DALTON
FULL PAPER

Synthesis, structure and magnetic properties of the one-dimensional chain compound $\{K[Fe(1,3,5\text{-triazine-}2,4,6\text{-tricarboxylate})(H_2O)_2]\cdot 2H_2O\}_\infty$

José-Ramón Galán-Mascarós,[a] **Juan-Modesto Clemente-Juan**[b] **and Kim R. Dunbar** *[a]

[a] *Department of chemistry, Texas A&M University, College Station, TX 77842-3012, USA. E-mail: dunbar@mail.chem.tamu.edu*

[b] *Instituto de Ciencia Molecular, Universidad de Valencia, Dr. Moliner, 50. 46100, Burjassot, Spain*

Received 3rd October 2001, Accepted 18th April 2002

First published as an Advance Article on the web 20th May 2002

The one-dimensional chain compound $\{[Fe(1,3,5\text{-triazine-}2,4,6\text{-tricarboxylate})(H_2O)_2]\}_n^{n-}$ was obtained from a reaction of 1,3,5-triazine-2,4,6-tricarboxylate with Fe(II) in water at room temperature. The high-spin Fe(II) centers adopt a pentagonal bipyramid geometry with unusual ligand binding modes. Magnetic measurements revealed weak magnetic interactions between paramagnetic centers; these were modeled with both axial and rhombic distortions.

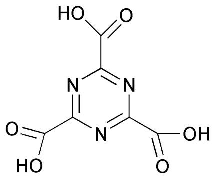
Introduction

The molecule-based approach to materials chemistry has been very succesful in recent years, producing new compounds with interesting optical,[1] electrical[2] and magnetic properties.[3] In the latter vein, novel magnets have been developed by the strategy of combining paramagnetic first row transition metals with appropiate bridging ligands. The nature of the bridging ligand is key to the properties of the material in the solid state since it dictates the sign and magnitude of the magnetic exchange between the paramagnetic metal centers. The size and topology of the ligand along with the connectivity pattern it adopts are all important parameters that need to be investigated *vis-à-vis* their effect on magnetic properties.

Small anions such as cyanide,[4] dicyanamide,[5] and oxalate are the successful bridging ligands for engendering strong magnetic coupling between transition metals in extended metal arrays.[6,7] Molecules such as TCNE[8] and TCNQ are also known to produce metal compounds with strong magnetic coupling because they form radicals that interact with the unpaired spins localized on the metal centers.[9] Large, diamagnetic π-ligands have not been particularly useful for preparing compounds with cooperative magnetic properties, but they have led to the discovery of new discrete and extended architectures of relevance to supramolecular chemistry. For example, ligands based on nitrogen heterocycles have been used to prepare molecular squares,[10] pentagons,[11] chains,[12] layers[13] and 3-D structures.[14]

One of our activities in the field of molecular magnetism is to use bridging ligands for paramagnetic metals whose binding topology is triangular. Metal compounds based on such ligands are interesting from the structural point of view, but, more importantly for the present discussion, they can lead to geometric spin-frustration.[15] Recent work in our laboratories,[16] and others,[17] involving the reactivity of hexaazatriphenylene (HAT) revealed that this ligand is capable of binding to three metal centers in a triangular fashion, but that the magnetic coupling between first row paramagnetic metal centers promoted by the HAT bridge is very weak. It occurred to us that triazine and its derivatives would also be interesting prospects for preparing triangular motifs, and that, perhaps due to the reduced distance between spin carriers, magnetic coupling would be stronger than with the HAT ligand. A perusal of the literature revealed that the only well-characterized triazine compounds are with Ag(I)[18] and Cu(I).[19] The limited scope of triazine chemistry is most likely due to the fact that the molecule is not particularly stable in solution with metal ions. In contrast, metal complexes of triazine derivatives are rather common;[20] these have been the subject of extensive studies with respect to photochemistry,[21] analytical chemistry[22] and biochemistry.[23] In recent years, supramolecular applications of various 2,4,6-tris(pyridyl)-1,3,5-triazine ligands has been a very active area as well.[24,25]

In spite of the considerable activity in the metal coordination chemistry of triazine derivatives, no reports of the use of this ligand with paramagnetic metal ions have been reported to our knowledge, although triazine itself has been investigated in the context of organic ferromagnets.[26] It occurred to us that the triazine derivative, 1,3,5-triazine-2,4,6-tricarboxylic acid (Scheme 1), offers interesting possibilities for metal-based molecular magnets due the presence of both nitrogen donors and three carboxylate groups that remain deprotonated even at very low pH values.



