43)	16.64 (16.76)	85	198
[Fe(DPFBP) ₂ (ClO ₄)](ClO ₄) ₂	C ₃₈ H ₃₆ Cl ₃ FeN ₈ O ₁₆	1022.98	5.40 (5.46)	29.01 (29.16)	44.52 (44.61)	3.48 (3.55)	10.98 (10.95)	89	263
[Fe(DPFBP) ₂ (NO ₃)](NO ₃) ₂	C ₃₈ H ₃₆ FeN ₁₁ O ₁₃	910.64	6.07 (6.13)	-	50.06 (50.12)	3.89 (3.98)	16.84 (16.92)	92	216
[Fe(DPFBP) ₂ (SCN) ₂](SCN)	C ₄₁ H ₃₆ FeN ₁₁ O ₄ S ₃	898.87	6.19 (6.21)	-	54.72 (54.78)	4.00 (4.04)	17.04 (17.14)	86	222
[Fe(DPFBP) ₂ Cl ₂]Cl	C ₃₈ H ₃₆ Cl ₃ FeN ₈ O ₄	830.99	6.68 (6.72)	12.74 (12.80)	54.86 (54.92)	4.32 (4.37)	13.42 (13.48)	87	220
[Fe(DPFBP) ₂ Br ₂]Br	C ₃₈ H ₃₆ Br ₃ FeN ₈ O ₄	964.36	5.70 (5.79)	24.80 (24.86)	47.36 (47.32)	3.70 (3.76)	11.57 (11.62)	89	244

washed several times with hot benzene to remove the excess ligand. It was recrystallized from acetonitrile and dried under vacuum over phosphorous(V) oxide.

All the complexes were analyzed for metal contents by the standard methods¹⁴. The electrical conductance of the complexes in DMF, methanol and nitrobenzene (10⁻³ M) were measured at room temperature using a Toshniwal conductivity bridge with a dip type conductance cell (cell constant = 1.098). The infrared spectra of the ligand and complexes were recorded in the range 4,000-400 cm⁻¹ on a Shimadzu IR 470 spectrophotometer in KBr disc in the range 400-200 cm⁻¹ on a Perkin-Elmer 983 IR spectrometer in polyethylene powder. Electronic spectra of the ligand and the complexes in the solid state (using Nujol paste) were measured on a Shimadzu UV 160A spectrophotometer. The elemental analyses (C, H and N) were carried out on a Heraeus CHNO rapid analyser. The magnetic moments were measured at room temperature by the Gouy method using mercury(II) tetrathiocyanatocobaltate(II) as the calibrant.

Results and discussion

The formation of the complexes may be represented by:



The complexes are dark brown non-hygroscopic solids. They are soluble in DMF, methanol and nitrobenzene but insoluble in benzene, chloroform, ethyl acetate and toluene. The analytical data (Table 1) show that the complexes can be represented as Fe(DPFBP)₂X₃ (X=ClO₄, NO₃, SCN, Cl or Br).

Table 2 — Molar conductance (ohm⁻¹ cm² mol⁻¹) data of the iron(III) complexes (10⁻³ M solution) of DPFBP

Complex	Molar conductance		
	DMF	CH ₃ OH	C ₆ H ₅ NO ₂
[Fe(DPFBP) ₂ (ClO ₄)](ClO ₄) ₂	164.70	186.66	56.00
[Fe(DPFBP) ₂ (NO ₃)](NO ₃) ₂	137.25	170.19	53.80
[Fe(DPFBP) ₂ (SCN) ₂](SCN)	81.25	109.80	23.05
[Fe(DPFBP) ₂ Cl ₂]Cl	71.37	85.64	21.96
[Fe(DPFBP) ₂ Br ₂]Br	70.27	84.54	20.86

Electrical conductance

The molar conductance of the complexes (Table 2) in DMF, methanol and nitrobenzene fall in the range suggested for 1:2 electrolytes for perchlorate and nitrate complexes¹⁵. The thiocyanate, chloride and bromide complexes behave as 1:1 electrolytes. Thus, the complexes may be formulated as [Fe(DPFBP)₂X]X₂ (where X = ClO₄ or NO₃) and [Fe(DBPP)₂X₂] X (X = SCN, Cl or Br).

