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EXTRACTION OF Cu(II) AND Ni(II) BY CAMPHORQUINONE DIOXIME

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(Received 26 January 1982)

Abstract—The extraction properties of three geometrical isomers (α-, β- and δ-) of D-camphorquinone dioxime (H₂CQD) with copper and nickel are described. Under extraction conditions isomerization occurred from α- and β-H₂CQD into δ-H₂CQD. The expected selectivity of δ-H₂CQD for nickel could not be established. On the contrary, copper formed complexes with lower pHₜ₅₀ values than nickel. An ESR study showed that this was due to the fact that copper did not form a NN coordinated complex, but just like nickel a NO coordinated complex. UV spectroscopy proved that besides the Cu(HCQD)₂ complex a Cu₂(HCQD)₂CQD complex is involved in copper extraction.

INTRODUCTION

The development of hydroxyoximes as commercial solvent extraction reagents for copper has prompted much research in the chemistry of such systems. Many attempts have been made to find a reagent that is selective for nickel above copper. In order to form stronger complexes with nickel than with copper, a reagent must be found that does not follow the normal Irving–Williams order of stabilities. This is only possible if nickel forms a different kind of complex with the reagent than copper does. Aliphatic α-dioximes did indeed extract nickel at lower pH than copper and this was explained by assuming that nickel formed a square planar complex with a low spin d⁹ configuration, while copper formed an octahedral complex by binding two additional water molecules. However, the extremely low rate of extraction does not make this system very attractive for commercial use.

Here we report on the separation properties of another kind of α-dioxime, camphorquinonedioxime H₂CQD. H₂CQD is known to exist in four isomeric forms (Fig. 1) which differ by the orientations of the OH groups. The rigid bicyclic skeleton is responsible for a larger NN distance than in aliphatic α-dioximes. NN coordination is the normal mode of coordination for vicinal dioximes but the large N...N distance in H₂CQD makes this kind of coordination less attractive. Recently it was reported that for copper only a NN coordinated H₂CQD complex could be isolated: Cu(α-HCQD)₂·H₂O·1 dioxane (Fig. 1).

In contrast to this it was published that nickel forms stable NO coordinated complexes with α-, γ- and δ-H₂CQD (Fig. 2a) and an unstable NN coordinated com-

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plex with $\beta$-H$_2$CQD. $\alpha$- and $\delta$-H$_2$CQD are likely to form NO coordinated complexes (Fig. 1) and if no isomerization takes place into $\beta$-H$_2$CQD it is to be expected that these two isomers react better with nickel than with copper. In this way the Irving-Williams order of stabilities might be broken.

For this reason we have studied the extraction properties of the camphorquinone dioxime isomers for copper and nickel and the kind of complexes which are responsible for the extraction.

**EXPERIMENTAL**

The optically active camphorquinone dioxime ligands were prepared from (+) camphor according to the procedures of Forster.\(^9\)

$\alpha$-H$_2$CQD: $[\alpha]_D$ (in 2 per cent sodium hydroxyde) = $-99.1 (-98.39); \delta$-H$_2$CQD: $[\alpha]_D$ = $-25.7 (-24.1)$; $\gamma$-H$_2$CQD could not be isolated pure. $\delta$-H$_2$CQD: $[\alpha]_D$ = +85.2 (+83.6$^\circ$).

Optical rotations were obtained at 20°C with a Kreis-Polarimeter 0.01/400 mm from Zeiss Winkel, while ESR measurements were done with a Varian E15 spectrometer at room temperature and UV-visible spectra were obtained on a Unicam SP.800D.

The extraction experiments were carried out in a three停止pered flask with a stirring device and continuous pH measurements. The starting volumes of water and organic solvent were both 250 ml. Stirring was stopped when no further change of the pH was noticed, indicating that equilibrium was reached. For analysis equally small volumes of water layer and organic layer were withdrawn from the system. To measure the distribution coefficient as a function of pH thereafter a small quantity of 4N acid or base was added, and the process of stirring until equilibrium and withdrawal of small portions of the aqueous and organic solutions was repeated at a different pH. Care was taken to keep the volumes of the aqueous and organic solutions equal. Although in this procedure the electrolyte concentration does not stay constant we referred this method because it is convenient to execute and because in a separate experiment it was shown that in the applied concentration range the influence of the electrolyte concentration is negligible. As organic solvents used were chloroform, pentanol and tributylphosphate and inorganic salts used were metal chlorides, nitrates or sulphates. NAOH was used as base and HCl, HNO$_3$ or H$_2$SO$_4$ as acids.