Scheme 1

Herein we report the first compound of the 1,3,5-triazine-2,4,6-tricarboxylic acid ligand with a first row transition metal, namely a one-dimensional chain compound of Fe(II) which was fully characterized by crystallographic techniques and magnetic properties.

Results and discussion

Synthesis and solid-state structure

The reaction of $Fe(NH_4)_2(SO_4)_2\cdot 6H_2O$ with the potassium salt of 1,3,5-triazine-2,4,6-tricarboxylate in water at room temperature yields $K\{Fe(1,3,5\text{-triazine-}2,4,6\text{-tricarboxylate})(H_2O)_2\}\cdot 2H_2O$ (**1**). The product of the bulk reaction is insoluble in water and all other common solvents. A slow diffusion reaction led

DOI: 10.1039/b109585b

This journal is © The Royal Society of Chemistry 2002

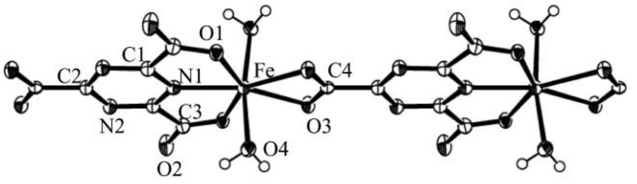


Fig. 1 ORTEP[35] diagram (50% probability) showing the 1-D chain $[Fe(1,3,5\text{-triazine-}2,4,6\text{-tricarboxylate})(H_2O)_2]_n^{n-}$ for **1**.

to the formation of single crystals of **1** which were analyzed by X-ray diffraction. The structure of **1** consists of one-dimensional chains (Fig. 1), composed of Fe(II) ions and the triazine ligand in a 1 : 1 ratio. The heptacoordinate Fe centers exhibit a pentagonal bipyramidal geometry. The five-coordinate positions in the equatorial plane are occupied by two chelating triazine ligands, one of which is bound through one nitrogen atom and two oxygen atoms from adjacent carboxylates, and the other of which is coordinated through a chelating carboxylate group. The axial positions of the pentagonal bipyramid are occupied by water molecules. Although examples of heptacoordination for Fe(II) centers are rather rare, in this case it is not unexpected, since it had been observed for a complex with the analogous ligand dipicolinate.[27] The chains run along the *b* axis, with Fe, K, N1, C2 and C4 lying on the crystallographic two-fold axis.

The shortest bonding distances in the chain are 2.120(3) Å (Fe–N1) and 2.117(2) Å (Fe–O4) to the axial water. The longest bond distance is 2.305(2) Å (Fe–O1) presumably due to the rigidity of the ligand. Indeed, the ligands are quite distorted as evidenced by the differences in the N1–O1 distance of 2.591(8) Å for the chelating carboxylate *versus* O2–N2 of 2.784(8) Å for the monodentate carboxylate sites. Both binding modes result in very small bite angles; the three-atom chelation site exhibits an angle of N1–Fe–O1 = 71.55(4)° which leaves ≈217° in the equatorial plane for the other ligands. The carboxylate of the adjacent triazine ligand exhibits an even smaller bite angle of O3–Fe–O3 = 59.35(8)°. These are extremely small values for an octahedral coordination environment, a situation that results in the adoption of a seven coordinate geometry. In spite of the distortions related to the angles between donor atoms, it is worth mentioning that the ligands maintain perfect planarity in this structure.

The 1-D chains adopt a pseudo-tetragonal packing along the *b* axis with K^+ cations and water molecules filling the interstices between the chains. The individual chains are connected to each other along the *a* and *c* axis by hydrogen bonding interactions (Fig. 2). The hydrogen atoms from the axial water molecule (O4) show very short contacts to an adjacent carboxylate group [H2–O1 = 2.05(3) Å] and to the interstitial water molecule [H1–O5 = 1.83(4) Å]. The uncoordinated water molecule is involved in an extended hydrogen bonded network to two adjacent chains [H3–N2 = 2.31(5) and H4–O2 = 1.87(4) Å], leading to an overall 3-D solid state structure.

