μ-Azido- and μ-Oxo-Complexes of Fe(III) with Schiff Bases

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μ-AZIDO- AND μ-OXO-COMPLEXES OF Fe(III) WITH SCHIFF BASES

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Two new azido-bridged Fe(III) Schiff base complexes, $[Fe(salen)N_3]$ and $[Fe(MeO-salen)N_3] \cdot 2H_2O$, [salen = N,N'-bis-salicylaldehyde(ethylenediimine) and MeO-salen = N,N'-bis-3-methoxysalicylaldehyde(ethylenediimine)] have been synthesized, characterized and studied cryo-magnetically. A new isomeric form of the complex $[\{Fe(salen)\}_2O]$ was obtained when attempts were made to grow single crystal of $[Fe(salen)N_3]$ from different solvents. The structure of $[Fe(salen)]_2O$ has been determined by single crystal X-ray analysis. Magnetic susceptibility measurements show the presence of antiferromagnetic interactions in $[Fe(salen)N_3]$ and $[Fe(MeO-salen)N_3] \cdot 2H_2O$. The theoretical fit of the susceptibility data yielded values for the spin exchange parameters $J = -10$ (± 0.2) and -13 (± 0.3) cm^{-1}, for $[Fe(salen)N_3]$ and $[Fe(MeO-salen)N_3] \cdot 2H_2O$, respectively.

Keywords: Antiferromagnetic interaction; Iron(III); μ-azido complex; Schiff bases

INTRODUCTION

Investigation of the magnetic properties of molecular materials has become a fascinating subject in the fields of condensed matter physics, materials chemistry as well as inorganic chemistry [1]. Considerable efforts have been directed towards preparing and characterizing these materials which can exhibit interesting magnetic properties [2]. The precondition for synthesizing these materials is for the metal ions having unpaired electrons being assembled in a molecule such a way that the said electrons can interact with each other. Coordination complexes possessing metal–metal bridges certainly fulfill this condition. Therefore, many complexes containing metal–metal bridges have been synthesized in the last decade [1–3]. Pseudohalogens are found to be suitable ligands for making the bridge. Amongst them, azide is the most efficient ligand for providing super-exchange pathways between paramagnetic centres such as

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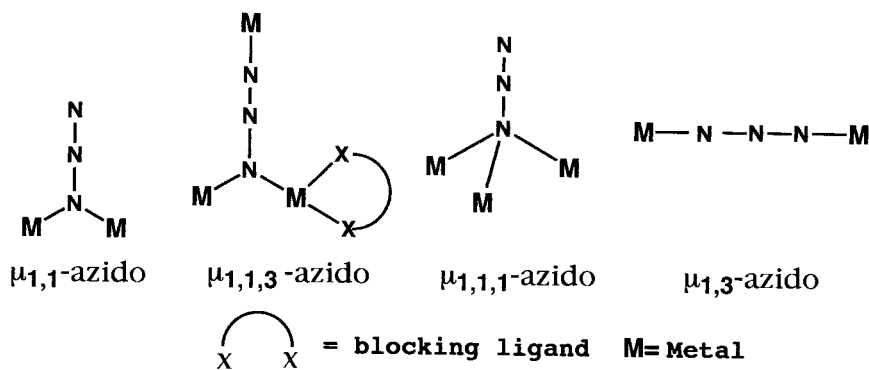
SCHEME 1