Infrared spectra

The important infrared spectral bands of DPFBP and its complexes are given in Table 3.

The band at 1674 cm⁻¹ characteristic of ν(C=O) of the pyrazolone ring of DPFBP is shifted to the region 1639-1642 cm⁻¹ in the complexes indicating the coordination of carbonyl oxygen¹⁶. The band corresponding to ν(C=O) of benzoyl moiety remain practically unaltered in all the complexes at about 1628 cm⁻¹ indicating the non-coordination of benzoyl oxygen¹⁷. The strong band observed at 1571 cm⁻¹ in DPFBP attributed to C=N stretching vibration is shifted to the range 1550-1560 cm⁻¹ indicating the coordination of azomethine nitrogen in the complexes⁷. The shifting of ν(N-N) band at 998 cm⁻¹ of DPFBP to higher frequencies (1008-1010 cm⁻¹) in

Table 3—Important infrared spectral bands (cm^{-1}) (s = strong, m = medium, w = weak) of DPFBP and its iron(III) complexes

DPFBP	$[\text{Fe}(\text{DPFBP})_2(\text{ClO}_4)](\text{ClO}_4)_2$	$[\text{Fe}(\text{DPFBP})_2(\text{NO}_3)](\text{NO}_3)_2$	$[\text{Fe}(\text{DPFBP})_2(\text{SCN})_2](\text{SCN})$	$[\text{Fe}(\text{DPFBP})_2\text{Cl}_2]\text{Cl}$	$[\text{Fe}(\text{DPFBP})_2\text{Br}_2]\text{Br}$	Assignment
1674 s	1642 s	1641 s	1642 s	1641 s	1639 s	$\nu(\text{C}=\text{O})$ ring
1630 s	1630 s	1628 s	1628 s	1630 s	1629 s	$\nu(\text{C}=\text{O})$
1571 s	1555 s	1550 s	1558 s	1560 s	1558 s	$\nu(\text{C}=\text{N})$
998 w	1008 w	1008 w	1009 w	1010 w	1007 w	$\nu(\text{N}-\text{N})$
	1144 m	-	-	-	-	ν_8 -coordinated ClO_4
	1112 s	-	-	-	-	ν_6 -coordinated ClO_4
	1018 s	-	-	-	-	ν_1 -coordinated ClO_4
	940 w	-	-	-	-	ν_2 -coordinated ClO_4
	632 w	-	-	-	-	ν_3 -coordinated ClO_4
	1090 s	-	-	-	-	ν_3 -uncoordinated ClO_4
	624 m	-	-	-	-	ν_4 -uncoordinated ClO_4
		1440 m	-	-	-	ν_4 -coordinated NO_3
		1244 m	-	-	-	ν_1 -coordinated NO_3
		1052 m	-	-	-	ν_2 -coordinated NO_3
		1383 s	-	-	-	ν_3 -uncoordinated NO_3
		821 m	-	-	-	ν_2 -uncoordinated NO_3
			2054 s	-	-	$\nu(\text{C}-\text{N})$
			854 w	-	-	$\nu(\text{C}-\text{S})$
			472 m	-	-	$\delta(\text{NCS})$
			-	310 w	-	$\nu(\text{Fe}-\text{Cl})$
			-	-	285 w	$\nu(\text{Fe}-\text{Br})$
	550 w	552 w	550 w	550 w	552 w	$\nu(\text{Fe}-\text{O})$
	455 w	457 w	455 w	457 w	455 w	$\nu(\text{Fe}-\text{N})$

the complexes further supports coordination through the azomethine nitrogen¹⁸.