**RESULTS**

Figure 3 shows the results for the extraction of Ni$^{2+}$ with $\delta$-H$_2$CQD. The pH$_{1/2}$ value of 5.20 means a (pH$_{1/2}$) value of 3.60. The slope (1.93) of the log D-pH curve agrees with the theoretical expected value of 2 for the Ni(HCQD)$_2$ complex. The H$_2$CQD recovered after the extraction experiment did not show a significant change in specific rotation (Table 1).

The extraction properties of $\alpha$-H$_2$CQD for Ni$^{2+}$ are constant, it follows that

$$\left(\frac{\partial \log D}{\partial \mathrm{pH}}\right)_{[\text{H}_2\text{CQD}]} = 2. \quad (5)$$

Introducing pH$_{1/2}$ as the pH value at which 50% of the metal is extracted (log D = 0) eqn (4) leads to:

$$\log K_E = 2 \log [\text{H}_2\text{CQD}] - 2 \mathrm{pH}_{1/2}. \quad (6)$$

Finally the value of pH$_{1/2}$ at 1.0 M equilibrium concentration of extractant in the organic phase, denoted by (pH$_{1/2}$)$_o$ can be obtained from eqn (6) as

$$(\mathrm{pH}_{1/2})_o = -\frac{\log K_E}{2}. \quad (7)$$

**TREATMENT OF EXTRACTION DATA**

The extraction is expected to follow eqn (1):

$$M^{2+} + 2\text{H}_2\text{CQD} \rightleftharpoons M(\text{HCQD})_2 + 2\text{H}^+ \quad (1)$$

where $M^{2+}$ represents the aquo metal ion, M(VCQD)$_2$, the extractable complex and bars indicate the organic layer. The equilibrium constant $K_E$ and the distribution coefficient D are defined as:

$$K_E = \frac{[\text{M(VCQD)}_2][\text{H}^+]^2}{[\text{M}^{2+}][\text{H}_2\text{CQD}]^2}. \quad (2)$$

$$D = \frac{[\text{M(VCQD)}_2]}{[\text{M}^{2+}]} \quad (3)$$

Combination of (2) and (3) gives

$$\log D = \log K_E + 2\mathrm{pH} + 2 \log [\text{H}_2\text{CQD}]. \quad (4)$$

When taking a large excess H$_2$CQD, so that H$_2$CQD is
Extraction of Cu(I) and Ni(I) by camphorquinone dioxime

Table 1. Specific rotation

<table>
<thead>
<tr>
<th>H₂CQD</th>
<th>fresh solution</th>
<th>after 7 days</th>
<th>after 45 days</th>
<th>after Cu extraction</th>
<th>after Ni extraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>-63.8</td>
<td>-64.3</td>
<td>-63.3</td>
<td>+51.9</td>
<td>+47.1</td>
</tr>
<tr>
<td>β</td>
<td>+3.7</td>
<td>+21.2</td>
<td>+23.9</td>
<td>+59.4</td>
<td>+45.5</td>
</tr>
<tr>
<td>δ</td>
<td>+78.6</td>
<td>+71.1</td>
<td>+70.2</td>
<td>+67.5</td>
<td>+67.8</td>
</tr>
</tbody>
</table>

α: pentanol as solvent  β: t.b.p. as solvent

quite analogous to those of δ H₂CQD (Fig. 4) with a pH₁/₂ value of 5.03 and a slope of 1.96. The recovered H₂CQD had a specific rotation of = +47.1 (Table 1) indicating that isomerization had taken place.

The only solvent that we could find which dissolves β-H₂CQD and is not soluble in water was tributylphosphate (TBP). In Fig. 5 a pronounced difference is seen between results from experiments with fresh solutions and results from extractions performed with solutions after contact times of two days. In the latter case the results correspond to those of the Ni δ-H₂CQD system: pH₁/₂ = 6.16, slope 1.99 and the recovered H₂CQD showed a specific rotation of +45.5, indicating that isomerization had occurred. Fresh solutions, however, show a slope of 0.97 and a slightly higher pH₁/₂ value of 6.33.