Cu(II), Ni(II), Mn(III) etc. [4–10]. The versatility and efficiency of azide lies in its functionality as a terminal monodentate, or bridging bi-, tri- and tetradentate ligand. In the case of a bridging bidentate, the coordination modes $\mu_{1,1}$ (end-on) and $\mu_{1,3}$ (end-to-end) azide have been observed (Scheme 1). It is well established that while a $\mu_{1,1}$-azide bridge generally gives ferromagnetic interaction pathways between two metal centers, a $\mu_{1,3}$-azide bridge gives an antiferromagnetic one [3]. As this type of interaction is important for the preparation of molecular magnetic materials, immense interest has been aroused to prepare azido-bridged metal complexes. A series of Ni(II) and Cu(II) complexes containing azide as bridging ligand has been synthesized in the last few years [4,5,7–9]. Quite a few such bridged complexes with Mn(III) have also been reported recently [11,12], but similar complexes with Fe(III) are very few in the literature [12,13]. On the other hand, magneto-structural behaviour of oxo-bridged Fe(III) Schiff base complexes for example, [{Fe(salen)}$_2$O]; salentH$_2$ = N,N'-bis-salicyl-aldehyde(ethylenediimine)] are well established [14]. This led us to attempt to introduce an azide in place of an oxo group as a bridging ligand in Fe(III) Schiff base complexes and we have successfully isolated two new azido-bridged complexes of this kind. During the course of our investigation the first azido-bridged Fe(III) Schiff base dimer complex has been reported [12], and which is very similar to the azido complexes prepared by us. In this article we discuss the preparation, characterization and cryomagnetic studies of [Fe(salen)N$_3$] and [Fe{MeO-salen)N$_3$]·2H$_2$O [MeO-salenH$_2$ = N,N'-bis-3-methoxysalicylaldehyde (ethylenediimine)].

EXPERIMENTAL

Materials and Reagents

All chemicals were of analytical grade and used without further purification. 3-Methoxysalicylaldehyde was purchased from Aldrich and used as such.

Preparation of the Complexes

The Complex [Fe(salen)N$_3$] (**1**) was prepared by mixing Fe(salen)C1 (1 mmol) and NaN$_3$ (1 mmol) dissolved in hot methanol. The dark red coloured product thus produced was

filtered and recrystallized from the same solvent. The complex Fe(salen)Cl was prepared by following the reported procedure [15]. The complexes Fe(MeO-salen)Cl and [Fe(Meo-salen)N$_3$]$\cdot$2H$_2$O (**2**) were prepared by following the same procedure using MeO-salen as ligand in place of salen. In both cases the yield was *ca.* 70%. Found by analysis (%): C, 52.51; H, 4.03; N, 19.25; Fe, 14.8 for (**1**) and C, 46.70; H, 5.21; N, 14.94; Fe, 11.6 for (**2**). Calculated for C$_{16}$H$_{14}$N$_5$O$_2$Fe (**1**) and C$_{18}$H$_{22}$N$_5$O$_6$Fe (**2**): C, 52.77; H, 3.85; N, 19.24; Fe, 15.3 for (**1**) and C, 46.93; H, 4.80; N, 15.19; Fe, 12.1 for (**2**). Despite several attempts we failed to grow single crystals suitable for X-ray analysis of the Complexes (**1**) and (**2**). Instead, in the case of [Fe(salen)N$_3$] (**1**), we obtained single crystals of [{Fe(salen)}$_2$O] (**3**) from CH$_3$OH. In the case of [Fe(MeO-salen)N$_3$] (**2**) such attempts only yielded polycrystalline [{Fe(MeO-salen)}$_2$O] (**4**) from the same solvent. The same oxo-products were also obtained for both complexes when C$_2$H$_5$OH was used as solvent for recrystallization. Found by analysis (%): C, 57.51; H, 4.11; N, 8.25; Fe, 16.4 for (**3**) and C, 54.70; H, 5.21; N, 6.94; Fe, 13.6 for (**4**). Calculated for C$_{32}$H$_{28}$N$_4$O$_5$Fe$_2$ (**3**) and C$_{36}$H$_{40}$N$_4$O$_9$Fe$_2$ (**4**): C, 58.15; H, 4.24; N, 8.48; Fe, 16.91 for (**3**) and C, 55.03; H, 5.14; N, 7.14; Fe, 14.24 for (**4**). The species [Fe(salen)N$_3$] (**1**) and [Fe(Meo-salen)N$_3$]$\cdot$2H$_2$O (**2**) are not soluble in any aprotic solvent.