The triply split band with maxima observed at around 1144, 1112 and 1018cm^{-1} due to ν_8 , ν_6 and ν_1 vibration, respectively of the perchlorate ion of C_{2v} symmetry indicates that the perchlorate ion may be coordinated in a bidentate fashion^{19,20}. But, the band at 1090cm^{-1} is attributed to the ν_3 vibration of uncoordinated perchlorate ion of T_d symmetry. Thus, the presence of both uncoordinated and bidentately coordinated perchlorate ions is observed in the perchlorate complex. The bands observed around 940 and 632cm^{-1} corresponding to ν_2 and ν_3 vibrations respectively of the coordinated perchlorate (C_{2v}) ion and the band at 624cm^{-1} due to the ν_4 vibration of the uncoordinated perchlorate (T_d) which are not present in the spectrum of the free ligand, also support the coexistence of both uncoordinated and bidentately coordinated perchlorate ions in the complex^{19,20}.

In the nitrate complex, a very strong band observed at 1383cm^{-1} due to the ν_3 vibration of the D_{3h} symmetry indicates the presence of uncoordinated nitrate ion²¹⁻²³. This is supported by the presence of another band of medium intensity at 821cm^{-1} due to

the ν_2 vibration of the uncoordinated nitrate ion²⁴. The presence of coordinated nitrate ion with C_{2v} symmetry is indicated by the bands observed at around 1440 and 1244cm^{-1} due to ν_4 and ν_1 vibrations respectively²². A medium intensity band observed around 1052cm^{-1} due to ν_2 vibration of the nitrate ion (C_{2v}) stands as an additional evidence for the coordination of nitrate ion²⁵. Since the difference between the two frequencies ($\nu_4 - \nu_1$) is 196cm^{-1} , the coordinated nitrate ion is bidentate²⁵.

In the thiocyanate complex, a sharp band at 2054cm^{-1} is attributable to N-coordinated thiocyanate ion. The presence of bands at 854 and 472cm^{-1} stands as an additional evidence for N-coordinated thiocyanate ion²⁶.

In the far infrared spectra of chloride and bromide complexes Fe-Cl and Fe-Br stretching vibrations are observed at 310 and 285cm^{-1} , respectively²⁵ which are not present in the spectrum of the free ligand. Further, $\nu(\text{Fe}-\text{O})$ and $\nu(\text{Fe}-\text{N})$ stretching vibrations are observed at about 550 and 455cm^{-1} , respectively in all these complexes²⁷. These results, which are in agreement with the conductance data, indicate that one of the perchlorate and nitrate ions as well as two

Table 4—Electronic spectral data and magnetic moments of the iron(III) complexes of DPFBP

Complex	Abs. Max. (cm ⁻¹)	Tentative assignment	μ_{eff} (B.M.)
DPFBP	23,866	$n \rightarrow \pi^*$	-
	41,153	$\pi \rightarrow \pi^*$	-
	23,952	$n \rightarrow \pi^*$	-
	39,370	$\pi \rightarrow \pi^*$	-
[Fe(DPFBP) ₂ (ClO ₄)](ClO ₄) ₂	33,112	Charge transfer	5.92
	19,685	${}^6A_{1g} \rightarrow {}^4T_{1g}$	
	24,154	$n \rightarrow \pi^*$	
	40,650	$\pi \rightarrow \pi^*$	
[Fe(DPFBP) ₂ (NO ₃)](NO ₃) ₂	33,783	Charge transfer	6.01
	19,230	${}^6A_{1g} \rightarrow {}^4T_{1g}$	
	24,449	$n \rightarrow \pi^*$	
	40,816	$\pi \rightarrow \pi^*$	
[Fe(DPFBP) ₂ (SCN) ₂](SCN)	33,783	Charge transfer	5.61
	20,080	${}^6A_{1g} \rightarrow {}^4T_{1g}$	
	24,630	$n \rightarrow \pi^*$	
	40,983	$\pi \rightarrow \pi^*$	
[Fe(DPFBP) ₂ Cl ₂]Cl	33,444	Charge transfer	5.50
	19,342	${}^6A_{1g} \rightarrow {}^4T_{1g}$	
	24,630	$n \rightarrow \pi^*$	
	40,160	$\pi \rightarrow \pi^*$	
[Fe(DPFBP) ₂ Br ₂]Br	33,557	Charge transfer	6.05
	19,801	${}^6A_{1g} \rightarrow {}^4T_{1g}$	

of the thiocyanate chloride and bromide ions are coordinated to the metal ion in these complexes.