Magnetic properties

The binding modes adopted by the ligands in this structure afford a rather long distance between paramagnetic metal centers (≈8.8 Å), which, we reasoned, would result in fairly weak magnetic interactions. In order to test this hypothesis, the temperature dependence of the magnetic susceptibility was measured for **1** from 2–300 K. The data show the characteristic features of a paramagnetic compound as indicated by the χ_m and $\chi_m T$ product *vs.* *T* plots depicted in Fig. 3. The χT product of 3.49 emu K mol^{-1} at room temperature is close to the expected value for magnetically dilute, high-spin Fe(II) ions (spin-only value is 3 emu K mol^{-1}). As the temperature is cooled, the $\chi_m T$ product decreases linearly and at 100 K the $\chi_m T$ product begins to decrease sharply and approaches zero at very low temperatures. The large distances between the paramagnetic centers in the chain preclude an assignment of this behavior to strong antiferromagnetic coupling between spin carriers; a more likely origin is single-ion anisotropy associated with the Fe(II) ions. Thus, the magnetic data were analyzed for Fe(II) ($S = 2$) with the following spin Hamiltonian that includes axial and rhombic single-ion zero-field splitting (ZFS) and a Zeeman interaction,

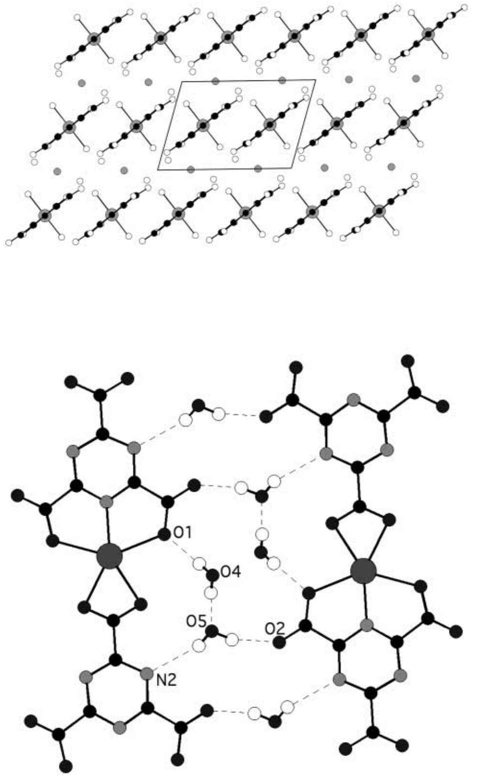


Fig. 2 Top: Packing diagram for **1**, showing the arrangement of the chains in the structure. (H atoms were omitted for clarity). Bottom: Representation of the hydrogen bonding connections between chains.

$$\hat{H} = D\hat{S}_z^2 + E(\hat{S}_x^2 - \hat{S}_y^2) + g\beta\vec{H}\vec{S} \qquad (1)$$

Calculations were performed with the magnetism package MAGPACK.[28] The best fit from a least-squares analysis of the $\chi_m T$ product is $D = 8.12$ cm^{-1}, $E/D = 0.089$, $g = 2.05$ and TIP = 1.1×10^{-3} emu K mol^{-1} ($R = \Sigma[((\chi_m T)^2_{exp} - (\chi_m T)^2_{calc})/(\chi_m T)^2_{exp}] = 1.3 \times 10^{-3}$). These values are in good agreement with typical values obtained for other high-spin Fe(II) compounds with axial and rhombic distortion, although in those cases the Fe centers are six-coordinate.[29]

Concluding remarks

A one-dimensional chain with heptacoordinate Fe(II) centers was prepared by reacting 1,3,5-triazine-2,4,6-tricarboxylate with ferric ions in water. The triazine ligands in this unusual polymer adopt a combination of chelating and monodentate binding modes in the five-coordinate equatorial plane of a distorted pentagonal bipyramid. The axial positions are occupied by water molecules. The Fe(II) ions are high-spin $S = 2$ with negligible magnetic interactions occurring through the ligand.