Physical Measurements

Carbon, hydrogen and nitrogen analyses were carried out using a Perkin-Elmer 2400 II instrument. ICP emission analysis data for iron were obtained with a Jarrell Ash ICAP-88 machine. Iron was also analyzed by standard spectrophotometric methods [16]. IR spectra (nujol mull) were recorded on a Jasco 7300 FT-IR spectrophotometer. Magnetic susceptibility measurements were carried out on powdered samples between 4.2–295 K by the Faraday method with a Cahn 2000 microbalance. After placing the sample in the measuring chamber, the chamber was thoroughly evacuated (1–2×10^{-6} Torr) for several days prior to the measurements in order to eliminate the effect of oxygen in magnetic susceptibilities. Finally a small amount of dry He gas was introduced into the chamber. The measurements were performed at 6.49 kG applied magnetic field and HgCo(SCN)$_4$ was used as calibrant. Diamagnetic corrections were made with Pascal's constants. Mössbauer spectra were recorded with a Wiessel 1200 spectrometer equipped with a proportional counter. Hyperfine parameters were obtained by least-squares fitting to Lorentzian peaks. Isomer shifts are reported relative to metallic iron foil.

Crystal Data

Fe$_2$C$_{32}$H$_{28}$N$_4$O$_5$, Triclinic, $a = 10.960(1)$, $b = 10.7590(7)$, $c = 13.915(1)$ Å, $\alpha = 85.193(5)$, $\beta = 66.162(4)$, $\gamma = 72.791(5)°$, $V = 1431.7(2)$ Å^3 (by least squares refinement of diffractometer angles for 20 automatically centred reflections, $\lambda = 0.71073$ Å), space group $P\bar{1}$, $Z = 2$, red blocky crystal, dimensions $0.23 \times 0.15 \times 0.15$ mm, $T = 298$.

Data Collection, Structure Solution and Refinement

X-ray intensities were recorded on a MAX Science DIP-3000 image processor with graphite-monochromated MoK$_\alpha$ radiation and an 18 kW rotating-anode generator. A total of 6703 reflections were collected using the Weisenberg method in the range

$2 < 2\theta < 29$ ($0 < h < 15$, $-10 < k < 11$, $-18 < l < 19$), but only 5375 reflections with $I > 2\sigma(I)$ were used in the structure analysis. The structure was solved with the Dirdif–Patty method in CRYSTAN-GM (software package for structure determination, MAC Science) and refined finally through full-matrix least-squares calculations. Aniostropic refinements were carried out for the non-hydrogen atoms. All of the hydrogen atoms, partially located in difference Fourier maps, were refined isotropically. The final $R\,[= \Sigma \|F_o| - |F_c\|/\Sigma|F_o|]$ and $Rw\{= \Sigma w(|F_o| - |F_c|^2/\Sigma w|F_o|^2]^{1/2}\}$ values were 0.050 and 0.062, respectively, using $w^{-1} = (F_o) + 0.003(F_o)^2$.

RESULTS AND DISCUSSION

Elemental analyses of the complexes convincingly demonstrate that (**1**) and (**2**) can be formulated as Fe(salen)N_3 and Fe(MeO-salen)$N_3 \cdot 2H_2O$, respectively. IR measurements of (**1**) and (**2**) show a band in the range 1630–1650 cm^{-1} attributable to the azomethine group [17]. This band for the free ligand occurs at frequencies higher by ~ 10 cm^{-1}. The ν_{as} band for azide group appears around 2050 cm^{-1}. The two distinct peaks (2056 and 2038 cm^{-1}) for ν_{as} band of N_3^- are observed in the case of (**2**) whereas only one broad peak (2052 cm^{-1}) for this band is found in IR spectra of (**1**). Similar characteristic bands for bridged azide have been observed in a number of μ-azido complexes of Ni(II) [18], Cu(II) [19] and Mn(III) [5]. From the abovementioned experimental evidence and considering the oxidation state of iron, the structure of Complexes (**1**) and (**2**) can be formulated either as a $\mu_{1,3}$-azido dimeric species or as a $\mu_{1,3}$-azido bridged polymeric chain species, as in Scheme 2. It is also noteworthy that the presence of strong antiferromagnetic interactions is indicative of the azide being bridged in an end-to-end fashion in these complexes (*vide supra*). The Complexes (**3**) and (**4**) were formed during recrystallilzation of (**1**) and (**2**), respectively.

