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Magnetic properties of hybrid molecular materials based on oxalato complexes

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Abstract

The use of $[M^{III}(ox)_3]^{3-}$ ($M^{III} = Ru, Rh$) complexes as building blocks for hybrid molecular materials is highlighted with two different synthetic approaches. The first strategy is the combination of organic donors and $[Ru^{III}(ox)_3]^{3-}$ units, resulting in the radical salt of formula $TTF_3[Ru(ox)_3]\cdot 0.5EtOH\cdot 4H_2O$ (**1**) which shows coexistence of paramagnetism and semiconducting properties. The second approach is the synthesis of extended 2D bimetallic oxalato-bridged networks of general formula $[FeCp_2^*][M^{II}Rh(ox)_3]$ in which paramagnetic layers of decamethylferricinium cations are alternated with paramagnetic bimetallic layers.

Keywords: Radical salts; Tetrathiafulvalene; Bimetallic oxalato complexes; Molecular magnetism; Conducting properties

1. Introduction

The oxalato (ox) ligand is well known for its ability to stabilize systems of different dimensionalities and its efficiency to transmit magnetic interactions [1]. The use of homoleptic $[M^{III}(ox)_3]^{3-}$ complexes provides an easy way for the preparation of oxalato complexes of the desired dimensionality. There are several examples of heterobimetallic oxalato-bridged compounds of dimensionalities 2 and 3 which display magnetic ordering. The 2D family is formed by compounds of general formula $A[M^{II}M^{III}(ox)_3]$ ($M^{II} = Mn, Fe, Co, \ldots$; $M^{III} = Cr, Fe, Ru$). When A is a quaternary onium cation, the oxalato network displays a staggered honeycomb-layered structure with the *n*-alkyl chains penetrating into the holes of the anionic layer [2]. Ferromagnetic ordering is achieved when $M^{III} = Cr$ [3], while the $Fe^{III}–M^{II}$ interaction is antiferromagnetic, giving rise to ferrimagnets and weak ferromagnets [4]. When the A cation is of the decamethylmetallocenium type $[Z^{III}Cp_2^*]^+$, the honeycomb alternating layers are eclipsed producing hexagonal channels where the cations lay [5]. This system represents a good example of magnetic multilayers. The 3D compounds have the general formulas $[M^{II}(bpy)_3][M_2^{II}(ox)_3]$ or $[M^{III}(bpy)_3][ClO_4][M_2^{II}(ox)_3]$ and crystallize with cubic chiral packing. They behave as weak ferromagnets when the spin-canting allows for non-cancelling magnetic moments [1,6]. Bimetallic analogues of general formula $[M^{II}(bpy)_3](ClO_4)[M^{II}Cr^{III}(ox)_3]$ have also been prepared. Their magnetic properties show the same trends as in the 2D compounds with slightly lower T_c and smaller coercive fields [7].

The cation plays an important role in the construction of both 2D and 3D families acting as template-agent. The introduction of cations possessing a physical property, like magnetism or optical activity, into magnetically ordered oxalato layers allows for the preparation of multifunctional molecular materials [7–10]. Organic donor molecules have also been used together with oxalato complexes in order to combine magnetism and conductivity in the same compound. The first example was $(BEDT\text{-}TTF)_4(NH_4)Fe(ox)_3\cdot C_6H_5CN$, a paramagnetic superconducting charge-transfer salt [11]. The oxalato complexes are not bridged but the overall inorganic structure is very similar to a honeycomb

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thanks to the solvent molecules that are occupying the hexagonal cavities. Many salts with different donors have been obtained since then giving rise to superconductors [12], metals [13] and semiconductors [14]. In some cases, the oxalato complexes form dimers [14b,14d] and trimers [15] that permit the interactions of the metallic centers. The combination of extended 2D bimetallic oxalato-bridged networks with organic donors has led to the preparation of the first molecular metal ferromagnet $(BEDT\text{-}TTF)_3[MnCr(ox)_3]$. This compound behaves as a metal down to 2 K, with no transition to a superconducting state observed, what could be prevented by the presence of magnetic ordering in the oxalato layers [16].

