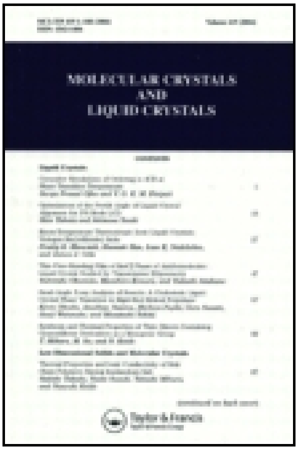


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Fe(II)-Fe(III) Alternate Ferrimagnetic Chain Constructed with Complexed-Ligand $[Fe(bpca)_2]^{\pm}$ (Hbpca = Bis(2-Pyridylcarbonyl) amine)

Takashi Kajiwara [a] & Tasuku Ito [a]

[a] Department of Chemistry, Graduate School of Science, Tohoku University, Sendai, 980-8578, JAPAN

Version of record first published: 24 Sep 2006

To cite this article: Takashi Kajiwara & Tasuku Ito (1999): Fe(II)-Fe(III) Alternate Ferrimagnetic Chain Constructed with Complexed-Ligand $[Fe(bpca)_2]^{\pm}$ (Hbpca = Bis(2-Pyridylcarbonyl) amine), Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 335:1, 73-80

To link to this article: http://dx.doi.org/10.1080/10587259908028852

Mol. Cryst. and Liq. Cryst., 1999, Vol. 335, pp. 73-80
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Fe(II)-Fe(III) Alternate Ferrimagnetic Chain Constructed with Complexed-Ligand $[Fe(bpca)_2]^+$ (Hbpca = Bis(2-Pyridylcarbonyl) amine)

TAKASHI KAJIWARA and TASUKU ITO

Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980–8578, JAPAN

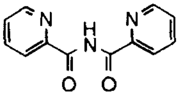
The reaction of $[Fe(bpca)_2]{\bullet}H_2O$ with $Fe(ClO_4)_3{\bullet}6H_2O$ in $MeNO_2$-$CHCl_3$ solution and $MeNO_2$-CH_2Cl_2 solution afforded black crystals of a trinuclear complex, $[Fe(H_2O)_2\{Fe(bpca)_2\}_2](ClO_4)_4$ (**1**), and a linear chain complex, *catena*-$[Fe(ClO_4)_2\{Fe(bpca)_2\}]ClO_4$ (**2**), respectively (Hbpca = bis(2-pyridylcarbonyl)amine). In both complexes, iron atoms in $\{Fe(bpca)_2\}^+$ units are in a low-spin 3+ state, whereas irons coordinated by four carbonyl oxygen atoms and two axial oxygen atoms (from coordinated water molecules or perchlorate anions) take a high-spin 2+ state. In both **1** and **2** antiferromagnetic interactions operated between high-spin Fe(II) and low-spin Fe(III) ions. **2** shows the ferrimagnetic ordering at 2.5 K. The plot of $1/\chi_m$ *vs* T above 50 K for **2** obeys the Curie-Weiss law with a negative Weiss constant of $\theta = -15.3$ K.

Keywords: complexed-ligand; Fe(II)-Fe(III) alternate arrangement; ferrimagnetic chain

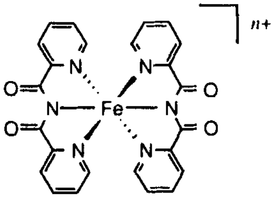
INTRODUCTION

The chemistry of multi-metal-centered complexes or metal complex assemblies with highly ordered solid state structures has attracted much attention.[1] In such chemistry, "complexed-ligands" are known to be beneficial in the construction of multi-metal complexes and the control of their properties. Monomeric complexes of tridentate ligand $bpca^-$ (Hbpca = bis(2-pyridyl carbonyl)amine), $[M(bpca)_2]^{n+}$ (n = 0 for M = Fe(II), n = 1 for M = Fe(III))[2] could be an example of this type of complexed-ligand. They have four free

C=O groups which, upon reaction with a metal ion M, may act as a bis-bidentate bridging ligand to give a linear chain complex of the type •••M(μ-bpca)Fe(μ-bpca)M•••, and the delocalized π-system on $\{Fe(bpca)_2\}^{n+}$ unit has the possibility to mediate magnetic interactions between Fe and M. It has been reported that oximato and oxamido complexes can act as a similar complexed ligand to give di-,[3] tri-,[4] and tetranuclear complexes.[5] One of the characteristics of the present system is that monomeric complexes $[Fe(bpca)_2]^{n+}$ can be isolated both in Fe^{II} and Fe^{III} state stably, and that they show reversible Fe^{II}/Fe^{III} redox wave at ca. 600 mV (vs SSCE). This suggests the potential of charge transfer interactions through delocalized π-system. We here report two complexes, a Fe(II)-Fe(III)-Fe(II) trimeric structure and Fe(II)-Fe(III) alternate chain structure.