In contrast to the results obtained in the extraction of nickel a value of 2.50 is found (2 was expected on ground of eqn 1) for the slope of the extraction curve for copper with δ-H₂CQD (Fig. 3). A clearly lower pH₁/₂ value of 2.75—leading to a (pH₁/₂)₀ of 1.15—is found. Also for copper no significant change in the specific rotation of δ-H₂CQD could be noted (Table 1).

As with the Ni α-H₂CQD system the Cu α-H₂CQD system gives almost the same figures as found for Cu δ-H₂CQD (Fig. 4). In this case also isomerization had taken place (Table 1) a pH₁/₂ value of 3.08, a slope of 2.67 and a change in specific rotation from -63.8 to +51.9 are found.

With a fresh solution of β-H₂CQD in TBP (Fig. 6) a pH₁/₂ value of 4.21 is obtained for the copper extraction, quite larger than with the Cu δ-H₂CQD pentanol system. The slope of 1.47 indicates that the extraction chemistry must deviate considerably from that represented by the extraction eqn (1). Just as in the experiment with nickel and β-H₂CQD, after two days the picture had dramatically changed. The pH₁/₂ value was lowered to 3.66 and the slope had increased to 2.37. Specific rotation measurement from the recovered H₂CQD showed that most of the β-H₂CQD had isomerized. This isomerization was more pronounced than the isomerization that occurred without contact with the aqueous copper solution (Table 1).

The slopes of the log D-pH curves for the copper extraction deviate from 2 and point to an extraction chemistry which is different from that assumed in eqn (1). To find out which stoichiometry the copper camphorquinone dioxime complex had during extraction an experiment was carried out with equivalent moles of copper and δ-H₂CQD. If Cu(HCQD)₂ would be the only extraction complex at most 50% of the copper can be extracted. Figure 7 shows that definitely more than 50% of the copper can be extracted, but that even at high pH 100% extraction is not reached. At pH 5.0 65% of the copper was extracted.

VIS-spectroscopy (Fig. 8) shows that two different copper complexes are present in the organic phase after extraction. When the pH is relatively low a complex is formed with a maximum absorbance at 25,300 cm⁻¹. At higher pH's a new band appears with a maximum at 22,400 cm⁻¹ and the corresponding complex becomes prevalent at pH 3.20.

Also ESR measurements, correlated with the two different Cu-HCQD complexes are carried out. The ESR spectrum of the complex with λₘ₉₉ 25,300 cm⁻¹ is presented in Fig. 9. It is exactly the same as that found...
Fig. 7. % copper extraction as a function of pH for the extraction of Cu(II) with δ-camphorquinone dioxime. The initial concentration of δ-H$_2$CQD in chloroform and the initial copper nitrate concentration in H$_2$O are both 0.002 M.

by Ma$^5$ for Cu(β-HCQD)$_2$-H$_2$O·½ dioxane. For the complex with $\lambda_{max}$ at 22,400 cm$^{-1}$ no ESR signal could be observed.

DISCUSSION

From Table 1 it can be clearly seen that under extraction conditions isomerization takes place when α- or β-H$_2$CQD are used.

Without contact with an aqueous solution containing metal ions α-H$_2$CQD does not isomerize at all and β-H$_2$CQD isomerizes only to a certain extent.

This phenomenon can be readily explained by the bonding of metal ions or protons to the dioxime; by this interaction the double bond character of the CN bond will be weakened and thus the rotation barrier of this bond will be lowered. δ-H$_2$CQD is the only isomer which possesses hydrogen bridge stabilization and no steric repulsion (Table 2). Therefore it is not surprising that it is the most stable isomer.

Pedersen and Larsen$^6$ found isomerization of Ni(α-

HCQD)$_2$ in chloroform to an equilibrium mixture of 85–90% Ni(δ-HCQD)$_2$ 5–10% Ni(α-HCQD)$_2$ and 5% Ni(β-HCQD) (δ-HCQD). This means that after recovering of H$_2$CQD a specific rotation is expected of 0.90 × (+ 78.6) + 0.075 × (− 63.8) + 0.025 × (+ 3.7) = + 66.0.