In this paper, we report the synthesis and characterization of new materials based on the $[Ru^{III}(ox)_3]^{3-}$ and $[Rh^{III}(ox)_3]^{3-}$ units with the aim of extending the work devoted to molecular magnetism based on 4d transition metal oxalato complexes. These 4d ions possess different characteristics than the 3d ions: (1) more orbital diffuseness character of the singly occupied orbitals; (2) more covalent ligand–metal bonds; and (3) more important spin-orbit coupling effects. These must influence the interactions between magnetic centers. Kahn and coworkers [17] published a pioneering work about 2D bimetallic oxalate layers of formula $Nbu_4[M^{II}Ru(ox)_3]$ (Nbu_4 = tetrabutyl ammonium; M^{II} = Mn, Fe, Cu) where a variety of magnetic behaviors was observed. Our group published an extensive work about this family employing decamethylmetalloceniums as cations. The magnetic ordering was settled to be of ferromagnetic nature when M^{II} = Fe, Co [18]. In the present communication, we present an analogue family substituting Ru^{III} by Rh^{III}. The use of this diamagnetic 4d ion represents a good opportunity to observe the behavior of the divalent metals on the coordination sphere imposed in the layer and to check if the layers can be synthesized with bigger ions.

We are also presenting the results of the combination of the trisoxalatometalate complexes with the tetrathiafulvalene (TTF) organic donor (salt **1**).

2. The radical salt $TTF_3[Ru(ox)_3]\cdot 0.5EtOH\cdot 4H_2O$ (1)

Electrochemical oxidation of the organic donor TTF in the presence of $THA_3[Ru(ox)_3]$ (THA = tetraheptylammonium) in a mixture of organic solvents leads to the synthesis of black crystals with general formula $TTF_3[Ru(ox)_3]\cdot 0.5EtOH\cdot 4H_2O$ [19].

This radical salt is formed by layers of the organic radical TTF, alternating with layers of inorganic oxalato complexes and solvent molecules. The trisoxalato complexes display a pseudohexagonal arrangement on the *ab*-plane (see Fig. 1). Both Δ and Λ isomers are present and give rise to a racemic salt. Solvent molecules (ethanol and water) are hosted in the cavities left by the anions, keeping them far apart. Many short intermolecular distances are found between anions and solvent molecules. The organic sublattice is formed by infinite chains and dimers of TTF. Three crystallographically independent TTF molecules are found named A, B and C. The dimers are composed of A-type molecules while the chains contain the other two types following the sequence ...BBCC... (see Fig. 2(a)). The shorter intermolecular distances within the chain are found between molecules B and C that are parallel to each other. Two molecules of the same type are displaced by their long axis to maximize the intermolecular interactions originating the zigzag form of the chains. Two consecutive organic layers are related by a C_2-axis and translation creating a repeating pattern ...abab... (see Fig. 2(b)).

Short distances have been found between the anions and the A-type molecules, and this is not surprising since these dimers are placed on the cavities formed by the non-coordinating oxygens. This closeness implies a high degree of partial oxidation, almost +1, on this kind of molecules. The partial oxidation degree on each TTF molecule has been calculated from their C–C and C–S intramolecular bond distances [20]. The molecules of A- and B-type are completely ionized, while the C molecules remain neutral. This balance indicates that the dimers are completely charged, while the chains are composed by completely ionized molecules alternating with neutral molecules.

Even taking into account the limitations of this method for the estimation of the charge of organic radicals based on bonding distances, it is clear that for the charge balance we have around two positive charges from the organic sublattice against three negative charges from the anion. So, the electroneutrality in the solid is probably achieved by the presence of a H_3O^+ molecule. Such a specie could not be located by X-ray diffraction, although some candidates were found among the O atoms located near the anions, as it has been observed in other radical salts [11b].

We have performed conductivity measurements on single crystals of **1** from 300 to 180 K. The plot of the conductivity vs. T is shown in Fig. 3(a). The thermal dependence of the conductivity is typical of a semiconducting regime. At room temperature, σ has a value of 1.5×10^{-4} S cm^{-1} and decreases down to 4×10^{-5} S cm^{-1} when cooling. The activation energy is 61.1(1) meV. This behavior is expected due to the charge localization found in the organic layer.

The magnetic susceptibility of this salt has been measured (see Fig. 3(b)). χ_m, presents a smooth increase from 300 to 50 K when an exponential rise begins. This thermal dependence has been fitted by a Curie–Weiss law considering two contributions, one from the Ru^{III} ion and a second one arising from the organic molecules.