Analogous reactions with Co(II), Ni(II), and Mn(II) have also been performed, but single crystals were not obtained. Preliminary analyses by X-ray powder methods, however, indicate that these metal products are not isostructural to the title compound. This hints at a versatility for the chemistry of 1,3,5-triazine-2,4,6-tricarboxylate that may be useful for the construction of a variety of solid state architectures.

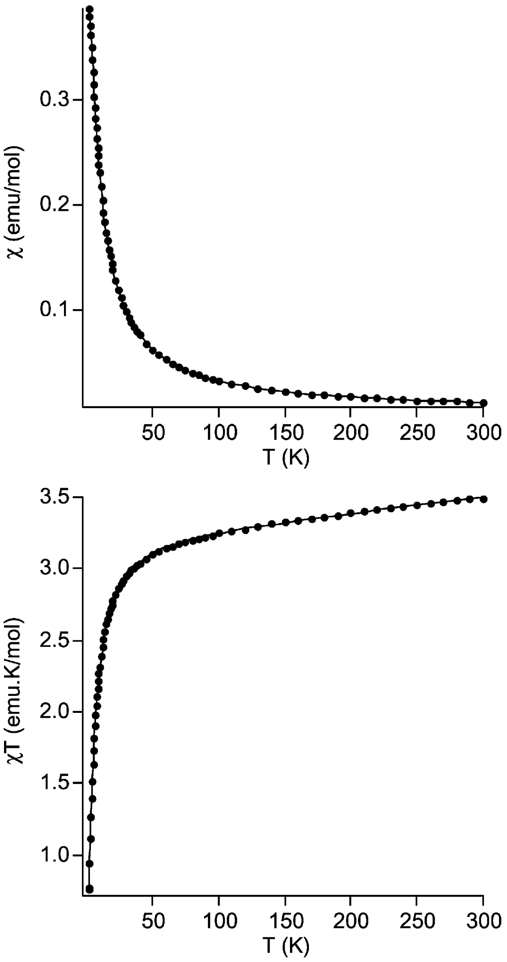


Fig. 3 Magnetic behavior for **1** (H = 1000 G) as a function of temperature. The line represents the theoretical model use to fit the experimental data (g = 2.05; D = 8.12 cm^{-1}; E/D = 0.089; TIP = 1.1 × 10^{-3} emu K mol^{-1}).

Experimental

Materials

The potassium salt of 1,3,5-triazine-2,4,6-tricarboxylate was prepared by treating a suspension of the corresponding trisacetyl-ester[30] with a 2 M KOH water solution at 0 °C. After the starting material had dissolved, precipitation of the product was induced by the addition of ethanol. All other reagents were obtained from commercial sources and used without further purification.

K{Fe(1,3,5-triazine-2,4,6-tricarboxylate)(H_2O)}·2H_2O (1)

A solution of $Fe(NH_4)_2(SO_4)_2·6H_2O$ (0.12 g, 0.3 mmol) in water (5 mL) was added drop-wise to a solution of K_3(1,3,5-triazine-2,4,6-tricarboxylate) (0.065 g, 0.2 mmol). An instantaneous reaction ensued with the deposition of a blue precipitate of the title compound, which was filtered, washed with water, acetone and ether, and finally dried under a dynamic vacuum. Yield: 0.062 g, 82%. Calc. for $C_6H_8FeKN_3O_{10}$ C, 19,11; N, 11.14; H, 2.14. Found, C, 19.66; N, 11.60; H, 2.13%.

When the same reaction was carried out by slow diffusion, the compound was obtained as single crystals after one month. These crystals were used for both single crystal X-ray studies and for the magnetic measurements. For the magnetic studies, the crystals were crushed to a powder to avoid anisotropic effects due to preferential orientation.

