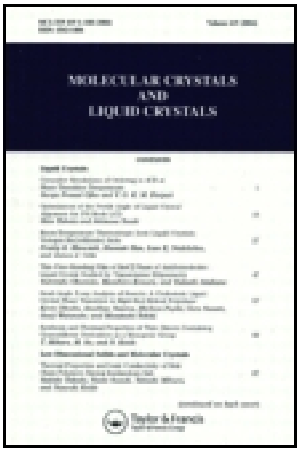

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Christian Rimbaud [a] , Lahcéne Ouahab [a] , Jean Pascal Sutter [b] & Olivier Kahn [b]

[a] Groupe Matèriaux Moléculaires, Laboratoire de Chimie du Solide et Inorganique Moléculaire, URA/CNRS 1495, Université Rennes I, 35042, Rennes cedex, France

[b] Laboratoire des Sciences Moléculaires, Institut de Chimie de la Matière Condensée de Bordeaux, UPR CNRS 9048, F33608, Pessac, France

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FERROMAGNETIC INTERACTIONS IN SUPRAMOLECULAR ASSEMBLIES CONSTRUCTED FROM NITRONYL NITROXIDE RADICAL CATIONS AND LARGE INORGANIC POLYOXOMETALATES

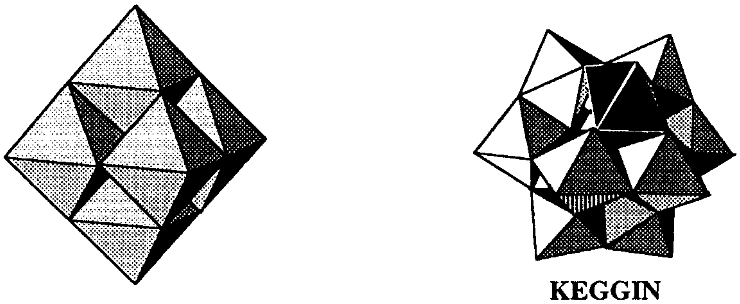
Christian RIMBAUD[a], Lahcène OUAHAB[a], Jean Pascal SUTTER[b] and
Olivier KAHN[b]

[a]Groupe Matériaux Moléculaires, Laboratoire de Chimie du Solide et Inorganique Moléculaire, URA/CNRS 1495, Université Rennes I, 35042 Rennes cedex France.
[b]Laboratoire des Sciences Moléculaires, Institut de Chimie de la Matière Condensée de Bordeaux, UPR CNRS 9048, F33608 Pessac France.

Abstract The synthesis, crystal structures and magnetic properties of two nitronyl nitroxide radical salts of polyoxometalates are reported. The para-radical 2-(4-N-methylpyridinium-4,4,5,5-tetramethylimidazoline)-1-oxyl-3-oxide was associated to Lindquist polyoxometalates $[M_6O_{19}]^{2-}$ with M=Mo,W to give (para-rad)$_2$-Mo_6O_{19} **(1)** and (para-rad)$_2$-W_6O_{19} **(2)** which are isostructural. The magnetic measurements show ferromagnetic interactions for **(1)** and **(2)**.

INTRODUCTION

The molecule based magnetic materials involves two kinds of compounds. On one hand those materials in which a spin-spin interactions occur through chemical bridges, the spin carriers being either transition metal ions or both transition metal ions and organic radicals[1]. On other hand the materials with weak through-space interactions between isolated molecules. These salts include charge transfer complexes such as TCNE-Fe(Cp*)$_2$ [2] and radical ions salts such as those containing nitronyl-nitroxide organic radicals. For this latter particular class, the magnetic interactions depend on the dimensionality of the materials. In this way, we have recently observed ferromagnetic interactions in such compounds containing hexacyanometalates[3]. In this paper we report the preparation, X-Ray crystal structures and ferromagnetic interactions of a new class of nitronyl-nitroxide radical salts containing polyoxometalates. These inorganic anions (Scheme1) have been used as components in conducting or magnetic TTF derivatives radical ions salts[4,5,6]. Their structure can be discribed as condensed MO_6 octahedra sharing edges or vertices, and they constitute a wide class of discrete molecular anions with different charges, shapes, sizes and electronic and magnetic properties[7]. Their association with organic radicals of the nitronyl nitroxide family can give rise to new molecular agencements with new kinds of magnetic interactions. Thanks to the richness of their substitution chemistry, it is possible to modulate their geometrical and physical properties. In particular, it can be introduced as spin carriers in these organic radical materials.