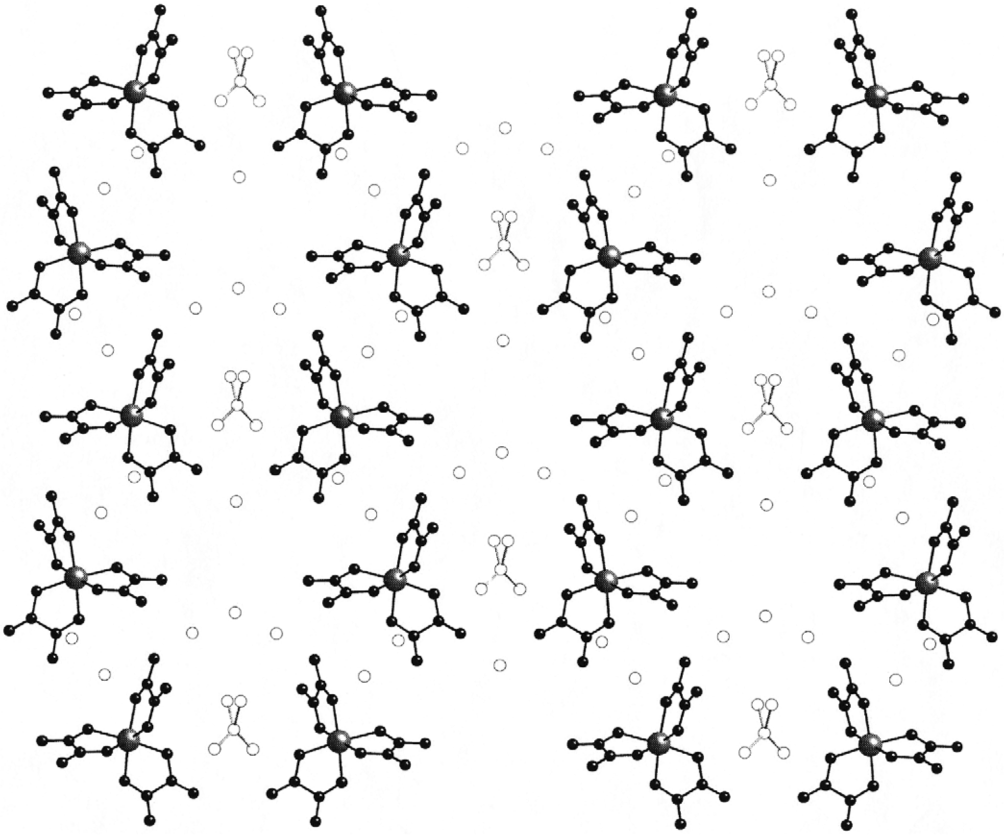

Fig. 1. General view of the anionic layer of the $TTF_3[Ru(ox)_3]\cdot 0.5EtOH\cdot 4H_2O$ on the *ab*-plane. Solvent molecules are shown in empty circles.

The equation that we have employed is:

$$\chi_m = \frac{C_{Ru}}{T - \Theta_{Ru}} + \frac{C_{TTF}}{T}$$

in which the first term stands for the Ru^{III} ion and the second one for the organic molecules. The parameters employed for the Ru^{III} are: C_{Ru} for the Curie constant and Θ_{Ru} for the Weiss constant, that accounts for the spin-orbit coupling on the Ru^{III} ion. A prior study on the precursor $K_3[Ru(ox)_3]$ allowed us the determination of the Θ_{Ru} parameter (−1.11 K) for a fixed literature value of C_{Ru} (0.3896 emu K mol^{-1} [21]). The organic term contains the Curie constant for the TTF molecules

