JOURNAL OF
Materials
CHEMISTRY

Ferrimagnetism in dicarboxylate-bridged cobalt hydroxide layers

M. Kurmoo

Institut de Physique et Chimie des Matériaux de Strasbourg, 23 rue du Loess,
67037 Strasbourg Cedex, France. E-mail: kurmoo@friss.u-strasbg.fr

Received 8th April 1999, Accepted 8th July 1999

The synthesis, characterisation (XRD, DTA, IR, UV-Vis) and magnetic properties of the layered compound $Co_5(OH)_8(O_2CC_4H_8CO_2)\cdot 5H_2O$ are reported. It is characterised by a triangular magnetic lattice with a metal–metal distance of 3.1 Å and an interlayer distance of 14.3 Å. The layers are bridged through the carboxylate groups of the adipate anions. Long range ferrimagnetic (three octahedrally coordinated cobalt centres with spin α and two tetrahedrally coordinated cobalt centres with spin β) ordering is characterised by spontaneous magnetization, an out-of-phase component in the AC susceptibility and a hysteresis loop. The Curie temperature is 52 K and the coercive field is 11 200 Oe at 2 K. Complete reversal of moment to the expected saturation of 3 μ_B was not observed due to the large anisotropy field. The long range ordering does not depend on whether the layers are covalently linked, confirming therefore the importance of dipolar interaction between layers having large effective moments as a consequence of short range intralayer interactions. The large coercive field is due to perpendicular alignment of the moment with respect to the layers and the synergy of crystalline shape and single ion anisotropies.

There is a long standing debate regarding long range magnetic ordering in two-dimensional (2D) Heisenberg systems.[1,2] The consensus is that no long range ordering is possible. Verifying the various arguments experimentally has been difficult because perfect two-dimensional compounds are rare. Consequently, there is a strong drive to create artificial magnetic systems; the physicist's method employs deposition of thin magnetic layers separated by non magnetic ones of variable thickness,[3] while the chemist resorts to supramolecular engineering to arrive at such systems. One avenue of investigation for the chemist is the insertion of non-magnetic insulating organic entities between existing magnetic layers. The current trend in this type of chemistry is intercalation of, or ion-exchange in, transition metal halides, -phosphates, -sulfides, -oxyhydroxides and -hydroxides.[4–12] Most recently, developments in Langmuir–Blodgett techniques are opening other possibilities in this area.[13,14]

In an attempt to answer some of these questions, we have developed a one-pot synthesis for layered magnetic compounds with interlayer spacers of varying length.[15–17] These are based on the rigid brucite-like metal-hydroxide triangular lattice (M–M distance of *ca.* 3 Å) where the interlayer separation can be tuned from 7 to 29 Å by changing the shape and size of the inserted ion, for example, the alkyl chain length of the anion separating the layers. Several anions containing alkyl carboxylate, -sulfate, -sulfonate and polycyanide have been employed. Furthermore, it is possible to vary the moment carriers from $S=1/2$ (Cu) to $S=1$ (Ni) and $S=3/2$ (Co) and between $S=1$–$3/2$ by synthesising Ni–Co solid solutions. Several of the copper salts have been reported previously; a range of ground states, antiferromagnetic, metamagnetic or canted antiferromagnetic and ferromagnetic, have been proposed.[18–23] The reason for the variable ground state is still unclear. The nickel compounds are ferromagnetic with Curie temperatures reaching 25 K and coercive fields less than 1000 Oe.[15] The cobalt compounds crystallise in two structural types;[17,24] the first contains both octahedral and tetrahedral sites and behaves as a ferrimagnet with a Curie temperature reaching 60 K and a coercive field approaching 20 000 Oe. The other contains only octahedral sites and behaves as a metamagnet with very strong anisotropy that results in a coercive field in excess of 50 000 Oe at 2 K.[17] Here, we report the results of a representative compound of cobalt, $Co_5(OH)_8$(adipate)$\cdot 5H_2O$ (adipate$=O_2CC_4H_8CO_2{}^{2-}$), which has layers bridged by the adipate dianion. The results of the present study demonstrate that bonding between layers has no influence on the long range magnetic ordering for this family of compounds.