LINDQUIST
$[M_6O_{19}]^{2-}$

KEGGIN
$[XM'M_{11}O_{40}]^{n-}$
X= Si, P; M'= Fe, Cu; M= W
X= Fe, Cu; M'= M= W

SCHEME 1: Representation of Lindquist and Keggin Polyoxometalates.

EXPERIMENTAL SECTION:

Synthesis:

Nitronyl nitroxide radical salt[8] and Lindquist polyoxometalates[9,10] were prepared using the literature procedure.

The synthesis of compounds is achieved by metathesis between the tetrabutylammonium salts of polyanions and the radical salt $Rad^+ I^-$ in acetonitrile solution. Well shapped green and brown crystals (respectively for (**1**) and (**2**)) were obtained by slow evaporation in acetonitrile. The stoichiometries were determined by X-Ray crystal structure and elemental analysis. Analysis calculated (found) gives for **(1)** : C, 22.78 (22.80); H, 2.77 (2.82); N, 6.13 (6.45); Mo, 42.02 (42.17). Analysis calculated (found) gives for **(2)** : C, 16.44 (16.42); H, 2.00 (2.01); N, 4.42 (4.39); W, 58.14 (58.89).

X-Ray Diffraction[11]:

The X-Ray data collections were performed on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromatized MoKα (λ=0.71073Å) radiation. The unit cell parameters were determined and refined from setting angles of 25 accurately centred reflections. Data were collected with the θ-2θ scan method. Three standard reflections were measured every hour and revealed no fluctuations in intensities for **(1)** and **(2)**. Intensities were corrected for Lorentz and polarisation effects. The structures were solved by direct methods and successive Fourier difference synthesis. An empirical absorption correction was applied using the Ψ-scan procedure[12]. The refinements were performed by the full-matrix least-squares method [H-atoms, both found by Fourier synthesis and placed at computed positions (C-H: 1Å, B=4Å^2). All the calculations were achieved on a Micro VAX 3100 using the Molen programs[13].

Magnetic Measurements:

These were carried out with a Quantum Design MPMS-5S SQUID magnetometer, with an external magnetic field of 10^3 Oe.

STRUCTURAL AND MAGNETIC CHARACTERISATIONS:

Crystal Structure:

The unit cell of **(1)** and **(2)** contains one polyoxometalate $[MO_{16}]^{2-}$ centered on the origin and one radical. The intramolecular bond lengths and bond angles are close to those reported for such units[14,15]. The angle between the nitronyl nitroxide and the pyridinium rings is 33.4(2)°. The radicals form centrosymetric dimers A-B which are located in the middle of the (ab) plane. Figure 1 shows the projection of the crystal structure. The most significant intermolecular interactions are observed following the directions [100] and [001]. Theses distances are reported in Table 1. The shortest O...H distances between the radicals are 2.322(3)Å and 2.368(6)Å for $[Mo_6O_{19}]^{2-}$ and $[W_6O_{19}]^{2-}$, respectively. The shortest contact between the radical and the polyoxometalate is observed for a O...H interaction at 2.21(4)Å and 2.294(4)Å for $[Mo_6O_{19}]^{2-}$ and $[W_6O_{19}]^{2-}$ respectively.