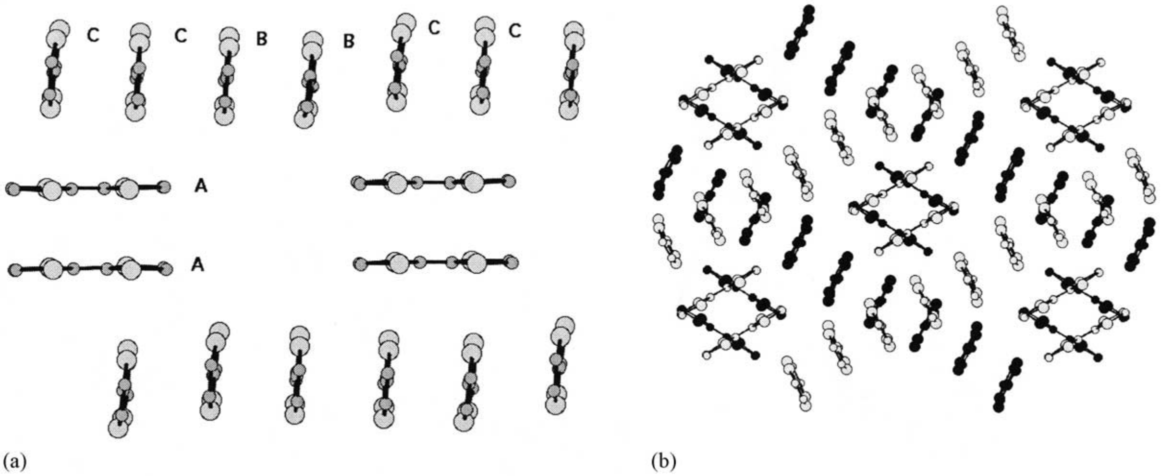

Fig. 2. View of the organic layer on the *ab*-plane (a) and two consecutive organic layers (b).

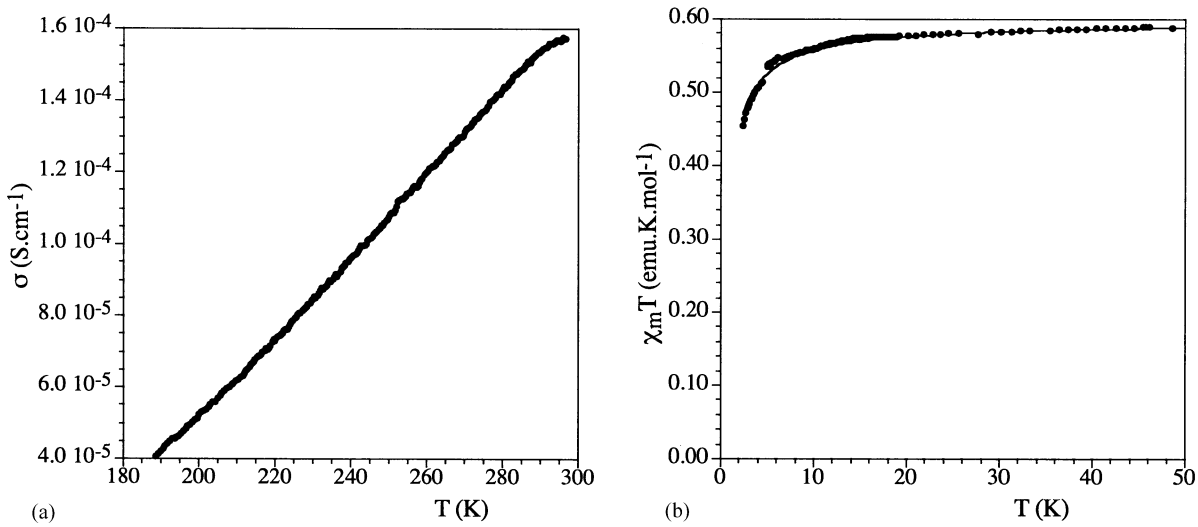

Fig. 3. (a) Plot of the conductivity vs. T and (b) thermal dependence of the fitting of the χ_mT product for the radical salt **1** under an applied field of 2 T.

(C_{TTF}), and the best-fit is obtained for $C_{TTF} = 0.2073(5)$ emu K mol^{-1}. The small value of the C_{TTF}, that corresponds to less than one unpaired electron per formula, indicates that the charge on the TTF molecules is either partially delocalized (as in the chain) or strongly coupled in antiferromagnetic way (as in the dimers). Then, the paramagnetic response observed from the organic layer should arise from crystallographic defects, as it has been observed in other TTF derivatives radical salts [22].

3. Hybrid 2D bimetallic compounds

We have synthesized 2D bimetallic M^{II}–Rh^{III} oxalato-bridged networks interleaved by decamethylferricinium cations of general formula $[FeCp_2^*][M^{II}Rh(ox)_3]$ (M^{II} = Mn, Fe, Co, Ni, Cu, Zn). All these materials were obtained as microcrystalline powders and the salt $[FeCp_2^*][MnRh(ox)_3]$ was also obtained as single crystals. As detected by X-ray powder analysis, these compounds are isostructural and possess the same unit cell than the published $[FeCp_2^*][MnFe(ox)_3]$ [5]. This is the first example of this type of magnetic multilayer systems where the Ni^{II} derivative has been synthesized.