An ORTEP [20] view of the complex [{Fe(salen)}$_2$O] (**3**) with the atom numbering scheme is given in Fig. 1. Final atomic coordinates and selected bond distances and angles are listed in Tables I and II and these are in good agreement with reported
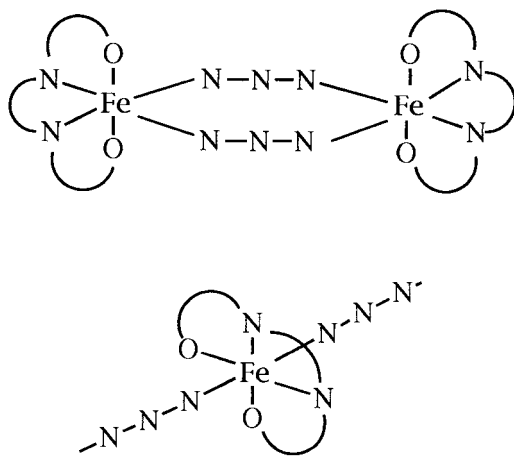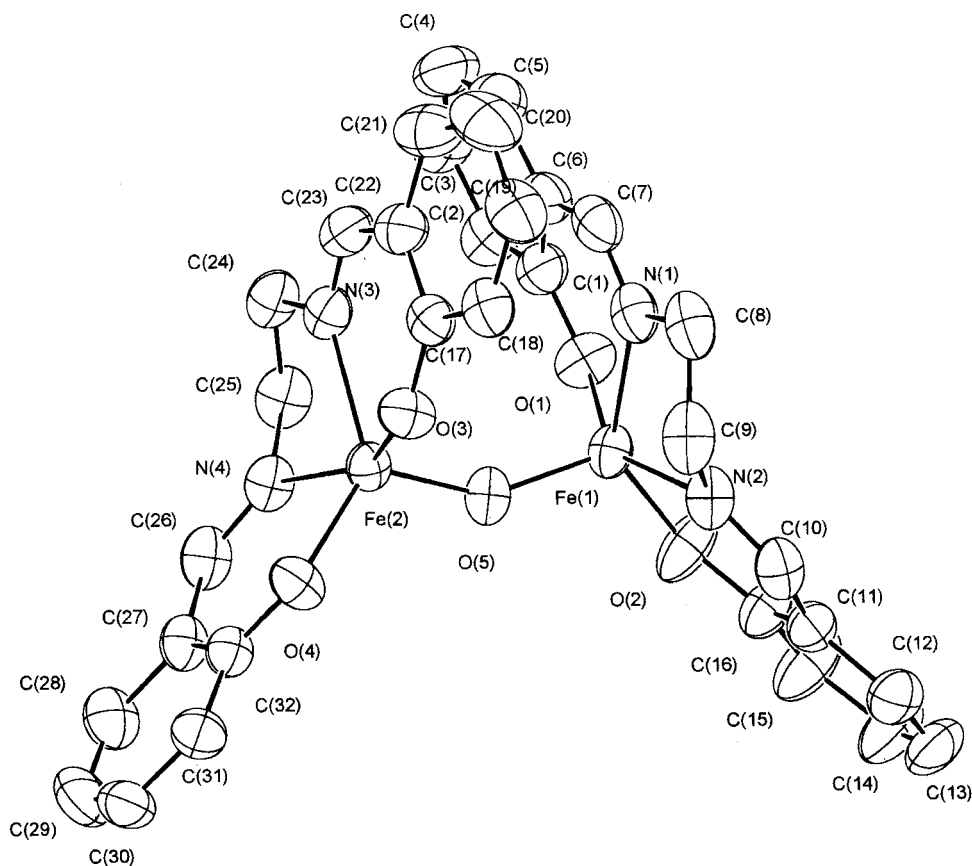

SCHEME 2

FIGURE 1   ORTEP drawing of [{Fe(salen)}$_2$O] (**3**) with the atom numbering scheme.