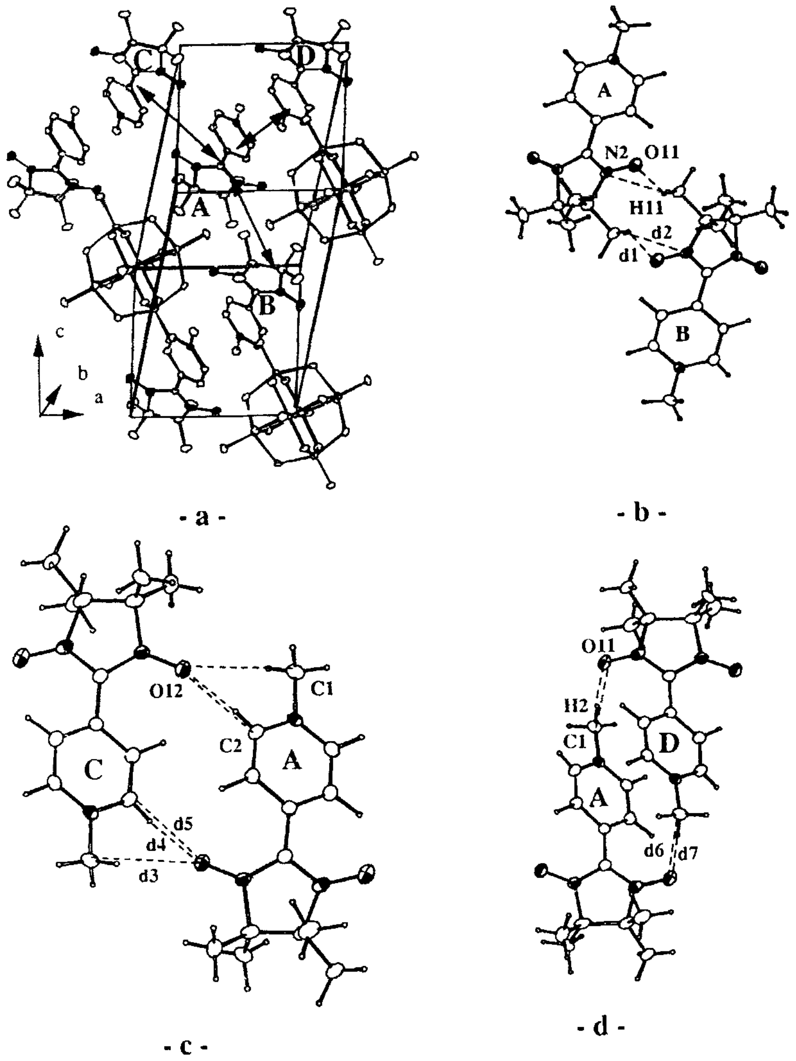


FIGURE 1 : a) Projection of the crystal structure. b, c and d give shortest intermolecular contacts according to Table 1. Symmetry code: A (x,y,z) ; B (1-x, 1-y, 1-z); C (-x, 1-y, 2-z); D (1-x, 1-y, 2-z).

TABLE1 : Significant intermolecular contacts for **(1)** and **(2)**.

		(para-rad)$_2$-Mo$_6$O$_{19}$	**(para-rad)$_2$-W$_6$O$_{19}$**
radical-radical :			
d1(O11-H11)	(i)	2.53(6) Å	2.452(6) Å
d2(N2-H11)	(i)	2.83(5) Å	2.751(5) Å
d3(O12-C1)	(ii)	3.169(4) Å	3.137(8) Å
d4(O12-H4)	(ii)	2.38(3) Å	2.337(4) Å
d5(O12-C2)	(ii)	3.045(3) Å	3.020(6) Å
d6(O11-C1)	(iii)	3.322(4) Å	3.317(9) Å
d7(O11-H2)	(iii)	2.322(3) Å	2.368(6) Å
polyoxometalate-radical :			
d8(O5-H6)	(iv)	2.21(4) Å	2.294(4) Å
d9(O7-H5)	(v)	2.45(5) Å	2.212(4) Å
d10(O3-H12)	(vi)	2.47(4) Å	2.430(4) Å

Symmetry code: (i): 1-x, 1-y, 1-z ; (ii): -x, 1-y, 2-z ; (iii): 1-x, 1-y, 2-z ; (iv): 1-x, -y, 1-z ; (v): -x, 1-y, 1-z, (vi): x, y-1, z.