Experimental

$Co_5(OH)_8(O_2CC_4H_8CO_2)\cdot 5H_2O$ was prepared by dissolving $Co(H_2O)_6(NO_3)_2$ (3 g) and adipic acid, $HO_2CC_4H_8CO_2H$ (1 g) in 200 ml of a 1 : 1 mixture of distilled water and absolute ethanol warmed to 40 °C. To this solution, 3 ml of aqueous ammonia (30%) was added dropwise to attain a pH of *ca.* 8 while stirring for 30–60 min. A dark blue precipitate formed which was collected by filtration, washed with water, ethanol and acetone and dried in air.

Chemical analysis found C 10.77, H 3.75 and N 0.23%; required for $Co_5(OH)_8(O_2CC_4H_8CO_2)\cdot 5H_2O$, C 10.84, H 3.94 and N 0%. Thermogravimetric results were characterised by a weight loss of 13% at 150 °C corresponding to the five molecules of water (calculated 13.5%) and a residual mass of 44.43% after combustion of the organic matter at 1000 °C, equivalent to the weight of the five cobalt atoms (calculated 44.32%).

X-Ray powder diffraction data were collected on a Seimens D-500 instrument using Co-Kα radiation (1.789 Å). Thermogravimetric analysis was performed in air on a SETARAM TGA–DT system. IR data were recorded by transmission through fine particles deposited on a KBr plate using a Mattson FTIR spectrometer. UV-Vis spectra were recorded by transmission through a thin film of the compound dispersed in paraffin oil on a Hitachi U-3000 spectrometer. A piece of thin tissue paper soaked with the paraffin oil was used in the reference arm to compensate for the scattering by the sample. Temperature dependent (4–300 K) magnetisation measurements were made on a Pendulum magnetometer in fields of up to 1.3 T. Isothermal field dependent magnetisation data were collected on a Princeton Applied Research vibrating sample magnetometer (operating in a field of up to ± 1.6 T) and a Quantum Design SQUID MPMS-XL (AC and DC modes and maximum static fields of ± 5 T).

Results and discussion

The family of metal hydroxides, *e.g.* brucite, bottalactite or hydrotalcite, is known to host guest molecules.[12] Both neutral and charged (anionic and cationic) organic or inorganic guests having specific properties can be inserted. The inserted species may bond to the metal atoms, but this is not always the case. In the brucite structure,[25] $Mg(OH)_2$, magnesium is octahedrally coordinated with six oxygen ions in the form of hydroxide; the octahedral units then, through edge sharing, form infinite sheets. The sheets are stacked on top of each other through hydrogen bonding. Layered double hydroxides (LDH) form a subset where some of the magnesium in the layer is replaced by a cation with a greater charge resulting in a positively charged single layer (*e.g.* Mg–Al–OH), while insertion of hydrated anions renders the structure electrically neutral.

$Co_5(OH)_8(O_2CC_4H_8CO_2)\cdot 5H_2O$ powder appears as irregular plates under a high resolution electron microscope. It displays concentric rings of electron diffraction overlaid by a hexagonal pattern of diffused spots with a periodicity corresponding to a *d*-spacing of *ca.* 2.7 Å. The XRD pattern (Fig. 1) is characterised by a progression of the 00*l* reflections to $l=4$ and two broad in-plane reflections at $d=2.69$ and 1.55 Å. The latter two reflections have a sharp rise in intensity followed by a pronounced asymmetry, which is typical of turbostratic faults. This would imply that there is two-dimensional order within a layer but the layers are orientationally disordered. We had anticipated that bridging the layers with the dicarboxylate anion would reduce this disorder. Its presence may originate from the flexibility of the long alkyl chain of the inserted acid. On this basis, and the lack of diffraction, information it is difficult to assign a hexagonal or a monoclinic unit cell corresponding to those found for $Zn_5(OH)_8X_2\cdot nH_2O$ ($X=NO_3$ or Cl).[26] Within the layer, the structure of the latter is characterised by a brucite-type layer of octahedral Zn–OH where one in four of the Zn atoms is replaced by two tetrahedral Zn centres above and below the vacant position. In our case, three cobalt atoms octahedrally coordinated with hydroxide ions form a layer which is sandwiched by two layers of cobalt atoms tetrahedrally coordinated by three hydroxide ions and an oxygen atom of the carboxylate. An idealised structure based on the layered structure found for $Zn_5(OH)_8X_2\cdot nH_2O$ is shown in Fig. 2. It can be considered as a triple-deck structure, *i.e.* one layer of octahedral Co–OH sandwiched by two layers of tetrahedral cobalt. The distance (14.3 Å) between the layers in the adipate ($C_4H_8C_2O_4^{2-}$) compound is shorter than those observed for the equivalent alkane-backbone hexanoate ($C_6H_{11}CO_2^-$) compound (19.4 Å) and methyladipate compound (18.5 Å), confirming that in the former the layers are bridged by the dicarboxylate anion while in the latter the hexanoate anions are interdigitated between the layers. The distance between terminal oxygen atoms of the two carboxylate groups is calculated as 8.7 Å for an energy-minimised structure of the adipate dianion. Therefore the minimum thickness of the cobalt layer, including the Co_{tet}–O bonds to the carboxylate, is 5.6 Å, in close agreement with the observed Zn_{tet}–Zn_{tet} distance of 3.4 Å for $Zn_5(OH)_8X_2\cdot nH_2O$.[26] From this observation and the stoichiometry of the compounds, the formation of bilayers can be ruled out. Interestingly, the interlayer distance alternates, as expected, for even and odd numbers of carbon atoms in the alkyl chain of the series of dicarboxylates.[16] This alternation is more pronounced for the dicarboxylates than for the carboxylates, suggesting more flexibility in the latter.