The structure of these materials present the well known eclipsed honeycomb bimetallic layers that are achiral with the $[FeCp_2^*]^+$ cations intercalated between the inorganic layers [5].

Magnetic measurements have been performed. The plot of χ_mT vs. T is shown in Fig. 4. The data have been fitted by a Curie–Weiss law $\chi_m = C/(T-\Theta)$ between 300 and 150 K. The magnetic parameters are shown in Table 1. We should state that the Rh^{III} ion has a spin $S = 0$, and so it is diamagnetic, and that the Fe^{III} ion from the $[FeCp_2^*]^+$ shows high C-values between 0.5 and 0.9 [23], due to its high single ion anisotropy. Below 150 K, the experimental points diverge from the calculated ones, what can be due to different phenomena like zero field splitting and spin-orbit coupling of the Fe^{II}, Co^{II} and Ni^{II} ions, or the Jahn-Teller distortion typical of the Cu^{II}. When compared to other salts of these divalent metal ions, we observed that in this series the magnetization of the sample decreases at higher temperatures and more abruptly, what indicates in this case the presence of weak antiferromagnetic interactions between the paramagnetic metals through the ox–Rh–ox bridges. The observed Curie constants agree, within experimental error, with the calculated ones that arise from the sum of the spins of the M^{II} ions and the spin of the Fe^{III} from the organometallic cations. Measurements of the magnetization as a function of the applied magnetic field confirm this behavior.

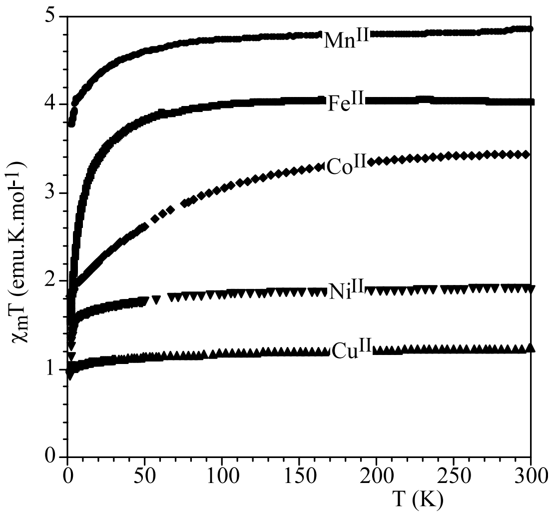

Fig. 4. Plot of the χ_mT product vs. T for the family $[FeCp_2^*][M^{II}Rh(ox)_3]$ (M^{II} = Mn (●) Fe (■), Co (◆), Ni (▲), Cu (▼), Zn (○)).

Table 1
Magnetic parameters obtained for the family $[FeCp_2^*][M^{II}Rh^{III}(ox)_3]$

$M^{II}Rh^{III}$	S total	C (emu K mol^{-1})	C calculated (emu K mol^{-1})	Θ (K)	$M_{5\ T,\ 2\ K}$ (μ_B)
MnRh	1/2+5/2	4.899(4)	5.12	−3.3(1)	5.08
FeRh	1/2+2	4.055(4)	3.75	−0.5(4)	3.07
CoRh	1/2+3/2	3.665(9)	2.625	−18.8(5)	2.78
NiRh	1/2+1	1.955(3)	1.75	−6.7(3)	2.70
CuRh	1/2+1/2	1.266(1)	1.125	−7.9(3)	2.05
ZnRh	1/2	0.732(1)	0.75	2.7(3)	1.14

C: Curie constant; Θ: Weiss constant; $M_{5\ T}$: magnetization reached at 5 T.

4. Conclusions

Here we report the results obtained when using $[M^{III}(ox)_3]^{3-}$ (M^{III} = Ru, Rh) complexes to construct novel hybrid organic/inorganic molecular materials by different approaches. The preparation of the radical salt **1** has yielded an inorganic layer constituted by $[Ru^{III}(ox)_3]^{3-}$ units, that have not dimerized, surrounded by solvent molecules that isolate them and avoid magnetic interactions. The resulting paramagnetic salt shows also semiconducting properties due to the arrangement of the TTF molecules. More radical salts of this kind are being synthesized in order to explore the structural and magnetic effects that can arise from the combination of organic donors and 4d transition metal ions.