Electronic spectra

The electronic spectral data of the ligand and complexes with their tentative assignments are given in Table 4.

DPFBP shows two absorption maxima at 23,866 and 41,153 cm⁻¹ corresponding to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions, respectively. In complexes $n \rightarrow \pi^*$ bands are found to be blue-shifted to the region 23,952-24,630 cm⁻¹, while $\pi \rightarrow \pi^*$ bands are red-shifted to the region 39,370-40,983 cm⁻¹, respectively when compared to that of DPFBP. The spectra of all the complexes exhibit a band in the region 19,230-20,080 cm⁻¹ corresponding to ${}^6A_{1g} \rightarrow {}^4T_{1g}$ transition consistent with octahedral iron(III) complexes²⁸. A strong band observed in the region 33,112-33,783 cm⁻¹ may be due to a charge transfer process.

Magnetic moment data

The molar magnetic moments of the complexes are given in Table 4. The values vary in the range 5.61 to 6.05 B.M. This suggests a high spin octahedral configuration (Fig. 1) around the metal ion²⁹.

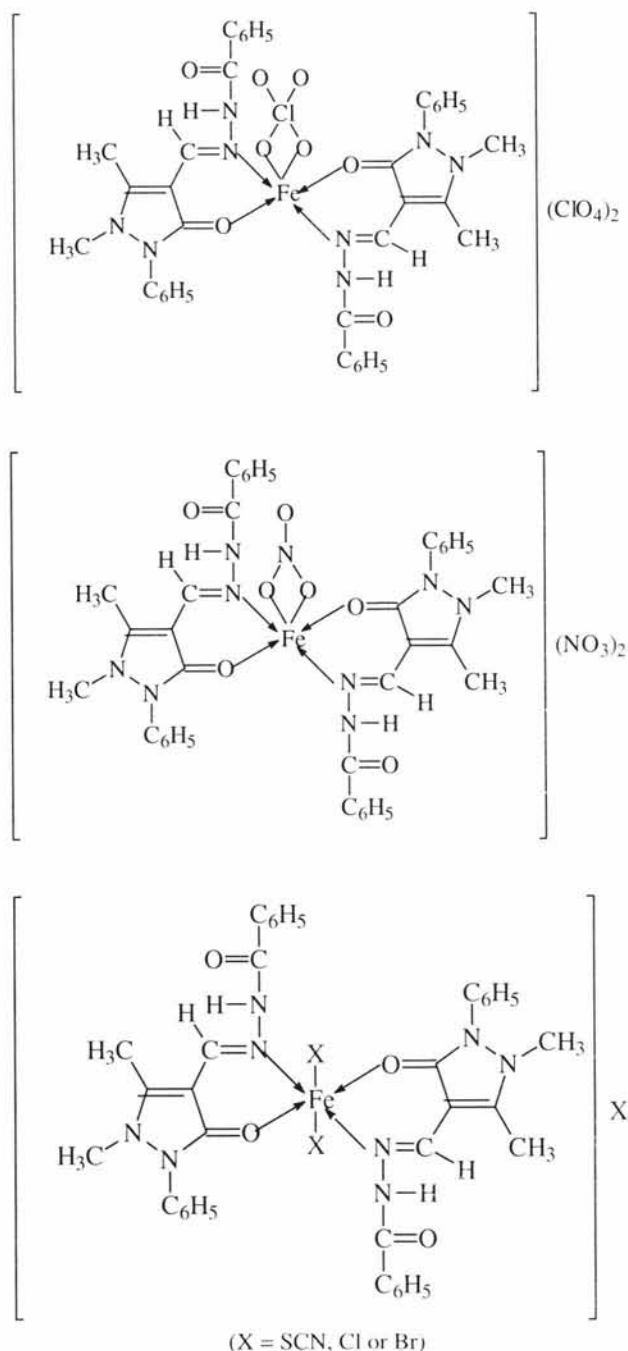


Fig. 1 — Tentative structures of iron(III) complexes of DPFBP.