Structural determination

A blue prism crystal of **1** was mounted on a glass fiber and cooled to 110 ±2 K. The X-ray data were collected on a Bruker SMART 1K CCD platform diffractometer with graphite monochromated Mo-Kα radiation (λ_α = 0.71073 Å). The frames were integrated in the Bruker SAINT software package,[31] and the data were corrected for absorption using the SADABS program.[32] The structure was solved using the SIR-97 program[33] and refined by full matrix least-squares calculations on F^2 using the SHELXL-97 program.[34] All non-hydrogen atoms were located and refined anisotropically. The good quality of the data also allowed for the location of all the hydrogen atoms, that were refined isotropically without any constraints. Crystallographic data and refinement parameters are summarized in Table 1.

Table 1 Main crystallographic and refinement parameters for $\{K[Fe(1,3,5\text{-triazine-}2,4,6\text{-tricarboxylate})(H_2O)_2]·2H_2O\}_\infty$ (**1**)

Formula	$C_6H_8FeKN_3O_{10}$
M_w	377.10
T/K	110 ± 2
Space group	$P2/c$
a/Å	7.0800(14)
b/Å	8.828(2)
c/Å	10.299(2)
β/°	106.24(3)
V/Å^3	618.0(2)
Z	2
μ(Mo-Kα)/cm^{-1}	16.17
Reflections/independent	4749/1475
$I > n\sigma(I)$	2
Reflections/parameters	1191/115
R_{int}	0.0232
$R1^a$	0.0380
$wR2^b$	0.0976

^{a} $R1 = \Sigma[(F_o - F_c)]/\Sigma(F_o)$. ^{b} $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0681P)^2 + (0.2635P)]$ where $P = (F_o^2 + 2F_c^2)/3$.

CCDC reference number 173765.

See http://www.rsc.org/suppdata/dt/b1/b109585b/ for crystallographic data in CIF or other electronic format.

Magnetic measurements

Magnetic susceptibility measurements were carried out on single crystals of **1** that had been ground to a fine powder. The data were collected at 0.1 Tesla in the temperature range of 2–300 K with the use of a Quantum Design MPMS-XL-5 magnetometer equipped with a SQUID sensor. Diamagnetic contributions were calculated from Pascal's constants.

Acknowledgements

K. R. D. gratefully acknowledges the National Science Foundation for generous support of this project (PI grant: NSF CHE-9906583, CCD diffractometer: CHE-9807975, and SQUID magnetometer: NSF-9974899). J.-R. G.-M. thanks the Ministerio de Educación y Ciencia for a postdoctoral fellowship.

References

1 *Molecular Nonlinear Optics*, ed. J. Zyss., Academic Press, New York, 1994.
2 J. M. Williams, J. R. Ferraro, R. J. Thorn, K. D. Carlson, U. Geiser, H. H. Wang, A. M. Kini and M. H. Whangbo, in *Organic Superconductors (Including Fullerenes). Synthesis, Structure, Properties and Theory*, ed. R. N. Grimes, Prentice Hall, Englewood Cliffs, New Jersey, 1992.
3 C. P. Landee, D. Melville and J. S. Miller, in *Magnetic Molecular Materials*, ed. D. Gatteschi, O. Kahn, J. S. Miller and F. Palacio, Kluwer Academic Press, NATO-ASI Series, 1996, E198, p. 395.
4 T. Mallah, S. Thièbault, M. Verdaguer and P. Veillet, *Science*, 1993, **262**, 1554; K. R. Dunbar and R. A. Heintz, *Prog. Inorg. Chem.*, 1996, **35**, 4449; M. Verdaguer, A. Bleuzen, V. Marvaud, J. Vaissermann, M. Seuleiman, C. Desplanches, A. Scullier, C. Train, R. Garde, G. Gelly, C. Lomenech, I. Rosenman, P. Veillet, C. Cartier

and F. Villain, *Coord. Chem. Rev.*, 1999, **190–192**, 1285; M. Ohba and H. Okawa, *Coord. Chem. Rev.*, 2000, **198**, 313; W. R. Entley and G. S. Girolami, *Inorg. Chem.*, 1994, **33**, 5156; O. Sato, Y. Einaga, A. Fujishima and K. Hashimoto, *Inorg. Chem.*, 1999, **38**, 4405; J. Larionova, R. Clérac, J. Sanchiz, O. Kahn, S. Golhen and L. Ouahab, *J. Am. Chem. Soc.*, 1998, **120**, 13088.