In Table 1 it is seen that after extraction with α-, β- or
$\delta$-H$_2$CQD the specific rotation had changed into the direction of this figure, but apparently equilibrium had not been reached.

The expected selectivity of $\delta$-H$_2$CQD could not be established. On the contrary, copper was extracted at a much lower pH than nickel (Fig. 3). This result is surprising because if copper forms a NN complex as suggested by Ma for then rotation around the CN double bond is necessary. Furthermore it might have been expected that copper extraction with $\beta$-H$_2$CQD, for which no rotation is needed would have a lower pHi$_{1/2}$ value than copper extraction with $\delta$-H$_2$CQD. However, in Fig. 6 it can be seen that after a contact time of two days, in which isomerization from $\beta$- to $\delta$-H$_2$CQD has taken place, the pHi$_{1/2}$ value is lowered and not raised.

These results can only be explained if we assume that copper does not form a NN complex but a NO complex just like nickel.

To investigate this possibility we took a closer look at the ESP spectrum of the extracted complex, which is completely identical with the ESP spectrum found by Ma for Cu($\beta$-HCQD)$_2$H$_2$O.4 dioxane. Ma has interpreted the ESP spectrum of Cu($\beta$-HCQD)$_2$ by assigning the four main lines to copper ($^{63}$Cu, $^{65}$Cu; I = 3/2) nuclear hyperfine interactions and the extra lines as being due to the nitrogen ($^{14}$N; I = 1) superhyperfine interaction. By counting 9 nitrogen superhyperfine lines he concluded that four nitrogen atoms were bonded to copper. We therefore conclude that only two instead of four nitrogen atoms are bonded to copper, and so an intensity ratio of 1:2:3:2:1 occurs in the nitrogen superhyperfine structure. As a consequence the Cu($\beta$-HCQD)$_2$ complex of Ma and the extracted complex with $\lambda$ of 25,300 cm$^{-1}$ do not have the NN structure but just like nickel a NO structure (Fig. 2).

The results found in the extraction experiments are in good agreement with this interpretation. For, when copper and nickel form the same kind of complex with H$_2$CQD, copper will have a lower pHi$_{1/2}$ value than nickel according to the Irving and Williams law.

The low values of the slopes of the log D vs pH curves found in the extraction of copper and nickel by fresh $\beta$-H$_2$CQD (1.47 for Cu and 0.97 for Ni) can now also be explained if we assume that $\beta$-H$_2$CQD is not active in the extraction. Only the small portion of the $\delta$-H$_2$CQD that is present will be active. As a consequence the extractant concentration in eqn (4) is not a constant when the equilibrium is changed by adding acid or base. This means that the slope of log D vs pH will not give a value of two, but will give a value which is considerably lower. After two days, during which most of the $\beta$-H$_2$CQD is isomerized to $\delta$-H$_2$CQD, excess $\delta$-H$_2$CQD will be present and indeed the slopes are increased to values (2.37 for Cu and 1.99 for Ni) which are almost equal to the values found in the extraction by $\delta$-H$_2$CQD.

This result of the slope analysis of 1.93 for the extraction of nickel(II) by $\delta$-H$_2$CQD is consistent with the theoretically expected value of 2 (eqn 3) and thus the extraction equation can be represented by

$$\text{Ni}^{2+} + 2\text{H}_2\text{CQD} \rightarrow \text{Ni}($$\text{HCQD})$_2$ + 2H$^+$.  

With copper(II) on the contrary, a deviating value of 2.50 was found for the extraction by $\delta$-H$_2$CQD.
According to Fig. 8 it was shown that two different complexes are involved during the extraction: complex A with \( \lambda_{\text{max}} = 25300 \text{ cm}^{-1} \) and complex B with \( \lambda_{\text{max}} = 22400 \text{ cm}^{-1} \). Their ratio is strongly pH-dependent; at low pH the spectrum is dominated by A, at relatively high pH values B is more important. Since the spectrum of A correlates with the presence of the copper ESR described above, complex A may be assumed to be \( \text{Cu(HCQD)}_2 \).