Hbpca



$[Fe(bpca)_2]^{n+}$

EXPERIMENTAL

Syntheses

The reaction of $[Fe(bpca)_2]{\bullet}H_2O$ with $Fe(ClO_4)_3{\bullet}6H_2O$ in $MeNO_2/CHCl_3$ solution in 1:1 ratio and $MeNO_2/CH_2Cl_2$ solution in 1:1.25 ratio afforded, respectively, black crystals of a trinuclear complex, $[Fe(H_2O)_2\{Fe(bpca)_2\}_2](ClO_4)_4$ (**1**), and black crystals of a linear chain complex, *catena*-$[Fe(ClO_4)_2\{Fe(bpca)_2\}]ClO_4$ (**2**).

RESULTS AND DISCUSSION

Description of the Structure

Figure 1 shows an ORTEP diagram of the complex ion in **1**. The trinuclear structure consists of two $\{Fe(bpca)_2\}^{n+}$ units (with filled bonds) and central

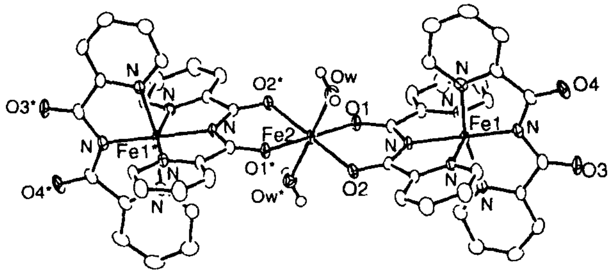


FIGURE 1 ORTEP drawing of cation part of **1**. Frameworks with filled bonds represent $\{Fe(bpca)_2\}^+$ units.

$Fe(H_2O)_2$, the former acting as terminal ligands to the central unit. Four perchlorate anions par a trinuclear unit were found, suggesting that three iron atoms have total charge of 8+, i.e, $Fe^{III}{}_2Fe^{II}$. X-ray structures for both $[Fe^{II}(bpca)_2]$ and $[Fe^{III}(bpca)_2]NO_3$ were reported,[2] and bond lengths and bond angles around metal centers are not much different between the Fe(II) and Fe(III) complexes (Table I). Fe-N bond lengths in **1** were close to those in both $[Fe^{II}(bpca)_2]$ and $[Fe^{III}(bpca)_2]NO_3$, therefore the oxidation states of the terminal iron atoms were not inferred crystallographically. In **1**, terminal $\{Fe(bpca)_2\}^{n+}$ units were related by a crystallographic inversion center at the central iron, Fe2, hence two irons at terminal positions must be equivalent. Then the oxidation numbers of three irons are regarded as (3+, 2+, 3+). The

TABLE I. Fe-N distances in **1**, **2**, and related complexes.

Compounds	Oxidation state	Fe-N(py) / Å	Fe-N(amide) / Å
$[Fe(bpca)_2]$2)	2+	1.929(8), 1.941(7), 1.943(8), 1.957(7)	1.918(7), 1.929(7)
$[Fe(H_2O)_2\{$*Fe*$(bpca)_2\}_2]$ $(ClO_4)_4$ (**1**)	3+	1.952(6), 1.957(6), 1.979(6), 1.982(6)	1.864(5) (free site) 1.961(5) (Fe site)
catena-$\{Fe(ClO_4)_2\{$*Fe*$(bpca)_2\}\}$ (ClO_4) (**2**)	3+	1.968(5), 1.975(5), 1.976(5), 1.976(5)	1.900(4), 1.905(4)
$[Fe(bpca)_2](NO_3)$2)	3+	1.943(6), 1.955(6), 1.963(6), 1.971(6)	1.908(5), 1.908(5)

TABLE II. Fe-O distances in **1**, **2**, and a related complex.