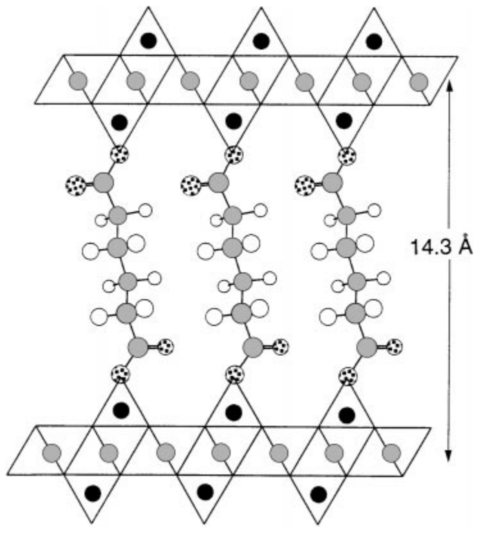

Fig. 2 Idealised triple-deck layer structure for $Co_5(OH)_8(O_2CC_4H_8CO_2)\cdot 5H_2O$ showing a single layer of octahedral cobalt (grey circles) sandwiched by two layers of tetrahedral cobalt (dark circles) and the adipate anion in a bridging position which has been arbitrarily chosen.

The IR spectrum is characterised by a broad band in the 3200–3500 cm^{-1} region, characteristic of the OH stretching vibration and ν(C–H) at 2940 cm^{-1}. The carboxylate asymmetric and symmetric vibrations are observed at 1540 and 1395 cm^{-1}; the difference in energy between the two bands is less than expected for a unidentate carboxylate and is close to the value found in solution.[27] This may be accounted for by the effect of hydrogen bonding by the solvent to the C=O group. The observation of only one of each type of vibration suggests the two terminal carboxylate groups of the adipate are equivalent. The UV-Vis absorption spectrum (Fig. 3) is characterised by three bands, a pair at 15 470 and 16 600 cm^{-1} and one at 19 700 cm^{-1} which are respectively assigned to the $^4A_2 \rightarrow {}^4T_1(P)$ of the tetrahedral cobalt and to $^4T_{1g}(F) \rightarrow {}^4A_{2g}(P)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ of the octahedral cobalt.[28] It appears that the colour in this family of compounds, ranging from green to blue, is due to the relative intensity of the two low energy bands and their energies rather than a difference in structure. Preliminary XANES measurements[16] on related compounds exclude the presence of trivalent cobalt as has been suggested.[29] The absence of cobalt(III) has

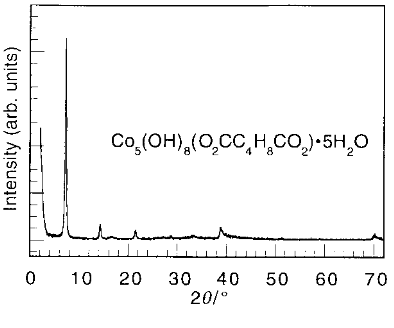

Fig. 1 Powder X-ray diffraction pattern of $Co_5(OH)_8(O_2CC_4H_8CO_2)\cdot 5H_2O$ (Co-Kα_1, $\lambda=1.789$ Å).

