MAGNETOSTRUCTURAL J-CORRELATIONS IN Fe(III) COMPLEXES – A REVISION

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Abstract: The magnetostructural correlations in Fe(III) complexes, originally outlined by Gorun and Lippard has been revised. Other correlation variants have been tested and the dataset enlarged for more recent entries possessing the Fe-O-Fe bridge including dinuclear, tetranuclear and hexanuclear Fe(III) complexes. The resulting relationships confirm that instead of the original suggestions, the correlation could stay as a linear relationship which covers the possibilities of positive values of exchange coupling constants.

Key words: exchange coupling, X-ray structure, magnetostructural correlation, Fe(III) complexes

1. Introduction

Relationships between structural and magnetic parameters attract attention of scientists for a long time. Invented by Hatfield (CRAWFORD *et al.,* 1976; HATFIELD *et al.,* 1985), the exchange coupling constant occurring in the Heisenberg form of the spin Hamiltonian

$$\hat{H}_{AB} = -J_{AB}(\hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B) \qquad (1)$$

depends upon certain structural parameters such as bond lengths and bond angles. In the series of dinuclear Cu(II) complexes of the $[Cu(OH)_2Cu]$ type the values of J correlate with the bonding angle α = Cu-O-Cu along a straight line with the negative slope as shown in Fig. 1. (Notice, the original definition of the J-constant utilizes a numerical prefactor −2, so that all the data below are rescaled to the definition that matches eq. (1)). The critical angle when the positive coupling constant alters to the negative value is close to 98 deg. Thus the ground state $S = 1$ ($J > 0$) and/or $S = 0$ ($J < 0$) can be controlled by the bonding angle α.

The correlations of the above type have been extended also to some other types of dinuclear Cu(II) complexes, such as alkoxido- or phenoxido-bridged complexes (THOMPSON *et al.,* 1996). A further progress has been achieved by proposing the magnetostructural correlations in dinuclear Cr(III) complexes of the $[Cr(OH)_2Cr]$ type by HODGSON *et al.* (GLERUP *et al.,* 1983; HODGSON *et al.,* 1985). In dinuclear Mn(IV) complexes of the $[Mn(O)_2Mn]$ type a magnetostructural correlation has been outlined by LAW *et al*. (2000).

Contrary to the previous cases, GORUN and LIPPARD (1991) proposed a magnetostructural correlation in Fe(III) oxido-bridged complexes in a different form: the value of $-J$ has been found to correlate with the shortest Fe-O contact (abbr. P)

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along a decreasing exponential function: $-J[\mathrm{cm}^{-1}] = A \cdot \exp(BP)$ with the constants $A = 8.763 \times 10^{11}$ and $B = -12.663$.

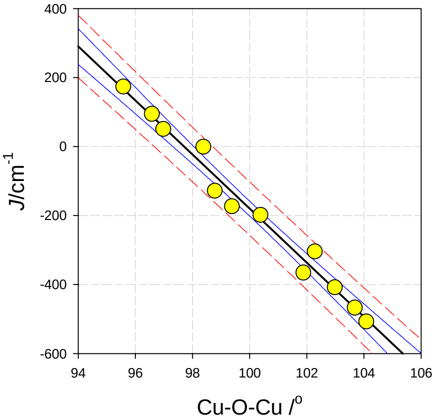

Fig. 1. Magnetostructural correlation in $[\mathrm{Cu^{II}(OH)_2Cu^{II}}]$ complexes by Hatfield et al. (CRAWFORD *et al.*, 1976) Regression line: $J[\mathrm{cm}^{-1}] = -78.33 \cdot \alpha[^\circ] + 7653$, $r^2 = 0.98$.

2. Results and discussion

The dataset compiled by GORUN and LIPPARD (1991) has been subjected to a non-linear regression using contemporary software. To this end the correlation displayed in Fig. 2 has been reconstructed; the regression line is $-J[\mathrm{cm}^{-1}] = a \cdot \exp(-bP)$ with parameters $a = 2.360 \times 10^{10}$ and $b = 10.661$ and it is drawn by bold-solid line. The outer bands refer to the confidence and prediction intervals (95 %), respectively.

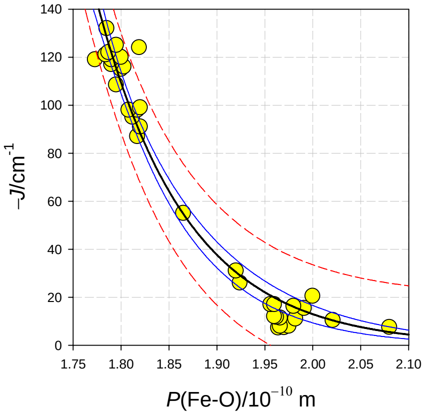

Fig. 2. Magnetostructural correlation for $[\mathrm{Fe^{III}(O)Fe^{III}}]$ complexes by GORUN and LIPPARD (1991). Regression line: $-J[\mathrm{cm}^{-1}] = (2.360 \times 10^{10}\ ) \cdot \exp(-10.661 \cdot P[10^{-10}\,\mathrm{m}])$, $r^2 = 0.95$.