Magnetic properties:

The magnetic properties of **(1)** are represented in Figure 2 in the form of the $\chi_M T$ versus T plot, χ_M being the molar magnetic susceptibility and T the temperature. At room temperature, $\chi_M T$ is equal to 0.75 cm^3.K.mol^{-1}, which corresponds to what is expected for two uncorrelated radical spins, remains constant down to ca. 60K, then increases as T is lowered further, and reaches 0.85 cm^3.K.mol^{-1}. These experimental data may be fitted with the Curie-Weiss law $\chi_M = 0.750/(T-0.286)$. Such a behaviour reveals dominant ferromagnetic interactions between the radicals spins. There are three kinds of intermolecular interactions within the lattice, namely: (i) the A-B interaction, B being deduced from A through the operation (1-x, 1-y, 1-z). The shortest contact is observed between a nitroxide oxygen atom of a unit and a hydrogen atom bound to a methyl group of the nitronyl nitroxide ring of the other unit (2.53(6) Å); (ii) the A-C interactions between the units related through the operation (-x, 1-y, 2-z). The shortest contact is then between the nitroxide oxygen atom of a unit and the hydrogen atom bound to the pyridinium carbon atom in 2-position of the other unit (2.38(3) Å); (iii) the A-D interaction, D being deduced from A through the operation (1-x, 1-y, 2-z). In that case, the shortest contact involves a nitroxide oxygen atom of a unit and a hydrogen atom of the methyl pyridinium group of the other unit (2.322(3) Å). It is not obvious to see what interaction is responsible for the observed ferromagnetic coupling. The best candidate seems to be the interaction A-B in which the nitronyl nitroxide groups are closer to each other. In any case, the interaction is rather weak. If we assume that one of the three interactions described above is operative and the other two are negligibly small, the experimental data could be described by a dimer law. Such a law leads to a singlet-triplet energy gap $J=0.84\ cm^{-1}$.

The data for compound (**2**) are very similar to that for compound (**1**). In the dimer hypothesis, J is found to be equal to $0.93\ cm^{-1}$. The fact that the ferromagnetic interaction is larger than for **1** is in line with the fact that the intermolecular contacts in (**2**) are shorter than in (**1**).

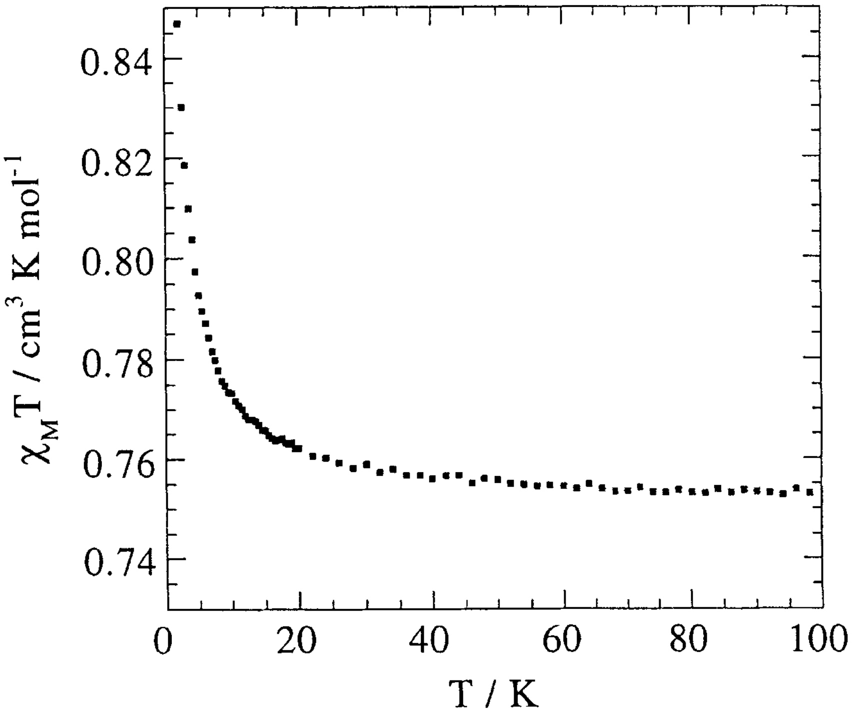


FIGURE 2 : $\chi_M T$ versus T curve in the 2-100 K temperature range for compound (1).