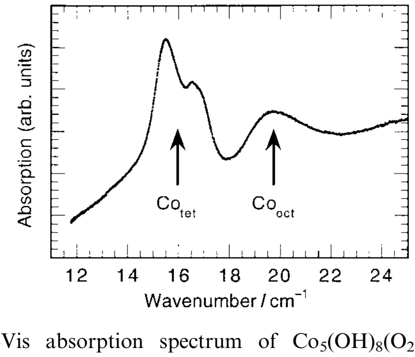

Fig. 3 UV-Vis absorption spectrum of $Co_5(OH)_8(O_2CC_4H_8CO_2)\cdot 5H_2O$.

also been noted by Kamath and coworkers.[30] The greater the down shift (maximum of *ca.* 1000 cm^{-1} observed) of the low energy bands the more blue the compound becomes. For example, the green cobalt compound $Co_5(OH)_8(C_{12}H_{25}SO_3)_2{\cdot}5H_2O$ shows two sharp peaks at 16 600 and 17 300 cm^{-1} and a broad weak band at 21 500 cm^{-1} (ref. 15).

The temperature dependence of the inverse susceptibility and the products of susceptibility and temperature are shown in Fig. 4. The data were analysed by fitting those in the temperature range 150–300 K ($T \geqslant 2.5$ times the Weiss constant) to the Curie–Weiss law.[31] The compound shows a linear dependence of the inverse susceptibility with temperature above 150 K ($\Theta = -63 \pm 2$ K). The value of the Curie constant (13.753 cm^3 K mol^{-1} or 2.75 cm^3 K mol^{-1} cobalt) obtained from the fit is consistent with the weighted average of those expected for cobalt in octahedral and tetrahedral environments. The effective moment decreases gradually to a minimum at 120 K, consistent with short range antiferromagnetic interaction between moments.

Spontaneous magnetisation is observed on cooling the sample from above the Curie temperature at 52 K in an applied field of 1 Oe (Fig. 5). AC magnetisation in an alternating field of 1 Oe oscillating at 20 Hz (Fig. 5) shows a maximum at 52 K which is accompanied by the observation of an out-of-phase component emerging at 52 K. The possibility of a spin glass transition can be eliminated due to the observation of spontaneous magnetisation in a very small DC field of *ca.* 1 Oe and the large coercive field (*vide supra*). The observation of bifurcation in the ZFC and FC magnetisation data near the Curie temperature is in agreement with long range magnetic ordering. Isothermal magnetisation measurements above the Curie temperature are weakly field dependent. Just below the transition at 50 K (Fig. 6) hysteresis is observed, which widens along the field axis as the temperature is lowered. At 30 K and in a field of 16 000 Oe the hysteresis loop has a remnant magnetisation of 1 μ_B and a coercive field of 2200 Oe. At 2 K, and in a field of 50 000 Oe, we observed a wider loop characterised by a remanant magnetisation of 1 μ_B and a coercive field of 11 200 Oe. We also note that the saturation magnetisation at +50 000 Oe is slightly larger than at −50 000 Oe, suggesting incomplete reversal of the moments. This suggests that the anisotropy field is larger than the limiting 50 000 Oe of our SQUID. The observed value of the coercive field (11 200 Oe) for $Co_5(OH)_8(O_2CC_4H_8CO_2){\cdot}5H_2O$ is consequently lower than that found (19 000 Oe) for $Co_5(OH)_8(C_{12}H_{25}SO_3)_2{\cdot}5H_2O$, where saturation was reached. The slanting shape of the hysteresis loop is also indicative of a large demagnetising field due to the flat plate geometry of the particles.[32] Common for this family of compounds is the large single-ion anisotropy and the shape anisotropy, which have a large contribution to the magnetocrystalline anisotropy. This situation is analogous to the large coercive fields observed for hexagonal ferrites compared to tridimensional ferrites. A large coercive field has also been observed for the hard molecule-based magnet $[(Etrad)_2Co_2\{Cu(opba)\}_3]{\cdot}S$ where Etrad$^+$ = 2(1-ethyl-4-pyridinio)-4,4,5,5-tetramethylimidazolin-1-oxyl3-oxide, opba = *o*-phenylenebis(oxamato) and $S = (DMSO)_{1.5}(H_2O)_{0.25}$ (ref. 33).