In can be seen that the data is aggregated to two clusters: one for short $P \sim 1.8$ Å referring to a strongly negative J; the second cluster is around "normal" $P \sim 1.95 - 2.00$ Å and it is associated with weakly negative J. The correlation of the above type excludes the occurrence of positive J (no such a data has been reported so far).

There is a clear difference between the J-α correlations proposed for Cu(II) complexes and J-P correlations proposed for Fe(III) ones. Therefore we tested some other variants of the magnetostructural correlations for Fe(III) complexes.

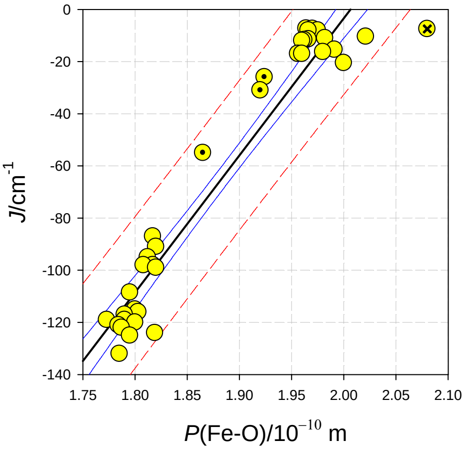

Fig. 3. Redrawn magnetostructural J-P correlation for Fe(III) complexes in a linear mode.

First, the original ($-J$)-P correlation has been redrawn to the usual ($+J$)-P picture and subjected to the linear regression (Fig. 3). The resulting regression line is $J[\mathrm{cm}^{-1}] = 525.7 \cdot P[10^{-10}\,\mathrm{m}] - 1055$, $r^2 = 0.92$, and it can be concluded that the correlation coefficient adopts the acceptable value. Moreover, the linear relationship allows passing to the region of positive J. There are three datapoints in the intermediate region ($P = 1.85 - 1.95$) that do not fall the straight line (highlighted by a dot). However, a detailed inspection to the dataset reveals that these data refer to *triangulo*-[μ_3-O-Fe_3] complexes where the bond angles are fixed to 120 deg so that the bond lengths are more constrained. There is another datapoint that does not match the linear correlation referring to the [Fe(salen)Cl]$_2$ complex (marked by a cross). Omission of these four points improves the regression to $r^2 = 0.958$ that is a better value relative to the original exponential regression.

Second, the correlation J-α has also been tested for Fe(III) oxido-bridged complexes and the results are displayed in Fig. 4. The problematic datapoint is marked by a cross and excluded from the correlation: $J[\mathrm{cm}^{-1}] = -3.98 \cdot \alpha[^\circ] + 396$, $r^2 = 0.70$. Having some more datapoints at the disposal from recent structural and magnetic investigations (NESTEROV *et al.*, 2012; CHYGORIN *et al.*, 2012; NESTEROVA *et al.*, 2013), the original dataset has been enlarged and subjected the linear regression (Fig. 5). Finally, the regression line is $J[\mathrm{cm}^{-1}] = 520.9 \cdot P[10^{-10}\,\mathrm{m}] - 1047$, $r^2 = 0.93$.

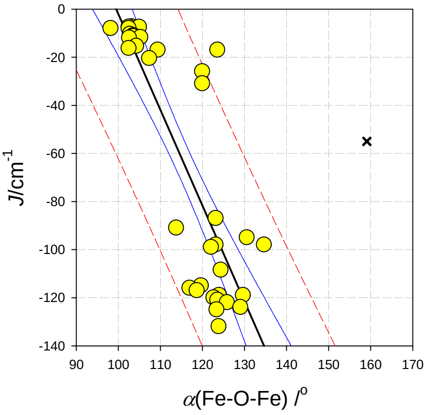

Fig. 4. Probing of magnetostructural correlation *J*-α in Fe(III) complexes using original dataset. A point excluded from the correlation is marked by a cross.

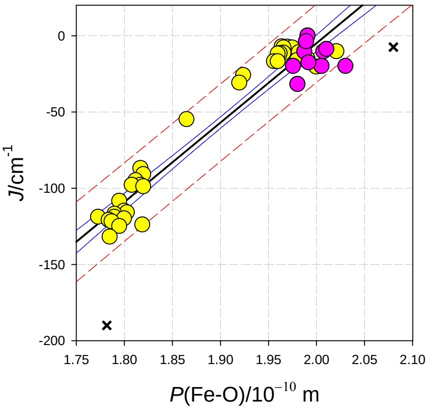

Fig. 5. Magnetostructural correlation in Fe(III) complexes using enlarged dataset. Two points excluded from the correlation are marked by cross.

3. Conclusions

It has been demonstrated that the original (exponential) magnetostructural J-correlation for Fe(III) complexes with μ-oxido bridge suffers of a number of weaknesses. It can be substituted by a linear dependence that is approximately of the same quality. The original dataset can be enlarged by points obtained from recent magnetic and structural studies. The data need be filtered for the quality of the X-ray structure determination, different structural motif, and also the quality of experimental magnetic data-taking and theoretical analysis.

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