data for similar complexes [14b,c,21]. The asymmetric unit of the complex contains one [{Fe(salen)}$_2$O] molecule. The crystal structure determination of a complex having the same chemical formula has been reported earlier [14a], but the significant difference between the structure of (**3**) reported here and that of the earlier one is clearly apparent from the bond distances and angles (Table II). The most striking difference is found in the Fe(1)–O(5)–Fe(2) angle. In the case of Complex (**3**) the angle is 147.8° whereas for the complex reported earlier it is 144.6°. This difference makes the two Fe(salen) moieties of Complex (**3**) disposed further apart in comparison to the earlier complex. Therefore, Complex (**3**) is a new isomer of [{Fe(salen)}$_2$O].

   The temperature dependence of solid state magnetic susceptibilities of both complexes has been measured from 4.2–295 K. The χ_m values of both the complexes increase when the temperature decreases and reaches a maximum (at *ca.* 60 K). It then decreases as the temperature approaches 4.2 K (Figs. 2 and 3). The μ_{eff} values of Complexes (**1**) and (**2**) at 295 K are 5.25 and 5.31 BM, respectively. These values decreases on cooling and at 4.2 K they were calculated to be 0.59 and 0.53 BM for (**1**) and (**2**). Overall antiferromagnetic interaction is evident from the characteristic folded knee-type curves (Figs. 2 and 3) of Complexes (**1**) and (**2**) [1a,22]. This magnetic

TABLE I   Atomic coordinates and isotropic thermal factors for [{Fe(salen)}$_2$O] (**3**)

Atom	x/a	y/b	z/c	U_{iso}
Fe(1)	0.16655(2)	0.13597(2)	−0.45409(1)	0.04439(7)
Fe(2)	0.15898(2)	0.17736(2)	−0.21001(1)	0.04145(6)
O(1)	0.30894(9)	−0.02791(10)	−0.50415(7)	0.0556(4)
O(2)	0.24325(9)	0.21497(12)	−0.58463(8)	0.0666(5)
O(3)	−0.03510(9)	0.18523(9)	−0.12916(8)	0.0519(4)
O(4)	0.14237(8)	0.33104(9)	−0.13987(8)	0.0528(4)
O(5)	0.18056(10)	0.19486(10)	−0.34423(7)	0.0560(4)
N(1)	0.02786(11)	0.02040(12)	−0.38370(7)	0.0535(5)
N(2)	−0.02788(10)	0.25990(12)	−0.44462(8)	0.0526(4)
N(3)	0.20514(11)	−0.02467(10)	−0.18141(7)	0.0477(4)
N(4)	0.37093(9)	0.12339(11)	−0.23672(7)	0.0456(4)
C(1)	0.32210(14)	−0.14052(13)	−0.45952(9)	0.0528(5)
C(2)	0.45642(17)	−0.22849(16)	−0.48365(11)	0.0647(7)
C(3)	0.4728(2)	−0.3467(2)	−0.4374(1)	0.0814(9)
C(4)	0.3582(3)	−0.3850(2)	−0.3658(2)	0.085(1)
C(5)	0.2278(2)	−0.3020(2)	−0.3432(1)	0.0775(9)
C(6)	0.20477(16)	−0.17927(15)	−0.38827(10)	0.0596(6)
C(7)	0.06408(16)	−0.09895(16)	−0.35946(9)	0.0603(7)
C(8)	−0.12149(13)	0.08834(18)	−0.35331(9)	0.0630(6)
C(9)	−0.14101(13)	0.23375(17)	−0.35104(10)	0.0616(6)
C(10)	−0.05290(12)	0.34952(14)	−0.50593(10)	0.0540(5)
C(11)	0.04941(12)	0.37668(12)	−0.60259(10)	0.0496(5)
C(12)	0.00469(15)	0.47252(15)	−0.66657(13)	0.0641(7)
C(13)	0.09323(18)	0.49581(17)	−0.76273(15)	0.0761(8)
C(14)	0.23394(18)	0.42365(20)	−0.79957(15)	0.0834(9)
C(15)	0.28276(15)	0.33303(19)	−0.73797(14)	0.0773(8)
C(16)	0.19228(12)	0.30512(14)	−0.63828(10)	0.0545(6)
C(17)	−0.10055(12)	0.09557(13)	−0.10626(8)	0.0484(5)
C(18)	−0.24605(13)	0.13295(16)	−0.07694(9)	0.0553(6)
C(19)	−0.31906(17)	0.04170(20)	−0.05277(12)	0.0710(8)
C(20)	−0.2510(2)	−0.0900(2)	−0.0534(1)	0.083(1)
C(21)	−0.1105(2)	−0.1283(2)	−0.0795(1)	0.0721(9)
C(22)	−0.03156(14)	−0.03865(14)	−0.10827(9)	0.0529(6)
C(23)	0.11729(15)	−0.08968(13)	−0.14096(9)	0.0531(6)
C(24)	0.35420(14)	−0.09392(14)	−0.21259(10)	0.0529(5)
C(25)	0.44025(13)	−0.00845(14)	−0.28329(10)	0.0557(5)
C(26)	0.43921(11)	0.19222(15)	−0.22022(10)	0.0539(5)
C(27)	0.37737(12)	0.31998(13)	−0.17000(9)	0.0504(5)
C(28)	0.46418(14)	0.38469(18)	−0.15512(12)	0.0670(7)
C(29)	0.41440(18)	0.50210(19)	−0.10422(14)	0.0766(9)
C(30)	0.26994(17)	0.56340(17)	−0.06434(12)	0.0640(7)
C(31)	0.18187(13)	0.50540(14)	−0.07905(10)	0.0544(6)
C(32)	0.23138(11)	0.38389(12)	−0.13097(9)	0.0458(5)