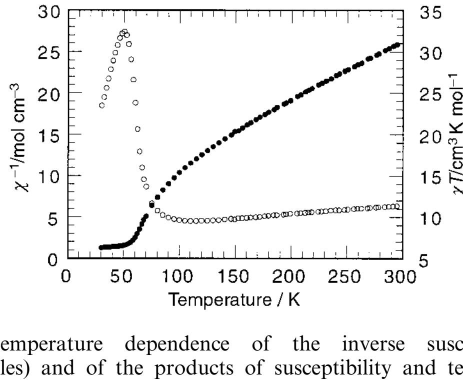

Fig. 4 Temperature dependence of the inverse susceptibilities (full circles) and of the products of susceptibility and temperature (open circles) measured in an applied field of 12 000 Oe for $Co_5(OH)_8(O_2CC_4H_8CO_2){\cdot}5H_2O$.

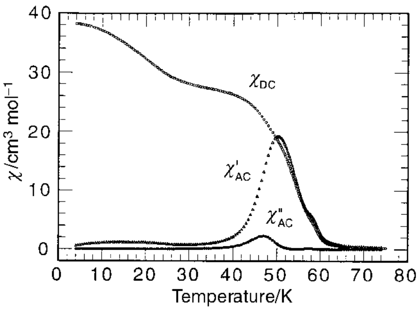

Fig. 5 Temperature dependence of the DC (open circles) and the in-phase (triangles) and out-of-phase (full circles) AC magnetization at 20 Hz for $Co_5(OH)_8(O_2CC_4H_8CO_2){\cdot}5H_2O$ in an applied field of 1 Oe.

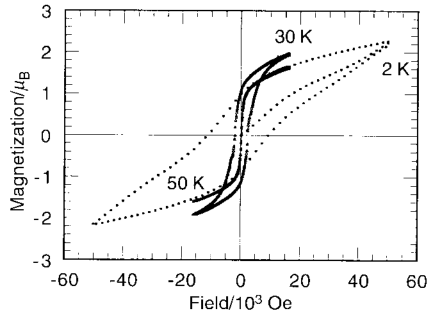

Fig. 6 Isothermal magnetization of $Co_5(OH)_8(O_2CC_4H_8CO_2){\cdot}5H_2O$

For the proposed structure there are two antiferromagnetically coupled sublattices within a layer, one comprising cobalt in octahedral sites (3 per formula unit) and the other Co in tetrahedral sites (2 per formula unit). The expected saturation magnetisation per mol in the ordered ferrimagnetic state is given by

$$M_{sat} = |3 \times g_{oct} \times 3/2\mu_B - 2 \times g_{tet} \times 3/2\mu_B|$$

Therefore, the saturation magnetisation is expected to be nearly 3 μ_B if we assume the *g*-values to be 2. The observed value at 2 K in 50 000 Oe is 2.4 μ_B (Fig. 6).

As noted previously,[15–17] the most striking observation for this class of compounds is the three-dimensional long range magnetic ordering at fairly high temperatures for spin carriers in layers separated by up to 25 Å. In the reported dodecylsulfonate compounds there is no bonding between the layers, thus magnetic exchange interactions between cobalt on adjacent layers is expected to be negligible. However, if the layers are covalently bridged the exchange interaction through the bonds is expected to follow a R^{-10} dependence, where R is the distance between the spin centres.[34] At a distance of 14.3 Å for the adipate derivative, the exchange interaction is still too small to result in long range magnetic ordering at 52 K.[35] On the other hand, a purely electrostatic dipolar interaction between the layers is proportional to R^{-3}. Since the short range interaction between the metals within the layer is large compared to that between layers, the correlation length within the layer increases as the temperature of the sample is lowered.[36] These correlated regions may be considered as a large spin cluster. Therefore, the average effective spin per cluster gets very high, such that even at large distances there will be sufficient dipole interaction to effect long range 3D-ordering. The critical temperature of the transition is expected to depend on the most dominant exchange interaction within the layer, as this defines the size of the correlated cluster. The interaction may be ferromagnetic or antiferromagnetic between sites of different sublattices. Furthermore, the critical temperature will be a very slow varying function of the distance when R is large (>10 Å). This is a point we have verified by comparing the experimental results for compounds within the series with different interlayer distances. It appears that there is little dependence of the Curie temperatures on the interlayer spacing. For the three cobalt compounds, $Co_5(OH)_8(X^-)_2 \cdot nH_2O$ where $X = N(CN)_2$, $(OC_2C_4H_8CO_2)_{0.5}$ or $C_{12}H_{25}SO_3$ the d-spacings are 11.5, 14.3 and 24.4 Å, respectively and the T_C are 58, 52 and 50 K, respectively. This is in good agreement with the proposed mechanism. Furthermore, one would expect T_C to increase with the value of S for the central metal. Indeed, this is the case for all the compounds studied. We have also verified this point for mixed metal (Ni and Co) solid solutions, where a continuous increase of T_C is observed with increasing average spin value. Most importantly, introducing an exchange pathway through alkyl or aryl dicarboxylate bridges between the layers has no discernible effect on the transition temperature. This, therefore, confirms that dipolar interactions at these distances are more important than exchange interactions through bonds. The fact that we have ferromagnetically coupled layers is a good indication that the moments are perpendicular to the planes, which is expected for spin carriers having large spin–orbit coupling as evidenced by the magnitude of the coercive force observed. In general, the most energetically favourable configuration when the moments are in the plane of a Heisenberg system is antiferromagnetic stacking.