CONCLUSION

The materials presented here constitute the first example of molecular assemblies of nitronyl nitroxide radicals with polyoxometalates. Despite the large size of the anions, ferromagnetic interactions between the nitronyl nitroxide radicals are observed. Other radical cation salts containing paramagnetic Keggin polyoxometalates $[XM'W_{11}O_{40}]^{n-}$ (X= Si, P and M'= Fe, Cu; X= Fe, Cu and M'= W) are under current investigation in our group. This kind of polyoxometalates gives the possibility to introduce paramagnetic centers on the inorganic part.

REFERENCES

1. O. Kahn, Molecular Magnetism; VCH: New York (1993).
2. J.S. Miller, J.C. Calabresse, A.J. Epstein, W. Bigelow, J.H. Zhang, W.M. Reiff, J. Chem. Soc., Chem. Commun, 1026 (1986).
3. C. Michaut, L. Ouahab, P. Bergerat, O. Kahn, and A. Bousseksou, J. Am. Chem. Soc., 118, 3610 (1996).
4. L. Ouahab, M. Bencharif, D. Grandjean, C. R. Acad. Sci. Paris, Sér. 2, 307, 749 (1988).
5. S. Triki, L. Ouahab, J. Padiou, D. Grandjean, J. Chem. Soc., Chem. Commun., 1608 (1989).
6. C. J. Gomez-Garcia, L. Ouahab, C. Gimenez-Saiz, S. Triki, E. Coronado, P. Delhaès, Angew. Chem., Int. Ed. Engl., 33, 223 (1994).
7. M. T. Pope, A. Müller, Angew. Chem., 103, 56 (1991); Angew. Chem., Int. Ed. Eng., 30, 34 (1991); Polyoxometalates: from Platonic Solids to Anti-retroviral activity, Eds. Kluwer Acad. Pub.: Dordrecht, The Netherlands (1994).
8. E.F.Ulman, J.H. Osiecki, D.G.B. Boocock, and R. Darcy, J. Am. Chem. Soc., 94, 7049 (1972).- P.W. Kopf, R. Kreilick, D.G.B. Boocock, and E.F.Ulman, J. Am. Chem. Soc., 92, 4531 (1970).
9. M. Che, M. Fournier, and J.P. Launay, J. Chem. Phys, 71(4), 1954 (1979).
10. C. Sanchez, J.Livage, J.P. Launay, and M.Fournier, J. Am. Chem. Soc., 105, 6817 (1983).
11. Crystal data: **(para-rad)$_2$-Mo$_6$O$_{19}$** crystallises in the $P\bar{1}$ triclinic space group with cell parameters a=8.240(8)Å, b=11.394(4)Å, c=12.059(1)Å, α=65.89(1)°, β=79.64(3)°, γ=84.27(5)°, V=1016 Å^3, Z=1, d_{calc}=2.252 g.cm^{-3}. Full-matrix least-squares refinements gave R(F)=0.022 and Rω(F)=0.040 based on 3666 reflections with

$I>3\sigma(I)$. **(para-rad)$_2$-W$_6$O$_{19}$** crystallises in the $P\bar{1}$ triclinic space group with cell parameters a=8.268(1)Å, b=11.418(6)Å, c=12.076(2)Å, α=65.77(2)°, β=79.27(2)°, γ=84.02(3)°, V=1021 Å^3, Z=1, d_{calc}=3.099 g.cm^{-3}. Full-matrix least-squares refinements gave R(F)=0.019 and Rω(F)=0.030 based on 3808 reflections with $I>4\sigma(I)$. The full X-Ray data will be reported elsewhere.

12. A.C.T. North, D.C. Phillips and F.S. Mathews, Acta. Cryst., A24, 351 (1968).
13. Crystal Structure Analysis, Molecular Enraf-Nonius (MolEN) 1990, delft Instruments X-Ray Diffraction B.V Rontgenweg 1 2624 BD Delft. The Netherlands.
14. S. Triki, L. Ouahab, J.F. Halet, O. Peña, J. Padiou, D. Grandjean, C. Garrigou-Lagrange, and P. Delhaes, J. Chem. Soc. Dalton Transactions, 1217 (1992).
15. K. Awaga, A. Yamaguchi, T. Okuno, T. Inabe, T. Nakamura, M. Matsumoto, and Y. Maruyama, J. Mater. Chem., 4(9), 1377 (1994).