The second synthetic strategy has originated a new inorganic/organometallic family. In this case, the $[Rh^{III}(ox)_3]^{3-}$ units are connected to first row transition divalent metal ions giving rise to extended bimetallic networks. The use of a slightly bigger trivalent ion has not affected the construction of the network, and has helped in the preparation of the Ni^{II} derivative that could not be obtained when using A = $[ZCp_2^*]$ (Z = Fe, Co) and M^{III} = Cr, Fe or Ru. In addition, short-range weak antiferromagnetic interactions have been observed through the diamagnetic Rh^{III} bridges.

The combination of the extended bimetallic oxalato networks with organic donors leads to the preparation of radical salts like $(BEDT\text{-}TTF)_3[MnCr(ox)_3]$. The use of the Rh^{III} ion instead of Cr^{III} in the inorganic layer has allowed the synthesis of a paramagnetic analogue of formula $(BEDT\text{-}TTF)_3[MnRh(ox)_3]$ [24]. This radical salt will permit us to check the influence of the magnetic ordering in the bimetallic oxalato network over the metallic properties observed in the Cr derivative.

5. Supplementary material

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 201318. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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References

[1] S. Decurtins, R. Pellaux, A. Hauser, M.E. von Arx, in: O. Kahn (Ed.), Magnetism: A Supramolecular Function, NATO-ASI Series C484, Kluwer Academic Publishers, Dordrecht, 1996, p. 487.

[2] R. Pellaux, H.W. Schmalle, R. Huber, P. Fisher, T. Hauss, B. Ouladdiaf, S. Decurtins, Inorg. Chem. 36 (1997) 2301.

[3] H. Tamaki, Z.J. Zhong, N. Matsumoto, S. Kida, M. Koikawa, N. Achiwa, Y. Hashimoto, H. Okawa, J. Am. Chem. Soc. 114 (1992) 6974.

[4] (a) H. Okawa, N. Matsumoto, H. Tamaki, M. Ohba, Mol. Cryst. Liq. Cryst. 233 (1993) 257;
(b) C. Mathionère, S.G. Carling, D. Yusheng, P. Day, J. Chem. Soc., Chem. Commun. (1994) 1551.;
(c) C. Mathionère, C.J. Nutall, S.G. Carling, P. Day, Inorg. Chem. 35 (1996) 1201;
(d) C.J. Nutall, C. Bellito, P. Day, J. Chem. Soc., Chem. Commun. (1995) 1513.

[5] E. Coronado, J.R. Galán-Mascarós, C.J. Gómez-García, P. Gütlich, Chem. Eur. J. 6 (2000) 552.

[6] (a) S. Decurtins, H.H. Schmalle, P. Schneuwly, R. Pellaux, J. Ensling, in: J.S. Miller, A.J. Epstein (Eds.), Proceedings of the IV International Conference on Molecule-based Magnets, Molecular Crystals and Liquid Crystals, Gordon & Breach, London, 1995;
(b) S. Decurtins, H.W. Schmalle, P. Schneuwly, J. Ensling, P. Gütlich, J. Am. Chem. Soc. 116 (1994) 9521;
(c) M. Hernández-Molina, F. Lloret, C. Ruiz-Pérez, M. Julve, Inorg. Chem. 37 (1998) 4131;
(d) S. Decurtins, H.W. Schmalle, R. Pellaux, P. Schneuwly, A. Hauser, Inorg. Chem. 35 (1996) 1451.

[7] E. Coronado, J.R. Galán-Mascarós, C.J. Gómez-García, J.M. Martínez-Agudo, Inorg. Chem. 40 (2001) 113.

[8] (a) G. Ballester, E. Coronado, C. Giménez-Saiz, F.M. Romero, Angew. Chem. Int. Ed. 40 (2001) 792;
(b) R. Sieber, S. Decurtins, H. Stoeckli-Evans, C. Wilson, D. Yufit, J.A.K. Howard, S.C. Capelli, A. Hauser, Chem. Eur. J. 6 (2000) 361.

[9] (a) S. Bénard, P. Yu, J.P. Audière, E. Rivière, R. Clément, J. Guilhem, L. Tchertanov, K. Nakatani, J. Am. Chem. Soc. 122 (2000) 9444;
(b) S. Bénard, E. Rivière, P. Yu, K. Nakatani, J.F. Delouis, Chem. Mater. 13 (2001) 159;
(c) P.G. Lacroix, I. Malfant, S. Bénard, P. Yu, E. Rivière, K. Nakatani, Chem. Mater. 13 (2001) 441.