Conclusion

$Co_5(OH)_8(O_2CC_4H_8CO_2) \cdot 5H_2O$ has been synthesised and characterised by several techniques. Its proposed structure, comprising layers of divalent cobalt in an octahedral environment sandwiched by two layers of cobalt in a tetrahedral environment, is in good agreement with the magnetic properties observed. Long range magnetic ordering between the two uncompensated sublattices results in a ferrimagnet with a Curie temperature of 52 K, a coercive field of 11 200 Oe and a magnetization of 2.4 μ_B at 2 K. By comparison of its Curie temperature and coercive field to those of other members in this family of compounds we can conclude that the introduction of covalent bonds between the magnetic layers has no influence on the magnetic properties and the long range ordering mechanism. The latter is due purely to dipolar interactions between the moments which are aligned perpendicularly to the planes, due to the strong spin–orbit coupling. The large coercive field is a consequence of synergetic alignment of crystallite shape, surface and single-ion anisotropies.[37]

Acknowledgements

This work was funded by the CNRS-France and the EEC (Molecular Magnetism: from Materials toward Devices; ERBFMRXCT 980181). The technical assistance of N. Finck, R. Poinsot and A. Derory is much appreciated. I am grateful to Dr M. Richard-Plouet for the electron microscopy and Dr S. Vilminot for fruitful discussions.