Figure 7 shows that at pH = 5, 65% of the copper is extracted and from Fig. 8 it can be concluded that at this pH complex B is almost exclusively responsible for the extraction. The value of about 65% extraction at high pH can be explained if a complex with a copper:HCQD = 2:3 ratio is assumed to be present during extraction. In that case the maximum concentration of copper in the organic phase is expected to be 66.7%. To check the hypotheses on the stoichiometry of the two copper complexes accurate values of the intensities of the bands of both (overlapping) bands were necessary. The separation at different pH values was carried out by means of computer simulation.

The best fit was obtained by using a corrected Lorentz function with the general form \( y = a(1 + bx + cx^2)^{-1} \) as used by Baker et al.\(^1\) for IR band simulation. A strong absorption near 35000 cm\(^{-1} \) with some overlap around 25000 cm\(^{-1} \) has been taken into account. In Fig. 10 one of the simulations is shown, and the excellent fit is noteworthy. In this way the real intensities of the bands at \( \lambda_{\text{max}} \) could be obtained and these values are according to Lambert-Beer's law proportional to the concentrations of complex A (25300 cm\(^{-1} \)) and B (22400 cm\(^{-1} \)). By using the trial and error method the best extinction coefficients for A and B could be determined. These extinction coefficients are 4940 for A and 8700 for B. In Fig. 11 it is shown what happens with the different species as a function of pH.

For complex A we assume that the same reaction equation applies as used in eqn (1) and \( k_A \) is then given by eqn (8)

\[
k_A = \frac{[\text{Cu(HCQD)}_2][\text{H}^+]^2}{[\text{Cu}^2+][\text{H}_2\text{CQD}]} = \frac{[A][\text{H}^+]^2}{[\text{Cu}^2+][\text{H}_2\text{CQD}]}.
\]

\[\text{(8)}\]

In eqns (8) and (10) all concentrations can be measured ([H\(^+\)] with pH measurements, [Cu\(^{2+}\)] with atomic absorption, [A] and [B] with UV/visible spectroscopy) with the exception of [H\(_2\)CQD]. To eliminate [H\(_2\)CQD] we combine (8) and (10)

\[
\frac{k_A}{k_B} = \frac{[\text{Cu}_2(\text{HCQD})_3\text{CQD}][\text{H}^+]^4}{[\text{Cu}^2+][\text{H}_2\text{CQD}][\text{H}_2\text{CQD}][\text{H}^+]^3} = \frac{[B][\text{H}^+]^4}{[\text{Cu}^2+][\text{H}_2\text{CQD}][\text{H}^+]^3}.
\]

\[\text{(10)}\]

resulting in

\[
\frac{\delta \log [B] - 3 \log [A] - \log [\text{Cu}^{2+}]}{\delta \text{pH}} = 2.
\]

In Fig. 12 we see that a plot of 2 log B - 3 log A - log [Cu\(^{2+}\)] vs pH indeed gives a straight line with a slope of 1.99 confirming our assumptions concerning complex B. However, the requirements of a neutral complex with a copper ligand ratio of 2:3 are also fulfilled with the assumption of the complex \( \text{Cu}_2(\text{HCQD})_3\text{OH} \), replacing the double negative charge of CQD by HCQD\(^-\) plus OH\(^-\):

\[
2\text{Cu}^{2+} + 3\text{H}_2\text{CQD} + \text{H}_2\text{O} \rightleftharpoons \text{Cu}_2(\text{HCQD})_3\text{OH} + 4\text{H}^+.
\]

\[\text{(13)}\]

Because [H\(_2\)O] can be assumed to be constant, replacing (9) by (13) gives no difference in expressions (11) and
**Extraction of Cu(II) and Ni(II) by camphorquinone dioxime**

Fig. 12. 2 log B - 3 log A - log Cu'' as a function of the pH for the extraction of copper(Ii) with S-camphorquinone dioxime. A and B are the calculated values of the maxima of the complex with $\lambda_{max} = 25300 \text{ cm}^{-1}$ and of the complex with $\lambda_{max} = 22400 \text{ cm}^{-1}$ respectively. For initial concentrations see Fig. 7.

(12) so complex B might also be represented by Cu(CQD)$_2$OH.