Acknowledgement

Sincere thanks to the heads of the Regional Sophisticated Instrumentation Centres at the Indian Institute of Technology, Chennai, and the Indian Institute of Technology, Mumbai, for the instrumental analysis. We also thank Mahatma Gandhi University, Kottayam, Kerala, India, for providing facilities and the University Grants Commission for awarding a

Teacher Fellowship to one of us (KCR) under the faculty improvement programme.

References

- Alaudeen M, Abraham A & Radhakrishnan P K, *Proc Indian Acad Sci*, 107 (1995) 123.
- Singh L, Parashar R K, Tripathi S P & Sharma R C, *Curr Sci*, 55(1986) 484.
- Alice C J & Prabhakaran C P, *Indian J Chem*, 29A (1990) 491.
- Schwieter C W & Mc Cue J P, *Coord Chem Rev*, 184 (1999) 67.
- Radhakrishnan P K, *J Indian Chem, Soci*, LXI (1984) 838.
- Nair M K M & Radhakrishnan P K, *Synth React Inorg Met Org Chem*, 26(2) (1996) 263.
- Joseph S & Radhakrishnan P K, *Synth React Inorg Met Org Chem*, 28 (3) (1998) 423.
- Madhu N T & Radhakrishnan P K, *Synth React Inorg Met Org Chem*, 31 (2) (2001) 315.
- Madhu N T & Radhakrishnan P K, *Synth React Inorg Met Org Chem*, 31 (9) (2001) 1663.
- Raju K C & Radhakrishnan P K, *Synth React Inorg Met Org Chem*, 32 (6) (2002) 1117.
- Raju K C & Radhakrishnan P K, *Synth React Inorg Met Org Chem*, 32 (10) (2002) 1719.
- Raju K C & Radhakrishnan P K, *Synth React Inorg Met Org Chem*, 33 (1) (2003) 23.
- Ram A N S, Sarasukutty S & Prabhakaran C P, *Curr Sci*, 45 (1976) 45.
- Jeffrey G H, Bassett J, Mendhem J & Denny R C, *Vogel's Text Book of Quantitative Chemical Analysis*, 5th Edn (ELBS, London) 1961.
- Geary W J, *Coord Chem Rev*, 7 (1971) 81.
- Silverstein R M, Bassler G C & Morrill T C, *Spectrometric Identification of Organic Compounds*, 5th Edn (John Wiley & Sons Inc., New York) 1991.
- Kumar P A, *Synth React Inorg Met Org Chem*, 27 (1997) 577.
- Singh B, Narang K K & Srivastava Rachana, *Synth React Inorg Met Org Chem*, 31 (2002) 1375.
- Hathway B J & Underhill A E, *J Chem Soc*, (1961) 3091.
- Scholer R P & Merbach A E, *Inorg Chim Acta*, 15 (1975) 15.
- Giri V & Indrasenan P, *Polyhedron*, 2 (1983) 573.
- Gatehouse B M, Livingstone S E & Nyholm R S, *J Inorg Nucl Chem*, 8 (1958) 75.
- Muraleedharan M K & Radhakrishnan P K, *Polyhedron*, 12 (1993) 1227.
- Agarwal R K, Agarwal H & Sarin R K, *Synth React Inorg Met Org Chem*, 24 (1994) 1681.
- Lever A B P, *Inorg Chem*, 4 (1965) 1042.
- Nakamoto K, *Infrared and Raman Spectra of Inorganic and Coordination Compounds* (Wiley, New York) 1986.
- Donia A M & El Saied F A, *Polyhedron*, 7 (1988) 2149.
- Lever A B P, *Inorganic Electronics Spectroscopy*, 2nd Edn (Elsevier, Amsterdam) 1984.
- Cotton F A & Wilkinson G, *Advanced Inorganic Chemistry*, 6th Edn (Wiley Eastern, New Delhi) 1999.