5 M. Kurmoo and C. J. Kepert, *New J. Chem.*, 1998, **22**, 1515; J. L. Manson, C. R. Kmety, Q.-Z. Huang, J. W. Lynn, G. M. Bendele, S. Pagola, P. W. Stephens, L. M. Liable-Sands, A. L. Rheningold, A. J. Epstein and J. S. Miller, *Chem. Mater.*, 1998, **10**, 2552; J. L. Manson, C. R. Kmety, A. J. Epstein and J. S. Miller, *Inorg. Chem.*, 1999, **38**, 2552; S. R. Batten, P. Jensen, B. Moubaraki, K. S. Murray and R. Robson, *Chem. Commun.*, 1998, 439; S. R. Batten, P. Jensen, C. J. Kepert, M. Kurmoo, B. Moubaraki, K. S. Murray and D. J. Price, *J. Chem. Soc., Dalton Trans.*, 1999, 2987.

6 E. Coronado, J. R. Galán-Mascarós and C. J. Gómez-García, *Adv. Mater.*, 1999, **11**, 558; H. Tamaki, Z. J. Zhong, N. Matsumoto, S. Kida, M. Koikawa, N. Achiwa, Y. Hashimoto and H. Okawa, *J. Am. Chem. Soc.*, 1992, **114**, 6974; R. Pellaux, H. W. Schmalle, R. Huber, P. Fisher, T. Hauss, B. Ouladdiaf and S. Decurtins, *Inorg. Chem.*, 1997, **36**, 2301; M. Hernández-Molina, F. Lloret, C. Ruiz-Pérez and M. Julve, *Inorg. Chem.*, 1998, **37**, 4131; E. Coronado, J. R. Galán-Mascarós, C. J. Gómez-García, J. Ensling and P. Gütlich, *Chem. Eur. J.*, 2000, **6**, 552.

7 M. Verdaguer, A. Gleizes, J. P. Renard and J. Seiden, *Phys. Rev. B: Condens. Matter.*, 1984, **29**, 5144; A. Gleizes and M. Verdaguer, *J. Am. Chem. Soc.*, 1981, **103**, 7373.

8 J. M. Manriquez, G. T. Yee, R. S. McLean, A. J. Epstein and J. S. Miller, *Science*, 1991, **252**, 1415; J. S. Miller and A. J. Epstein, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 385; J. S. Miller and A. J. Epstein, *Chem. Ind.*, 1996, **2**, 49; J. Zhang, J. Ensling, V. Ksenofontov, P. Gütlich, A. J. Epstein and J. S. Miller, *Angew. Chem., Int. Ed.*, 1998, **37**, 657; G. T. Yee, J. M. Manriquez, D. A. Dixon, R. S. McLean, D. M. Groski, R. B. Flippen, K. S. Narayan, A. J. Epstein and J. S. Miller, *Adv. Mater.*, 1991, **3**, 309; J. S. Miller, D. T. Glatzhofer, D. M. O'Hare, W. M. Reiff, A. Chakraborty and A. J. Epstein, *Inorg. Chem.*, 1989, **28**, 2930.

9 K. R. Dunbar, J. Cowen, H. Zhao, R. A. Heintz, X. Ouyang and G. Grandinetti, in *NATO ASI: Supramolecular Engineering of Synthetic Metallic Materials: Conductors and Magnets*, ed. J. Veciana, Kluwer Academic Publishers, Dordrecht, 1999, 518, p. 353; J. Cowen, R. Clérac, R. A. Heintz, S. O'Kane, X. Ouyang, H. Zhao and K. R. Dunbar, *Mol. Cryst. Liq. Cryst.*, 1999, **335**, 113.