References

1. L. J. De Jongh and A. R. Miedema, *Adv. Phys.*, 1974, **23**, 1; L. J. De Jongh (ed.), *Magnetic Properties of Layered Transition Metal Compounds*, Kluwer Academic Publishers, Dordrecht, Boston, MA, 1990.
2. O. Kahn (ed.), *Magnetism: A Supramolecular Function, NATO ASI Ser., Ser C*, Kluwer Academic Publishers, Dordrecht, 1996, vol. 484.
3. B. Heinrich and J. A. C. Bland (ed.), *Ultrathin Magnetic Structures*, Springer Verlag, Berlin, 1994.
4. R. Schollhorn, *Intercalation Compounds*, Academic Press, London, 1984.
5. A. Clearfield, *Chem. Rev.*, 1988, **88**, 125; A. Clearfield, *Curr. Opin. Solid State Chem.*, 1996, **1**, 268; A. Clearfield (ed.), *Inorganic Ion Exchange Materials*, CRC Press Inc., Boca Raton, FL, 1991.
6. A. J. Jacobsen, in *Solid State Chemistry: Compounds*, ed. P. Day and A. Cheetham, Oxford University Press, Oxford, 1992.
7. D. O'Hare, in *Inorganic Materials*, ed. D. W. Bruce and D. O'Hare, Wiley, London, 1993.
8. T. Pinnavaia, *Science*, 1983, **220**, 365.
9. I. V. Mitchell (ed.), *Pillared Layered Structures; Current Trends and Applications*, Elsevier, London, 1990.
10. M. Jakupca and P. K. Dutta, *Chem. Mater.*, 1995, **7**, 989.
11. S. Carlino, *Solid State Ionics*, 1997, **98**, 73.
12. M. Meyn, K. Beneke and G. Lagaly, *Inorg. Chem.*, 1993, **32**, 1209; S. P. Newman and W. Jones, *New J. Chem.*, 1998, **22**, 105.
13. G. E. Fanucci, C. M. Nixon, M. A. Petruska, C. T. Seip, D. R. Talham, G. E. Granroth and M. W. Meisel, in *Supramolecular Engineering of Synthetic Metallic Materials, NATO ASI Ser., Ser. C*, ed. J. Veciana, C. Rovira and D. B. Amabilino, Kluwer Academic Publishers, Netherlands, 1999, vol. 518, p. 465.
14. M. Clemente-León, H. Soyer, E. Coronado, C. Mingotaud, C. J. Gómez-García and P. Delhaès, *Angew. Chem., Int. Ed.*, 1998, **37**, 2842.
15. M. Kurmoo, P. Day, A. Derory, C. Estournès, R. Poinsot, M. J. Stead and C. J. Kepert, *J. Solid State Chem.*, , 1999, **145**, 452.
16. M. Kurmoo, *Mol. Cryst. Liq. Cryst.*, 1999, in press; *Chem. Mater.*, 1999, in press.
17. M. Kurmoo, *Proc. R. Soc. London, Ser. A*, 1999, in press.
18. V. Laget, Thèse doctorat, Université Louis Pasteur, Strasbourg, France, 1998; M. Drillon, C. Hornick, V. Laget, P. Rabu, F. M. Romero, S. Rouba, G. Ulrich and R. Ziessel, *Mol. Cryst. Liq. Cryst.*, 1995, **273**, 125.
19. W. Fujita and K. Awaga, *Inorg. Chem.*, 1996, **35**, 1915.
20. V. Laget, P. Rabu, C. Hornick, F. Romero, R. Ziessel, P. Turek and M. Drillon, *Mol. Cryst. Liq. Cryst.*, 1997, **305**, 291.
21. V. Laget, M. Drillon, C. Hornick, P. Rabu, F. Romero, P. Turek and R. Ziessel, *J. Alloys Compd.*, 1997, **262**, 423.
22. M. A. Girtu, C. M. Wynn, W. Fujita, K. Awaga and A. J. Epstein, *Phys. Rev. B*, 1998, **57**, R11058.
23. V. Laget, C. Hornick, P. Rabu, M. Drillon and R. Ziessel, *Coord. Chem. Rev.*, 1998, **178–180**, 1533 and references therein.
24. S. Rouba, Thèse doctorat, Université Louis Pasteur, Strasbourg, France, 1996.
25. A. F. Wells, *Structural Inorganic Chemistry*, Oxford University Press, Oxford, 1984.
26. R. Allmann, *Z. Kristallogr.*, 1968, **126**, 417; W. Stählin and H. R. Oswald, *Acta Crystallogr. Sect. B*, 1970, **26**, 860; P. Benard, J. P. Auffredic and D. Louer, *Thermochim. Acta*, 1994, **232**, 65.
27. K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley, New York, 1986, p. 230.
28. A. P. B. Lever, *Inorganic Electronic Spectroscopy*, Elsevier, Amsterdam, 1986.
29. L. Markov, K. Petrov and V. Petrov, *Thermochim. Acta*, 1986, **106**, 283; H. C. Zeng, Z. P. Xu and M. Qian, *Chem. Mater.*, 1998, **10**, 2277; Z. P. Xu and H. C. Zeng, *Chem. Mater.*, 1999, **11**, 67.
30. R. S. Jayashree and P. V. Kamath, *J. Mater. Chem.*, 1999, **9**, 961; P. V. Kamath, G. H. A. Therese and J. Gopalakrishnan, *J. Solid State Chem.*, 1997, **128**, 38.
31. O. Kahn, *Molecular Magnetism*, VCH Publishers Inc., New York, 1993.
32. S. Chikazumi, *Physics of Magnetism*, John Wiley, New York, 1978.
33. M. G. F. Vaz, L. M. M. Pinheiro, H. O. Stumpf, A. F. C. Alcântara, S. Golhen, L. Ouahab, O. Cador, C. Mathoniere and O. Kahn, *Chem. Eur. J.*, 1999, **5**, 1486.
34. D. Bloch, *J. Phys. Chem. Solids*, 1966, **27**, 881.
35. J. Cano, G. De Munno, J. L. Sanz, R. Ruiz, J. Faus, F. Lloret, M. Julve and A. Caneschi, *J. Chem. Soc., Dalton Trans.*, 1997, 1915.
36. M. Drillon and P. Panissod, *J. Magn. Magn. Mater.*, 1998, **188**, 93.
37. M. Kurmoo and C. J. Kepert, *New J. Chem.*, 1998, **22**, 1515.

Paper 9/02807B