U_{iso} is defined as one third of the orthogonalized U_{ij} tensor.

behaviour of these complexes is quite similar to that observed in other complexes with oxo bridge [23a,b]. Susceptibility data were fitted for both possible structures, viz, dimeric and polymeric chain. For the polymeric structure the susceptibility data were fitted with Eqs. (1) and (2) derived by Fisher [24].

$$\chi_m - Ng^2\beta^2\{S(S+1)\}(1+u)/\{3kT(1-u)\} \tag{1}$$

$$u = \coth[\{JS(S+1)\}/kT] - [kT/\{JS(S+1)\}] \tag{2}$$

TABLE II   Selected bondlengths (Å) and angles (°) for complex [{Fe(salen)}$_2$O] (**3**)

Fe(1)–O(1)	1.931(1)	Fe(1)–O(2)	1.913(2)
Fe(1)–O(5)	1.781(1)	Fe(2)–O(3)	1.942(1)
Fe(2)–O(4)	1.915(1)	Fe(2)–O(5)	1.786(1)
Fe(1)–N(1)	2.128(2)	Fe(1)–N(2)	2.111(2)
Fe(2)–N(3)	2.123(2)	Fe(2)–N(4)	2.100(1)
C(6)–C(7)	1.434(3)	C(8)–C(9)	1.516(3)
C(24)–C(25)	1.521(2)	N(2)–C(10)	1.276(2)
N(1)–C(7)	1.286(3)	C(11)–C(12)	1.413(3)
O(1)–Fe(1)–O(2)	92.0(1)	O(1)–Fe(1)–O(5)	108.2(1)
O(5)–Fe(1)–O(2)	116.0(1)	O(3)–Fe(2)–O(4)	92.8(1)
O(4)–Fe(2)–O(5)	115.3(1)	O(3)–Fe(2)–O(5)	106.5(1)
N(1)–Fe(1)–N(2)	76.3(1)	N(3)–Fe(2)–N(4)	76.3(1)
Fe(1)–O(5)–Fe(2)	147.8(1)	O(2)–Fe(1)–N(2)	85.5(1)
O(1)–Fe(1)–N(2)	148.0(1)	O(1)–Fe(1)–N(1)	85.4(1)
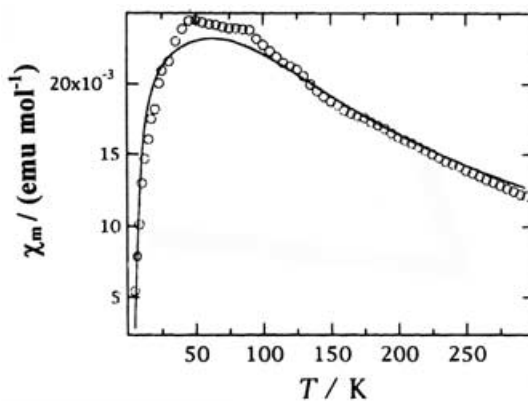
FIGURE 2   Plot of the temperature dependence of χ_m for [Fe(salen)N$_3$] (**1**). The solid line results from a least-squares fit of the data to the theoretical values mentioned in the text.
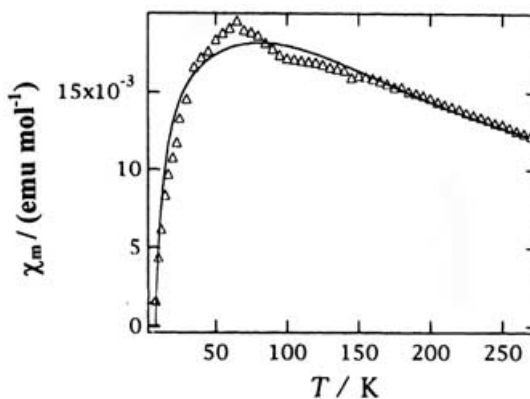
FIGURE 3   Plot of the temperature dependence of χ_m for [Fe(MeO-salen)N$_3$]·2H$_2$O (**2**). The solid line results from a least-squares fit of the data to the theoretical values mentioned in the text.