[10] (a) M.E. von Arx, A. Hauser, H. Riesen, R. Pellaux, S. Decurtins, Phys. Rev. B 54 (1996) 15800;
(b) A. Hauser, H. Riesen, R. Pellaux, S. Decurtins, Chem. Phys. Lett. 261 (1996) 313;
(c) V.S. Langford, M.E. von Arx, A. Hauser, J. Phys. Chem. A 103 (1999) 7161.

[11] (a) A.W. Graham, M. Kurmoo, P. Day, J. Chem. Soc., Chem. Commun. (1995) 2061.;
(b) M. Kurmoo, A.W. Graham, P. Day, S.J. Coles, M.B. Hurthouse, J.L. Caufield, J. Singleton, F.L. Pratt, W. Hayes, L. Duchase, P. Guionneau, J. Am. Chem. Soc. 117 (1995) 12209.

[12] S. Rashid, S.S. Turner, P. Day, J.A.K. Howard, P. Guinonneau, E.J.L. McInnes, F.E. Mabbs, R.J.H. Clark, S. Firth, T. Biggs, J. Mater. Chem. 11 (2001) 2095.

[13] L. Martin, S.S. Turner, P. Day, K.M.A. Malik, S.J. Coles, M.B. Hurthouse, J. Chem. Soc., Chem. Commun. (1999) 513.

[14] (a) L. Martin, S.S. Turner, P. Day, F.E. Mabbs, E.J.L. McInnes, J. Chem. Soc., Chem. Commun. (1997) 1367.;
(b) S. Rashid, S.S. Turner, P. Day, M.E. Light, M.B. Hursthouse, Inorg. Chem. 39 (2000) 2426;
(c) L. Martin, S.S. Turner, P. Day, P. Guionneau, J.A.K. Howard, M. Uruichi, K. Yakushi, J. Mater. Chem. 9 (1999) 2731;
(d) E. Coronado, J.R. Galán-Mascarós, C.J. Gómez-García, J. Chem. Soc., Dalton Trans. (2000) 205.

[15] (a) E. Coronado, J.R. Galán-Mascarós, C. Giménez-Saiz, C.J. Gómez-García, C. Ruiz-Pérez, S. Triki, Adv. Mater. 8 (1996) 737;
(b) E. Coronado, J.R. Galán-Mascarós, C. Giménez-Saiz, C.J. Gómez-García, C. Ruiz-Pérez, Eur. J. Inorg. Chem., 2003, in press.

[16] E. Coronado, J.R. Galán-Mascarós, C.J. Gómez-García, V. Laukhin, Nature 408 (2000) 447.

[17] J. Larionova, B. Mombelli, J. Sanchiz, O. Kahn, Inorg. Chem. 37 (1998) 679.

[18] E. Coronado, J.R. Galán-Mascarós, C.J. Gómez-García, J.M. Martínez-Agudo, E. Martínez-Ferrero, J.C. Waerenborgh, M. Almeida, J. Sol. State Chem. 159 (2001) 391.

[19] Crystal data for $C_{25}H_{23}O_{16.50}RuS_{12}$ (**1**): monoclinic, $C2/c$, $a = 24.477(6)$ Å, $b = 15.089(5)$ Å, $c = 21.219(6)$ Å, $\beta = 93.043(8)^\circ$, $V = 7826(4)$ Å^3, $M = 1073.24$ g mol^{-1}, $Z = 8$, R1 = 6.46%. The structure was solved by direct methods using the SIR97 program and was refined on F^2 using the SHELX97 program (G.M. Sheldrick, University of Göttingen, 1997).

[20] T.C. Umland, S. Allie, T. Kulhmann, P. Coppens, J. Phys. Chem. 92 (1988) 6456.

[21] R.L. Carlin, Magnetochemistry, Springer, Berlin, 1986.

[22] J.M. Williams, J.R. Ferraro, R.J. Thorn, K.D. Carlson, U. Geiser, H.H. Wang, A.M. Kini, M.H. Whangbo, in: R.N. Grimes (Ed.), Organic Superconductors (Including Fullerenes): Synthesis, Structure, Properties and Theory, Prentice-Hall, Englewood Cliffs, NJ, 1992.

[23] D.N. Hendrickson, D.N. Sohn, H.B. Gray, Inorg. Chem. 10 (1971) 1559.

[24] Manuscript in preparation.