Compounds	Oxidation state	Fe-O(eq) / Å	Fe-O(ax) / Å
$[Fe(acac)_2(H_2O)_2]$5)	2+	2.034(3), 2.041(3)	2.212(4) (H_2O)
$[\mathit{Fe}(H_2O)_2\{Fe(bpca)_2\}_2](ClO_4)_4$ (**1**)	2+	2.057(5), 2.095(4)	2.116(7) (H_2O)
catena-$[\mathit{Fe}(ClO_4)_2\{Fe(bpca)_2\}](ClO_4)$ (**2**)	2+	2.030(4), 2.035(4), 2.065(4), 2.067(4)	2.134(5), 2.135(5) (ClO_4^-)

oxidation state assignments appear to be reasonable when Fe-O distances in **1** and related complexes are compared (Table II). Fe2 in **1** has coordination environment very similar to *trans*-$[Fe^{II}(acac)_2(H_2O)_2]$; for **1**, Fe-O(bpca$^-$) = 2.057(5) and 2.095(4), Fe-O(H_2O) = 2.116(7) ; for *trans*-$[Fe(acac)_2(H_2O)_2]$, Fe-O(acac$^-$) = 2.034(3) and 2.041(3) Å, Fe-O(H_2O) = 2.212(4) Å. And the Fe-O distances in **1** are clearly longer than those found in $[Fe(acac)_3]$ and their Fe(III)-acac derivative complexes, Fe(III)-O = 1.955-2.026 Å.[7] These facts supports that Fe2 in **1** is in the +2 state.

The C=O distances for C-O1 and C-O2 (av. 1.243 Å) are definitely longer as compared with those in the monomer and uncoordinated C=O bonds in **1** (C-O3 and C-O4 ; av. 1.208 Å). This fact suggests that minus charge of bpca$^-$ is delocalized on the O1-C-N-C-O2 moiety in the trinuclear complex, whereas it is localized mainly on the amide nitrogen in monomeric $[Fe(bpca)_2]$ and $[Fe(bpca)_2]X$.

Figure 2 shows an ORTEP diagram of a cation part of chain complex **2**. In **2**, asymmetric unit consists of a $\{Fe(bpca)_2\}^{n+}$ (with filled bonds), and an Fe atom(Fe2) with two coordinating perchlorate anions. With one noncoordinating perchlorate anion, total oxidation number of two iron atoms in an asymmetric unit becomes 5+. Based on the same discussion as compound **1**, Fe1 and Fe2 are assigned to +3 and +2, respectively. As seen in Figure 2, $\{Fe(bpca)_2\}^+$ units are acting as a bridging bis-bidentate complexed ligand, and alternating arrangement of $\{Fe(bpca)_2\}^+$ and $\{Fe(ClO_4)_2\}$ units forms the one dimensional chain structure. Fe-N bond lengths found in **2** were close to those in $[Fe^{II}(bpca)_2]$ and $[Fe^{III}(bpca)_2]NO_3$ (Table I), and Fe-O(eq) bond length were close to those in $[Fe^{II}(H_2O)_2(acac)_2]$, indicating that Fe2 in **2** is in

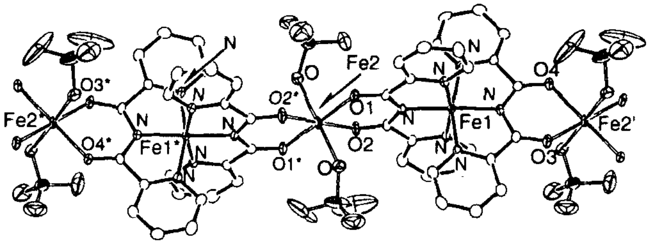


FIGURE 2 ORTEP drawing of cation part of **2**. Frameworks with filled bonds represent $\{Fe(bpca)_2\}^+$ units.