10 S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853; S.-S. Sun, A. S. Silva, I. M. Brinn and A. J. Lees, *Inorg. Chem.*, 2000, **39**, 1344; C. S. Campos-Fernández, R. Clérac and K. R. Dunbar, *Angew. Chem., Int. Ed.*, 1999, **38**, 3477; R. V. Slone, K. D. Benkstein, S. Belanger, J. T. Hupp, A. I. Guzei and A. L. Rheingold, *Coord. Chem. Rev.*, 1998, **171**, 221; M. Fujita, M. Aoyagi, F. Ibukuro, K. Pgura and K. Yamaguchi, *J. Am. Chem. Soc.*, 1998, **120**, 611; P. J. Stang and B. Olenyuk, *Acc. Chem. Res.*, 1997, **30**, 502; B. Olenyuk, J. Whiteford and P. J. Stang, *J. Am. Chem. Soc.*, 1996, **118**, 8221; M. Fujita, O. Sasaki, T. Mitsushashi, T. Fujita, J. Yakazi, K. Yamaguchi and K. Ogura, *Chem. Commun.*, 1996, 1535; M. Fujita, J. Yazaki and K. Ogura, *J. Am. Chem. Soc.*, 1990, **112**, 5645; P. M. Stricklen, E. J. Volcko and J. G. Verkade, *J. Am. Chem. Soc.*, 1983, **105**, 2494.

11 C. S. Campos-Fernandez, R. Clerac, J. M. Koomen, D. H. Russell and K. R. Dunbar, *J. Am. Chem. Soc.*, 2001, **123**, 773.

12 J. L. Manson, A. M. Arif, C. D. Incarvito, L. M. Liable-Sands, A. L. Rheingold and J. S. Miller, *J. Solid State Chem.*, 1999, **145**, 369; M.-L. Tong, J.-W. Cai, X.-L. Yu, X.-M. Chen, S. W. Ng and T. C. Mak, *Aust. J. Chem.*, 1998, **51**, 637.

13 S. Triki, F. Thetiot, J. R. Galán-Mascarós, J. Sala-Pala and K. R. Dunbar, *New J. Chem.*, 2001, **25**, 954; A. M. Chippindale, A. R. Cowley and K. I. Peacock, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 2000, **56**, 651; M. A. Lawandy, X. Huang, R.-J. Wang, J. Li, J. Y. Lu, T. Yuen and C. L. Lin, *Inorg. Chem.*, 1999, **38**, 5410.

14 B. F. Abrahams, P. A. Jackson and R. Robson, *Angew. Chem., Int. Ed.*, 1998, **37**, 2656; R. L. LaDuca Jr., C. Brodkin, R. C. Finn and J. Zubieta, *Inorg. Chem. Commun.*, 2000, **3**, 248.

15 P. W. Anderson, *Mater. Res. Bull.*, 1973, **8**, 153; A. S. Wills and A. Harrison, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 2161; J. E. Greedan, N. P. Raju, A. Maignan, C. Simon, J. S. Pedersen, A. M. Niraimathi, E. Gmelin and M. A. Subramanian, *Phys. Rev. B: Condens. Matter.*, 1996, **54**, 7189.

16 J. R. Galán-Mascarós and K. R. Dunbar, *Chem. Commun.*, 2001, 217.

17 H. Grove, J. Sletten, M. Julve and F. Lloret, *J. Chem. Soc., Dalton Trans.*, 2001, 1029.

18 D. Venkataraman, S. Lee, J. S. Moore, P. Zhang, K. A. hirsch, G. B. Gardner, A. C. Covey and C. L. Prentice, *Chem. Mater.*, 1996, **8**, 2030; M. Bertelli, L. Carlucci, G. Ciani, D. M. Proserpio and A. S. Sironi, *J. Mater. Chem.*, 1997, **7**, 1271.

19 A. J. Blake, N. R. Brooks, N. R. Champness, P. A. Cooke, A. M. Deveson, D. Fenske, P. Hubberstey, W.-S. Li and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1999, 2103.

20 L. K. Mishra, Y. Jha, B. K. Sinha, R. Kant and R. Singh, *J. Indian Chem. Soc.*, 1999, **76**, 65; J. Granifo, *Polyhedron*, 1999, **18**, 1061; M. F. Iskander, J. Stephanos, N. El Kady, M. El Essawi, A. El Toukhy and L. El Sayed, *Transition Met. Chem.*, 1989, **14**, 27.