If $\text{OH}^-$ is replaced by another anion, for example $\text{NO}_3^-$ (to adjust pH $\text{HNO}_3$ is used), elimination of $[\text{H}_2\text{CQD}]$ from the expressions for $k_A$ and $k_B$ gives:

$$\frac{k_A}{k_B} = \frac{[A]}{[B]} [\text{NO}_3^-]^2 [\text{Cu}^{2+}]^{-1}.$$  \hspace{1cm} (14)

This would mean that $[A]/[B]$ would be independent from the pH, which does not fit with Fig. 11. We therefore conclude that this reaction does not take place.

Although the extraction experiments strongly point to the formation of a 2:3 Cu:HCQD complex, we checked if a 1:1 complex could explain the extraction results

$$\text{Cu}^{2+} + \text{H}_2\text{CQD} \rightleftharpoons \text{Cu(CQD)} + 2\text{H}^+.$$ \hspace{1cm} (15)

In combination with eqn (8) and by eliminating the [H$_2$CQD] we obtain

$$\frac{k_A}{k_B} = \frac{[A]}{[B]} [\text{Cu}^{2+}] [\text{H}^+]^{-2}.$$ \hspace{1cm} (16)

Therefore a plot of $2 \log B - 3 \log A - \log [\text{Cu}^{2+}]$ vs pH must give a straight line with slope 2. From Fig. 13 it is clear that this is not the case so we may safely reject eqn (15). Also Cu(HCQD) (NO$_3$) could be rejected by this way of analysis. Because of all these arguments for complex B we conclude that complex B must have the composition Cu$_2$(HCQD)$_2$CQD or Cu$_3$(HCQD)$_2$OH.

In agreement with this conclusion no ESR signal could be observed for complex B. This is not an unknown phenomena$^{13,14}$ for binuclear Cu(II) complexes in which the antiferromagnetic coupling between the two copper ions is so large that the singlet ground state has a very pronounced energy difference from the triplet state. As a result the complex is diamagnetic at room temperature. Since only binuclear copper(II) complexes can have such an antiferromagnetic complexing and mononuclear copper(II) complexes always have an unpaired electron, this confirms the conclusion that the composition of complex B must be Cu$_2$(HCQD)$_2$OH or Cu$_3$(HCQD)$_2$CQD.

**CONCLUSIONS**

The expected selectivity of $\delta$-H$_2$CQD for the extraction of nickel above copper has not been confirmed. On the contrary, copper was found to have a pH$_{1/2}$ value that was much lower (2.75 vs 5.20) than that of nickel. This expected selectivity of camphorquinone dioxime for nickel above copper was based on a publication of Ma, claiming that the dioxime in Cu(p-HCQD)$_2$H$_2$O.dioxane, had a NN coordination around copper. However, a study of the ESR spectrum showed, however, that this product does not have a NN coordination but a NO coordination like nickel. With the knowledge that there is no difference in coordination of H$_2$CQD around copper and nickel, it is not surprising that $\delta$-H$_2$CQD has no selectivity for nickel above copper, and that the normal order of stabilities according to Irving and Williams is followed.

Under extraction conditions isomerization occurred from $\alpha$- and $\beta$-H$_2$CQD into $\delta$-H$_2$CQD. Without contact with metal ions or protons the $\alpha$-H$_2$CQD is stable in solution. We therefore conclude that metal ion or proton attaches on the nitrogen atoms and lowers the double
bond character of the CN bond, thus making rotation around this bond more easy.

Analysis of the slope of $\log D$ vs pH confirmed the expected reaction equation for nickel: $\text{Ni}^{2+} + 2\text{HCQD} \rightleftharpoons \text{Ni(HCQD)}_2 + 2\text{H}^+$. With copper two different complexes are involved in the extraction which is clearly seen by UV spectroscopy. Computer simulation showed that these two complexes are $\text{Cu(HCQD)}_2^-$ with an absorption at 25300 cm$^{-1}$ and $\text{Cu}_2(\text{HCQD})_2\text{CQD}$ or $\text{Cu}_2(\text{HCQD})_2\text{OH}$ with an absorption at 22400 cm$^{-1}$. ESR spectroscopy proved the $\text{Cu(HCQD)}_2^-$ complex to have an NO structure. For the $\text{Cu:HCQD} = 2:3$ complex no ESR signal could be observed, which is not uncommon for binuclear copper(II) complexes with a very strong antiferromagnetic coupling.

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