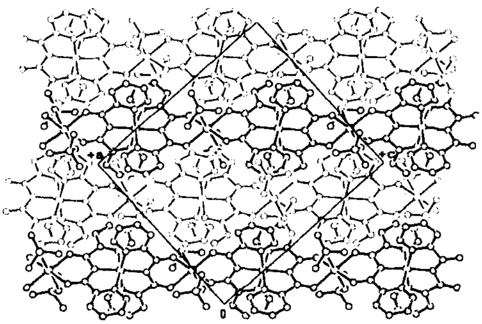


FIGURE 3 Packing diagram of cation part of **2**.

the 2+ state. One of the characteristics of the system is that two perchlorate anions axially coordinate to Fe2 in extremely short Fe-O separations of 2.134(5) and 2.135(5) Å. A few complexes are known with coordination of perchlorate to iron, and the Fe-$OClO_3$ separations fall in the range of 2.093 to 2.148 Å.[9] They are all porphyrin complexes with iron(III), and the present Fe^{II}-$OClO_3$ bonds would be very novel. Coordination environment around Fe2 *is again similar to that of* $[Fe^{II}(H_2O)_2(acac)_2]$.

As in complex **1**, the C=O distances (av. 1.235 Å) are definitely longer than those in the monomer, suggesting again the charge delocalization on the O-C-N-C-O moiety in **2**.

Magnetic Properties

Temperature dependence of magnetic susceptibility of complexes **1** and **2** were measured down to 2.0 K. Room temperature $\chi_m T$ value of **1** was 5.62 emu K mol^{-1}, decreased to 4.26 emu K mol^{-1} at 50 K, and then went smoothly to a value of 1.50 emu K mol^{-1} at 5.0 K. $\chi_m T$ value at room temperature is higher than the spin-only value of 3.75 emu K mol^{-1} for the magnetically dilute three-spin system with low-spin Fe(III), $(S_{\mathrm{Fe(III)}}, S_{\mathrm{Fe(II)}}, S_{\mathrm{Fe(III)}})$ = (1/2, 2, 1/2), but lower than that with high-spin Fe(III), $(S_{\mathrm{Fe(III)}}, S_{\mathrm{Fe(II)}}, S_{\mathrm{Fe(III)}})$ = (5/2, 2, 5/2) 11.74 emu K mol^{-1}. It is reported that monomeric [Fe(bpca)$_2$]X show different magnetic properties depending on counter anion, X.[2] With NO$_3^-$, Fe(III) atom is practically in the low-spin state. On the other hand, μ_{eff} of the ClO$_4^-$ salt shows a gradual decrease from 4.4 BM to 3.3 BM on lowering the temperature, and this was explained as a continuous high-spin to low-spin transition on lowering the temperature which is not completed even at 20 K. The same phenomenon as the latter case may cause the curious magnetic behavior of **1**.

Figure 4 shows the temperature dependence of $\chi_m T$ per repeating unit for **2**. Room temperature $\chi_m T$ value of **2** is 3.46 emu K mol^{-1}, which is compatible with the spin-only value of 3.37 emu K mol^{-1} for the magnetically dilute two-spin system with low-spin Fe(III) and high-spin Fe(II), $(S_{\mathrm{Fe(III)}},$

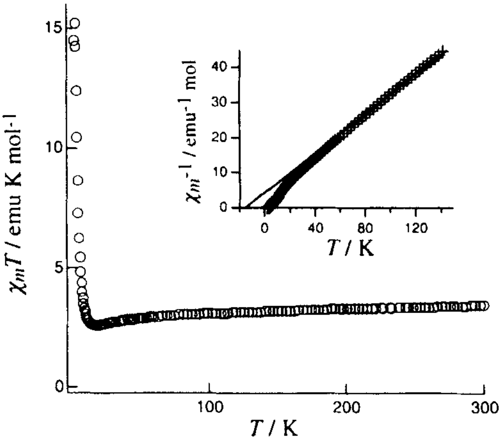


FIGURE 4 $\chi_m T$ per Fe$_2$ repeating unit *vs* T for **2**. The inset shows χ_m^{-1} *vs* T.

$S_{Fe(II)}$) = (1/2, 2) with g = 2.00. This room temperature $\chi_m T$ value is consistent with the assignment of of iron atoms, 3+ to Fe1(N_6 site) with low-spin state and 2+ to Fe2(O_6 site) with high-spin state. On lowering the temperature, $\chi_m T$ gradually decreases and shows a minimum at *ca.* 20 K, and then it increases abruptly to reach a value of 15.2 emu K mol^{-1} at 2.5 K, which is significantly higher than the largest possible value of 4.37 emu K mol^{-1} with g = 2.0. The plot of $1/\chi_m$ *vs* T above 50 K obeys the Curie-Weiss law with a negative Weiss constant of θ = -15.3 K, indicating the presence of antiferromagnetic interactions. These facts suggest the ferrimagnetic ordering within the linear chain through Fe(II)-π-system-Fe(III) linkages.