taking $S = 5/2$ as a classical spin vector. No acceptable as obtained, especially in the low temperature region. For dimeric species the susceptibility data can be interpreted in terms of the Heisenberg–Dirac–Van Vleck spin Hamiltonian for isotropic dinuclear magnetic exchange interaction ($H = -2JS_1S_2$). The equation used to fit the corrected molar susceptibility data is [22] given in (3),

$$
\chi_m = 2Ng^2\beta^2/kT(e^{2x} + 5e^{6x} + 14e^{12x} + 30e^{20x} + 55e^{30x})/
$$
$$
(1 + 3e^{2x} + 5e^{6x} + 7e^{12x} + 9e^{20x} + 11e^{30x})
\tag{3}
$$

where N, g, β and k have their usual meaning and $x = J/k$. Equation (3) gives an acceptable fit for both Complexes (1) and (2) (Figs. 1 and 2). For Complex (1) J is found to be $-10(\pm 0.2)\,\text{cm}^{-1}$ and $g = 2.01$ while for (2) J is calculated to be -13 $(\pm 0.3)\,\text{cm}^{-1}$ and $g = 2.0$. The residual (R) values for (1) and (2) were 7.2×10^{-5} and 3.1×10^{-5}. The magnetic behaviour of the Fe(III) complexes under zero-field-cooled (ZFC) and field-cooled (FC) conditions was essentially the same. Mössbauer spectra were composed of a single quadrupole doublet showing paramagnetism in the full temperature range. Isomer shifts and quadrupole splittings were in the range of 0.54 and 1.04 mm/s, respectively, at 4.2 K. This suggests the absence of any bulk magnetic interaction in the complexes up to 4.2 K.

It is evident from the abovementioned studies that we have succeeded in preparing azido-bridged Fe(III) complexes containing Schiff bases. As the complexes showed antiferromagnetic coupling, the bridging fashion of azide in this complex is expected to be end-to-end (1,3 bridge). The syntheses of such complexes are of importance to study the role of azide as a bridging ligand with several complexes, especially with Fe(III), which are rare in the literature. It is also noteworthy that the azido complexes reported here are not very stable in solvents like alcohols. The complexes undergo hydrolysis or solvolysis (even crystallization of azido complexes from super-dry solvent does not afford azido complexes on slow evaporation) on crystallization to form oxo-bridged dimers.

Acknowledgment

Supplementary Data

Crystallographic data have been deposited with the CCDC (Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK) and are available upon request, quoting the deposition number CCDC 181275.

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