21 H. Brunner, A. Winter and B. Nuber, *J. Organomet. Chem.*, 1998, **558**, 213; R. M. Berger and J. R. Holcombe, *Inorg. Chim. Acta*, 1995, **232**, 217; S. Chirayil, V. Hegde, Y. Jahng and R. P. Thummel, *Inorg. Chem.*, 1991, **30**, 2821; R. Hage, J. H. Van Diemen, G. Ehrlich, J. G. Haasnoot, D. J. Stufkens, T. L. Snoeck, J. G. Vos and J. Reedijk, *Inorg. Chem.*, 1990, **29**, 988; C.-T. Lin, W. Bottcher, M. Chou, C. Creutz and N. Sutin, *J. Am. Chem. Soc.*, 1976, **98**, 6536.

22 P. Collins, H. Diehl and G. F. Smith, *Anal. Chem.*, 1959, **31**, 1862; W. A. Embry and G. H. Ayres, *Anal. Chem.*, 1968, **40**, 1499; M. J. Janmohamed and G. H. Ayres, *Anal. Chem.*, 1972, **44**, 2263; H. Katano, H. Kuboyama and M. Senda, *J. Electroanal. Chem.*, 2000, **483**, 117; Y. Sasaki, *Anal. Chim. Acta*, 1978, **98**, 335; S. K. Undra, M. Katyal and R. P. Singh, *Anal. Chem.*, 1974, **46**, 1605.

23 Z. H. Hohan and M. A. Farooq, *J. Chem. Soc. Pak.*, 1995, **17**, 14; H. J. Keller and B. Keppler, *PCT Int. Appl.*, 1986, 39.

24 P. Fischer, A. Fettig, W. U. Frey, S. Henkel, H. Hoier, H. E. A. Kramer, M. Roessler and J.-L. Birbaum, *J. Chem. Soc., Perkin Trans. 2*, 2001, 90; M. Hong, Y. Zhao, W. Su, R. Cao, M. Fujita, Z. Zhou and A. S. C. Chan, *Angew. Chem., Int. Ed.*, 2000, **39**, 2468; R. K. R. Jetti, F. Xue, T. C. W. Mak and A. Nangia, *Cryst. Eng.*, 2000, **2**, 215; S. N. G. Acharya, K. Venkatesan, S. Bhattacharya, R. S. Gopalan and G. U. Kulkarni, *Chem. Commun.*, 2000, 1351.

25 T. Kusukawa, M. Yoshizawa and M. Fujita, *Angew. Chem., Int. Ed.*, 2001, **40**, 1879; M. Fujita, K. Umemoto, M. Yoshizawa, N. Fujita, T. Kusukawa and K. Biradha, *Chem. Commun.*, 2001, 509; F. A. Cotton, C. Lin and C. A. Murillo, *J. Chem. Soc., Dalton Trans.*, 2001, 499.

26 J. Zhang and M. Baumgarten, *Chem. Phys.*, 1997, **214**, 291.

27 P. Lainé, A. Gourdon, J.-P. Launay and J.-P. Tuchagues, *Inorg. Chem.*, 1995, **34**, 5150.

28 J. J. Borrás-Almenar, J. M. Clemente-Juan, E. Coronado and B. S. Tsukerblat, *Inorg. Chem.*, 1999, **38**, 6081; J. J. Borrás-Almenar, J. M. Clemente-Juan, E. Coronado and B. S. Tsukerblat, *J. Comput. Chem.*, 2001, **22**, 985–991.

29 M. P. Hendrich, P. D. Day, C. Wang, B. S. Synder, R. H. Holm and E. Münck, *Inorg. Chem.*, 1994, **33**, 2848.

30 We thank Professor Robin Hicks for providing the ester starting material.

31 SAINT 1000, Bruker Analytical X-Ray Instruments, Madison, WI 53719, 1999.

32 G. M. Sheldrick, SADABS, Siemens Area Detector Absorption (and other) Correction, University of Göttingen, Göttingen, Germany, 1997.

33 SIR-97, A. Altomare, M. C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori and R. Spagna, *J. Appl. Crystallogr.*, 199, **32**, 115.

34 SHELXL-97, G. M. Sheldrick, University of Göttingen, Germany, 1997.

35 M. N. Burnett and C. K. Johnson, ORTEP3, Report ORNL-6895, Oak Ridge National Laboratory, Oak Ridge, TN, 1996.