CONCLUSION

This study shows that $[M(bpca)_2]^{n+}$ could be a potential building block for supramolecular compounds. In fact, two-dimensional honeycomb structure has been constructed *via* the reaction of $[Ni(bpca)_2]$ and Fe^{2+}, in which $[Ni(bpca)_2]$ is acting as a building block.[10] Such studies are now in progress in our laboratories.

ACKNOWLEDGMENT

This work was supported by Grant-in-Aid for Scientific Research on Priority Areas(No. 10149102) from the Ministry of Education, Science and Culture, Japan.

References

[1] For example, H.O. Stumpf, L. Ouahab, Y. Pei, D. Grandjean, and O. Kahn, *Science*, **261**, 447 (1993); S. L. Suib, *Chem. Rev.*, **93**, 803 (1993).

[2] S. Wocadlo, W. Massa and J.-V. Folgado, *Inorg. Chim. Acta* **207**199(1993).

[3] D. Marcos, R. Martinez-Mane, J.-V. Folgado, A. Beltran-Porter, D. Beltran-Porter and A. Fuertes, *Inorg. Chim. Acta*, **159**, 11(1989).

[4] F. Birkelbach, M. Winter, U. Flörke, H.-J. Haupt, C. Butzlaff, M. Lengen, E. Bill, A.X. Trautwein, K. Wieghardt, and P. Chaudhuri, *Inorg. Chem.*, **33**, 3990(1994); P. Basu, S. Pal, and A. Chakravorty, *J. Chem Soc Dalton Trans.*, 3217(1991); A. Escuer, R. Vicente, J. Ribas, R. Costa, and X. Solans, *Inorg. Chem.*, **31**, 2627(1992).

[5] For example, S. Chattopadhyay, P. Basu, S. Pal, and A. Chacravorty, *J. Chem. Soc. Dalton Tans.*, 3829(1990); R. Costa, A. Garcia, R. Sanchez, J. Ribas, X. Solans, and V. Rodriguez, *Polyhedron*, **12**, 2697(1993).

[6] M.V. Tsodikov, O.V. Bukhtenko, O.G. Elbert, I.A. Petrunenko, A.S. Antsyshkina, G.G. Sadikov, Yu.V. Marsimov, Yu.V. Titov, and V.M. Novotnortsev, *Izv.Akad. Nauk, Ser. Khim.*, 1454(1995).

[7] I.A. Baidina, P.A. Stabnikov, I.K. Igumenov, and S.V. Borisov, *Koord. Khim.*, **12**, 258(1986); L.R. Nassimbeni and M.M. Thackeray, *Acta Crystallogr., Sect. B*, **30**,

1072(1974) ; R.W. Saalfrank, R. Burak, A. Breit, D. Stalke, R. Herbst-Irmer, J. Daub, M. Porsch, E. Bill, M. Muther, and A.X. Trautwein, *Angew. Chem., Int. Ed. Engl.,* **33,** 1621(1994) ; H. Soling, *Acta Chem. Scand. Ser. A,* **30,** 163(1976).

[8] Cambridge Structural Database (1998). Version 5.15. Cambridge Crystallographic Datacentre, 12 Union Road, Cambridge, England.

[9] G. Buisson, A. Deronzier, E. Duee, P. Gans, J.-C. Marchon, and J.-R. Regnard, *J. Am. Chem. Soc.,* **104,** 6793(1982) : P. Gans, G. Buisson, E. Duee, J.-C. Marchon, B. S. Erler, W. F. Scholz, and C. A. Reed, *J. Am. Chem. Soc.,* **108,** 1223(1986) : W. R. Sheidt, H. Song, K. J. Haller, M. K. Safo, R. D. Orosz, C. A. Reed, P. G. Debrunner, and C. E. Schulz, *Inorg. Chem.,* **31,** 939(1992).

[10] T. Noguchi, T. Kajiwara, and T. Ito, unpublised results.